Thermal processing of thin films using ultra-short laser pulses

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Applied to photovoltaic materials

D. Scorticati

THERMAL PROCESSING OF THIN FILMS USING ULTRA-SHORT LASER PULSES

APPLIED TO PHOTOVOLTAIC MATERIALS

Davide Scorticati

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THERMAL PROCESSING OF THIN FILMS USING ULTRA-SHORT LASER PULSES

APPLIED TO PHOTOVOLTAIC MATERIALS

DISSERTATION

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Summary

In this thesis a novel approach to raise the thermal selectivity of superficial heat treatments, exploiting ultra-short laser pulses, is proposed and studied.

That is, the effective applicability of ultrafast lasers for selective heat treatments is proven by increasing the performance of different films of materials adopted for manufacturing thin film photovoltaic devices - i.e. SnO_2 , ZnO and Mo . At the same time, the scalability of surface processing with ultrafast lasers for future possible industrial applications is evaluated and shown to be in practice only limited by the available laser power.

First, a finite-element model was developed for ZnO and Mo thin films.

It is analytically demonstrated that ultra-short pulses can be exploited to increase the selectivity during thermal processes, via numerical comparison of the induced temperature-cycles induced by ns- and ps-pulses. It is also numerically demonstrated that the heat selectivity is preserved when the beam is expanded, hence showing the scalability of the process.

Next, the effect of selective thermal processing of SnO_2 , ZnO and Mo thin films is studied experimentally.

More specifically, thermal annealing by ultra-short laser pulses of SnO_2 thin films (thickness $\sim 1 \mu\text{m}$) is studied. The effect of the laser annealing on the electrical and optical properties was analyzed. A marked increased optical transmittance of light in the visible-UV range and a simultaneous modest decrease of the electrical properties of the laser treated films were found. Combining these two contributions via the so-called Figure of Merit, an overall improvement of the performance, up to 59%, of the films after the laser treatment was observed. At high laser fluence levels, modification of the surface texture of the films was also observed. The origin of the observed macroscopic changes (i.e. the optical and electrical properties) in the SnO_2 thin films are explained on a microscopic level. The increased optical transmittance was mainly attributed to the removal of the thin interfacial carbon-rich layer present in the as-deposited samples and to the new surface morphology, while the

small decrease of the electrical performance was ascribed to the generation of laser-induced defects, upon laser processing, especially in the molten-resolidified region.

Also the effects of ultra-short pulsed laser treatment on Al-doped ZnO thin films (thickness $\sim 130\text{-}800$ nm) deposited by industrially scalable deposition techniques, such as sputtering and plasma enhanced chemical-vapor- deposition was studied. The conductivity of these films increases sharply after laser exposure from 1 and 10^{-3} $\Omega\cdot\text{cm}$ to 10^{-2} and 10^{-4} $\Omega\cdot\text{cm}$, while keeping an excellent transparency in the visible range ($85 - 90\%$). The morphology and nanostructure of the films were analyzed in detail. The doping efficiency of Al atoms was improved by laser exposure, which was shown to promote their incorporation in the ZnO lattice via the creation of zinc vacancies.

Finally, thin molybdenum films (thickness $\sim 150\text{-}400$ nm) deposited on glass were textured by ultra-short laser pulses. On the surface of the films, nano-sized gratings formed which are known as Laser-Induced Periodic Surface Structures (LIPSSs). These structures modify the optical properties of the films by increasing the scattering of light in the near infra-red part of the spectrum. Focusing on the technical side of laser nano-fabrication of long regular LIPSSs on thin Mo films, the aim of this study was also to give an understanding of the correct laser parameters to apply during laser texturing of these brittle thin films, in order to avoid thermal damage. It was found that the brittle-ductile transition must be taken into account when optimizing the laser parameters during laser processing.

The conclusion of this thesis is positive regarding the beneficial effects of ultra-short laser pulses exploited for highly selective thermal processing of thin films.

Samenvatting

Dit proefschrift beschrijft een innovatieve toepassing van ultra-kort gepulste lasers om de thermische selectiviteit van warmtebehandelingen te vergroten. De effectiviteit van het gebruik van ultra-kort gepulste lasers voor selectieve warmtebehandelingen wordt aangetoond aan de hand van de verbeterde eigenschappen van laser-behandelde materialen die worden toegepast in zonnecellen; SnO_2 , ZnO en Mo . Ook de schaalbaarheid van deze laserbewerking naar toekomstige industriële toepasbaarheid wordt geëvalueerd en blijkt enkel te worden beperkt door het beschikbare laservermogen.

Allereerst wordt, aan de hand van een-eindige elementen model van een dunne laag ZnO en een dunne laag Mo , dewelke het door de laser geabsorbeerde laserenergie geïnitieerde de thermische cycli beschrijft, aangetoond dat de thermische selectiviteit van picoseconden laserpulsen groter is dan van nanoseconde laserpulsen. De simulaties tonen tevens aan dat de selectiviteit behouden blijft als de diameter van de laserspot wordt vergroot. Dit laatste toont de schaalbaarheid van het proces aan. Vervolgens wordt experimenteel het effect van selectief thermische bewerken van dunne film SnO_2 , ZnO en Mo bestudeert. Eerst wordt het effect van thermisch gloeien van een dunne laag (dikte $\sim 1 \mu\text{m}$ SnO_2) met ultra-korte pulsen op de optische en elektrische eigenschappen van de laag bestudeerd. De lagen vertonen een significante verbetering van de optische transparantie t.g.v. de laserbewerking, met slechts een beperkte achteruitgang van de elektrische eigenschappen van de laag. De zogenaamde Figure of Merit, combineert deze twee eigenschappen in één grootheid, dewelke verbetert tot wel 59% ten gevolge van de laserbewerking. Verder bleek de oppervlakte textuur van de lagen te worden gewijzigd indien werd bewerkt met hoge laser energiedichtheden. De oorzaak van de gewijzigde optische en elektrische eigenschappen van SnO_2 ten gevolge van de laserbewerking werden gezocht en gevonden in de laser genduceerde effecten op micro- en atomaire schaal.

De toegenomen optische transparantie kon zowel worden toegedicht aan de gewijzigde oppervlakte textuur, als aan het verwijderen van een koolstofrijke laag in de

oorspronkelijke SnO_2 laag. De beperkte teruggang van de elektrische eigenschappen kon worden toegedicht aan de vorming van defecten in met name de laser gesmolten, en vervolgens gestolde, delen van de laag.

Vervolgens zijn de effecten onderzocht van ultra-korte pulse laser bewerkingen van dunne, Al-gedoteerde, ZnO lagen (dikte $\sim 130\text{-}800$ nm), dewelke werden aangebracht met industriële depositie technieken, zoals 'sputtering' en 'plasma enhanced chemical-vapor-deposition'. De elektrische geleidbaarheid van deze lagen verbeteren sterk van $1\ \Omega\cdot\text{cm}$ tot $10^{-3}\ \Omega\cdot\text{cm}$ naar $10^{-2}\ \Omega\cdot\text{cm}$ and $10^{-4}\ \Omega\cdot\text{cm}$ ten gevolge van de laserbewerking, terwijl de de excellente transparantie (85 - 90%) voor zichtbaar licht behouden blijft. De morfologie en nanostructuur van de lagen werd in detail onderzocht. De efficiëntie van de Al doteringen bleek te zijn verhoogd ten gevolge van de laserbewerking, doordat Al atomen op vacante Zn posities in de ZnO kristalstructuur worde opgenomen.

Tot slot zijn, met behulp van ultra-korte laser pulsen, dunne lagen van molybdeen (dikte $\sim 150\text{-}400$ nm), op glas substraten, getextureerd. Als gevolg van de laserbewerking vormen zogenaamde 'Laser-induced Periodic Surface Structures' (LIPSSs) op de laag. Deze structuren beïnvloedden de optische eigenschappen van de laag, doordat de verstrooiing van met name infra-rood licht toeneemt. Met het oog op het produceren van grote oppervlakken met homogene LIPSSs op dunne brosse lagen van Mo, is onderzocht hoe de juiste bewerkingsparameters te kiezen teneinde thermische schade aan de lagen te voorkomen. De zogenaamde 'brittle-ductile transition' blijkt hierin een belangrijke materiaaleigenschap waarmee rekening gehouden moet worden.

De hoofdconclusie van dit proefschrift is dat ultra-kort gepulste lasers inderdaad effectief en efficiënt kunnen worden gebruikt voor het thermische bewerken van dunne lagen.

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Chapter 1

Introduction

1.1 Background

Laser processing has become an important aspect of industrial micromachining, where precision, selectivity and processing speed are key parameters to evaluate the efficiency of a process [1].

In micromachining, lasers are mainly adopted for ablation, which is the removal of material by laser irradiation via direct sublimation of the target material within the focused laser spot [2]. The continuous demand of machining with higher precision and selectivity drove the application of lasers toward the so called cold ablation, where the Heat Affected Zone (HAZ) around the removed material is effectively reduced and is in some cases negligible [3]. Ultra-short pulsed lasers, with pulse durations in the order of tens of femtoseconds up to tens of picoseconds, are replacing nanosecond pulsed laser sources in industrial applications where cold ablation is needed. Decreasing the interaction time between a single laser pulse and the material, i.e. reducing the pulse duration, reduces the amount of heat propagating in the material during the laser pulse. Therefore, a higher *thermal* selectivity is provided with shorter pulse durations compared to longer pulse durations [4,5].

In the present work, the *thermal* selectivity of ultra-short pulsed lasers is exploited for thermal processes, where their effect is studied on the target material below the ablation threshold. This uncommon use of ultra-short pulsed lasers represents a novel approach to achieve an excellent level of selectivity during surface heat treatments.

When this selectivity confines the thermal effect of the absorbed laser energy to only the very top layer of the material, the particular interaction between the ultra-short laser pulses and material can lead to a new microstructure, changing the material properties such as electrical and optical, as well as the to a new surface morphology

[6-9].

Compared to other conventional techniques used for rapid thermal annealing (i.e. furnaces, lamps, or cw and ns-pulsed lasers)[10-14], ultra-short pulsed laser annealing can provide the advantage of reducing the heat affected zone to a depth which, in first approximation, corresponds to the optical absorption length of the material at the laser wavelength. The resulting localized heating may also reduce the transport and intermixing of different atomic species between adjacent layers, for instance when processing a multi-layered device. Furthermore, the high selectivity of ultra-short pulsed laser processing is particularly suitable for thermal processing of thin films, where a high degree of controllability of the heat input is crucial to avoid thermal damage of the film and/or of the substrate.

A good understanding of the laser-material interaction as well as knowledge of the effects of the laser treatment on the micro and macro scale properties of the films are needed to establish laser optimal processing conditions, in order to achieve the best performance of the treated films.

A relevant application of thermal processing with ultra-short laser pulses can be found, as a future prospect, in technologies adopting thin films. In this thesis, materials common in photovoltaics (PV) were chosen.

1.2 Problem definition

The timescale of the heating-cooling cycle time induced by ultra-short laser pulses in the material is extremely short, hence limiting the time available for modifications of the microstructure. Therefore the main problem definition in this thesis is formulated as a research questions, namely:

- *Can ultra-short laser pulses be exploited for thermal processing of thin films?*

Different thin films relevant for photovoltaic applications were selected (see table 1.1), namely tin dioxide doped with fluorine ($\text{SnO}_2:\text{F}$), zinc oxide doped with aluminum ($\text{Al}:\text{ZnO}$) and molybdenum (Mo), which are all materials commonly adopted as electrodes in thin film solar cells [15].

To answer the main research question, other four (sub-)questions are answered in this work.

The first research question (Q1) is:

- *What is the effect of laser pulses with different time durations (i.e. nano- and picosecond) on the temperature profiles in the films during, as well as after, their absorption and how this does affect the thermal selectivity of the process?*

To evaluate the effect of ultra-short laser pulses on PV films, electrical and optical properties were evaluated. Therefore, the second research question (Q2) is:

- *What are the optical and electrical properties of the films before and after laser processing with ultra-short laser pulses?*

Observable macroscopic changes of the optical, as well as of the electrical, properties can be induced by several causes at the microscopic scale. Therefore, the third research question (Q3) is:

- *What is, at the microscopic level, the origin of the measured macroscopic changes?*

A critical aspect of laser micro-processing of thin films composed of brittle material is to control the input of heat in order to avoid thermal damage of the films. This means avoiding thermo-mechanical cracking, delamination and excessive thinning by ablation. Therefore, a careful choice of the laser parameters is required for process optimization. To this end, the fourth research question (Q4) is:

- *What are the optimal laser parameters to be chosen in order to avoid any thermally related damage of the films?*

1.3 Scope

This work is based on a collection of scientific peer-reviewed articles (see pag. 113). Therefore, the reader is forewarned that the introductions of the different chapters may show partial repetition. A general overview of the structure and scope of this thesis is shown in table 1.1.

Chapter 2 presents and discusses a model which was developed in order to answer research question Q1. Chapters 3 to 6 study the effect of using ultra-short laser pulses for thermal processing of different films for future applications in PV and thin film technology in general.

More specifically, chapters 3 and 4 focus on thermal annealing by ultra-short laser pulses of SnO₂ thin films (thickness $\sim 1 \mu\text{m}$). In chapter 3, the effect of the laser annealing on the electrical and optical properties is studied, answering research question Q2. Chapter 4 focuses on the explanation, at a microscopic level, of the observed changes in the SnO₂ thin films, answering question Q3.

In chapter 5, ultra-short pulsed laser annealing of Al:ZnO thin films (thickness $\sim 130\text{-}800 \text{ nm}$) is investigated. In this chapter, first the effect of the laser annealing on the electrical and optical properties is studied, again answering question Q2. Next, an explanation, at a microscopic level, of the observed changes is presented, answering Q3.

In chapter 6, molybdenum films (thickness $\sim 150\text{-}400 \text{ nm}$), deposited on glass, were textured by ultra-short pulses. The results discussed in this chapter answer both questions Q2 and Q3. Moreover, this chapter focuses on the technical side of laser nano-fabrication of Laser-Induced Periodical Surface Structures (LIPSSs) on thin brittle molybdenum films. The aim of this chapter is also to understand the optimal laser parameters to apply during laser texturing of these thin films in order to avoid or minimize thermal damage. This answers question Q4.

Finally, in chapter 7, conclusions are drawn regarding the overall results of the use of ultra-short laser pulses for selective heat treatment of thin films.

Table 1.1: General overview of the structure and scope of this thesis.

Chapter	Material	Thickness [nm]	τ [ps]	Process	Answered questions
1				introduction	
2				modeling	Q1
3	SnO ₂	900 – 1000	6.7	annealing and texturing	Q2
4	SnO ₂	900 – 1000	6.7	annealing and texturing	Q3
5	Al:ZnO	130 – 800	6.7	annealing	Q2, Q3
6	Mo	150 – 400	0.23 – 10	texturing nanosized gratings of LIPSSs	Q2,Q3,Q4
7				conclusions	

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Ultra-short pulsed laser-material interaction: a physical background

2.1 Introduction

The aim of this chapter is to provide a background of the physics that govern the absorption of light and subsequent diffusion of heat in semiconductor and metallic materials, when exposed to picosecond or nanosecond laser pulses. This background is required to support the main claim asserted in the first chapter of this thesis. Namely, ultra-short pulsed lasers have benefits over nanosecond pulsed lasers for selective (i.e. superficial) heat treatment of materials in general, and for selective heat treatment of thin films in particular.

To this end, a numerical model was implemented using a commercial Finite Element Modeling (FEM) package, to simulate the temperature fields in thin films induced by laser pulses. The results of the simulations provide insight in the temperature-time cycles, as function of the processing parameters, such as fluence, pulse duration, pulse repetition frequency and laser wavelength.

The simulations were run for thin films of molybdenum (Mo) and zinc oxide (ZnO) on a glass substrate. ZnO, which is a semiconductor, is modeled as undoped, due to the unavailability of the material properties for doped ZnO in literature. No simulations were carried out for SnO₂ due to lack of data on material properties. Moreover, single pulse simulations were performed, since main insights (i.e. maximum temperature, time scales, heat selectivity) can be gained from a single

Based on the submitted article: D. Scorticati, G.R.B.E. Römer, D.F. de Lange, A.J. Huis in 't Veld, Modeling of temperature cycles induced by pico- and nanosecond laser pulses in ZnO and Mo thin films, Journal of Heat Transfer (2015).

temperature cycle.

In section 2.2, two models will be presented to describe the interaction of a laser pulse with semiconductors and metals, respectively. Then in section 2.3, simulation results will be presented and discussed. Finally, section 2.4 summarizes the main results and observations.

2.2 Modeling

Since semiconductors and metals respond differently to laser radiation, two different models are needed. First, the interaction of the laser with semiconductors will be discussed and modeled. Next, a model for metals will be derived, by introducing general simplifications to the model for semiconductors.

For an overview of symbols and quantities used in this chapter and in the simulations, see tables 2.1, 2.2, 2.3 and 2.4*.

2.2.1 Semiconductors

The interaction between ultra-short laser pulses and materials is commonly expressed by a multi-step absorption mechanism. That is, after the initial absorption of the laser energy by the electron gas of the material, and subsequent generation of hot carriers, the heat is transferred to the lattice via electron-phonon scattering and finally dissipated, mainly via diffusion [1,2].

The physics of these phenomena are described by a set of four equations: (i) An equation describing the absorbed laser intensity in time and space, inside the targeted material. (ii) A conservation equation, which accounts for the generation, diffusion, and recombination of photo-generated carriers. Two more equations are required to calculate the temperatures fields of the electron gas (iii) and of the lattice (iv), respectively.

When the duration of the laser pulse τ_p is much longer than the scattering time τ_{e-p} between electrons and phonons of the material, the electron temperature T_e is close or even indistinguishable from the temperature of the lattice T_l . The latter is the case for nanosecond pulses or longer pulse durations. With ultra-short pulsed lasers, where $\tau_p \leq \tau_{e-p}$, T_e and T_l can be in non-equilibrium (i.e. strongly differ). Hence a two-temperature model (TTM) is required to describe the system [1].

To derive the presented set of equations, the formulation of ultra-fast transport dynamics in semiconductors presented by van Driel was followed [2].

*It should be noted that, the symbols used in this chapter may differ from the symbols employed in subsequent chapters.

2.2.1.1 Conservation equation for the free carriers

The absorbed energy of ultra-short focused laser pulses generate a dense plasma of electrons-holes pairs ($\approx 10^{21} \text{ cm}^{-3}$), inside the targeted semiconductor material, which is well above the typical carrier densities of intrinsic ZnO. The Dember field, which builds up due to charge separation, prevents the densities (n_e and n_h) and currents (j_e and j_h), related to electron and holes respectively, to differ significantly [3]. Therefore one can assume $n_h = n_e = n_c$ and $\vec{j}_h = \vec{j}_e = \vec{j}$, where n_c is the density of the electron-hole pairs and $\vec{j}$ their current density. The conservation law of photo-generated carriers can then be expressed as

$$\frac{\partial n_c}{\partial t} = -\nabla \cdot \vec{j}/e + G - R, \quad (2.1)$$

where e is the electron charge, G describes the generation of carriers (electron-hole pairs) and R represents their recombination, i.e. electrons crossing the band gap from the valence to the conduction band and viceversa, respectively. Using the ambipolar diffusion coefficient D_0 , the current can be expressed as $\vec{j}/e = -D_0 \nabla n_c$ [2] and equation (2.1) becomes

$$\frac{\partial n_c}{\partial t} = \nabla \cdot (D_0 \nabla n_c) + G - R. \quad (2.2)$$

Considering the single- and double-photon electronic transitions from the valence to the conduction band and the impact ionization, the generation term G reads [2]

$$G = \frac{\alpha I}{h\nu} + \frac{\beta I^2}{2h\nu} + \delta n_c, \quad (2.3)$$

with I the intensity of the laser, α and β the single[†] and double photon absorption coefficients respectively, δ the impact ionization coefficient and $h\nu$ the energy of the photons, where ν denotes the frequency at the laser wavelength and h denotes the Planck constant.

The recombination term R accounts for three recombination mechanisms, namely, Shockley-Read-Hall recombination, radiative recombination and Auger recombination [2], and reads

$$R = \gamma_{srh} (n_c - n_0) + \gamma_{rad} (n_c - n_0)^2 + \gamma_{aug} (n_c - n_0)^3, \quad (2.4)$$

[†]The absorption coefficient of intrinsic ZnO depends on the carrier concentration. This can vary between $5 \cdot 10^6$ - 10^5 cm^{-1} , depending on the density of oxygen vacancies. In simulations, the smallest value was adopted in order to simulate the worst possible case.

where n_0 is a constant and γ_{srh} , γ_{rad} and γ_{aug} are the coefficients for Shockley-Read-Hall, radiative and Auger recombination, respectively.

2.2.1.2 Electron heat equation

To derive the conservation equation for the electron heat, the Maxwell-Boltzmann distribution is adopted, as an approximation for the distribution of the carriers at high temperatures. Then, the total energy density U of the electronic system reads [2]

$$U = n_c E_g + \frac{3}{2} n_c k_b T_e, \quad (2.5)$$

where E_g denotes the energy band gap between the minimum of the conduction band and the maximum of the valence band and where k_b denotes the Boltzmann constant. Clearly, the first term on the right side describes the potential energy of the free carriers, while the second term represents their kinetic energy.

The conservation of the energy in the electronic system can then be expressed as [2]

$$\frac{\partial U}{\partial t} = -\nabla \cdot \vec{W} - \Gamma (T_e - T_l) + S, \quad (2.6)$$

where C_e denotes the volumetric electron heat capacity, $\vec{W}$ the ambipolar energy current [2], Γ the electron-phonon coupling coefficient and S the source term, accounting for the absorbed laser energy. Here, $-\Gamma (T_e - T_l)$ describes the exchange of energy between the electrons and the lattice.

Few steps are at this point needed to express equation (2.6) into its final form (equation (2.13)). Since, by definition, the heat capacity is the derivative of the energy U with respect to temperature, C_e takes the form

$$C_e = \frac{\partial U}{\partial T_e} = \frac{3}{2} k_b n_c. \quad (2.7)$$

Deriving U as a function of time t , using equation (2.5) yields

$$\frac{\partial U}{\partial t} = \frac{\partial n_c}{\partial t} E_g + n_c \frac{\partial E_g}{\partial t} + \frac{3}{2} k_b \frac{\partial n_c}{\partial t} T_e + \frac{3}{2} k_b n_c \frac{\partial T_e}{\partial t}. \quad (2.8)$$

Reordering the terms in equation (2.8), and substituting the mathematical equality $\frac{\partial E_g}{\partial t} = \frac{\partial E_g}{\partial T_l} \frac{\partial T_l}{\partial t}$, as well as substituting equation (2.7) yields

$$\frac{\partial U}{\partial t} = \frac{\partial n_c}{\partial t} \left(E_g + \frac{3}{2} k_b T_e \right) + C_e \frac{\partial T_e}{\partial t} + n_c \frac{\partial E_g}{\partial T_l} \frac{\partial T_l}{\partial t}. \quad (2.9)$$

Focusing on the last term on the right side of equation (2.9), the term $\frac{\partial E_g}{\partial T_l}$ is considered. The band gap E_g of ZnO is commonly expressed as a function of T_l as

$$E_g(T_l) = E_g(0) - \frac{a T_l^2}{b + T_l}, \quad (2.10)$$

with a and b being constants [4] and $E_g(0)$ the band gap at $T = 0$ K.

Since $\frac{d}{dx} \left(\frac{ax^2}{b+x} \right) = a \cdot \frac{d}{dx} \left(\frac{x^2}{b+x} \right) = a \left(\frac{2x}{b+x} - \frac{x^2}{(b+x)^2} \right)$, it follows from equation (2.10) that

$$\frac{\partial E_g}{\partial T_l} = a \left(\frac{2T_l}{b + T_l} - \frac{T_l^2}{(b + T_l)^2} \right). \quad (2.11)$$

Finally, the ambipolar energy current W in equation (2.6) needs to be considered. Referring to the work of van Driel [2], the ambipolar energy current $\vec{W}$ of generated electron-holes pairs can be expressed as

$$\vec{W} = (E_g + 4k_b T_e) \vec{j}/e - k_e \nabla T_e. \quad (2.12)$$

Recalling that the divergence is a linear operator and that $\vec{j}/e = D_0 \nabla n_c$ (see section 2.2.1.1), substitution of equations (2.9), (2.11) and (2.12) into (2.6) yields

$$\begin{aligned} C_e \frac{\partial T_e}{\partial t} = & -\nabla \cdot [(E_g + 4k_b T_e) D_0 \nabla n_c] + \nabla \cdot (k_e \nabla T_e) - \Gamma (T_e - T_l) \\ & + S - \left(E_g + \frac{3}{2} k_b T_e \right) \frac{\partial n_c}{\partial t} + n_c \frac{\partial T_l}{\partial t} \left[a \left(\frac{2T_l}{b + T_l} - \frac{T_l^2}{(b + T_l)^2} \right) \right]. \end{aligned} \quad (2.13)$$

2.2.1.3 Lattice heat equation

The conservation of lattice heat is given by the classical heat equation [2]

$$C_l \frac{\partial T_l}{\partial t} = -\nabla \cdot \vec{q}_l + \Gamma (T_e - T_l), \quad (2.14)$$

where C_l is the volumetric heat capacity of the lattice and $\vec{q}_l$ the lattice heat flux described by Fourier's law

$$\vec{q}_l = -k_l \nabla T_l, \quad (2.15)$$

where k_l is the thermal conductivity of the lattice. Hence, substituting equation (2.15) into equation (2.14) yields

$$C_l \frac{\partial T_l}{\partial t} = \nabla \cdot (k_l \nabla T_l) + \Gamma (T_e - T_l). \quad (2.16)$$

The term $+\Gamma (T_e - T_l)$, already discussed in respect to equation (2.6), has now an opposite sign to account for the total conservation of energy.

2.2.1.4 Laser source

The source term S , in equation (2.13), can be expressed as

$$S = (\alpha + \beta I + \theta n_c) \cdot I, \quad (2.17)$$

where θ is the free carrier absorption coefficient and I is the solution of

$$\frac{\partial I}{\partial z} = \alpha I + \beta I^2 + \theta n_c I, \quad (2.18)$$

which accounts for the decreasing laser intensity I in time and space inside the targeted material, observing that the laser beam is directed in negative z direction.

Assuming a Gaussian beam shape, in both time and space, a proper Dirichlet boundary condition (I_b) must be imposed to solve equation (2.18). To that end, assume that the single pulse energy is E_p . Then the power P of a single pulse can be expressed as a function of time as

$$P = \frac{E_p}{\sqrt{2\pi}\tau_\sigma} \cdot \exp \left[-\frac{(t - 2\tau_\sigma)^2}{2\tau_\sigma^2} \right], \quad (2.19)$$

where $\tau_\sigma = \tau_p/2.355$ is the standard deviation, with τ_p the Full Duration at Half Maximum (FDHM) of the laser pulse (i.e. the pulse duration). The Gaussian intensity profile in space I_b is described as [5]

$$I_b = \frac{2P}{\pi\omega_0^2} \exp \left[-2 \frac{r^2}{\omega_0^2} \right], \quad (2.20)$$

where r is the radial coordinate in cylindrical coordinates and ω_0 is the radius of the laser spot on the surface of the material.

Finally, since the peak fluence F_0 is related to the pulse energy E_p as [6]

$$F_0 = 2E_p/\pi\omega_0^2, \quad (2.21)$$

I_b takes the final form of

$$I_b = 0.94 \cdot \frac{F_0}{\tau_p} (1 - R_f) \exp \left[-2 \frac{r^2}{\omega_0^2} \right] \exp \left[-2.77 \cdot \frac{(t - 2\tau_p)^2}{\tau_p^2} \right], \quad (2.22)$$

where R_f denotes the reflectivity of the material.

2.2.1.5 Reflectivity

The optical length L_{opt} ($= 1/\alpha$, also known as the optical penetration depth of light in an opaque material) of ZnO at the laser wavelength considered in this thesis for processing ZnO ($\lambda = 343$ nm) is more than two times smaller than the thickness of the film considered in this thesis, which is typically in the range of 200-1000 nm. It is then assumed that interference effects between the incident electromagnetic wave of the laser and the reflected wave at the interface of the glass substrate and the film do not occur.

The reflectivity of ZnO at normal incidence of the laser beam on the surface can then be simply expressed as

$$R_f = \frac{(n_a - n)^2}{(n_a + n)^2}, \quad (2.23)$$

where n_a and n are the refractive indexes of air and ZnO, respectively. Here, n denotes the real part of the complex refractive index $\tilde{n} = n + ik$, with k the extinction coefficient and i the imaginary number.

Next, equation (2.23) is to be expressed in known quantities of ZnO at a high excitation level, which will be discussed in the remainder of this subsection.

The complex refractive index $\tilde{n}$ and the complex dielectric function of a material $\epsilon = \epsilon_1 + i\epsilon_2$ are linked by the relations [7]

$$n = \sqrt{\frac{\sqrt{\epsilon_1^2 + \epsilon_2^2} + \epsilon_1}{2}} \quad (2.24)$$

and

$$k = \sqrt{\frac{\sqrt{\epsilon_1^2 + \epsilon_2^2} - \epsilon_1}{2}}. \quad (2.25)$$

Following the description given by Sokolowsky-Tinten and von der Linde [8], the complex dielectric function ϵ^* of a semiconductor at a high level of excitation, which is the case when a semiconductor is exposed to intense laser radiation, can be described by

$$\epsilon^* = \epsilon_g + \Delta\epsilon_{pop} + \Delta\epsilon_{bgs} + \Delta\epsilon_{fcr}, \quad (2.26)$$

where $\epsilon_g = \epsilon_{g1} + i\epsilon_{g2}$ is the dielectric constant of the unexcited material at the laser wavelength. Here, ϵ_{g1} and ϵ_{g2} can be deduced by equations (2.24) and (2.25), knowing the linear absorption coefficient α and the reflectivity R_{f0} of the unexcited material. In fact, $k = \alpha \cdot \lambda / 4\pi$ while n can be expressed as function of R_{f0} inverting equation (2.23).

Further, $\Delta\epsilon_{pop}$, $\Delta\epsilon_{bgs}$ and $\Delta\epsilon_{fcr}$ represent the changes of the dielectric constant due to state and band filling, renormalization of the band structure, and the free-carrier response, respectively [8]. Sokolowsky-Tinten and von der Linde showed that the dielectric function of an optically excited semiconductor can be generally expressed as [8]

$$\epsilon^*(\hbar\omega) = 1 + [\tilde{\epsilon}_g(\hbar\omega + \Delta E_g) - 1] \cdot \frac{N_v - n}{N_v} - \frac{n \cdot e^2}{\epsilon_0 \cdot m_{eff} \cdot \omega} \cdot \frac{1}{1 + i \cdot \frac{1}{\omega\tau_D}}, \quad (2.27)$$

where $\tilde{\epsilon}_g(\hbar\omega)$ is the complex dielectric constant of the unexcited material, N_v , n , m_{eff} , ω , τ_D and ϵ_0 represent the valence band electron density, the carrier density, the effective mass of the carriers, the frequency of the laser wavelength, the Drude damping time and the dielectric constant in vacuum, respectively.

Taking the expression of the plasma frequency

$$\omega_p = \sqrt{\frac{n \cdot e^2}{\epsilon_0 \cdot m_{eff}}} \quad (2.28)$$

and assuming the effect of the band gap for the pulse intensities under consideration negligible [9], yields

$$\tilde{\epsilon}_g(\hbar\omega + \Delta E_g) = \tilde{\epsilon}_g(\hbar\omega), \quad (2.29)$$

and equation (2.27) can be rewritten in the convenient form $\tilde{\epsilon}(\hbar\omega) = \epsilon_1 + i\epsilon_2$, where

$$\epsilon_1 = 1 + (\epsilon_{g1} - 1) \cdot \frac{N_v - n}{N_v} - \frac{\omega_p^2}{\omega^2} \cdot \frac{1}{1 + \frac{1}{\omega^2 \tau_D^2}} \quad (2.30)$$

and

$$\epsilon_2 = \frac{\omega_p^2}{\omega^2} \cdot \frac{1}{\omega \tau_D + \frac{1}{\omega \tau_D}} + \epsilon_{g2} \cdot \frac{N_v - n}{N_v}. \quad (2.31)$$

Finally, substituting equation (2.30) and (2.31) into (2.24) and the latter into (2.23), the reflectivity of ZnO at high excitation is obtained.

2.2.1.6 Geometry

In order to reduce the computational load of the numerical model, the set of equations (2.2), (2.13), (2.16) and (2.18) was solved on a 2D-axis-symmetric geometry, the symmetry axis being the optical axis of the laser beam, see figure 2.1. Since the glass is a dielectric, the electronic conduction of heat in the substrate is considered to be negligible. Furthermore, the laser intensity is totally absorbed in the thin film layer. Hence, equations (2.2), (2.13) and (2.18) are only solved on the thin film layer, and a zero flux condition was applied at the film-glass interface in equation (2.13). Only equation (2.16) is solved both on the film and the glass domain.

Since irradiation losses are assumed to be negligible, a zero flux condition was chosen for equation (2.13) as well as for (2.16), at the top surface of the film. Further, regarding equations (2.13) and (2.16), natural boundary conditions were also imposed on the lateral surface of the cylinder and at the bottom of the glass substrate, considering that the boundaries are sufficiently far from the zone of interest. Alternatively, Dirichlet boundary conditions were applied, to verify the indifference of the results to the type of boundary conditions applied on the far boundaries. Similarly, natural boundary conditions were imposed on all boundaries

Figure 2.1: Sketch of the simulated geometry in the cylindrical coordinates r and z . The slab of material rotates around the z axis (optical axis of the laser beam). The dimensions in r and z of the slab are taken large enough to avoid errors in the computational results. The laser beam impinges the film (thickness t_f) from the top.

to solve equation (2.2).

To increase the computation speed, a coarser meshing was used in the glass than in the film. For the same reason, an increasingly coarser grid was used in the glass going towards the bottom. The grid size was reduced until convergence of final results was obtained.

The time stepping was adapted automatically by the numerical solver (of the Multiphysics Comsol[®] software) at every time-step to ensure convergence of the solutions.

2.2.2 Metals

A model that describes the laser absorption and heat propagation in metals is obtained, by simplifying the model derived for the semiconductors in section 2.2.1. This approach arises from the physical description of metals [24]. That is, for metals, the Fermi energy does not lie in the band gap, but lies within the conduction band. Therefore the band gap does not exist and the density of free carriers is considered to be constant. By considering that $E_g = 0$, $\nabla n_c = 0$ and $\frac{\partial n_c}{\partial t} = 0$, the set of equations (2.2), (2.13), (2.16) and (2.18) will reduce to a set of three equations, i.e. equations (2.32), (2.33) and (2.35). That is, equation (2.13) reads

$$C_e \frac{\partial T_e}{\partial t} = \nabla \cdot (k_e \nabla T_e) - \Gamma (T_e - T_l) + S. \quad (2.32)$$

While equation (2.16) remains unchanged

$$C_l \frac{\partial T_l}{\partial t} = \nabla \cdot (k_l \nabla T_l) + \Gamma (T_e - T_l). \quad (2.33)$$

For metals, the electron volumetric heat capacity C_e is usually described as being proportional to T_e [22], and takes the form $C_e = A_e \cdot T_e$.

The bulk thermal conductivity of metals measured at equilibrium (i.e. $T_e = T_l$), k_{eq} , is the sum of electron thermal conductivity, k_e , and the lattice thermal conductivity, k_l . Since diffusion of free electrons is the main mechanism for heat conduction in metals, k_e is dominant, accounting for about 99 % of the total thermal heat conductivity [21]. Therefore, the value $k_l = k_{eq}/100$ was set in the model [21]. Moreover, at non-equilibrium conditions (that is when T_e and T_l differ significantly), the electronic heat conductivity k_e is proportional to the ratio between T_e and T_l [26]. Hence, the electronic thermal conductivity is expressed as

$$k_e = \frac{99}{100} k_{eq} \cdot \left(\frac{T_e}{T_l} \right). \quad (2.34)$$

Since the absorption is linear for metals, the source term of equation (2.32) becomes $S = \alpha \cdot I$, and equation (2.18) reduces to

$$\frac{\partial I}{\partial z} = \alpha \cdot I, \quad (2.35)$$

which is solved with the same boundary conditions as equation (2.18). Here, the absorption coefficient α and the reflectivity R_f are constant [23]. So the Lambert-Beer solution is obtained $I = I_0 \cdot e^{(\alpha \cdot z)}$.

2.3 Results

In this section simulation results will be presented and discussed. First, in section 2.3.1, the results of simulations of ZnO thin films will be shown. Then, in section 2.3.2, the results of simulations of Mo thin films will be shown.

2.3.1 Zinc oxide

Simulations were run for two different laser pulse durations, i.e. 10 ps and 10 ns. The latter were chosen to represent two typical pulse durations for OEM laser sources in the ultra-short and so-called ns range (i.e. between 1 ns and hundreds of ns), respectively.

In both cases, the fluence was set in order to reach the same surface lattice temperature of the film (about 1000 K) in the center of the laser spot. The laser spot diameter D ($= 2 \cdot \omega_0$) was initially set to 15 μm , in order to simulate a tightly focused laser beam on the surface, and the film thickness t_f equals 500 nm, which is an average value for the common thickness of ZnO films for PV applications (200-1000 nm).

Figures 2 and 3 show the calculated electron and lattice temperatures, for the two

pulse durations, as a function of time at different positions along the optical axis ($r = 0$). The electron temperature T_e is shown at the top surface ($z = 0$) of the film, while three curves of the lattice temperature T_l are shown at different positions, i.e. top surface ($z = 0$), at a depth of 100 nm ($z = -100$ nm) and at the ZnO/glass interface ($z = -t_f$). As can be concluded from figures 2.2 and 2.3, the maximum lattice temperature T_l at the surface is about 1000 K (as targeted) for both pulse durations, while different maximum lattice temperatures are reached in the other locations for the two pulse durations. For the 10 ps laser pulse, a maximum lattice temperature of 580 K and 410 K are calculated, at locations $z = -100$ nm and $z = -t_f$, respectively. For the pulse of 10 ns, at the same locations, the lattice temperatures are as high as 945 and 700 K. Hence, the lower temperatures in the ps pulse duration reveal a higher thermal selectivity, confining high temperatures more in the top section of the film.

Also different timescales are revealed by the two simulations of the two pulse durations. The time period τ^* during which the material is above a pre-defined temperature provides an objective measure for timescales.

Taking a temperature of 500 K as a reference, the lattice temperature T_l can be compared at $z = 0$, as well as at $z = -100$ nm, for both simulations. At the two locations, τ^* equals ~ 5 ns (coincident for the two locations) for the pulse duration of 10 ps and $\sim 0.55 \mu\text{s}$ (coincident for the two locations) for the 10 ns pulse.

To compare τ^* at the film/substrate interface ($z = -t_f$), the reference for the temperature is set at 400 K, since, as previously shown, the maximum lattice temperature reaches 410 K at $z = -t_f$ for the 10 ps pulse duration. For the 10 ps pulse $\tau^* \sim 50$ ns, while for the 10 ns pulse $\tau^* \sim 1.5 \mu\text{s}$.

Finally, the time needed by the sample to return below 300 K is about $6 \mu\text{s}$ for the 10 ps pulse and $80 \mu\text{s}$ for the 10 ns pulse. Hence, very different time cycles are achieved with the two different pulse durations. The latter can in principle lead to new properties of a material when treated by shorter pulses during processing (i.e. ultra-fast annealing).

Figure 2.4 shows the effect of a laser spot with a larger diameter of $50 \mu\text{m}$ (instead of $15 \mu\text{m}$) on the temperatures of the material. The parameters used for this simulation are the same as those used to generate figure 2.2. On one hand, when comparing figure 2.4 to figure 2.2, it can be concluded that the differences in the maximum temperatures reached at the various locations are very small, if not negligible. On the other hand, the cooling time after which the initial room temperature is reached again differs in figure 2.2 when compared to figure 2.4. The latter is due to the fact that the heat flux is more constrained towards the axial direction while its radial component is suppressed when the ratio D/t_f increases. Hence, the simulations show the possibility, without affecting the thermal selectivity, to increase the spot size. The latter can be adopted to speed up the processing velocity, when a higher throughput is needed.

However, it is also clear that when increasing the diameter of the laser spot, it is important to select an appropriate repetition frequency and fluence level in order to achieve the same temperatures in the film. A correct combination of the latter

Figure 2.2: Simulated electron and lattice temperatures of ZnO thin film on glass, irradiated at 10 ps and $F_0=0.028 \text{ J}\cdot\text{cm}^{-2}$ and $15 \mu\text{m}$ focus diameter. T_e is probed at the film surface in the center of the laser spot ($z = 0$), while T_l is probed at three positions in the beam center, i.e. $z = 0$ (surface), $z = -100 \text{ nm}$ and $z = -t_f$.

parameters will control the heat accumulation in a range that prevents thermal damage of the film. Thermal damage occurring as a result of beam expansion can be avoided by selecting a lower fluence or, in some cases, also by a lower repetition rate.

2.3.2 Molybdenum

For simulations of Mo films, the laser spot diameter D was again initially set to $15 \mu\text{m}$ and the film thickness t_f to 400 nm , which resembles a typical thickness of Mo films used for PV applications. The other parameters were chosen such that different pulse durations reach a surface lattice temperature T_l equal to the melting temperature, since this is the highest temperature reachable in solid state. Figures 2.5 and 2.6 show the simulated temperatures for pulse durations of 10 ps and 10 ns respectively.

Comparing the calculated temperatures shown in figure 2.5 and figure 2.6, a striking difference between the two pulse durations can be noticed.

Figure 2.3: Simulated electron and lattice temperatures of ZnO thin film on glass, irradiated at 10 ns and $F_0=0.106 \text{ J}\cdot\text{cm}^{-2}$ and $15 \mu\text{m}$ focus diameter. T_e is probed at the film surface in the center of the laser spot ($z = 0$), while T_l is probed at three positions in the beam center, i.e. $z = 0$ (surface), $z = -100 \text{ nm}$ and $z = -t_f$.

Whereas for the 10 ps pulse, the material reaches a maximum lattice temperature T_l of 1190 and 770 K at $z = -100 \text{ nm}$ and at $z = -t_f$ respectively, for the 10 ns pulse, the material reaches about the same temperature as the surface, i.e. $T_m \approx 2896 \text{ K}$ at both locations.

Hence, for metallic films, where the thermal conductivity is higher and the optical absorption length is shorter, when compared to ZnO, the thermal selectivity is greatly enhanced in the case of ps pulses.

Remarkably, while a pulse duration of 10 ps, at the top surface of the Mo film reaches $T_l = T_m$ with $F_0 = 0.135 \text{ J}\cdot\text{cm}^{-2}$, for the 10 ns pulse the same temperature is only reached at a much higher fluence level of $F_0 = 0.84 \text{ J}\cdot\text{cm}^{-2}$. The latter also implies that the energy per pulse increases from $0.12 \mu\text{J}$ to $0.74 \mu\text{J}$, raising therefore the total absorbed energy by the film of about 6 times. The higher energy compensates for the effect of the high thermal conduction of a metallic film at longer pulse durations, with the final effect of an increased heating of the whole layer. Therefore, surface processing with ultra-short laser pulses can generally reduce the

Figure 2.4: Simulated electron and lattice temperatures of ZnO thin film on glass, irradiated at 10 ps and $F_0=0.028 \text{ J}\cdot\text{cm}^{-2}$ and $50 \mu\text{m}$ focus diameter. T_e is probed at the film surface in the center of the laser spot ($z = 0$), while T_l is probed at three positions in the beam center, i.e. $z = 0$ (surface), $z = -100 \text{ nm}$ and $z = -t_f$.

effect of excessive heat injection on delicate substrates or, in principle, multi-layered structures.

Regarding the timescales, a further comparison can be made between figures 2.5 and 2.6. Again, the comparison is made using the time period τ^* that the material is over a pre-defined temperature for the different simulations.

Taking as a reference 1000 K, T_l is comparable at $z = 0$ as well as at $z = -100 \text{ nm}$. At the two locations, τ^* equals 0.6 ns and 0.5 ns for the pulse duration of 10 ps and $0.4 \mu\text{s}$ (coincident for the two locations) for the 10 ns pulse.

To compare τ^* at the film/substrate interface ($z = -t_f$), the reference for the temperature was set at 500 K. For the 10 ps pulse $\tau^* = 0.14 \mu\text{s}$, while for the 10 ns pulse $\tau^* = 1.4 \mu\text{s}$.

Moreover, the time needed by the sample to return below 300 K is in the order of $3 \mu\text{s}$, for the 10 ps pulse, and about $40 \mu\text{s}$, for the 10 ns pulse. From these results, a clear difference in the material response time is predicted. Interestingly, a combination of high thermal selectivity and a shorter timescale for cooling can

Figure 2.5: Simulated electron and lattice temperatures of Mo thin film on glass, irradiated at 10 ps and $F_0=0.135 \text{ J}\cdot\text{cm}^{-2}$ and $15 \mu\text{m}$ focus diameter. T_e is probed at the film surface in the center of the laser spot ($z = 0$), while T_l is probed at three positions in the beam center, i.e. $z = 0$ (surface), $z = -100 \text{ nm}$ and $z = -t_f$.

”freeze” the flow of molten material just after the pulse, allowing for metastable morphologies to form. This combination is of particular interest for superficial treatments on thin films (e.g. surface texturing or cleaning).

Figure 2.7 shows the effect of a larger laser spot diameter of $50 \mu\text{m}$, with the same set of parameters used for the simulation shown in figure 2.5. Similar to what was observed for the ZnO computations, while the maximum T_l at the same locations are very close, slightly different cooling times are observable. Again, a correct choice of the laser process parameters will control the heat accumulation in order to prevent thermal damage of the film.

2.4 Conclusions

Two models were devised in this paper, one for semiconductors and one for metals, which were adopted to simulate the interaction of different laser pulses with ZnO

Figure 2.6: Simulated electron and lattice temperatures of Mo thin film on glass, irradiated at 10 ns and $F_0=0.84 \text{ J}\cdot\text{cm}^{-2}$ and $15 \mu\text{m}$ focus diameter. T_e is probed at the film surface in the center of the laser spot ($z = 0$), while T_l is probed at three positions in the beam center, i.e. $z = 0$ (surface), $z = -100 \text{ nm}$ and $z = -t_f$.

and Mo thin films, respectively. These models include physical phenomena, such as absorption, photo-generation and recombination of carriers, non-equilibrium between lattice and electron temperatures using a TTM approach and the relative transport phenomena. Using these two models, simulations were run for two different pulse durations, i.e. 10 ps and 10 ns, and the obtained results were presented and discussed.

The results of these simulations showed that mainly three parameters affect the thermal selectivity for a film of fixed thickness, i.e. the absorption length of the material at the laser wavelength, the thermal conductivity of the material and the pulse duration.

For the materials studied, given the fixed laser wavelength, the choice of a shorter pulse duration implies an increased thermal selectivity. That is, the ultra-short pulses can reach the same temperature at the surface of the targeted material, but inducing a much lower temperature within the rest of the film, as well as at the film-substrate interface, when compared to the ns pulses.

Figure 2.7: Simulated electron and lattice temperatures of Mo thin film on glass, irradiated at 10 ps and $F_0=0.135 \text{ J}\cdot\text{cm}^{-2}$ and $50 \mu\text{m}$ focus diameter. T_e is probed at the film surface in the center of the laser spot ($z = 0$), while T_l is probed at three positions in the beam center, i.e. $z = 0$ (surface), $z = -100 \text{ nm}$ and $z = -t_f$.

Taking as a reference a point at the center of the laser beam at a depth of 100 nm below the top surface, the maximum temperatures reached simulating the nanosecond pulses were almost indistinguishable from the maximum temperatures reached at the top surface, for both ZnO and Mo. At the same location, when simulating the effect of picosecond pulses, the maximum temperature for ZnO and Mo was about one third and half of the relative maximum temperatures reached at the surface, respectively.

It was also shown that a shorter pulse duration not only increases the thermal selectivity but also has an impact of about three orders of magnitude on the duration of the thermal cycle, when comparing simulations of nanosecond with picosecond pulses.

The energy per pulse needed to reach a pre-defined temperature at the surface is reduced with a factor four to six when processing with ultra short pulses, compared to ns pulses. The latter can have a positive impact when processing thin films on thermally sensitive substrates or multi-layered structures.

Finally, it was pointed out that an increase of the laser spot diameter does not affect the thermal selectivity of the process, but must only be balanced by an appropriate choice of the fluence and repetition rate of the laser. The latter result shows that the process speed is not constrained by the dimension of the spot diameter, but by the available average laser power. As a result, large areas can be processed in relatively short processing times.

2.5 Validation and link to the following chapters

Due to the unavailability of all exact material properties, as already hinted, the two models devised are not simulating the particular experimental conditions of chapters 5 and 6 for Al:ZnO and Mo films, respectively.

However few remarks help to understand the overall agreement between the simulation results in this chapter with the experimental observations in the following chapters.

The validation of the ZnO model is first described.

Initially, each material, as well as laser parameter, was singularly varied over a wide range and simulations were run to see their impact on the final results. This helps to obtain knowledge of the most critical parameters within the fluence range under consideration.

Then, a simple experimental test was performed on the Al:ZnO samples used in chapter 5 to measure nonlinear optical effects, within the adopted fluence range. The latter was simply performed by measuring the power of the transmitted and reflected (under a low incidence angle) laser beam as function of the initial laser power. It was found that the influence of any nonlinear optical effect on the absorption and reflectivity was negligible (affecting less than 5% of the total). The latter was in good agreement with the simulations.

This finding allowed to consider the model originally devised for intrinsic ZnO also valid ZnO which is heavily doped with Al, under the experimental irradiation conditions of chapter 5.

Following, simulations were run choosing the measured optical properties of the samples (i.e. linear absorption coefficient α and reflectivity R_f), the thickness and adopted laser fluence.

Two indirect but very important indications could be concluded by the comparison of the simulation results with the experiments presented in chapter 5.

Firstly, the temperature was found to be in the expected range for the annealing (800-1500 K). Moreover, direct inspection by microscopy showed no occurrence of melting at the surface, as predicted by the simulations.

Secondly, the predicted timescales were in strong agreement with the experimentally observed diffusion lengths of laser induced defects as well as atomic species within the films.

These two indications are an experimental proof of the validity of this model, regarding the expected maximum temperatures and timescales involved in the

process.

Regarding the results for Mo thin films, a first validation was obtained by comparison of the simulation results with reference [23]. However, since reflectivity and absorption coefficient are related to the surface quality of the material, deviations from the experimental results can be related to the specific sample under examination.[‡] Oxidation, roughness and presence of subsurface defects, can have a strong influence on the optical properties of the metallic films. The latter will have an impact on the threshold fluence level to obtain a certain temperature (i.e. the melting temperature).

However, a different choice of these parameters, will not affect the qualitative results obtained by the simulations, i.e. order of magnitude of the response cycle time of the material and of the fluence needed to reach a certain temperature.

Unfortunately, no test were performed using a ns-pulsed laser for both materials under investigation. However, if the results are in the correct range for ultra-short pulse durations, a closer agreement is expected for longer pulse durations, where all non-linear material related phenomena become negligible.

[‡]The reader will also notice that the definition of fluence in chapter 6 will differ from the previous chapters, being F_0 the average fluence instead of the peak fluence.

Table 2.1: List of symbols.

Quantity	Symbol	value	Units
Dielectric constant in vacuum	ϵ_0	$8.854 \cdot 10^{-12}$	F m ⁻¹
Boltzmann constant	k_b	$1.38 \cdot 10^{-23}$	kg m ² s ⁻² K ⁻¹
Planck constant	h	$6.626 \cdot 10^{-34}$	m ² kg s ⁻¹
Reduced Planck constant	$\hbar$	$h/2\pi$	m ² kg s ⁻¹
Frequency of laser light	ν	$8.74 \cdot 10^{14}$	Hz
Angular frequency of laser light	ω	$\nu/2\pi$	Hz
Electron mass	m_e	$9.1 \cdot 10^{-31}$	kg
Electron charge	e	$1.6 \cdot 10^{-19}$	C
Optical penetration length	L_{opt}	$1/\alpha$	cm
Laser peak fluence	F_0		J cm ⁻²
Electron temperature	T_e		K
Lattice temperature	T_l		K
Laser intensity	I		W cm ⁻² s ⁻¹
Boundary condition for I	I_b		W cm ⁻² s ⁻¹
Electron-hole pairs density	n_c		cm ⁻³
Electron density	n_e		cm ⁻³
Hole density	n_e		cm ⁻³
Hole-pairs current density	$\vec{j}$		C s ⁻¹ cm ⁻²
Electron current density	$\vec{j}_e$		C s ⁻¹ cm ⁻²
Hole current density	$\vec{j}_h$		C s ⁻¹ cm ⁻²
Generation term for carriers	G		cm ⁻³ s ⁻¹
Recombination term for carriers	R		cm ⁻³ s ⁻¹
Energy density of the electron system	U		J cm ⁻³
Ambipolar energy current vector	$\vec{W}$		W cm ⁻²
Source term	S		W cm ⁻³
Real part of the refractive index	n		
Complex refractive index	$\tilde{n}$		
Real part of the dielectric function	ϵ_1		
Imaginary part of the dielectric function	ϵ_2		
Dielectric function	ϵ		
Imaginary number	i		
Pulse duration	τ_p		s
Lattice heat flux	$\vec{q}_l$		W cm ⁻³
Standard deviation	τ_σ		
Radial coordinate	r		cm
Axial coordinate	z		cm
Time	t		s
Spot radius	ω_0		cm
Spot diameter	D		cm
Pulse energy	E_p		J
Laser power	P		W

Table 2.2: Values of the parameters used in the numerical simulations of ZnO.

Quantity	Symbol	Value/expression	Units	Ref.
Effective Electron mass	m^*	$0.22 \cdot m_e$	kg	11
Electron heat capacity	C_e	$3k_b n_c / 2$	$\text{J m}^{-3} \text{K}^{-1}$	2
Electron heat conductivity	k_e	$\pi^2 n_c k_b^2 T_e \mu_e / 3e$	$\text{W m}^{-1} \text{K}^{-1}$	10
Lattice heat capacity	C_l	3422100	$\text{J m}^{-3} \text{K}^{-1}$	12
Lattice heat conductivity	k_l	$3 \cdot 10^{-11} \cdot T_l^4$ $-1 \cdot 10^{-7} \cdot T_l^3$ $+3 \cdot 10^{-4} \cdot T_l^2$ $-0.2239 \cdot T_l$ $+82.692$	$\text{W m}^{-1} \text{K}^{-1}$	13
El.-phonon collision time	τ_{ep}	$5 \cdot 10^{-13}$	s	14
El.-phonon coupling factor	Γ	C_e / τ_{ep}	$\text{W m}^{-3} \text{K}^{-1}$	2
Melting temperature	T_m	1975	K	15
Ambipolar diff. coeff.	D_0	1.4	$\text{cm}^2 \text{s}^{-1}$	16
Linear abs. coeff.	α	10^5	cm^{-1}	
Extinction coefficient	k	$\alpha \lambda / 4\pi$		
Two-photon abs. coeff.	β	10^{10}	W cm^{-1}	17
Free carrier abs. coeff.	θ	$5 \cdot 10^{-18}$	cm^2	18
Impact ionization coeff.	δ	10^5	s^{-1}	19
S.R.H. rec. coeff.	γ_{srh}	$10^{12} / 210$	s^{-1}	20
Radiative rec. coeff.	γ_{rad}	$3.2 \cdot 10^{-11}$	$\text{cm}^3 \text{s}^{-1}$	20
Auger rec. coeff.	γ_{aug}	10^{-34}	$\text{cm}^6 \text{s}^{-1}$	11
Constant	n_0	$6 \cdot 10^{18}$	cm^{-3}	20
Band gap at $T = 0$	$E_g(0)$	3.5	eV	4
Constant	a	$2 \cdot 10^{-4}$	eV K^{-1}	4
Constant	b	325	K	4
Valence band electron density	N_v	$8.32 \cdot 10^{22}$	cm^{-3}	9
Drude damping time	τ_D	10^{-14}	s	9
Refractive index of air	n_a	1		

Table 2.3: Values of the parameters used in the numerical simulations of Mo.

Quantity	Symbol	Value/expression	Units	Ref.
Constant for el. heat capacity	A_e	350	$\text{J m}^{-3} \text{K}^{-2}$	22
Equilibrium heat conductivity	k_{eq}	135	$\text{W m}^{-1} \text{K}^{-1}$	22
Lattice heat capacity	C_l	$2.8 \cdot 10^6$	$\text{J m}^{-3} \text{K}^{-1}$	22
Melting temperature	T_m	2896	K	22
El.-phonon coupling	Γ	$13 \cdot 10^{16}$	$\text{W m}^{-3} \text{K}^{-1}$	22
Optical absorption coefficient	α	$1.189 \cdot 10^6$	cm^{-1}	25
Reflectivity	R_f	0.54		25

Table 2.4: Values of the parameters used in the numerical simulations for the glass substrate.

Quantity	Symbol	Value/expression	Units	Ref.
Heat conductivity	k_{eq}	1.2	$\text{W m}^{-1} \text{K}^{-1}$	22
Heat capacity	C_l	$2.8 \cdot 10^6$	$\text{J m}^{-3} \text{K}^{-1}$	
Optical absorption coefficient	α	0	cm^{-1}	

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Chapter 3

3

Optical and electrical properties of SnO₂ thin films after ultra-short pulsed laser annealing

Abstract

Ultra-short pulsed laser sources, with pulse durations in the ps and fs regime, are commonly exploited for cold ablation. However, operating ultra-short pulsed laser sources at fluence levels well below the ablation threshold allows for fast and selective thermal processing. The latter is especially advantageous for the processing of thin films. A precise control of the heat affected zone, as small as tens of nanometers, depending on the material and laser conditions, can be achieved. It enables the treatment of the upper section of thin films with negligible effects on the bulk of the film and no thermal damage of sensitive substrates below. By applying picosecond laser pulses, the optical and electrical properties of 900 nm thick SnO₂ films, grown by an industrial CVD process on borofloat[®]-glass, were modified. The treated films showed a higher transmittance of light in the visible and near infra-red range, as well as a slightly increased electrical sheet resistance. Changes in optical properties are attributed to thermal annealing, as well as to the occurrence of Laser- Induced Periodic Surface Structures (LIPSSs) superimposed on the surface of the SnO₂ film. The small increase of electrical resistance is attributed to the generation of laser induced defects introduced during the fast heating-quenching cycle of the film. These results can be used to further improve the performance of SnO₂-based electrodes for solar cells and/or electronic devices.

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3.1 Introduction

Tin-dioxide (SnO_2), also known as stannic oxide, is a widely used and studied ceramic material [1]. Stoichiometric SnO_2 is an insulator, while shallow doping (i.e. with F or Sb) or small shifts from its perfect stoichiometry (i.e. SnO_{2-x} , with $x < 1$) associated with oxygen vacancies, lead to n -type semi-conductive behavior of the material. For this reason, optimized SnO_2 is grouped with a category of materials that combines high electrical conductivity with optical transparency. Such materials are usually referred to as Transparent Conductive Oxides (TCOs). They constitute an important component for opto-electronic devices [2].

Due to their low fabrication cost, SnO_2 thin films find application in different areas, including: glass coatings for thermal insulation, oxidation catalysts, gas sensor materials, flat panel displays, touch panels, flexible electronics, dye-sensitized solar cells (DSSC), thin film $a-Si$ solar cells, light-emitting diodes (LEDs), etc. [2].

Strong interest for TCO materials led recent research to investigate the effects of post-deposition annealing by nanosecond (ns) pulsed lasers on the optical and electrical properties of different TCOs [3-10]. The use of rapid thermal laser annealing, as an alternative process to conventional furnace annealing, is a cost effective solution. It also reduces thermal damage on thermally sensitive low cost substrates (i.e. with low melting points) [3].

A next step in this research is the investigation of (thermal) effects of ultra-short pulsed lasers on the optical and electrical properties of TCOs. Compared to ns-pulses, ultra-short laser pulses in the pico- and femtosecond regime, can induce the same high surface temperatures of the film, but at a significantly lower energy input. This is advantageous for thin film processing where a precise control of the heat affected zone is necessary.

The present research aims to investigate the effects of picosecond laser irradiation on the optical and electrical properties of industrially optimized thin SnO_2 films.

3.2 Experimental setup

3.2.1 laser setup

An Yb:YAG (TruMicro 5050 of Trumpf) laser source was used. This laser source is characterized by a fixed pulse duration of 6.7 ps, 50 W maximum power output (P_{out}) at a central wavelength of 1030 nm (IR) and maximum pulse repetition frequency (f_p) of 400 kHz. The laser radiation was linearly polarized. The power density profile shows a nearly Gaussian distribution, $M^2 < 1.3$. The source is equipped with a pulse-picker, allowing the user to change the repetition frequency without affecting the energy per pulse. A Third Harmonic Generation (THG) unit was employed to convert the central wavelength to 343 nm (UV).

The diameter d of the focused laser beam on the surface was determined using the D^2 method [4] and was found to be 17 μm . Given the spot diameter d , the peak laser fluence F_0 -here defined as: $F_0 = (8E_0)/(\pi \times d^2)$, where E_0 is the pulse energy

was then calculated for single pulses. We also define the term overlap (OL) as the spatial overlap ratio of the laser spots of successive pulses as $OL = 1 - v(d \times f_p)$, where v (m/s) denotes the velocity of the laser spot relative to the substrate, and f_p (Hz) the repetition frequency of the laser source. Note that, for increasing velocity, OL goes to zero, or will even become negative, indicating no spatial overlap between subsequent laser pulses on the surface.

A galvano-scanner (IntelliScan14 of Scanlab) was used to scan the focal spot at defined velocities (v) over the surface of the samples. A telecentric F-theta lens (Ronar of Linos) with 100 mm focal length was used to focus the laser beam. A polarizer ($\lambda/2$ plate) was used to rotate the linear polarization direction of the laser in order to study the effect of the polarization direction on the laser-induced surface modifications.

3.2.2 Analysis tools

Morphological inspection of surfaces was performed by High-Resolution Scanning Electron Microscopy (HRSEM, Merlin of Zeiss, equipped with X-Max detector of Oxford Instruments), as well as Atomic Force Microscopy (AFM, VEECO Dimension 3100 Atomic Force Microscope). Spectroscopic techniques were employed to determine the thickness (spectroscopic ellipsometry, using a variable angle rotating compensator spectroscopic ellipsometer M2000X from J.A. Woollam Co., with Xe arc discharge lamp as light source and light spot size ~ 2 mm) of the SnO_2 layers and their composition (Raman spectroscopy, home built apparatus described elsewhere [18]) before and after laser processing.

The optical properties (transmittance, reflectance and haze in transmittance) of the samples were measured in the near-ultraviolet, visible and near-infrared, by a UV-3600 Shimadzu spectrophotometer equipped with an integrating sphere. The electrical properties were determined by using a Jandel universal 4-point probe and, finally, X-Ray Diffraction (XRD) (XPert, Panalytical equipped with a $\text{Co-K}\alpha$ source), was used to determine changes of the grain size and lattice structure after laser processing.

3.2.3 Samples

SnO_2 coatings of 900 nm thickness deposited by chemical vapor deposition (CVD) on 1 mm thick borofloat-glass were used. The latter combination of thin SnO_2 layers on glass is meant for the production of $a - \text{Si}$ thin film solar cells. Deposition of the samples was performed at TNO in the Netherlands using an industrial process [21].

3.3 Results and discussion

3.3.1 Experimental procedure

The experimental procedure consisted of three steps. During the first step, laser lines were created by scanning the focal spot over the sample. Lines with varying pulse-to-pulse overlap (OL), number of overscans (OS) and fluence levels were produced. During these experiments the repetition frequency f_p was fixed at 100 kHz. After initial SEM analysis, to find laser conditions for damage-free (crack-free and no ablation) layers, we iterated this step by choosing finer variation of the processing parameters (OL , OS and fluence). The third and final step of the experimental procedure consisted of choosing one set of processing parameters from the second step to create areas composed of several parallel overlapping laser lines. Here the pitch (distance) between parallel lines was varied in order to obtain samples free of thermal damage.

Finally, three samples were selected for further analysis, namely:

- As-deposited SnO_2 , without laser treatment applied;
- Low fluence regime ($F_0 = 0.17 \text{ J/cm}^2$, 1 OS , $OL = 98.7\%$, $pitch = 3 \mu\text{m}$);
- High fluence regime ($F_0 = 0.26 \text{ J/cm}^2$, 1 OS , $OL = 98.7\%$, $pitch = 3 \mu\text{m}$).

These two laser processed samples were chosen based on their initial enhanced transparency by a first naked eye inspection.

3.3.2 Surface morphology, optical properties and electrical properties

3.3.2.1 Surface morphology

The surface morphology of the as-deposited sample is characterized by relatively big and sharp crystals, as is depicted in Fig. 3.1(a) and Fig. 3.2(a). These crystals show low electric resistance and scatter light in the $NIR - VIS - UV$ range. The latter enhances the so-called light trapping mechanism, as is required in thin film solar cells in order to enhance the short circuit current (I_{ss}). A similar morphology was observed in the sample processed at low laser fluence (Fig. 3.1 (b)). Here, only small dissimilarities were observed between the as-deposited material and the laser treated sample. Only small cuts on the edges of the crystals, as shown in Fig. 3.1(d), were observed. In the case of the sample treated at high(er) laser fluence, a remarkable difference was observed. Here, small oriented nano-ripples were induced by the laser-material interaction (Fig. 3.1 (c) and (e)). These wavy structures, with amplitudes and periodicity Λ in the nanometer regime, are usually referred to as Laser Induced Periodic Surface Structures (LIPSSs) [11]. In particular, the LIPSSs observed in the sample are ascribed to a particular type, usually referred to as High Spatial Frequency LIPSSs (HSFLs) [16]. HSFLs are ripples with a spatial periodicity Λ significantly smaller than the wavelength of the laser radiation λ .

Figure 3.1: HRSEM pictures of the three samples: (a) as-deposited (bar = 1 μm), (b) laser processed at low fluence (bar = 1 μm), (c) laser processed at high fluence (bar = 1 μm). Laser processing conditions as listed in section 3.3.1. (d) Detail of the small cuts visible at the edges of the crystals in the samples treated at low fluence (bar = 100 nm). (e) Enlarged view of the observed nanostructures (ripples) on the surface of the high fluence sample (bar = 200 nm).

Figure 3.2: AFM height measurements of the three samples: (a) as deposited, (b) low fluence, (c) high fluence. The gray scale (fixed from 0 to 500 nm) shows the height of the different morphologies. The dimension of the analyzed area was $3 \times 3 \mu\text{m}^2$. R_a values measured for (a) and (b) are 37 nm and for (c) 42 nm.

Their periodicity can be as small as $\Lambda = 0.08\lambda$ [17]. HSFLs have been reported to be orthogonal [16] or parallel [17] to the laser beam polarization. Similar to our laser conditions, HSFLs have been observed mostly for laser pulse durations in the femtosecond and picosecond regime. Moreover, they are reported by researchers upon irradiation with hundreds to thousands of laser pulses per spot and at fluence levels typically below the single-pulse ablation threshold [13].

To ascertain that the observed nano-ripples are indeed LIPSSs, an experiment was carried out where the polarization of the laser radiation was varied. That is because it is known [12] that the orientation of LIPSSs depends on the polarization direction of the laser radiation. Using a $\lambda/2$ -plate the polarization was rotated. As is shown in Fig. 3.3, the orientation of the ripples follows the angle of the polarizer. This implies that the observed nano-ripples are indeed LIPSSs.

Further inspection of the surface morphologies was carried out by AFM measurements (see Fig. 3.2), revealing an increased roughness for the high fluence sample ($R_a = 42$ nm), when compared to the other two samples ($R_a = 37$ nm). To characterize the frequencies and periodicities of the surface morphology, a fast Fourier transform (FFT) of the HRSEM measurements was calculated (see Fig. 3.4) from the data (shown in Fig. 3.1 (a) and (b)). Fig. 3.4 shows that the nano-ripples are superimposed on the as-deposited surface morphology of the film, creating a double-scale roughness.

Figure 3.3: SEM images of nano-ripples, obtained at three different polarization directions of the laser radiation. The dashed arrow shows the scanning direction of the laser spot. The fixed solid black arrow shows the initial orientation of the LIPSSs. From left to right, the position of the polarizer was rotated from initial position (0°) to 36° and 72° respectively. As the polarization is rotated, the orientation of the ripples follows the polarization direction (white solid arrow).

Figure 3.4: Fast Fourier Transforms (FFT) of the as-deposited surface morphology (left) and of the high fluence sample (right), plotted in the K -space (normalized frequency domain). The ring in the as-deposited material shows spatial isotropy of the analyzed structures. In the right picture, the ring can still be observed, but its oriented and elongated lobes reveal an orientation of the LIPSSs, which are characterized by high spatial frequencies. It is known that the orientation of LIPSSs depends on the polarization direction of the laser radiation. It can be concluded from these images that the LIPSSs are superimposed on the original morphology of the material.

Figure 3.5: Measured transmittance (T), reflectance (R) and calculated absorption (A), with $A + T + R = 1$, of the glass substrate. Negligible absorption is displayed for wavelengths over 380 nm. For this reason, the transmittance (Fig. 3.6) and haze (Fig. 3.9) of the samples are only shown for wavelengths over 380 nm.

3.3.2.2 Optical properties

When compared to the as-deposited samples, both laser treated samples displayed an enhanced transparency in the wavelength range relevant to photovoltaic cells (i.e. $NIR - VIS - UV$), see Fig. 3.6. These samples also showed a decreased reflectance,

see Fig. 3.7.

Calculated linear absorption coefficients α from transmittance ($T = e^{-\alpha \cdot t}$, where t is the thickness of the layer), depicted in Fig. 3.8, show the effect of the laser treatment on the bulk optical properties of the layer. As expected after thermal annealing [3], SnO_2 becomes more transparent for wavelengths below 1100 nm. This points out that increased transmittance is not only the result of a reduced reflectance (due to morphological changes of the surface), but also the result of decreased absorptivity of the SnO_2 layer. Probably, also part of the decreased reflectance is due to changed bulk properties (i.e. reduced refractive index). Further analysis is ongoing, to confirm the latter.

Figure 3.6: (a): Transmittance of the three samples as function of the wavelength. Low transmittance in the long wavelength region over 1500 nm is expected due to strong absorption near the plasma frequency ω_p of SnO_2 . An increase of the transmittance of the high fluence sample indicates a slightly reduced carrier density due to the laser treatment. (b) Relative increase of transmittance of the low fluence and high fluence samples compared to the as-deposited material.

Figure 3.7: (a) Measured reflectance of the three samples as function of the wavelength. (b) Relative decrease of reflectance of the low fluence and high fluence samples compared to the as-deposited material.

Figure 3.8: Absorption coefficients α , calculated from transmittance T data in Fig. 3.6 - i.e. $T = e^{-\alpha t}$, where t is the thickness of the layer. Absorption of the glass substrate was taken into account.

Of interest is the increased haze observed in the high fluence sample, while only small differences can be observed between the as-deposited film and the low fluence samples (see Fig. 3.9 (a)). The role of the morphology and the increased roughness R_a on the increase of haze are demonstrated by the increase of the absolute scattering level, as shown in Fig. 3.9 (b). The absolute scattering level of transmitted light from a textured interface is described by the haze parameter for transmittance, $H_T(\lambda)$, which is the ratio between the total and the diffused transmittance (*haze*).

Figure 3.9: (a) Measured haze for the three different samples. (b) Ratio between the haze in transmittance and the transmitted light at an angle of 90° $H_T(\lambda)$. This ratio is higher at each wavelength in the case of the high fluence sample, compared to the as-deposited sample. This demonstrates the beneficial effect of LIPSSs on the haze.

A higher optical transmittance could be attributed to a thinning of the laser treated SnO_2 layer due to laser ablation. Spectroscopic ellipsometry (SE) was applied to measure the thickness of the samples, see Fig. 3.10. SE measurements showed negligible thinning of the SnO_2 layers. Hence, the increased transmittance of the

laser treated samples is not simply due to thinning of the layers. Moreover, it can be concluded from this measurement that no significant reduction of the thickness between the three samples was induced by ablation. For the samples treated at high fluence, SE analysis also predicted an increased width of the transition from air towards full density bulk SnO_2 of about 30 nm. The latter matches with the cumulative height distributions from AFM data (see Fig. 3.11). Here, the slopes of the two curves of the samples differ and show a longer transition in the textured sample, in agreement with the SE prediction. This figure proves that the nano-ripples, superimposed on the original morphology, increase the transition region between air and SnO_2 , thus creating a smoother change from one refractive index to the other and thereby decreasing the reflectance.

Figure 3.10: Measured and fitted Ψ and Δ parameters from SE. Data were fitted using the Cauchy relationship from 600 to 950 nm range, where the material was supposed to be highly transparent (setting the extinction coefficient $k = 0$). A good fit ($MSE < 20$) was provided for both the as deposited and the high fluence samples.

Figure 3.11: Cumulative height distributions from AFM data for as-deposited material and high fluence sample, showing the integrated solid/void ratio along a plane, parallel to the surface, starting from the outside and proceeding deep into the bulk material.

Table 3.1: Average values of the sheet resistance, measured by the 4 point probe technique, at several locations of the samples.

Sample	Sheet resistance $R_s[\Omega/sq]$
As-deposited	13.5 ± 2
Low fluence	14.5 ± 2
High fluence	16.1 ± 2

3.3.2.3 Electrical properties

Measurements of the electrical sheet resistances did not show differences (within the experimental error) between the as-deposited film and the film processed at low fluence, see table 3.1. Variations in the resistance between the as-deposited film and the film treated at low fluence is within the experimental error (possibly arising from thickness variations of the SnO_2 layers during deposition), while for the high fluence sample R_s is slightly higher than as-deposited. A slightly higher value was found for sheet resistance of the high fluence sample. The latter confirms the observed higher optical transmittance in the long wavelength range (see Fig. 3.6 (a)).

3.3.3 Bulk material properties: phase composition and grain structure

3.3.3.1 Phase composition

As the changes in absorptivity showed that the bulk properties of the film were modified by the laser treatment (see Fig. 3.8), Raman spectroscopy was employed to investigate the composition of the bulk material before and after the laser treatment. Fig. 3.12 reveals that only peaks (namely at 244, 293, 475, 500, 618, 630, 687 cm^{-1}) corresponding to SnO_2 in its rutile phase [14,19] were present in all samples. This implies that only small stoichiometry changes (SnO_{2-x} , with $x < 1$) are present and therefore it can be concluded from these measurements that only small stoichiometric shifts from SnO_2 are possible. And that neither SnO_1 nor Sn_3O_4 phases are present in the thin film, neither before, nor after laser irradiation.

Figure 3.12: Raman spectra of the three samples as well as of the bare glass (substrate) used. The observed peaks correspond to the SnO_2 spectrum.

3.3.3.2 Micro structure

From exploratory XRD measurements (see Fig. 3.13), the average grain sizes of the crystallites were determined from the widths and shapes of the reflections. Here, employing the $\{110\}$ and $\{220\}$ SnO_2 reflections, the contribution to the broadening from small diffracting crystallites was determined from the respective integral breadths. The contribution to the broadening from the instrument itself was removed. On average, the crystallite size is in the range of 70-150 nm for the as-prepared sample and approximately 100 nm for the other samples, showing no significant differences between the as-deposited material and the laser treated samples. However, the structural broadening of the second order $\{220\}$ SnO_2 reflection is larger than that of the first order $\{110\}$ reflection for all samples. The latter indicates the presence of additional micro-strain sources. The contribution of these micro-strain sources increases with the amount of fluence. Another indication for the presence of micro-strain sources is the highly anisotropic character of the line broadening as a function of the reflection $\{hkl\}$, which is not expected if all structural broadening is due to the finite size of the diffracting crystallites only. Further study is currently carried out in this direction. It is not unlikely that the observed micro-strain sources also influence the electrical properties of the samples.

3.3.4 Overall efficiency of the treated SnO_2

A way to characterize the overall performance of the SnO_2 layers is via the so called figure of merit (ϕ), combining the total contribution of the increased optical transmittance and the increased sheet resistance. A common formula for the figure of merit is present in literature for TCO layers. This figure is meant for the production of photovoltaic devices [20] and reads:

$$\phi = \frac{T^{10}}{R_{sh}} \quad (3.1)$$

where T is the average transmittance in the wavelength range from 400 to 1100 nm.

Figure 3.13: XRD measurements of the three different samples using Co radiation. Small differences can be observed between the as-deposited and the low fluence samples, where the relative numbers of counts for different peaks start to differ. More evident are the differences between the as-deposited and the high fluence samples. Analysis of the peaks revealed a broadening in the high fluence sample, indicating a lower crystalline quality (i.e. smaller size of the grains, more crystallographic defects) with respect to the as-deposited material.

Table 3.2: Figure of merit ϕ of the three different samples and their ratio to the ϕ of the as-deposited film.

	As-deposited	Low fluence	High fluence
$\phi \times 10^3 [\Omega^{-1}]$	2.55	3.05	4.07
ϕ/ϕ_{as-dep}	1	1.20	1.59
Improvement [%]		20	59

An increase of the ϕ in the laser treated layers is clearly shown from calculated data (see table 3.2).

3.4 Conclusions

Thin SnO_2 films on Borofloat[®]-glass were irradiated by 6.7 ps *UV* laser pulses using two different laser conditions: (i) $F_0 = 0.17 \text{ J/cm}^2$, 1 *overscan*, *overlap* = 98.7%, *line – to – line pitch* = $3\mu\text{m}$, $f_p = 100 \text{ kHz}$, and (ii) $F_0 = 0.26 \text{ J/cm}^2$, 1 *overscan*, *overlap* = 98.7%, *pitch* = $3\mu\text{m}$, $f_p = 100 \text{ kHz}$. Nano-ripples were found on samples irradiated at the higher fluence level. It was shown that these nano-structures are Laser Induced Periodic Surface Structures (LIPSSs). An increased optical transparency was found in the wavelength range from 380 to 1100 nm -i.e. the working range of photovoltaic cells. Increased optical transmission was found not due to a thinning of the layers after the laser treatment, but due to morphological changes on the surface, as well as the effect of the annealing on the bulk properties of the treated SnO_2 . Both combined result in a decrease of the reflectivity, and also in a lower absorption within the annealed layer. It was shown that the changed morphology also resulted in an increase of the absolute scattering level, which is strongly dependent on the small-scale LIPSSs roughness superimposed on roughness of the as-deposited layer. This latter result can be used to further optimize the SnO_2 layer.

Measurement of the sheet resistance of the films revealed a light detrimental effect of the picosecond laser radiation on the sheet resistance of the SnO_2 layer; a detailed explanation of these effects on the electrical properties needs further study.

The overall contribution of the changes in optical and electrical properties was evaluated by using a figure of merit usually applied for TCO layers for solar cells application, showing a 20 to 59% improvement in the laser treated samples compared to the as-deposited sample.

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Chapter 4

Annealing of SnO₂ thin films by ultra-short laser pulses

4

Abstract

Post-deposition annealing by ultra-short laser pulses can modify the optical properties of SnO₂ thin films by means of thermal processing. Industrial grade SnO₂ films exhibited improved optical properties after picosecond laser irradiation, at the expense of a slightly increased sheet resistance [Proc. SPIE 8826, 88260I (2013)]. The figure of merit $\Phi = T^{10}/R_{sh}$ was increased up to 59% after laser processing. In this paper we study and discuss the causes of this improvement at the atomic scale, which explain the observed decrease of conductivity as well as the observed changes in the refractive index n and extinction coefficient k . It was concluded that the absorbed laser energy affected the optoelectronic properties preferentially in the top 100-200 nm region of the films by several mechanisms, including the modification of the stoichiometry, a slight desorption of dopant atoms (F), adsorption of hydrogen atoms from the atmosphere and the introduction of laser-induced defects, which affect the strain of the film.

4.1 Introduction

Tin-dioxide (i.e. SnO₂), also known as stannic oxide, is a widely applied and studied ceramic material [2]. Un-doped and stoichiometric SnO₂ is a semiconductor with a wide bandgap (~ 3.6 eV). Shallow doping of SnO₂ (e.g. with F , Cl or Sb) or small shifts from its perfect stoichiometry (i.e. SnO_{2-x}, with $x < 1$), which are

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associated with oxygen vacancies, lead to n-type semi-conductive behavior. Doped SnO_2 combines a high electrical conductivity with optical transparency and belongs to a class of materials referred to as Transparent Conductive Oxides (TCOs). These TCOs are important for opto-electronic devices [2, 3]. Due to the low fabrication cost, SnO_2 thin films find application in different areas, including glass coatings for thermal insulation, oxidation catalysts, gas sensors, flat panel displays, touch panels, flexible electronics, dye-sensitized solar cells (DSSC), thin film silicon and cadmium telluride (CdTe) solar cells, light-emitting diodes (LEDs), etc [3]. A strong interest for TCO materials led research into the effects of post deposition annealing by nanosecond (ns) laser pulses on the optical and electrical properties of different TCOs [4-11]. The use of Rapid Thermal Laser Annealing (RTL) is an alternative process to conventional furnace annealing. Compared to furnace annealing RTL reduces thermal damage of sensitive low cost substrates with low melting points [4]. For a given wavelength of the laser radiation, ultrashort laser pulses -with pulse durations in the order of tens of picoseconds or less- can induce same high surface temperatures of the film, but at a significantly lower energy input per pulse, when compared to nanosecond laser pulses. This can be attributed to the fact that the Heat Affected Zone (HAZ) due to ultra-short laser pulses is significantly smaller than due to ns- laser pulses. Hence, ultra-short laser pulsed processing is highly selective in depth of the laser induced transformations. This can be exploited for processing either thin films or selectively process a thin top layer of the substrate under consideration. Moreover, due to the small timescales at which the annealing process occurs during ultra-short laser processing, new and original material structures can be obtained. Despite low heat input during laser annealing, heat accumulation might occur, especially at high pulse rates. However, by careful selection of the laser parameters (i.e. laser fluence, repetition rate, and pulse overlap), heat accumulation can be controlled in order to increase the duration of the heating cycle time, while ensuring that the temperature at the film/substrate interface remains below the damage threshold for the substrate.

Laser annealing is an alternative use of ultra-short pulsed laser sources, as a future prospect, in thermal processing, e.g.: extremely selective annealing, laser selective evaporation (either for removal of unwanted impurities or for tailoring the stoichiometry), ultra-selective laser doping, etc. To fully exploit this alternative use of ultra-short pulsed laser sources, a detailed understanding is required of the heat-related phenomena in a laser fluence range below the ablation threshold and their effects on the material.

In an earlier study [1], the effects of UV ($\lambda = 343$ nm) picosecond (ps) laser irradiation on the macroscopic optical and electrical properties of thin SnO_2 films was demonstrated and discussed. It was shown that the total average optical transmittance (T) in the wavelength range from 400 to 1100 nm increased from 71.4% to 76.1%, while the electrical properties were only slightly deteriorated. That is, the sheet resistance (R_{sh}) increased from 13.5 to 16.1 Ω/sq . The Figure-of-Merit $\Phi = T^{10}/R_{sh}$ [12], which combines the optical and electrical properties in a single performance quantity, increased up to 59% due to the laser treatment. Moreover, it was found that when nanostructures (also known as Laser-Induced Periodic Surface

Structures, or LIPSSs) form on the surface of the film, due to the laser irradiation, the optical reflectivity of the film reduces and the haze of the film increases. This was attributed, in part, due to the morphology of LIPSSs, which was superimposed on the original morphology. Other possible causes, which could smoothen the mismatch of refractive index with air, as well as could explain the decreased optical absorption by the bulk of the material, were not discussed [1]. Moreover, it was also pointed out that processing with ultra-short pulses may introduce microscopic modifications in the lattice, which do result in measurable changes in optical and electrical properties.

The present research aims to study the effect of *UV* ($\lambda = 343$ nm) picosecond laser-material interaction on the microscopic structure of SnO_2 thin films in order to explain the origin of the macroscopic changes observed in the optical, as well as electrical properties of the film. We discuss the causes at the atomic scale, which can explain the observed decrease of conductivity, such as modification of the density of oxygen vacancies, changes in average grain size, amorphization due to fast quenching, introduction of quenched-in defects during fast thermal processing, as well as stress/strain induced by the defects in the lattice. Also the observed changes in the refractive index n and extinction coefficient k can be understood at the atomic level. That is, the presence of detrimental impurities, formation of different material phases, presence of amorphous structure of the lattice and different carrier densities. The possible causes, which induce a modification of the carrier density, electronic mobility and optical constants n and k , due to the laser treatment, were examined by means of several inspection techniques. The results of these analyses were cross-checked to give an overall exhaustive comprehensive interpretation of the observed effects. The results of this study can be used to further improve the performance of SnO_2 -based electrodes for solar cells and/or other electronic devices.

4.2 Experimental

4.2.1 Laser setup

In the experiments, an Yb:YAG laser source was used, showing a nearly Gaussian power density profile ($M^2 < 1.3$) and with fixed pulse duration of about 6.7 ps. A Third Harmonic Generation (THG) unit was employed to convert the central wavelength $\lambda = 1030$ nm of the laser source to 343 nm (UV) and a Galvano-scanner, equipped with an F-theta-lens (focal length 103 mm), was used to scan the focal spot (diameter $d = 17$ μm) over the surface of the samples. The spot diameter, combined with the scan velocity v and the pulse frequency f_p determine the spatial pulse-to-pulse overlap (OL), which is defined here as $OL = 1 - v/(d \times f_p)$. More details on the experimental laser setup can be found in [13].

4.2.2 Analysis tools

Several analysis techniques were adopted to study the effects of the laser radiation on the material. A high resolution Scanning Electron Microscope (SEM), as well as an

Atomic Force Microscope (AFM) were utilized to investigate the surface morphology of the samples, as well as their cross sections. For the investigation of the crystalline structure of the outermost atomic layers, Transmission Electron Microscope (TEM) was used. X-ray diffraction (XRD) experiments were performed on a system using a mixture of $K\alpha_1$ and $K\alpha_2$ of Co radiation with an average wavelength of $K\alpha = 0.17903$ nm, to determine the crystallographic structure of the film. To identify changes in stoichiometric composition of the SnO_2 thin films and the concentration of impurities, we employed X-ray photoelectron spectroscopy (XPS). Depth profiling of impurities with low concentrations was performed using the Time of Flight Secondary-Ion Mass Spectrometry (TOF-SIMS) technique. The electrical properties of the films, such as electron mobility, carrier density and sheet resistance, were determined by Hall effect measurements and the 4-point probe technique. Last, positron annihilation was adopted to inspect the occurrence of laser-induced defects in the layers after the laser treatment. The Doppler broadening of positron annihilation radiation was measured with a low-energy Variable Energy Positron beam (VEP) using positrons with a kinetic energy in the range of 0- 25 keV [14]. The depth profiles of the S and W parameters, extracted from the Doppler broadened 511 keV γ -ray photopeak, were analyzed using VEPFIT software [15].

4.2.3 Samples

Fluorine-doped SnO_2 samples of 980 nm thickness, deposited by chemical vapor deposition (CVD) on 1 mm thick Borofloat®-glass, showing a sheet resistance of $R_{sh} = 13.5 \Omega/sq$ were used. This combination of a thin SnO_2 layer on glass is used for the production of silicon thin film solar cells. Deposition of the samples was performed at TNO in the Netherlands using an industrial process [16].

4.2.4 Experimental approach

The experimental procedure consisted of three steps. During the first step, laser tracks were created with varying pulse-to-pulse overlap (OL), number of over-scans (OS) and fluence levels (being F_0 the peak fluence) by scanning the focal spot over the sample at a fixed pulse repetition frequency of $f_p = 100$ kHz. The second step consisted of finding conditions for damage-free (crack-free and no ablation) treatment of the films. This second step was iterated by choosing finer variation of the processing parameters (OL , OS and fluence) and inspecting the sample afterwards by SEM. The third and final step of the experimental procedure consisted of creating laser treated (3 cm^2) areas by varying the pitch (distance) between parallel laser tracks. Following this procedure, three sets of samples were manufactured and subjected to subsequent analysis:

- As-deposited SnO_2 , without laser treatment applied;
- Low fluence regime ($F_0 = 0.17 \text{ J/cm}^2$, 1 OS , $OL = 98.7\%$, $pitch = 3 \mu\text{m}$);
- High fluence regime ($F_0 = 0.26 \text{ J/cm}^2$, 1 OS , $OL = 98.7\%$, $pitch = 3 \mu\text{m}$).

Figure 4.1: AFM measurements of the three samples. (a) as-deposited SnO_2 , (b) SnO_2 treated at low laser fluence and (c) at high laser fluence.

Figure 4.2: SEM images of the three samples. (a) and (b) show as-deposited SnO_2 surface at different magnifications. (c) and (d) show SnO_2 treated at low laser fluence sample at different magnifications. (e) and (f) show SnO_2 treated at high laser fluence sample at different magnifications.

4.3 Results and discussion

4.3.1 Surface morphology

When comparing the results of SEM and AFM measurements of the as-deposited SnO_2 sample (Fig. 4.1(a) and Figs. 4.2(a)-4.2(b)) to the results of the low fluence samples (Fig. 4.1(b) and Figs. 4.2(c)-(d)), only small differences are observed. However, a clearly modified surface morphology is found for the sample treated at high laser fluence (Fig. 4.1(c) and Figs. 4.2(e)- 4.2(f)). As already discussed in our previous work [1], the nano-structures observed in Fig. 4.1(c) and Figs. 4.2(e)-4.2(f) on the SnO_2 film treated at high laser fluence are Laser-induced Periodic Surface Structures (LIPSSs). In particular, the obtained LIPSSs were identified as High Spatial Frequency LIPSSs (HSFLs) [17].

For the sample treated at low fluence, where no LIPSSs were found (see Fig. 4.2(c)), the material remained entirely in the solid state during annealing. In the case

of treatment at high fluence, LIPPSs were formed, which only happens when either melting and/or ablation occurs due to laser irradiation. In both cases, the melting temperature must be reached to observe morphological modifications. Therefore, the maximum surface temperature reached during the laser processing of the sample treated at high fluence is expected to have exceeded the melting temperature T_M . Several mechanisms can induce melting of the surface in the sample treated at high fluence. First, if the peak fluence F_0 of a single pulse is above the fluence F_M , required for melting, the surface melts after one single pulse. Experiments based on the so called D^2 -method [18] were performed to identify the single pulse melting fluence threshold to equal $F_M = 0.56 \text{ J/cm}^2$. As the single peak fluence F_0 applied during the experiments (see section 4.2.4) was well below F_M , other mechanisms should be considered to explain the occurrence of surface melting. Two other mechanisms are most likely inducing the melting of the surface. First, inter-pulse heat accumulation and secondly, a reduction of the melting threshold due to laser induced defects when a high overlap (OL) is applied. Usually, a reduction of the thresholds of melting and ablation is observed only upon irradiation with hundreds to thousands of laser pulses. This particular phenomenon is explained by the formation of numerous defects just below the surface of the irradiated material, which in turn reduces the thresholds [19]. The latter can also be understood as the chemical storage of heat in the material, by increasing the free Gibbs energy of the lattice, induced by an increasing disorder. However this reduction of the threshold for melting is expected to be a small fraction of F_M . At $F_0 = 0.26 \text{ J/cm}^2$, corresponding to the high laser fluence condition, the ratio between the peak fluence and the fluence for melting is small, i.e. $F_0/F_M \approx 0.5$. For ultra-short laser pulses, thermal dissipation due to heat conduction in the material is limited during the pulse. Hence, the maximum surface lattice temperature T_0 of SnO_2 at the center of the focal spot ($r = 0, z = 0$) at $F_0 = 0.26 \text{ J/cm}^2$ will be $T_0 \approx T_M/2$. The significant difference between T_M and T_0 cannot be explained by a reduction of the melting temperature in SnO_2 caused by the accumulation of defects with the current laser conditions. Therefore, the difference implies that heat accumulation occurs during the treatment and explains why the top surface of the film is melted. That is, heat accumulation allows to reach temperatures above the single-shot maximum temperature, which can explain observed surface modifications of the material after being irradiated with pulses having fluence levels $F_0 < F_M$. Moreover, the final structure of a material after the annealing process depends on the local thermal history of the heating-quenching cycle. The occurrence of controlled inter-pulse heat accumulation, which rules the timescale of the annealing cycle, is an important condition to prevent amorphization in material processing via ultra-short laser pulses. On the other hand, it should be mentioned that heat accumulation needs to be controlled by varying the laser parameters (e.g. λ , f_p and F_0) in order to avoid damage of thermally sensitive substrates.

4.3.2 Cross sections

SEM pictures of the cross sections (Fig. 4.3) show that the grain morphology in the bulk (close to the glass) of the sample treated at high fluence is similar to the

Figure 4.3: Cross section of SEM images of (a) as-deposited SnO_2 , (b) SnO_2 treated at high laser fluence causing surface melting and the LIPSSs depicted in Figs. 4.2(e) and 4.2(f).

morphology of the as-deposited sample. In both samples, small grains are visible near the glass substrate due to the fast nucleation process during deposition. Grain growth along a preferential direction with lower formation energy enables the development of bigger V-shaped grains on top of the small ones. XRD texture measurements performed on the samples indicated the presence of a strong fiber texture with $\langle 301 \rangle$ in the direction normal to the plane of the sample. This type of texture has been observed before [20] and is enhanced in relatively thick (over 500 nm) $\text{SnO}_2\text{:F}$ layers. The fiber texture was not significantly changed due to the laser irradiation. However, the top 100-200 nm of the high fluence laser-treated sample reveals a different contrast and structure than the as-deposited sample.

Arguably, the difference in contrast of the top 100-200 nm in Fig. 4.3(b) can be attributed either to an increased amount of defects, or to a different chemical composition in the top layer, as a result of a modified lattice structure in the high fluence sample. To investigate the possible presence of an amorphous lattice structure within the modified top part of the high fluence sample, due to fast quenching, the as-deposited and the high fluence samples were glued together and a lamella for TEM inspection was extracted and subsequently mechanically grinded and ion milled. The cross sections of the two samples are shown in Figs. 4.4(a) and 4.4(d). Figures 4.4(b) and 4.4(e) show a close-up view of the surface layers at the SnO_2 -glue interface, where lattice fringes indicate crystallinity of the samples all the way up to the surface. The latter is supported by the corresponding electron diffraction pattern recorded near the interfaces shown in Figs. 4.4(c) and 4.4(f), showing no amorphous halo. This result was also confirmed by XRD spectra, where no amorphous hump was observed when the same sample was inspected not locally, but over a bigger area (1×1 cm) [1]. Hence, both measurements indicate the absence of any amorphous structure in the lattice. Therefore, any observed effect of the laser process on the optical and electrical properties of the film cannot be attributed to amorphization.

Figure 4.4: (a) and (b): Bright field TEM images of as-deposited SnO₂ at two different magnifications. (d) and (e): Bright field TEM images of the sample treated with high laser fluence at two different magnifications. Pictures (c) and (f) show the electron diffraction pattern recorded near the interfaces, respectively corresponding to the as-deposited and high fluence samples.

4.3.3 Stoichiometry and chemical composition

The optical and electrical properties of an SnO₂ film greatly depend on its stoichiometry and chemical composition. Small shifts of stoichiometry, as well as the presence of impurities are associated to interstitial states and band tailing effects. Those can affect the transmittance of light in the bandgap of a semiconductor, as well as the carrier density and the electron mobility of the material. The latter are significant quantities contributing to the sheet resistance (R_{sh}), being $R_{sh} = 1/(n_e \mu_e q_e t)$, where n_e , μ_e , q_e and t respectively are the carrier density, the electron mobility, the electron charge and the thickness of the film. Therefore, to study the effect of laser annealing on the chemical composition and stoichiometry, we carried out XPS and TOF-SIMS analysis of the samples.

Oxygen desorption was inspected by the XPS technique. Tin and oxygen concentrations were measured along the depth of the samples and their signals (respectively the $Sn_{4d_{5/2}}$ and O_{1s} peaks) were divided in order to have their ratio O/Sn , see Fig. 4.5. In perfectly stoichiometric SnO₂, this ratio is 2. Irrespective of the fluctuations of the signals over depth, we observed a relative decrease of oxygen concentration in the laser-treated sample at high fluence compared to the concentration on the as-deposited film. The largest shifts in the stoichiometry from SnO₂ to SnO_{2-x}, with x as high as 0.1, were found in the sample treated with high fluence, but only in the top 250 nm of the film. We attribute this effect to desorption of surplus interstitial oxygen from the film during laser processing.

Traces of dopants and/or impurities in the SnO₂ matrix were measured by TOF-SIMS analysis, see Fig. 4.6. TOF-SIMS measurements were performed over $50 \times 50 \mu m$ spots, over the full depth of the layers. Fluorine (F) and hydrogen (H), known to act as n-doping impurities [21, 22], were found to be present in the samples.

Figure 4.5: O/Sn ratio from XPS measurements for the as-deposited SnO_2 and the sample treated at high fluence.

As impurities of F were not detected by XPS, it can be concluded that their concentrations are below the sensitivity ($0.1\%at$) of the instrument. Measured concentrations of F dopant atoms as function of depth were not showing appreciable changes in the shape of their concentration profiles between the three samples, with a typical peak at the SnO_2 /glass interface. Concentration profiles of H atoms over the depth of the sample treated at high-fluence display an appreciably increased density at the surface, compared to the as-deposited sample indicating an adsorption of H from air during the laser treatment. Diffusivity of impurities in a host material is related to the type of impurity and the state (liquid or solid) of the host material. Several orders of magnitude distinguish the diffusivity in the solid state from the diffusivity in the liquid state. Interestingly, the concentration over depth of the adsorbed H in the high fluence sample is not step-like. This implies that the time of resolidification of the laser-material interaction zone is faster than the time required by the dopant to reach the opposite end of the molten region. The latter implies that the molten state is reached for brief periods just after the laser pulse. Due to its atomic small size, H has the highest diffusion coefficient among the other atomic species present in atmosphere. Therefore its adsorption into the SnO_2 matrix will be the largest among the atmospheric species. Since the number of experimental counts in TOF-SIMS analysis is linearly proportional to the relative amount of impurities in the material, we integrated the counts in Fig. 4.6 along the depth and subsequently divided these values with respect to the thickness, in order to obtain an average density of each impurity. Calculated data were normalized by the averaged values found for the as-deposited sample. Table 4.1 lists the relative quantities of F and H in the three samples. As can be observed, the relative amounts of F and H show different trends with the applied laser fluence. On the one hand, the total amount of F reduces slightly in both laser-treated samples, with increasing laser fluence due to desorption. On the other hand, the total amount of H increases due to adsorption from the atmosphere, following the increase of the laser fluence applied.

Combined results from the XPS and TOF-SIMS analysis indicated the presence of carbon in the three samples, see Fig. 4.6(b). A high concentration of carbon was found at the surface of the as-deposited sample, quickly decreasing within the first 150

Table 4.1: From left to right: (i) Measured electrical properties of the as deposited (*AD*), low fluence (*LF*) and high fluence (*HF*) samples, (ii) Integrated counts of *F*, *H* and *C* from SIMS measurements of signals relative to different impurities found in the three samples, (iii) optical average transmittance *T* and reflectance *R* in the wavelength range from 400 to 1100 nm from previous investigation [1] and (iv) figure of merit Φ [1]. Carrier density n_e and electron mobility μ_e were measured by Hall technique (considering less than 5% instrumental error on the values), while sheet resistance R_{sh} was measured also by 4-point probe technique [1]. Percentile quantities in parenthesis in the carrier density, electron mobility and figure of merit columns show the relative shifts from the as-deposited layer.

	$n_e \times 10^{20}$ [cm ⁻³]	μ_e [cm ² /Vs]	R_{sh} [Ω/sq]	<i>F</i>	<i>H</i>	<i>C</i>	<i>T</i> [%]	<i>R</i> [%]	$\phi \times 10^3$ [Ω ⁻¹]
<i>AD</i>	2.32	19.1	13.5 (± 0.5)	1	1	1	71.4	9.9	2.55
<i>LF</i>	2.07 (-8.6%)	20.0 (+4.7%)	14.6 (± 0.5)	0.97	1.17	0.65	73.3	8.6	3.05 (+20%)
<i>HF</i>	2.17 (-4.3%)	17.2 (-9.9%)	16.1 (± 0.5)	0.95	1.48	0.39	76.2	7.2	4.07 (+59%)

Figure 4.6: TOF-SIMS results showing the concentrations of different impurities as a function of depth.

nm into the film. The latter distance matches with the measured transition from air to bulk SnO₂ from measured AFM data, as shown by the cumulative height distributions in our previous work [1]. This observation limits unambiguous interpretation of the actual carbon distribution in the samples. Two different interpretations of Fig. 4.6(b) are given. First, carbon is simply intermixed in SnO₂ up to the depth measurable by TOF-SIMS. Secondly, carbon is present as a very thin superficial coating (few tens of nanometers) after deposition, intermixed with SnO₂ just in the outermost atomic layers. In the latter case, the carbon signal is measured also at deeper depths since the superficial roughness affects the uniformity of the sputtering. The latter explanation would also fit with the concentration of carbon over depth. That is, Fig. 4.6(b) shows two different concentration slopes, which intersect at a depth of about 25 nm. Comparing the three samples, a significantly higher concentration of carbon within the first 150 nm was found in the as-deposited material than in the laser treated samples. The concentration reduces with increasing laser fluence (see Table 4.1 and Fig. 4.6), similarly to elsewhere reported [23]. Since the TOF-SIMS analysis shows only counts, XPS was adopted to obtain an absolute value of the carbon concentration. At the surface, the XPS signals showed a reduction of carbon concentration from 44%*at.* (15.8%*wt.*) in the as-deposited SnO₂ to 19.8%*at.* (4.99%*wt.*) in the SnO₂ treated at high fluence. It was found that, after the first 150 nm, TOF-SIMS counts showed a rather constant and similar profile in all samples (see Fig. 4.6). The high concentration of carbon in the as-deposited sample cannot be simply attributed to atmospheric contamination, but must have been caused by the carbon-rich precursor gases used during the CVD process in the last deposition stage of the SnO₂ layers [16]. Moreover, the crystalline structure of the outermost layers would not explain atmospheric contamination.

4.3.4 Lattice structure and presence of strain

X-ray Diffraction (XRD) was employed to obtain an average value of the SnO₂ grain size for the different samples. The grain size can be determined from the width of the measured XRD reflections since the grain size is inversely proportional to the width (the so-called coherent length), if no other sources of broadening are present. Often, significant contributions to the total broadening arise from the non-ideal optics of the diffractometer and the wavelength distribution (instrumental broadening) and/or from microstructural sources such as dislocations introducing non-homogeneous strain fields (strain broadening). The contribution from the instrument can be removed using separately measured reflections of a standard material employing the same instrumental configuration and X-ray wavelength. Here, a standard sample, LaB₆, was used for this purpose and an interpolation routine was employed to determine the instrumental line profile for the measured reflections. Subsequently, a deconvolution procedure was adopted to obtain the Fourier coefficients of the only structural broadened profiles [24]. The widths of these profiles were characterized by the integral breadths determined from the Fourier coefficients. A plot of the integral breadths as a function of $1/d_{\{hkl\}}$, with $d_{\{hkl\}}$ being the lattice spacing pertaining to the hkl reflection considered, is

Figure 4.7: Williamson Hall plot of the integral breadth versus the reciprocal lattice spacing for various SnO_2 reflections. The intercepts of the extrapolation of the line through the integral breadths of the $\{110\}$ and $\{220\}$ determine the size contribution to the broadening for the different samples.

shown in Fig. 4.7 for all the samples. If grain size broadening is the only source of structural broadening, then it can be shown [25] that the integral breadths of all SnO_2 reflections are equal. However, Fig. 4.7 shows that the integral breadth increases as a function of $1/d_{\{hkl\}}$ for all samples. Consequently, the samples exhibit lattice defects causing strain broadening. For the purpose of this study, we adopted a relatively straightforward approach to separate the size and strain sources employing multiple orders of the same reflection. Hence, the integral breadth values of the $\{110\}$ and $\{220\}$ SnO_2 reflections are extrapolated towards the intercept at $1/d_{\{hkl\}} = 0$ [20]. The so-obtained values represent the net broadening due to the small size of SnO_2 crystallites oriented with their $\langle 110 \rangle$ normal to the plane of the sample. Here, the integral breadths of the samples are approximately equal to 0.015 nm^{-1} resulting in an average grain size of 67 nm, when adopting a Scherrer constant equal to one. These results match with the observed grain dimensions obtained from SEM (Fig. 4.3) and TEM (Fig. 4.4) analysis, in which epitaxial recrystallization was found.

From the observed increasing trend of the broadening as a function of $1/d_{\{hkl\}}$ and the $\{hkl\}$ dependence of the broadening, the presence of micro-strain sources is also relevant in all samples. The particular dependence of the line broadening on $1/d_{\{hkl\}}$ shown in Fig. 4.7, suggests the presence of distributed defects, probably dislocations, even in the as-deposited sample [26-31]. The laser treatment causes a further broadening of the reflections only in case of the high fluence sample. Concomitantly to the peak broadening, also a peak shift, not shown here, was observed for this sample indicating the presence of strains at the macro level. Full quantitative analysis of the observed peak shifts and broadening is beyond the scope of this study.

4.3.5 Formation of defects

Positron annihilation is usually adopted to study the presence of defects, such as vacancies in materials for concentrations down to 10^{16} cm^{-3} . Signals collected by positron annihilation give information about the position of the trapping sites (lattice defects) for the positrons, thus precisely locating the extension of the affected zone where the changes observed in the SnO_2 films have a major impact on the optoelectronic properties. Laser-induced lattice defects (including Sn vacancies, ionized impurities, grain boundaries, or even substitutional atoms) lead to distortion of the lattice and act as traps or scattering centers for free carriers. In turn, these have a detrimental effect on the overall electrical properties, because these defects can induce a reduction of both the carrier density, as well as a reduced electron mobility [30]. In our samples, the measured signal will be a sum of the signals from all different contributions, from intrinsic vacancies to laser-induced defects, which play a primary role on the electrical properties.

In Fig. 4.8, the Doppler S and W parameters as function of the depth into the films are shown for the three samples. The S parameter gives a measure for the annihilation of positrons with valence electrons. That is, it provides information on the electronic structure of the inspected lattice and the presence of vacancies that are trapping sites for positrons. An increase of the S parameter is usually related to an increased density of defects in the lattice. The W parameter is a measure for positron annihilation with core electrons, which gives chemical sensitivity of the positron trapping site. More details on the interpretation of these parameters can be found in [14]. After measurement, the dependence of the parameters S and W , as function of depth, were analyzed using VEPFIT, which solves the implantation-diffusion equation for positrons implanted at selected energies, assuming a layered model of the sample, and fits calculated S and W curves to the experimental depth-profiles [14, 15]. From the implantation energy E [keV] and the mass density of the material ρ [g/cm³], the average implantation depth $\langle z \rangle$ [nm] can be calculated by the equality $\langle z \rangle = 36E^{1.62}/\rho$.

The depth-profiles and VEPFIT analysis clearly showed that the properties of the top 130 nm layer of the as-deposited $\text{SnO}_2:\text{F}$ film differ from the properties of the remainder of the film. That is, the thin sub-surface top 130 nm layer shows a low value of the S parameter of 0.4792 ± 0.0003 and high a high value of the W parameter of 0.0700 ± 0.0003 . The layer below, towards the glass substrate, shows a relatively higher value of S of 0.4915 ± 0.0003 and a lower value of W of 0.0643 ± 0.0003 , when compared to the top 130 nm layer. We attribute this difference in the top and bottom layer of the as-deposited $\text{SnO}_2:\text{F}$ film to the large carbon fractions present in the film in the depth-range up to about 150 nm below the surface (Fig. 4.6), with the highest concentrations at the surface of up to 44at.% as measured by TOF-SIMS. The concentration of carbon reduces beyond a depth of about 150 nm.

Figure 4.8 and the VEPFIT analysis show that the treatments by low and high laser fluence lead to an increase of the S parameter and a reduction of the W parameter in the 130 to 140 nm top layer, while the S and W parameter of the layer below

Figure 4.8: a) Doppler S -parameter and b) W -parameter as a function of the average positron implantation depth profiles for as-deposited (circles), low fluence laser treated (triangles) and high-fluence laser treated (crosses) $\text{SnO}_2\text{:F}$ films. Lines represent the fits obtained using VEPFIT.

have smaller shifts after the laser treatments. The variations of the W parameter show a strong correlation with the changes in S parameter, and thus indicate a common origin of the cause of the changes in S and W parameter. We attribute the increase in S parameter, as a results of the laser treatment, to two effects. Namely, first an increase in the number of oxygen vacancies present in $\text{Sn} - \text{O}$ vacancy complexes, which can trap positrons. And secondly, to the escape of carbon from the sub-surface region, due to laser annealing, as can be observed in Fig. 4.6. It is interesting to notice that the increase in the S parameter correlates with an increase in resistivity of the layer. The correlation resembles the trends reported by Mao et al. [32] for Sb-doped SnO_2 layers, where both the S parameter and the resistivity reduced significantly upon annealing under atmospheric conditions, leading to a reduction in oxygen vacancy concentration. In contrast, undoped SnO_2 showed an increase in resistivity due to annealing, as a result of a reduction in charge carrier concentration. Also, in the present case of doped $\text{SnO}_2\text{:F}$ films, the changes in the charge carrier mobility, due to scattering by vacancy complexes and extended defects in the lattice, help to understand the higher resistivity of the $\text{SnO}_2\text{:F}$ layer due to laser annealing [30]. An explanation for the observed trend of the S parameter, as function of the depth in the sample treated at high laser fluence, is that the laser pulse induces a relatively high concentration of defects in top part of the film, where the resolidification from the molten state takes place. The latter is attributed to an increase of the local strain of the lattice, induced by fast quenching after irradiation. Contemporarily, also the bottom part of the layer is indirectly affected by laser processing, being attached to the highly strained top part of the layer. This is in agreement with the results of Liu et al. [33].

4.3.6 Effects on the optical properties

The optical transmittance of the three samples was measured in the wavelength range of 400 to 1100 nm, see Fig. 4.9. The transmittance varies from an average value of 71.4% in the as-deposited sample to 76.1% in the sample treated at high fluence, see also Table 4.1. Three main causes can affect the optical transmittance of the films, namely: carbon impurities, stoichiometry and doping concentration.

Carbon impurities, either near the surface or in a TCO film, increase light absorption of the TCO over the complete range of wavelength a solar cell operates ($\sim 300\text{-}1100$ nm), resulting in a lower overall efficiency of the device. In TCOs, this high absorptivity should be avoided and optical transmittance should be as high as possible. In contrast, a high concentration of carbon at the surface of the film increases the refractive index mismatch at the air-TCO interface, resulting in a higher reflectivity. Taking an average value for the optical absorption coefficient of the carbon-rich outermost layer of about 104 to 105 cm^{-1} [34] in the visible range and considering its distribution with depth, a decrease in absorption of a few percent is predicted in the sample treated at high laser fluence, which is in the same order of the experimentally observed variations in Fig. 4.9.

The observed decrease in the O/Sn ratio after laser annealing see Fig. 4.5 might also affect the optical transmittance, since the density of oxygen interstitial states (with $O/Sn > 2$), which absorb visible radiation, is reduced by the laser annealing.

Optical transmittance is also related to the concentration of F . In section 4.3.3 it was found that the initial concentration of F in the as-deposited sample was less than 0.1% at. and it varies by about 5% from the as-deposited to the sample treated at high fluence. Hence this contribution is expected to affect the total increase of transmittance to a very small extent only if compared to the observations reported in literature [35].

In conclusion, the main effect of the laser treatment on the optical properties of the SnO_2 is due to a desorption of carbon impurities from the surface. Possibly, also the changed stoichiometry can have a non-negligible effect. The desorption of carbon due to the laser processing decreases both the extinction coefficient k and the refractive index n . This is consistent with the observed beneficial effect of the laser treatment on the increased transmittance and lowered reflectance, as measured in our previous work [1].

4.3.7 Effects on the electrical properties

Hall measurements (see Table 4.1) show only small differences in the carrier density in the three samples, displaying a maximum value for the as-deposited sample and slightly lower values for the laser-treated samples. The Hall measurements suggest that the decrease of carrier density does not simply follow the increase of the laser fluence. That is, the carrier density of the sample treated at low fluence is lower than the value of the sample treated at high fluence. The latter observation indicates that most likely different causes do affect the carrier density with opposite effects. The total of combined effects depends on the adopted fluence regime during

Figure 4.9: Measured optical transmittance for the three samples, reproduced from [1].

the laser treatment. Since the differences in the measurements are small between the three samples, we can only point out which of the measured properties can possibly play a role in the measured quantities, but not quantify the relative influence.

It is well-known that the carrier density of SnO_2 depends on point defects in the lattice associated with oxygen vacancies, which do provide free electrons in the conduction band [2]. The latter could arise from the presence of electrically active impurities acting as donors when they occupy substitutional oxygen sites, as well as from small shifts from the perfect stoichiometry, possibly caused by oxygen desorption [2]. The TOF-SIMS analysis in section 4.3.3, pointed out a variation in the amount of total ionized impurities, i.e. F and H , while XPS showed shifts in the stoichiometry after the laser treatment. The stoichiometric shift is relatively large, since most of the desorbed atoms are oxygen atoms which are present in excess as interstitials in the lattice above the perfect stoichiometric ratio ($O/\text{Sn} = 2$). Creation of intrinsic shallow donor defects can result in an increase of carrier density up to about 10^{20} cm^{-3} . Since a fraction of the observed desorbed oxygen can also originate from the lattice, hence increasing the density of oxygen vacancies, this effect is expected to increase the carrier density. Being the observed changes of the carrier density between the three samples in the order of 10^{19} cm^{-3} , stoichiometric shifts can be considered as one of the possible causes.

Resuming, on the one hand, the carrier density tends to decrease due to a slight desorption of F , but on the other hand, the laser process increases the carrier density by two factors: first, by reducing the stoichiometric ratio of O to Sn due to desorption of oxygen, and secondly, by increasing the amount of adsorbed H (see section 4.3.3). Presence of laser-induced defects in the lattice can also negatively affect the carrier concentration as well as the electron mobility, and will be discussed at the end of this section.

Table 4.1 shows a change in electron mobility, due to the laser treatment, measured

by the Hall technique. A modified electron mobility in a semiconductor can arise from several causes, such as: scattering by phonons, neutral and ionized impurities, lattice defects and grain boundaries. The total scattering rate is then the sum of the individual rates [36]. All the mentioned phenomena can be triggered by laser irradiation when a material is quickly heated and subsequently fast cooled by self-quenching. However, for a degenerate semiconductor the situation simplifies, as scattering by phonons and neutral impurities can be neglected.

The contribution of grain-boundary scattering is significant only if the grain size D_g is comparable to the mean electronic free path l_e , as determined by all scattering mechanisms [37]. In typical polycrystalline thin TCO films the mean electronic free path estimated in literature, based on the mobility and carrier concentration, is rather small-i.e. $l_e \sim 10$ nm, while $D_g \sim 100$ nm [38]. From the obtained XRD data, an estimation can be made about the effect of the laser treatment on the electron mobility of the material. Since the measured mean grain size of 67 nm as derived by XRD analysis is about one order of magnitude larger than l_e , in all the samples, we conclude that changes in electron mobility of the laser-treated samples are not due to a variation of grain boundary scattering.

In the sample treated at low fluence, where no LIPSSs were found, the main measurable effect on the electrical mobility is due to the reduction of the total amount of ionized impurities, as discussed in section 4.3.3. As already mentioned earlier in this section (4.3.7), the decreased concentration of ionized impurities affects the electronic mobility of a degenerate semiconductor. Table 4.1 shows the variation of the carrier densities in the three samples, which is strongly related to the density of ionized impurities in the SnO_2 matrix, such as F and H . This decreases the scattering rate from ionized impurities in the lattice and hence, increases the electron mobility. The latter can explain the slight increase of electron mobility in the low fluence sample, when compared to the electron mobility in the as-deposited sample.

Following the same reasoning, higher value of electron mobility in the sample treated at high fluence should be also expected if compared to the as deposited sample. However, Hall measurements show an opposite trend (see Table 4.1). Interestingly, the reduction of electron mobility is concomitant with a measured increase of strain, which was concluded from XRD data analysis. The explanation for the increased strain can be found in the formation mechanism of LIPSSs. The latter take place at high temperatures with high gradients and, when cooled down, the structured uppermost part remains strained by freezing defects in the lattice. Recent studies of SnO_2 related the effect of strain in the lattice to reduced electrical conductivity [33]. According to this report, strain in the lattice of ceramic and semiconducting materials causes elastic lattice deformation and lattice defects, such as dislocations, stacking faults and twin boundaries. The latter can trap electrons inducing electrostatic potential barriers near the trapping sites, thus reducing the carrier density and also reducing the electron mobility [31, 39].

4.4 Conclusions

Areas of 3 cm² SnO₂ films, with a thickness of 980 nm, on Borofloat[®]-glass were irradiated by 6.7 ps, $\lambda = 343$ nm laser pulses by two sets of laser conditions, referred to as low and high fluence conditions respectively: (i) peak fluence $F_0 = 0.17$ J/cm², 1 overscan, 98.7% pulse-to pulse overlap, track-to-track pitch of 3 μ m, pulse frequency of $f_p = 100$ kHz, and (ii) $F_0 = 0.26$ J/cm², 1 *OS*, *OL* = 98.7%, *pitch* = 3 μ m, $f_p = 100$ kHz. We observed two main different regimes as results of the laser treatment for the two laser treated samples. While at low fluence the SnO₂ layer remained completely in solid state, showing no changes in the surface morphology, the sample treated at high fluence showed that the top layer of 100-200 nm of the SnO₂ film was subjected to melting and resolidification. The latter was concluded on the basis of observed Laser-induced Periodic Surface Structures (LIPSSs). Careful analysis revealed a total absence of amorphous material, even in the outermost atomic layers of both laser treated samples. A tuning of the laser parameters (such as F_0 , f_p and *OL*) was necessary to achieve the optimal inter-pulse heat accumulation, which slows down the resolidification process and avoids amorphization. Simultaneously, the heat accumulation was moderate, which ensured a thermally damage-free film and substrate. The latter is an essential condition to exploit ultra-short pulsed lasers for ultra-shallow thermal treatments even above the melting threshold of the material without damaging the structure of the lattice.

Our investigation revealed multiple effects of the laser treatment on the properties of the SnO₂ film, where small changes in the observed macroscopical optoelectronic properties can arise from several combined different phenomena, whose contributions cannot be isolated easily. Chemically, desorption of fluorine was measured as well as of oxygen, which induce shifts in the stoichiometric O/Sn ratio after the laser treatment. Carbon contaminant impurities at the top surface was also reduced after the laser treatment. On the other hand, adsorption of hydrogen from surrounding atmosphere was measured. The presence of laser-induced lattice defects, related to different strains observed in the film, was found in the case of the sample treated at high laser fluence. Those defects are likely created during the rapid self-quenching phase of the process. That is, the velocity of the solid/melt interface is sufficiently high to freeze those defects in the lattice, which in turn generates strain in the film. Depending on the laser processing conditions, each of these contributions can play an important role or even dominate the final opto-electronic properties of the films.

In the two laser treated samples, different properties were identified in the top 100 to 200 nm layer of the SnO₂ films, when compared to the remaining layer of the film on glass. This difference is sharper in the sample treated at high fluence, where fast resolidification from the molten state has occurred, than in the sample treated at low fluence. This observation indicates that changes in the opto-electronic properties can be mainly attributed to the top 100 to 200 nm layer of the film and only secondarily to the rest of the layer, which remains almost unaffected by the laser annealing.

Finally, the overall performance of the SnO₂ films before and after the laser treatment were compared via the figure of merit $\Phi = T^{10}/R_{sh}$. It was found that the Φ of already industrially optimized SnO₂ films was increased up to 59% due to laser processing.

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4.5 References

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Chapter 5

Thermal annealing using ultra-short laser pulses to improve the electrical properties of Al:ZnO thin films

5

Abstract

Industrial-grade Al:ZnO thin films, were annealed by UV picosecond laser irradiation in argon atmosphere. A remarkable increase of both the carrier density and electron mobility was measured, while the optical properties in the 400-1000 nm range did not change significantly. We studied the microstructure of the films, in order to explain the observed macroscopical changes upon ultra-short pulsed laser annealing. The effects of the ps-laser irradiation are shown to be attributed to the formation of defects and a local atomic rearrangement on the sub-nm scale. This interpretation is rigorously based on the cross-referenced analysis of different experimental techniques (i.e. SEM, AFM, positron annihilation, optical spectroscopy, Hall measurements, Raman spectroscopy, XPS and XRD). The results of this study can be used to develop a new, viable, technological processing technique to further improve Al:ZnO electrodes.

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5.1 Introduction

Transparent Conducting Oxide (TCO) thin films have been extensively used in applications, such as transparent electrodes for solar cells, touch- and flat- panel displays, sensors, lasing material, and space applications.[1,2]

In the recent past, aluminum-doped zinc oxide (Al:ZnO or AZO) has attracted much attention as a material of the future for optoelectronic devices.[1,2] AZO combines electrical and optical properties comparable with indium doped tin oxide (ITO) but at a substantially lower cost. Different deposition techniques have been studied over the years for this kind of thin films.[1,2] Industrially mature techniques, in terms of deposition speed versus quality of the deposited films, are Magnetron Sputtering, Chemical Vapor Deposition (CVD), Atomic Layer Deposition (ALD) and Expanding Thermal Plasma Enhanced Chemical Vapor Deposition (ETP-PECVD).[1,3-5]

Post-deposition annealing can be adopted either to cure fast deposited films, or, generally, to further optimize their properties. Previous studies showed already the effect of Rapid Thermal Laser Annealing (RTLTA) with continuous-wave (CW) and nanosecond (ns) pulsed lasers at different wavelengths (Excimer, Nd:YAG) on thin AZO films, resulting in an increase of the electrical and/or optical properties of the films after laser annealing.[6,7]

However, for a given wavelength of the laser radiation, ultra-short laser pulses can induce the same surface temperatures, but at a significantly lower energy input per pulse as compared to ns-pulses. Depending on the thermal diffusivity of the irradiated material, this may result in a smaller heat-affected zone (HAZ). Therefore, a higher thermal selectivity is provided with decreasing pulse durations. The effect of ultra-short pulsed laser-material interaction can be exploited to process thin films deposited on thermally susceptible substrates, multi-layered structures, and/or selectively process a thin top layer of a bulk target. As a result of this approach, new material properties can be selectively generated in very shallow regions at the surface.

In the present work we investigate the effects of annealing of thin AZO films by ultra-violet (UV) picosecond (ps) laser pulses and the physical phenomena occurring in the material. These phenomena explain the observed changes at a macroscopic level, i.e. the changed electrical and optical properties of the film. The outcome of this research can be used to further increase the performance of ZnO-based electrodes for solar cells and/or other opto-electronic devices.

5.2 Experimental

5.2.1 Laser setup

In the experiments, an Yb:YAG laser source was used, showing a nearly Gaussian power density profile ($M^2 < 1.3$) and with fixed pulse duration of 6.7 ps. A third harmonic generation unit was employed to convert the central wavelength $\lambda = 1030$ nm of the laser source to 343 nm (UV). A galvano-scanner, equipped with an F-

theta-lens (focal length 103 mm), was used to scan the defocused beam over the surface of the samples.

5.2.2 Atmosphere

Samples were positioned in a sealed chamber filled with argon. A SiO₂ window, transparent to the laser light, allowed the laser beam to reach the sample.

5.2.3 Samples

AZO films of thicknesses ranging between 130 and 860 nm, deposited by RF-Magnetron Ar Plasma Sputtering, or ETP-PECVD on 0.7 and 1.1 mm thick borosilicate glass, were used. Typically, thin AZO films on glass are used for the production of thin film solar cells. Deposition of the sputtered samples was performed at ECN and TNO, while ETP-PECVD depositions were performed at Roth & Rau using industrial processes.

5.2.4 Analysis tools

A high resolution Scanning Electron Microscope (SEM), as well as an Atomic Force Microscope (AFM) were utilized to investigate the surface morphology of the samples, as well as their cross sections. Spectroscopic ellipsometry was used to measure the thickness of the samples.

The electrical properties of the films were determined by Hall effect measurements and 4-point probe technique, while the optical properties were inspected by a spectrophotometer equipped with an integrating sphere.

To identify changes in stoichiometric composition of the AZO thin films and the concentration of impurities, we employed X-ray photoelectron spectroscopy (XPS). XPS spectra were obtained using an aluminum anode (Al K α =1486.6 eV) operating at 72 W and a spot size of 400 μ m. Scans were measured in snapshot mode. The background pressure was $2 \cdot 10^{-8}$ mbar and during measurements $3 \cdot 10^{-7}$ mbar due to the charge compensation of the dual beam source. A full XPS profile along the depth of the films was determined, by sputtering the surface of the samples with Ar ions with a beam energy of 3000 eV at high current.

X-ray diffraction (XRD) experiments were performed on a system using a mixture of K α_1 and K α_2 of Co radiation with an average wavelength of K α =0.17903 nm with a Bragg-Brentano set-up, to determine the crystallographic structure of the film. Here, the instrumental contribution to the broadening was determined employing a standard LaB₆ specimen.

Raman spectroscopy was adopted to study the possible presence and evolution of amorphous phases, hardly detectable by XRD. The Raman spectroscope was equipped with a continuous wave laser probe (λ =647.1 nm) that acquired a spectrum from a 30 $\times$ 30 μ m area.

Last, positron annihilation was adopted to inspect the occurrence of laser-induced defects in the films after the laser treatment. The Doppler broadening of the 511

keV radiation, arising from the annihilation of positrons with electrons, was measured using positrons with a kinetic energy in the range of 0-25 keV. Momentum windows of $|\vec{p}| < (3.0 \times 10^{-3}) m_0 c$ and $(8.2 \times 10^{-3}) m_0 c < |\vec{p}| < (23.4 \times 10^{-3}) m_0 c$, where m_0 is the electron mass and c the speed of light, were used for the S and W parameters, respectively. The measured dependence of the S- and W-parameter as function of depth was analyzed and fitted using VEPFIT software,[8] which solves the implantation-diffusion equation for positrons implanted at selected energies, assuming a layered model of the samples.[8] From the implantation energy E and the mass density ρ_m of the material, the average implantation depth $\langle z \rangle$ can be calculated using $\langle z \rangle = a \cdot E_b / \rho_m$, where $a=3.6 \mu\text{g}\cdot\text{cm}^{-2}\text{keV}^{-b}$ and $b=1.62$ are two empirical constants.[9]

5.2.5 Method

Uniform areas, consisting of multiple parallel tracks at a fixed pitch, were processed on the samples by the laser. An empirical approach was adopted to establish optimal processing parameters, i.e. peak fluence (F_0), pulse frequency (f), pitch (p), beam diameter (D) and velocity of the spot over the surface of the sample (v). To demonstrate the achievable production rate of the process, the laser was initially run near the full average output power (~ 16 W) of the laser source, and the maximum pulse frequency (400 kHz). These parameters were only relaxed if thermal damage of the film was occurring. The number of overscans was fixed to 1 and adjacent lines were scanned in the opposite way (meandering) to reduce indexing time. The pitch was fixed to 40 μm .

Since different samples were showing a different absorption, the laser power and beam velocity were adjusted by an iterative procedure, measuring the sheet resistance (R_{sh}) of the samples after each treatment and selecting the set of parameters resulting in the lowest resistance. Following this procedure, four representative samples were selected for further analysis, namely: samples E1, E2 and TN deposited by sputtering and sample RR deposited by ETP. The designation E1, E2, TN and RR refers to the source of the samples (E=ECN, TN=TNO, RR=Roth & Rau). The thickness t_f of the films, found unaffected after the laser treatment, and the laser processing parameters adopted for the different samples are summarized in table 5.1.

5.2.6 Estimation of temperatures and timescales

An estimation of the temperatures and timescales of the heating-cooling cycle of the material helps understanding the observed changes in the materials properties as a result of the laser annealing discussed further on.

For ultra-short pulsed laser irradiation, the maximum temperature reached at the top surface of a film can be estimated by considering that, during the pulse, the thermal diffusivity in the material can be neglected. Moreover, it was experimentally determined that non-linear effects due to carrier generation during the pulse on the absorption and reflectivity are small ($< 5\%$ of the total) in the fluence range used for

Table 5.1: Thickness (t_f) and laser processing parameters adopted during the experiments. Repetition frequency (f), beam diameter (D), beam speed (v) and peak fluence (F_0). The temperatures T_{max}^{AD} and T_{max}^L are the estimated maximum temperatures reached at the surface of the films at the start (AD=as deposited) and at the end (L=laser treated) of the process, respectively.

Sample	t_f [nm]	f [kHz]	D [μ m]	v [mm/s]	F_0 [J/cm ²]	T_{max}^{AD} [K]	T_{max}^L [K]
E1	510	200	364	1700	0.052	1780	1620
E2	860	400	383	1950	0.049	1600	620
RR	460	400	390	1950	0.036	423	380
TN	137	400	331	1950	0.037	940	750

these experiments. It can therefore be assumed that, to a first approximation, the absorption and reflectivity are constant and equal to the linear coefficients measured with the spectrophotometer at the laser wavelength (see section 5.3.2). Considering that the recombination time of the photo-generated free carriers is in the order of few tens of ps for ZnO,[10] implies that, after few tens of ps after the pulse, the absorbed laser energy can be considered entirely kinetic. Hence, the maximum surface temperature will be about $T_{max} = T_0 + \alpha \cdot (1 - R) \cdot F_0 / C_v$, where T_0 is the initial temperature, α and R are the linear absorption coefficient and reflectivity of the film at the laser wavelength, respectively, and C_v the volumetric heat capacity of ZnO. It should be noted that during the laser process, the absorption of AZO films decreases, due to the Burstein-Moss shift, as will be shown in section 5.3.2. For this reason, the T_{max} was estimated using the values of α and R before, as well as after laser processing, see table 5.1. The estimated temperature is a maximum value to be expected at the surface just after the laser pulse, while the temperature in the rest of the film will be lower. And still well below the melting temperature of ZnO.

The timescale of the heating-cooling cycle time of the film can be estimated as follows. The thermal diffusion length L_{th} is calculated from the well-known relation $L_{th} = (4 \cdot D_{th} \cdot \tau)^{1/2}$ where D_{th} is the thermal diffusivity of a material ($\sim 10^{-2} \text{ cm}^2\text{s}^{-1}$ for ZnO) and τ a given diffusion time. During the ultra-short pulse of 6.7 ps, it holds that $L_{th} \ll L_{opt}$. Inverting the previous relation and considering a diffusion length L_{th} in the order of L_{opt} , it follows a thermal time τ_{th} that defines the timescale that the material spends at a relatively high temperature after a single laser pulse. Taking sample E1 as an example, it can be shown that $\tau_{th} < 10 \text{ ns}$. This is an overestimation of τ_{th} since the large temperature gradients right after the pulse are not taken into account.

5.3 Results and discussion

5.3.1 Effects on the electrical properties

Hall measurements showed a remarkable decrease of resistivity ρ for all samples after laser annealing (table 5.2). This decrease is related to the initial value of the film, i.e. the improvement of films showing a lower initial resistivity was relatively small compared to films which were initially more resistive. AZO films with initial resistivities ranging between 1 and $10^{-3} \Omega\cdot\text{cm}$, were improved upon laser annealing, showing final resistivities ranging between 10^{-2} and $10^{-4} \Omega\cdot\text{cm}$. Interestingly, the lowest obtained resistivity of $6.5\cdot 10^{-4} \Omega\cdot\text{cm}$ was achieved on a film of only 137 nm thickness, demonstrating the potential to achieve already low resistivities at relatively small film thickness.

It can be concluded from table 5.2, that the decrease of resistivity for all samples originated from a combined increase of both the carrier density (n_e) and the electron mobility (μ_e). This remarkable result will be discussed in section 5.4.

To mention, the films, kept in a nitrogen atmosphere, did not show degradation of their electrical properties over several weeks after irradiation.

5.3.2 Effects on the optical properties

The measured optical transmittance (T) and reflectance (R) and the calculated absorbance ($A=1-T-R$) of all films are shown in figs. 5.1a-5.1d, for wavelengths between 280 and 2500 nm. The transmittance T of only the films was derived as by $T=T_{tot}/(1-A_g)$, using the measured total transmittance T_{tot} of the samples and the absorbance of the glass substrate, $A_g=1-T_g-R_g$. The linear absorption coefficient was then calculated from $\alpha = -\ln(T)/t_f$. For all films an increased transmittance was observed towards higher photon energies in the UV range ($\lambda < 400$ nm), after laser annealing. Following the parabolic approximation for direct inter-band transitions $\alpha h\nu \propto (h\nu - E_g)^{1/2}$, where h is the Planck constant and ν the photon frequency, the optical bandgap E_g was extrapolated from the linear part of the $(\alpha h\nu)^2$ vs. $h\nu$ plot by linear regression, see fig. 5.1e. The optical bandgap increases with increasing n_e . This matches with the well-known BursteinMoss effect,[11] at high doping. According to the theory, the increase in the optical bandgap ΔE_g is related to n_e as:[12]

$$\Delta E_g = (h^2/8m_{eff}) \cdot (3n_e/\pi)^{2/3}, \quad (5.1)$$

being m_{eff} the effective electron mass. The experimentally extrapolated values of ΔE_g are shown in table 5.2. As already discussed elsewhere,[13] the theoretical values of ΔE_g calculated with equation (1) will be larger than the experimentally extrapolated values, especially at high n_e , as a result of many-body effects inside the heavily doped lattice.

When compared to as-deposited samples, all samples after laser processing show a

Figure 5.1: a-d) Optical transmittance (black), reflectivity (red) and absorbance (blue) for all samples as-deposited (solid curves) and laser treated (dashed curves). e) $(\alpha h\nu)^2$ vs. Energy plot before (AD) and after (L) the laser treatment. As an example, extrapolation of the optical E_g from the plot is shown for sample RR only.

comparable average transmittance T_{ave} ($\sim 85 - 90\%$), calculated between 400-700 nm wavelength (see table 5.1). Small shifts in T_{ave} after laser irradiation are associated with the density of defects present in the films.[11]

In the infrared range ($\lambda > 1100\text{nm}$), a lower transmittance was found in all films after laser annealing. This effect is related to the increase of A and R with the increase of n_e due to the shift of the plasma frequency ($\omega_p = (n_e \cdot e^2 / \epsilon_0 \cdot m_{eff})^{0.5}$ where e , ϵ_0 and m_{eff} are the electron charge, the dielectric permittivity in vacuum and the effective electron mass, respectively) towards the visible spectral region.[11] This increase, which is in agreement with the data shown in table 5.1, occurs due to free carrier absorption at frequencies below ω_p . Comparing differently deposited samples, different contributes from A and R to the total effect on T are observed. This effect is due to the different thickness of the samples, which affects the absorption.

Due to the small surface roughness of the samples, only negligible values of the haze were measured.

5.3.3 Surface morphology

In the top row of figure 5.2 the results of the AFM measurements are shown. The surface roughness R_a was extracted from the collected data for the as-deposited (AD) samples and laser irradiated (L) samples. No noticeable differences were observed between before and after laser treatment in the E1 ($R_a^{AD}=2.17$ nm and $R_a^L=2.15$ nm), TN ($R_a^{AD}=1.51$ nm and $R_a^L=1.46$ nm) and E2 ($R_a^{AD}=7.71$ nm and $R_a^L=8.67$ nm) samples. However, a larger increase in the roughness of sample RR ($R_a^{AD}=11.1$ nm and $R_a^L=17.3$ nm) was observed. This was attributed to a polishing effect of the laser on the surface.

Figure 5.2: Top row: AFM measurements of the films as-deposited (AD) and laser treated (L). The dimension of the x and y axes are identical for all measurements, while a different scaling is applied to the z -axis, as indicated. Bottom row: isometric SEM pictures of the cross sections of the films.

5.3.4 Cross sections

The samples were snapped and SEM pictures were taken after tilting the samples, showing the cross sections of the different films, see fig. 5.2 (bottom row). Typically, a thin interfacial layer (~ 50 nm) with small grains can be observed near the glass interface in the AZO films caused by the fast nucleation process during deposition. On top of this layer, big columnar crystals were formed, induced by the fast grain growth along a preferential direction with lower formation energy. The crystal structure appears not to be significantly affected by the laser irradiation. No signs of melting and resolidification (i.e. modified morphology, splashing, droplets, etc.) were found on the top part of the films after laser treatments.[14,15] Hence, we conclude that the laser annealing process indeed occurred in the solid state.

5.3.5 Stoichiometry and chemical composition

The ratio between the concentrations of aluminum and zinc ($\text{Al}\%/\text{Zn}\%$) from the XPS signals, provides a quantitative measure of the dopant concentration. From the $\text{Al}\%/\text{Zn}\%$ ratio, the atomic ratio x can be calculated, assuming the stoichiometry is $\text{Al}_x\text{Zn}_{1-x}\text{O}$.

For all samples, the relative stoichiometric shifts observed by XPS after the laser treatment were found within the intrinsic scattered deviations of the measurements (see fig. 5.3a). Considering the total number of laser pulses impinging on the surface ($N_p = f \cdot D^2 / (v \cdot p)$) and the thermal cycle time τ_{th} estimated for single laser pulses in section 5.2.6, an atomic diffusion length can be estimated. In

fact, from the atomic self-diffusion coefficient of Zn in ZnO as function of the temperature ($D_{dif} = 10^{-25} \cdot \exp(0.023 \cdot T[K])[1]$), an atomic diffusion length ($L_{dif} = N_p \cdot (4D_{dif} \cdot \tau^{th})^{0.5}$) in the order of only 10 to 30 nm is over-estimated as the temperature was calculated for the top region only of sample E1. For other samples L_{dif} was found to be smaller, i.e. $L_{dif} < 10$ nm for sample E2 and $L_{dif} < 1$ nm for samples TN and RR. The diffusion of oxygen interstitials (O_i) can be estimated to be less than 1 nm for all samples, since the atomic diffusion coefficient of oxygen in ZnO is approximately two orders of magnitude smaller than the one of Zn.[1]

Hence, the absence of stoichiometric shifts due to the laser treatment could have been expected, since the cycle-cooling time is so short to allow only negligible desorption.

However, two main differences were observed in the XPS spectra, when comparing the differently deposited samples.

First, the relative atomic concentration of aluminum differs considerably between different samples. XPS measurements show an average concentration of 3.7, 1.5, 2, and 5 at.% for the E1, E2, TN and RR samples, respectively (see fig. 5.3a). Then, from the atomic concentration of ZnO ($n_{at} = 8.3 \cdot 10^{22} \text{ cm}^{-3}$) and the carrier density, the average active percentage of aluminum ($Al_{\%}^{act} = n_e \cdot n_{at}^{-1} \cdot x^{-1}$) can be estimated for each sample. This is assuming that hypothetically all the free carriers are originated from active Al dopant atoms. As can be observed from the values listed in table 5.2, even in this extreme case, only a small part of the Al present in the films is active, i.e. between 0.8 and 24.9 at.%. The rest of the Al inside the ZnO films is present either as interstitial, clustered forming secondary phases (i.e. homologous phases, Al_2ZnO_4 or Al_2O_3) or located at the grain boundaries (GB), detrimental for the electrical conductivity.[16]

Secondly, while the sputtered samples (E1, E2 and TN) show a rather constant aluminum concentration profile along the depth, the ETP-PECVD sample (RR) shows an overall decreasing trend, see fig. 5.3a. This highlights a substantial dissimilarity in the level of control one can have over the inclusion of aluminum in the ZnO matrix during different depositions, which causes a peculiar interaction with the laser for each sample (i.e. an increased absorption near the surface of the film, which might explain the polishing effect).

The positions of single Al2p photoelectron peaks were observed to be constant along the depth for all samples within their standard deviation, in the energy window of 73.8-74.3 eV, see fig. 5.3b. Furthermore, as a result of laser annealing, the peaks shifts lie within the standard deviation of the measurements. This proves that the excess aluminum present in the films did not form any metallic precipitation, whose peaks are positioned at 72.8 eV.[17]

5.3.6 Lattice structure and presence of strain

The XRD diffractograms of all samples showed two strong reflections related to the ZnO {0002} and {0004} wurtzite planes. The diffractograms of the {0002} reflections are shown in figs 5.4a-5.4d. Additional measurements showed that all

Figure 5.3: (a) Atomic concentration of Al, as function of depth t_f (where 0% refers to the surface of the films and 100% to the interface with the substrate). (b) Al_{2p} photoelectron peak position for all samples. The error bars refer to the standard deviation of the measurements. The level of metallic Al from [17] is displayed as a reference.

Table 5.2: Resistivity ρ , carrier density n_e , electron mobility μ_e , average optical transmittance (400-700 nm) T_{ave} , measured optical energy gap E_g , measured optical absorption length L_{opt} at the laser wavelength ($\lambda = 343$ nm) and average active percentage of aluminum ($Al_{act}^{\%}$) of the samples as-deposited (AD) and laser treated (L), respectively.

Sample	ρ [$\Omega \cdot \text{cm}$]	n_e [cm^{-3}]	μ_e [$\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$]	T_{ave}	E_g [eV]	L_{opt} [nm]	$Al_{act}^{\%}$ [%]
E1 AD	$4.4 \cdot 10^{-2}$	$7.0 \cdot 10^{19}$	2.05	85.8	3.41	88	2.2
E1 L	$9.4 \cdot 10^{-3}$	$8.7 \cdot 10^{19}$	7.67	87.2	3.45	99	2.8
E2 AD	3.9	$1.0 \cdot 10^{19}$	0.16	86.9	3.36	101	0.8
E2 L	$1.5 \cdot 10^{-2}$	$3.1 \cdot 10^{20}$	1.35	84.6	3.7	410	24.9
TN AD	$1.7 \cdot 10^{-2}$	$3.4 \cdot 10^{20}$	1.12	88.5	3.84	726	8.2
TN L	$4.4 \cdot 10^{-3}$	$4.4 \cdot 10^{20}$	3.42	87.4	3.9	1044	10.7
RR AD	$1.3 \cdot 10^{-3}$	$3.9 \cdot 10^{20}$	13.8	85.3	3.55	145	10.4
RR L	$6.5 \cdot 10^{-4}$	$5.9 \cdot 10^{20}$	17.7	86.5	3.65	196	15.8

samples can be characterized by a strong texture with the [0001] direction as the axis normal to the plane of the sample. No other phases, like Al_2O_3 , Al_2O_4 nor metallic precipitates, were observed.

The diffractograms showed significant broadening of the measured reflections. The structural broadening of the measured line profile contained contributions due to the finite size of the diffracting crystallites (size broadening) and the presence of (micro-) strain fields (strain broadening). First, a linear Williamson-Hall (WH) plot was carried out to discriminate both contributions, exploiting the well-known order independence of the size-term, see figs. 5.4e-5.4h. In several cases the intercepts of the abscissae, constituting the size broadening term, have negative values, which is physically unrealistic. Leineweber et al.[18] showed that the dependence of the strain broadening on the order of reflection need not necessarily be linear of nature. A phenomenological, functional description of the shape of the reflections is given, which holds for multiple orders of reflection simultaneously. Therefore, in figs. 5.4e-5.4h also the determination of the size and strain contributions employing Leinwebers approach is shown (curved lines). The average crystallite sizes obtained from this approach are now positive and range between 15 to 100 nm for all as-deposited samples. These values comply with the SEM results shown in fig. 5.2 and are in accordance with similar types of specimens.[19]

Following the non-linear approach, samples E2 and TN do not show any change in the average crystallite sizes upon laser annealing, which is understandable from the extremely short duration of the laser treatment. Surprisingly, samples E1 and RR show a clear decrease of the respective sizes. However, the straightforward application of the non-linear approach is hampered by an increased asymmetry of these peak profiles after laser treatment. A full analysis of the asymmetries in the peak profiles is beyond the scope of this work and a separate paper is in preparation where the X-ray line profile analysis will be described in full detail. However, some observations help understanding the effect of laser pulses on the material here.

The peak positions, reflecting the average lattice parameter (c_l), change upon laser irradiation (see figs. 5.4i and 5.4l), as a consequence of changes in defect densities and distributions. For samples E2, TN and RR, the peaks shift toward higher 2θ values, which implies a correspondingly smaller average lattice parameter. Following the reasoning of Gondoni et al.,[19] who explained an increase of c_l from the stoichiometric ZnO value by the presence of Al^{3+} cations on interstitial positions, we propose the ps laser induced incorporation of Al^{3+} on substitutional Zn positions, where the atomic radius of Al is smaller than that of Zn, to explain a decrease of c_l . It also explains the large increase in the carrier density ($\Delta n_e > 10^{20} \text{ cm}^{-3}$) upon laser irradiation (see table 5.2) for these samples.

For sample RR the peak shapes are already asymmetrical in the as-deposited state, which can be understood from the varying Al concentration (see fig. 5.3a) and the corresponding differences in the average lattice constant through the sample thickness. After the laser treatment, with $L_{opt} > t_f$, the laser smoothens the gradients along the film thickness leading to corresponding changes in the peak shape (i.e. less asymmetry), as well as in peak width.

For sample E1 the peaks shift to a smaller diffraction angle and their shapes

Figure 5.4: a-d) Line profiles of the $\{0002\}$ reflections. e-h) Plots of the peak integral breadths (β) vs. reflection order (n). i) and l) peak positions for the first order $\{0002\}$ and second order $\{0004\}$ reflections, respectively.

become broader and more asymmetrical, after laser irradiation. Here $L_{opt} < t_f$, hence the laser treatment predominantly affects the top layer of the irradiated film, leading to a spatially varying c_l along the film thickness. In turn, this will cause a corresponding shift of the line profile position along the film thickness explaining the increased peak broadening and asymmetry. Moreover, the higher temperature (see T_{max} in table 5.1) reached in the top layer may simultaneously trigger the creation of oxygen vacancies (V_O) and related interstitials (O_i), as reported by Jiang et al..[20] Since for sample E1 $\Delta n_e \sim 10^{19} \text{ cm}^{-3}$, their combined effect may play a dominant role in increasing c_l , hence shifting the peaks toward lower 2θ values.

5.3.7 Evolution of other phases

The wurtzite crystal structure of intrinsic ZnO corresponds to the hexagonal system, with spacegroup C_{6v}^4 in the Schoenflies notation.[21] The wurtzite-structure optical phonons at the Γ -point of the Brillouin zone are part of the irreducible representation $\Gamma_{opt} = 1A_1 + 2B_1 + 1E_1 + 2E_2$. However, when ZnO is highly doped, additional modes (AM) complicate the vibrational spectra. Research regarding the explanation of these AM is still ongoing in literature.[1,21] A comprehensive description of the frequencies and degeneracy of the active vibrational modes of ZnO and Al:ZnO can be found in literature.[1,21]

Raman spectroscopy showed changes upon laser annealing in the recorded spectra only

Figure 5.5: a) Raman spectra of all samples. b) Detail of the E1 spectra obtained after subtracting the background in the range of $400\text{--}600\text{ cm}^{-1}$ to show the relative change of intensities of the two peaks of interest, i.e. $E_1(LO)$ and E_2^{high} .

for sample E1, while for all other samples (E2, TN and RR) the changes were very small if not negligible, as shown in fig. 5.5a. The main difference observed in sample E1 upon laser annealing concerns the ratio between the intensity of the peaks at 580 and 440 cm^{-1} , denoted $E_1(LO)$ and E_2^{high} , respectively (see fig. 5.5b). Russo et al.,[21] showed that this ratio increased when the oxygen pressure was reduced during deposition. That is, when the density of oxygen vacancies (V_O) was increased. The $E_1(LO)$ peak is known to be an active vibrational mode of the oxygen sub-lattice of ZnO,[2] as it depends on defects affecting its atomic configuration. As mentioned in section 5.3.6, the occurrence of V_O upon laser annealing is expected only in sample E1 due to the higher temperature reached in the top layer of this film, see T_{max} in table 5.1.

5.3.8 Vacancy related defects

Positron annihilation (PA) gives insights into the concentration and type of open volume defects.[8] These defects are trapping sites for positrons in the AZO films. Besides a possible contribution from annihilation in defect-free areas of the films, the PA signal can be the result of annihilation in point defects, as well as in extended defects (i.e. vacancy complexes and nano-voids). Both of these defects have a strong impact on the electron density and mobility of the TCO films.

An increase in the S-parameter indicates the formation (or increase in the concentration) of open-volume defects. The most likely vacancy-related defects in

AZO films are the zinc monovacancy (V_{Zn}), and also vacancy-complexes such as $V_{Zn} - V_O$. Both types of vacancies act as effective positron trapping centers, as demonstrated in previous PA studies of ZnO.[9,22,23] Interestingly, due to charge self-compensation in n-type ZnO, the formation energy of the V_{Zn} (< 2 eV)[24] is smaller than the photon energy of the laser beam (~ 3.6 eV). Indeed, Khan et al.[25] recently demonstrated that the UV irradiation of single crystals of ZnO, promotes the formation of V_{Zn} and V_{Zn} -complexes. A similar mechanism likely plays a dominant role in AZO films under consideration.

Fig. 5.6a shows that the S-parameter of sample E1 displays a strong increase upon laser-annealing for the ~ 140 nm (corresponding to $E \sim 5$ keV) top layer of the initially homogenous film. In contrast, the S-parameter of the bottom part of the film is nearly unaffected by the laser radiation.

When compared to the top layer of sample E1, samples E2 and RR show a smaller increase in the S-parameter, and satisfactory fits could be obtained for these samples assuming a homogeneous layer, also after the laser annealing process (see fig. 5.6b and 5.6c).

A fit of the measured depth profiles collected on the as-deposited sample TN was only possible when using a double layer model. The two layers showed quite distinct characteristics (fig. 5.6d). First, the bottom layer (~ 110 nm thick), which is characterized by a significantly larger S-parameter around $E \sim 3$ keV, strongly differs from the ~ 26 nm top layer in the as-deposited sample. This correlates with the disordered, nano-porous morphology near the interface with the substrate, as can be observed in the SEM image of fig. 5.2. Secondly, the S-parameter of sample TN reveals a distinct behavior upon laser annealing: whereas the top layer of sample TN responds to the laser treatment similarly to all other samples (i.e. the S-parameter slightly increases after laser irradiation), the bottom layer shows a strongly deviating behavior with a strong reduction of the S parameter. This indicates a densification of the bottom layer, due to the laser treatment, which is presumably rich in nano-voids in the as-deposited state as can be deduced from the observed high value for the S parameter.

The W-parameter showed a large shift toward lower values only for the top part of the E1 sample (fig. 5.6e). For sample E2, the reduction of the W-parameter is less marked and was observed along the whole thickness of the film (fig. 5.6f). Samples RR (fig. 5.6g) and TN (fig. 5.6h) only show small shifts of the W-parameter along their whole depth.

The formation of Zn-vacancies resulting from the laser annealing can be clearly observed in the S-W plot of fig. 5.6i, which facilitates the comparison of this work to the results of previous PA studies on ZnO. The S-W plot shows the S and W parameters of the investigated AZO films before and after laser annealing, as extracted from the VEPFIT analysis. In the same figure, the S-W point for a bulk reference ZnO crystal, as well as the S-W point for the Zn mono-vacancy V_{Zn} in ZnO, are plotted. The S-W reference value for ZnO was obtained from the VEPFIT fit parameters of S and W at high positron implantation energy of a reference ZnO single crystal (Mateck GmbH). The corresponding S-W value for the V_{Zn} is then calculated, based on the average of the values for $S(V_{Zn})/S_{bulk} \sim 1.055$

and $W(V_{Zn})/W_{bulk} \sim 0.825$ reported by Zubiaga et al.[23] and Kahn et al.[25]. Similarly to what was observed for as-deposited ZnO layers by Zubiaga et al.,[23] the S-W points of the as-deposited ZnO:Al films lie in the range starting from about halfway up to the end point of the line, connecting the bulk ZnO and monovacancy V_{Zn} S-W points. Only the S-W points (before and after laser annealing) of the bottom layer of sample TN do not fall on the line associated with vacancy defects, related to the trapping of positrons in nano-voids. The S-W values for samples E2 and RR seem to lie somewhat beyond that of the mono-vacancy, which presumably is due to the uncertainty in the S-W point for the Zn monovacancy, indicating saturation trapping of positrons in Zn monovacancies which occurs for concentrations beyond about $3 \cdot 10^{18} \text{ cm}^{-3}$.

The position of the S-W point can be used to estimate the vacancy concentrations,[23,25,26] indicating the presence of relatively low concentrations of $\sim 3 \times 10^{17} \text{ cm}^{-3}$ and $\sim 5 \times 10^{17} \text{ cm}^{-3}$ for the as-deposited samples E1 and TN (top part), respectively. In contrast, the as-deposited samples E2 and RR contain significantly higher vacancy concentrations, larger than about $3 \times 10^{18} \text{ cm}^{-3}$. This seems to correlate also with the differences in the cross sections of the films observed by SEM (fig. 5.2). The cross sections show to be fairly dense for the samples E1 and the top layer of sample TN, whereas samples E2 and RR are characterized by a nanostructure with semi-separated columns.

The creation of Zn vacancies in the more dense sample E1 after laser annealing can be clearly observed in the pronounced shift in the S-W point (fig. 5.6i), indicating an increase in the vacancy concentration from $\sim 3 \cdot 10^{17} \text{ cm}^{-3}$ to $\sim 1 \cdot 10^{18} \text{ cm}^{-3}$. Upon laser annealing, a less pronounced increase in the S-parameter was observed in samples E2, TN and RR.

Two main conclusions can be drawn from the PA study. First, the laser-induced defects extend up to the maximum depth reached by the UV laser radiation during the process. That is, the range of laser-induced defects strongly correlates with L_{opt} after the Burstein-Moss shift. This provides experimental proof that the ultra-short laser pulses indeed induce in the film an heating-cooling cycle time which is too short to allow diffusion of vacancies over relatively long distances, nor allow interstitials to diffuse from their original location. Second, a clear creation of Zn-vacancy related defects is observed. This is quantitatively consistent with the typical increase in concentration of active dopants (Al_{Zn}) according to the ab-initio calculations by Noh et al.[27] for the case of $\mu_0 \sim -2 \text{ eV}$ (where μ_0 is the chemical potential), e.g. sample E1 shows a vacancy concentration of $\sim 3 \cdot 10^{17} \text{ cm}^{-3}$ to $\sim 1 \cdot 10^{18} \text{ cm}^{-3}$ at a charge carrier concentration of $n_e \sim 7 - 9 \cdot 10^{19} \text{ cm}^{-3}$. This further shows that the concentration of Zn vacancy-related defects is about two orders of magnitudes less than the charge carrier concentration.

5.4 Proposed mechanism

A general mechanism is proposed to explain the effect of ultra-short pulsed laser annealing on AZO films, although different engineering-materials can have a specific

Figure 5.6: a-d) S-parameter as function of the positron implantation energy. e-h) W-parameter as function of the positron implantation energy. Closed and open circles indicate the as-deposited and laser treated samples, respectively, while lines show the fits. (i) S-W plot of the fitted values with VEPFIT software, compared to the reference values of ZnO bulk and the Zn monovacancy in ZnO V_{Zn} . The arrows indicate the shift from the as-deposited material to the laser treated. Various concentration levels of V_{Zn} are shown in the plot.

interaction with laser energy.

The absorbed laser energy induces defects, such as V_{Zn} , up to the depth reached by the UV photons (i.e. $\sim L_{opt}$ after the Burstein-Moss shift, as inspected by PA). Because the heating-cooling cycle time of the film is short, the diffusion of atomic species, or defects, is only possible on the nm scale (i.e. $L_{dif} < 10 \text{ nm}$), as confirmed by XPS and PA.

However, on the nm-scale, the effect of acceptor-like defects, i.e. V_{Zn} , can play an important role on the atomic rearrangement. In the AZO films under investigation, the majority of aluminum, not active, is primarily expected to be present interstitially in the ZnO matrix, and not to form other secondary phases, as shown by XPS and XRD results.

Moreover, evolution of secondary phases upon laser irradiation was not inspected by Raman spectroscopy. We expect that the local rearrangement of defects can increase the carrier density via a $V_{Zn}^- - Al_{Zn}^+$ substitutional mediated mechanism within the irradiated bulk of the grains, driven by the Coulombian interaction between charged

defects.[27]

Following this explanation, the laser provides the energy needed to move the Al into the most thermodynamically favorite state, i.e. Al substitutional,[28]not achieved during deposition because films are grown in a not equilibrium state. The increase of the Fermi Energy level, due to the increase of the carrier density, in turn lowers the effective height of the potential barriers at the GB.

Simoultaneously, local recombination of oppositely charged defects can induce a reduction of the density of defects at the surface of the GB,[29,30]which yields an increase of mobility, as well as a decreased amount of trap states for electrons in conduction. The latter effect also tends to increase the carrier density as well as dopant activation.

This interpretation is in agreement with the model proposed by Seto[1]for polycrystalline semiconductor thin films, which explains the simultaneous increase of carrier density and electron mobility of the laser treated samples, as reported in table 5.1. This model describes the barrier height at the GB Φ_{GB} as δ -shaped densities of the electron trap states, which can also be only partially filled, acting therefore as traps also.

The model by Seto was shown to be valid for ZnO up to a critical carrier density of $n_{crit} = 5 \cdot 10^{20} \text{ cm}^{-3}$,[31]which is approximately in the range of the carrier densities measured in this work.

5.5 Conclusions

Ultra-short laser pulses (6.7 ps, $\lambda = 343 \text{ nm}$) were applied to thermally anneal thin Al:ZnO films below the melting temperature. The initial resistivities of differently deposited films, ranging between 1 and $10^{-3} \Omega\cdot\text{cm}$, were significantly improved upon laser annealing, showing final resistivities ranging between 10^{-2} and $10^{-4} \Omega\cdot\text{cm}$. At the same time, the optical properties in the visible range remained nearly unchanged.

The physical mechanism that explains the observed macroscopical changes in the electrical properties only involves a local atomic rearrangements on the nm-scale. As previously reported in literature for ZnO, UV laser radiation was observed to create V_{Zn} related defects in Al:ZnO, up to the depth illuminated below the surface. Subsequently, the combined effect of high induced temperature and short time timescales, both during as well as just after the absorption of laser energy, enhances the nanometric movement of initially inactive Al_i into Zn substitutional locations, generating new active donors. This atomic rearrangement is allowed by the coulombian forces between oppositely charged defects. Surprisingly, not only the carrier density, but also the electron mobility was observed to increase. This was explained by two mechanisms. First, a reduction of the potential barriers at the GB following the increase of the Fermi Energy level due to the increased carrier density. Second, a local reduction of trap states at the GB. These results on Al:ZnO are in agreement with the model described by Seto on the transport of polycrystalline semiconductor films.

Finally, based on parameters studied in this paper, the time required for processing of a surface of 1 m^2 , using for example a 1 kW laser source, lies between 80 and 150 seconds with a calculated energetic cost of about few cents Euro/ m^2 , hence showing the potential for industrial applications.

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Chapter 6

Ultra-short-pulsed laser-machined nanogratings of laser-induced periodic surface structures on thin molybdenum layers

6

Abstract

Large areas of regular diffraction nanogratings were produced consisting of so-called laser-induced periodic surface structures (LIPSSs) on thin molybdenum layers (< 400 nm) deposited on a borosilicate glass substrate. The aim was to produce these structures without ablating nor cracking the molybdenum layer. Ultra-short laser pulses were applied using a focused Gaussian beam profile. Processing parameters such as laser fluence, pulse overlap, number of overscans, repetition frequency, wavelength and polarization were varied to study the effect on periodicity, height, and especially regularity of the obtained LIPSSs. It was found that a careful choice of the correct laser parameters is required to avoid detrimental mechanical stresses, cracking, and delamination during the laser processing of the layer in order to remain in its correct range of ductility as well as to ensure regular LIPSSs. A possible photovoltaic application of these nanogratings could be found in texturing of thin film cells to enhance light trapping mechanisms.

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6.1 Introduction

Laser-induced periodic surface structures (LIPSSs), also referred to as ripples, are wavy structures observed on the surface of many materials after laser irradiation. Although LIPSSs have been studied since 1965[1], their exact origin is still debated. However, it is well-known that the regularity, shape and dimensions of LIPSSs depend on the laser irradiation conditions as well as material properties. Periodicity, amplitude and orientation of LIPSSs depend on the wavelength of the laser radiation, fluence, polarization, angle of incidence and the refractive index of the material[24]. Under most laser conditions, LIPSSs show bifurcations and/or forking -i.e. when a single ripple splits into two ripples of half periodicity- and their length is limited to the diameter of the laser spot. Interestingly, by choosing proper laser parameters, the length of LIPSSs can be extended without bifurcations or forking to areas larger than the spot size, as has been shown on bulk materials[5]. A practical application of LIPSSs can be found in diffraction nanogratings[6].

In the present work, we investigated the feasibility of nanogratings consisting of LIPSSs on thin molybdenum (Mo) layers of a thickness ≤ 400 nm. The challenge, while texturing a thin molybdenum film, is to find the proper scanning conditions for obtaining a uniform area of LIPSSs -which occur only in a limited range of total deposited fluence on a given material (see Ref. [7])- and for avoiding thermo-mechanical damage during the laser treatment. The latter includes cracking, delamination, and excessive ablation of the thin layer. To avoid thermo-mechanical damage on a thin molybdenum film, the so-called brittle to ductile transition (BDT) plays a primary role and a careful choice of the correct single pulse fluence is required well below the total -or accumulated- fluence range needed for creating LIPSSs, as will be shown in Fig. 6.1. The particular behavior of the BDT on thin metallic layers during laser irradiation was first discussed for laser removal of thin chromium films by Lee et al. and Siegel et al. using an excimer laser[8,9].

When compared to other metals, in body centered cubic (bcc) lattice metals such as molybdenum, chromium and tungsten, the ductile range is reached abruptly above a certain temperature[9-11]. In such materials, because of the BDT, excessive thermal stresses can be avoided during the cooling down phase only when high temperature gradients lay in the ductile region above the BDT. For this reason, the thin molybdenum layer only can withstand thermal stresses during the laser treatment without cracking in the case where the absorbed fluence level is above a certain threshold. Khantha et al.[11] discussed, theoretically, the connection between the high generation of laser induced defects below the melting temperature and the BDT threshold temperature. However, if the absorbed fluence is too high, excessive ablation or chipping/delamination occurs. Therefore, damage-free surface texturing is possible only within a certain absorbed fluence range.

Moreover, when applying high spatial pulse-to-pulse overlap, the absorptivity of the material to laser energy varies as a function of the number of pulses and the laser fluence. After the first shots, incubation effects, due to laser-induced surface defects and increased roughness[12], lead to a lower surface reflectivity. The latter leads to an increased absorption of laser radiation and to subsequent thermal damage [as will

Figure 6.1: For creating LIPSSs on thin Mo layers without thermal damage, two requirements need to be fulfilled: (i) The absorbed fluence $F_{abs}(F_0, N)$ of each subsequent laser pulse shall be in the BDT range not to thermally damage the layer, and (ii) the accumulated fluence F_0^{tot} being in the range for obtaining LIPSSs[7].

be shown in Sec. 6.3.2, Fig. 6.2(c) and 6.2(d)]. The absorbed fluence F_{abs} (J/cm²) can be expressed as

$$F_{abs}(F_0, N) = F_0 \times A(F_0, N) \quad (6.1)$$

where F_0 (J/cm²) is the incident laser fluence and $A(F_0, N)$ is the changing absorptivity as function of the number of applied laser pulses N and the impinging averaged laser fluence F_0 .

6.2 Experimental setup

6.2.1 Laser setup

Two different laser sources were employed to study the effect of fluence, pulse duration and wavelength on LIPSSs formation in the molybdenum layer:

- the Pharos from Light Conversion Ltd., which is a Yb:KGW laser source, central wavelength of 1030 nm infrared (IR), with tunable pulse duration (ranging from 230 fs to 10 ps), maximum repetition frequency 200 kHz, 10 W maximum average output power (in IR) at 200 kHz and a beam quality of $M^2 < 1.2$.
- the TruMicro 5050 from Trumpf GmbH, which is a Yb:YAG laser source, central wavelength of 1030 nm (IR), with fixed pulse duration of 6.7 ps, maximum repetition frequency of 400 kHz, 50 W maximum average output power (in IR) at 400 kHz and $M^2 < 1.3$.

Figure 6.2: SEM pictures of the surface after multiple laser shots at a fixed fluence of 0.07 J/cm^2 , with fixed pulse duration of 6.7 ps , obtained at UV wavelength, fixed spot diameter of $12 \mu\text{m}$ and at different overscans on 150 nm molybdenum layer: (a) 1 shot, (b) 2 shots, (c) 5 shots and (d) 10 shots. This sequence shows that the fluence range to process the layer free of any damage, is changed due to the enhanced absorption, as described by Eq. (6.1). The latter is the result of increased roughness and subsurface defects induced by subsequent laser shots. The evidence of this statement is given by the different color of the laser-treated surface, due to different material properties and is well explained by Jee et al.[12].

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Both laser sources showed a Gaussian power density distribution and were equipped with a pulse-picker, allowing the adaptation of the repetition frequency without affecting the energy per pulse. To study the effect of the wavelength, a second harmonic generation or a third harmonic generation unit was employed to convert the central wavelength to 515 nm (green) or to 343 nm ultraviolet (UV).

In both systems, galvano-scanners (IntelliScan14 of Scanlab GbmH) were used to manipulate the focal spot over the surface of the sample. The scanners were equipped with telecentric F-theta lenses (Ronar of Linos GmbH) to focus the laser beam on the samples. In the case of the TruMicro laser source, the focal length of theta lenses used for IR , green, and UV were, respectively 80 , 100 , and 100 mm , while in the case of the Pharos source, only the IR wavelength was exploited and at a focal length of the lens of 100 mm . All experiments were carried out at normal incidence of the laser beam on the surface and at environmental conditions.

The optical $1/e^2$ diameter D of the focused laser beam on the surface was determined using the D^2 method for each wavelength used[4]. This diameter was found to range from 12 to $30 \mu\text{m}$, depending on the wavelength and setup used. Given the spot diameter D , the average laser fluence F_0 here defined as: $F_0 = \frac{E_0}{\pi \times D^2}$, where E_0 is the pulse energy was then calculated for single pulses. The effect of spatial pulse-to-pulse laser spot overlap (OL) on LIPSSs formation was also studied. We define the term OL as the physical displacement distance of the laser spot between successive pulses[13]:

$$OL = 1 - \frac{v}{D \times f_p} \quad (6.2)$$

where $v \text{ (m/s)}$ denotes the velocity of the laser spot relative to the substrate, and f_p

(Hz) the repetition frequency of the laser source. Note that, for increasing velocity, OL goes to zero, or even will become negative, indicating no spatial overlap between subsequent laser pulses on the surface.

6.2.2 Analysis equipment

Morphological inspection of the laser-treated areas was performed by optical microscopy, scanning electron microscopy (SEM, JCM-5000 NeoScope), atomic force microscopy (AFM, Nanosurf Easyscan 2) and confocal laser scanning microscopy (CLSM, Keyence VK-9700). A spectrophotometer (PerkinElmer Lambda 950 with ARTA accessory) was used to analyze the angular intensity distribution (AID) of the refracted light at different angles and wavelengths of the obtained nanogratings[14].

6.2.3 Samples

Molybdenum layers of different thickness were deposited on glass substrates. For initial tests, samples of 150 nm thickness deposited by physical vapor deposition (PVD) on borosilicate glass were used. For structuring larger areas with LIPSSs, molybdenum layers deposited by sputtering on soda lime glass by a third party were used. The latter combination of thin film molybdenum on soda lime glass is meant for the production of $Cu(In,Ga)Se_2$ solar cells. The molybdenum for this application has, in general, a high porosity[15], while molybdenum for other applications might require more dense layers and will react differently during laser texturing. The latter is not addressed in this work.

6.3 Experimental results and discussion

6.3.1 Experimental procedure

The experimental procedure to determine the processing window for damage-free LIPSSs on the thin molybdenum layers can be divided into three steps:

- First, determining processing conditions for single laser pulses (Sec. 6.3.2). This section will show the importance of reaching the BDT transition for each individual pulse, while texturing thin molybdenum layers as a function of the laser fluence.
- Next, determining processing conditions for (partly) spatial overlapping pulses (Sec. 6.3.3) resulting in lines, or tracks with LIPSSs. This section will show the effect of processing parameters -fluence, pulse overlap, pulse frequency, pulse duration, number of overscans and wavelength- on the characteristics of LIPSSs. As well as the importance of ensuring that the total (accumulated) fluence is in the right range for creating LIPSSs.

Figure 6.3: SEM pictures of the surface after single laser shots at different fluence levels, with fixed pulse duration of 6.7 ps, obtained using *UV* wavelength and fixed spot diameter of 12 μm on 150 nm molybdenum layer: (a) 0.05 J/cm^2 , (b) 0.07 J/cm^2 and (c) 0.09 J/cm^2 . The fluence of condition (b) is in the correct range to obtain a damage-free layer.

- Finally, determining the optimal pitch between laser tracks, and polarization direction required to generate uniform areas of bifurcation-free and forking-free LIPSSs.

6.3.2 Single laser shots

Figure 6.3 shows the surface morphology of a 150 nm-thick molybdenum layer on glass after laser processing, as function of laser fluence ranging from 0.05 to 0.09 J/cm^2 . If the applied laser fluence is too low, the layer is not able to withstand thermally induced stresses and will crack, as seen in Fig. 6.3(a). That is, for a fixed molybdenum film thickness,[8] below a certain fluence threshold the material will not reach the BDT, and the layer will crack. Above this threshold the BDT is reached and the ductility of the layer allows it to cope with thermal stresses, as seen in Fig. 6.3(b). If the laser fluence is too high, the layer will be chipped off, as in Fig. 6.3(c). It should be noted that the fluence range for damage-free processing is small. These results are comparable to those shown by Lee et al.[8] and Siegel et al.[9] on thin chromium layers.

Figure 6.2 shows the surface morphology after irradiation of multiple pulses on the same location at $F_0 = 0.07 \text{ J}/\text{cm}^2$. This fluence level was chosen as it allowed damage-free processing of the layer when applying single pulses. The time separation between subsequent pulses was on the order of tens of milliseconds or more. This allows the material to cool down before the next shot is applied avoiding inter-pulse heat accumulation. As can be observed from Fig. 6.2, the molybdenum layer starts to crack when the number of overscans is five. This can be attributed to an increase in absorptivity after the first few pulses, which leads to a high absorbed laser fluence, as described by Eq. (6.1). Similarly to the single-shot case, if the total absorbed fluence is too high, the layer will be damaged. To account for this effect, the fluence of the

individual pulses of a pulse train shall be lower than the single pulse fluence, in order to reach the BDT.

6.3.3 Single laser tracks

Based on the results of single and multiple pulses on the same location, lines (i.e. tracks) were produced by applying multiple partly overlapping laser pulses. The effect of spatial pulse-topulse overlap, number of overscans, and laser fluence on the surface morphology of the lines was studied. During these experiments the repetition frequency f_p was fixed at either 100 or 200 kHz. Figure 6.4 provides an overview of the experiment matrix. The overlap was calculated for different wavelengths using Eq. (6.2), where the beam diameter D was used as an input. After initial SEM analysis to identify the conditions which produce LIPSSs on damage-free layers, this step was iterated by finer variations of the parameters.

Again, the main goal of this set of experiments was to find conditions which induce the BDT in the layer, as this will result in damage-free textured lines. Whether the BDT was reached was found to mainly depend on the pulse overlap and single pulse fluence as is illustrated in Fig. 6.5. This figure shows the surface morphologies at constant laser fluence of 0.05 J/cm^2 and as a function of increasing overlap and overscans. The overlap was increased from none (i.e., separate, nonoverlapping pulses) in Fig. 6.5(a) to a pulse overlap of 97.9% in Fig. 6.5(d). As can be observed, the increase of overlap significantly reduces the formation of cracks, delamination and chipping. It was found that only for overlap values over 95% was the absorbed single pulse fluence F_{abs} , see Eq. (6.1), in the right range for damage free laser tracks, see Fig. 6.5(c) and 6.5(d). This can be explained by the increase in absorption to a steady condition after the first pulses, which shifts condition of Fig. 6.5(a) to the BDT range shown in Fig. 6.1.

When analyzing these results, both the overlap and the overscans (OS) should be accounted for the LIPSSs formation, since they only appear in a certain total accumulated fluence domain[7]. To that end, another quantity is here defined, which is the total optical accumulated laser fluence $F_0^{tot}(\text{J/cm}^2)$ impinging on the surface of the sample:

$$F_0^{tot} = F_0 \times \frac{OS}{1 - OL} \quad (6.3)$$

which is an approximation valid for $D \gg v/f_p$ and $OL > 60\%$. In Eq. (6.3), F_0 was used instead of $F_{abs}(F_0, N)$, which includes the material response to the laser material in the multi-pulse regime; in this sense we are only expressing here the incident fluence on the top surface of the layer.

Figure 6.6 shows the total fluence F_0^{tot} absorbed at the surface as a function of overlap and overscans, where circles correspond to the processing conditions shown in Fig. 6.5. Conditions d and e in Fig. 6.6 produce damage-free textured tracks on the layer, while conditions indicated by a , b , and c were found to damage the molybdenum layer.

Figure 6.4: Experiment matrix used to scan lines with different combinations of irradiation conditions. Repetition frequency was constant, while average laser power/fluence, speed (and by that overlap), and number of overscans (OS) were varied. To check the reproducibility of the results, several identical lines were processed using identical conditions.

Similar to what was concluded in Sec. 6.3.2 for single shots, damage-free lines can be attributed to reaching the BDT at each single laser pulse as a result of a reduced surface reflectivity at high overlap. The latter statement is consistent with the observed experimental results shown in Fig. 6.5(a) and 6.5(d). Figure 6.5(a) shows a surface which is damaged by a single laser shot on the untextured surface, but it is not damaged when the overlap is increased in Fig. 6.5(d). In Fig 6.5(a) the absorbed fluence F_{abs} is too low to reach the BDT; however, when the overlap is sufficiently high, the BDT can be reached due to increased absorption at steady processing regime after the first shots of the line. Moreover, the increase of OL also leads to an increase of F_0^{tot} and entry into the correct range to obtain LIPSSs[7]. In conclusion, the effect of a correct choice of OL , F_0 , and overscans is to keep F_{abs} (F_0, N) in the correct BDT range for each subsequent shot, while increasing the total deposited fluence F_0^{tot} until the fluence range to obtain LIPSSs is reached. This is illustrated in Fig. 6.1.

To study the effect of pulse duration on the formation of LIPSSs, four different pulse durations were applied: 0.230, 1, 6.7, and 10 ps. For pulse durations of 0.230 and 1 ps, processing conditions were found which resulted in LIPSSs, but the peak-to-valley amplitude of those LIPSSs were larger than the thickness of the molybdenum layer. Hence, the glass substrate was exposed in the valleys between peaks in these cases, as seen in Fig. 6.7. At pulse durations of 6.7 and 10 ps, the shape of the LIPSSs were smoother and more superficial. That is, the valleys were less deep and did not expose the glass carrier. Therefore, to create large areas of

Figure 6.5: SEM images of machined 150 nm PVD deposited molybdenum layers on soda lime glass textured by 6.7 ps, *UV* (343 nm) laser pulses, where overscans and scanning speed were varied while repetition frequency (100 kHz) and fluence (0.05 J/cm^2) were fixed. It should be noted, that the images are not all to the same scale. (a) Single pulse, (b) 1 overscan, 91.6% overlap, (c) 1 overscan, 93.7% overlap, (d) 1 overscan, 97.9% overlap, (e) 2 overscans, 97.9% overlap. Only at high pulse overlap is the layer damage-free. The total (or accumulated) fluence deposited in each condition is plotted in Fig. 6.6. This set of images clearly shows the effect of the overlap on the fabrication of textured lines without thermal damage. LIPSSs starts to grow when F_0^{tot} is increased enough to reach the correct LIPSSs fluence range[7].

LIPSSs, the pulse duration in subsequent experiments was fixed to 6.7 ps. The fact that these LIPSSs were smoother and more superficial can probably be attributed to the relatively short electron-phonon coupling time τ_{ep} of molybdenum, when compared to the pulse duration[6,16,17]. Further study would be required to confirm this.

6.3.4 Processing areas

The final step of the experimental procedure consisted of choosing a few sets of processing parameters from the previous step (Sec. 6.3.3), and creating areas of LIPSSs by varying the pitch (distance) between parallel lines, which were scanned in the same direction. This pitch is an additional parameter to be considered for texturing areas with LIPSSs.

Polarization is an essential factor for determining the direction of regular LIPSSs.

Figure 6.6: The total fluence F_0^{tot} (J/cm^2) incident on the sample from Eq. (6.3) is plotted as a function of the overlap (%) and overscans, at the fixed single pulse average fluence $F_0 = 0.05 \text{ J}/\text{cm}^2$. Circles indicate the total fluence of the conditions of the images in Fig. 6.5. Red circles *a*, *b*, and *c* refer to conditions inducing thermal damage of the layer, while green dots *d* and *e* refer to damage-free conditions.

Depending on the material and machining conditions, this direction can be either parallel or perpendicular to an applied linear polarization[18,19]. The observed LIPSSs on molybdenum thin layers were found to grow perpendicular to the linear polarization of the laser radiation. Long LIPSSs, without bifurcations and interruptions, can be obtained if the linear polarization is perpendicular to the scanning direction[20]. In this way, LIPSSs growth is not constrained by the width of the single laser line and regular nanogratings can be obtained over large areas. Conditions were found at which the surface was covered with long LIPSSs without bifurcations, as shown in Fig. 6.8(a). It was determined by CLSM that the material removed by ablation on this sample was below 150 nm in thickness. When required, the thinning of the processed layer could be compensated for by using a thicker layer.

The obtained nanogratings were inspected by SEM and AFM to determine the periodicity and amplitude of the LIPSSs obtained with *UV*, green, and *IR* laser light (Table 6.1). It is known from literature that the periodicity of the LIPSSs is correlated to the wavelength of the laser[20]. The results in Table 6.1 confirm this. It is also known that the amplitude of LIPSSs depends on the parameters applied[18,19]. However, the process window leading to LIPSSs on a damage-free thin molybdenum layer is so small that large areas were machined here with just one set of conditions, with respect to each wavelength. For each set of conditions

Figure 6.7: SEM images of LIPSSs in single lines on 400 nm molybdenum layer irradiated with *IR* light. (a) $\tau = 0.23$ ps, $fluence = 0.81$ J/cm², 93% overlap, 1 overscan. (b) $\tau = 10$ ps, $fluence = 1.26$ J/cm², 93% overlap, 1 overscan. Single arrows in the graphs indicate the processing direction, whereas the double arrows indicate the polarization direction of the laser radiation. LIPSSs in (b) are smoother and more superficial than those in (a).

Figure 6.8: (a) SEM image of a 870 nm grating composed by highly periodical LIPSSs on 400 nm molybdenum layer sputtered on soda lime glass. Processing conditions: $\lambda = 1030$ nm, 6.7 ps, 98% overlap, 0.013 J/cm², 100 kHz, 0.3 μ m pitch between different lines and 30 μ m spot size. The LIPSSs length is not limited by the dimensions of the laser spot (indicated by the white circle). Single arrow indicates the scanning direction, while double arrow indicates the polarization. This picture clearly shows that there is no fundamental limitation in the size of the processable area, since the length of the LIPSSs is not constrained by the size of the lasers spot. (b) AFM image showing the smooth 3D topography of the same sample. (c) 2D cross-section of the surface in Fig. 6.8(b).

Table 6.1: Averaged periodicity and amplitude (obtained by AFM and SEM) of LIPSSs obtained with the three different lasers wavelengths.

	<i>UV</i> ($\lambda = 343nm$)	<i>Green</i> ($\lambda = 515nm$)	<i>IR</i> ($\lambda = 1030nm$)
Aver. periodicity (<i>nm</i>)	270	390	890
Aver. amplitude (<i>nm</i>)	29	21	13
Improvement [%]		20	59

this leads to a single amplitude of the LIPSSs, as seen in Table 6.1. Their 3-D morphology is shown in Fig. 6.8(b). In addition, Fig. 6.8(c) shows the smooth sinusoidal shape of its cross-section. Figure 6.9(a) and 6.9(b), demonstrates the uniformity of large areas with LIPSSs as a uniform color at fixed visual angle due to diffracted light. To confirm the uniformity, Fig. 6.9(c) shows the AID of the gratings of Fig. 6.9(a) and 6.9(b). In Fig. 6.9(c), two different lobes are visible, one representing the zeroth order and the other representing the first order of diffraction. The first order of diffraction subtracts part of the intensity from the zeroth order as shown in Fig. 6.9(c). The measured data from Fig. 6.9(c) matches with a nanograting of 390 nm periodicity, which is the same value observed with SEM and AFM inspection. As expected for a nanograting of such periodicity, the first order of diffraction disappears at wavelengths longer than the periodicity of the grating. Hence, this confirms that the optical diffraction shown in Fig. 6.9(a) and 6.9(b) originates from the LIPSSs and not from geometrical features, such as grooves formed by ablation during laser processing. The latter would show a larger periodicity.

Since theoretical and numerical models of LIPSSs -or more specifically, models predicting periodicity of LIPSSs describing the absorbed laser energy below the rough surface of the material- are known only for bulk material, we compared the periodicity predicted by one of those bulk models, known as the efficacy factor theory[21,22], to the experimentally obtained periodicity in the thin molybdenum layers[23]. We found that the periodicity of LIPSSs produced on thin films was in good agreement with the theoretical expectations for LIPSSs on bulk material.

6.4 Conclusions

By applying ultra-short laser pulses, very regular and damage-free nanogratings consisting of laser-induced periodic surface structures (LIPSSs) of various periodicities (890 and 390 nm) were fabricated over areas as large as $6 \times 6 \text{ mm}^2$ on 400 nm thin molybdenum films deposited on borosilicate glass. It was found that the optical diffraction effect of the nanograting was indeed produced due to the LIPSSs and not by laser ablated grooves of larger periodicity. Furthermore, it was shown that there is no fundamental limitation in the size of the processable area, where the only

Figure 6.9: (a) and (b) Photographs of the same laser textured sample at different angles showing the feasibility of large area nanogratings (LIPSSs) on 400 nm molybdenum layer. (c) AID obtained by spectrophotometry: the intensity I is plotted as function of the scattering angle θ and the incident lights wavelength λ . The measurement was taken over an area of $6 \times 6 \text{ mm}^2$. Notice that the first order of diffraction subtracts part of the intensity from the zeroth order. Measured data match with a grating of 390 nm periodicity, confirming that the optical diffracting effect was produced by the LIPSSs and not by other geometrical features of larger periodicity.

constraint is given by the beam manipulation system and the size of the sample. Focusing on the technical side of laser nanofabrication of long regular LIPSSs on thin molybdenum layers, the aim of this work was also to give an understanding of the correct laser parameters to apply during laser texturing of the thin layers. It was discussed in detail and demonstrated experimentally that the primary role played by laser parameters, such as fluence and spatial pulse overlap, is to reach the ductile range of molybdenum. Only then thermal damage of the thin layer can be avoided. On the other hand, the laser parameters should be chosen such as to reach the right range of accumulated fluence to initiate LIPSSs. It is expected that an analogous approach could be taken to texture thin layers of materials similar to molybdenum, such as chromium and tungsten.

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6.5 References

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Chapter 7

Conclusions and recommendations

7.1 Conclusions

Thermal processing of thin films by ultra-short pulsed lasers has been shown to be an innovative approach to process thin films, showing combined encouraging results on the optical and electrical performance of the treated films.

In chapter 2, the first research question (Q1) (what is the effect of laser pulses with different time durations (i.e. nano- and picosecond) on the temperature profiles in the films during as well as after their absorption and how this affects the thermal selectivity of the process?) was answered. A finite-element model was developed for ZnO and Mo thin film and it was analytically demonstrated that ultra-short pulses can be exploited to increase the selectivity during thermal processes. Moreover, linking the fundamental research to the industrial need of high throughput, the simulation results clearly indicate that, when using an unfocused beam, the only limitation to the processing speed is given by laser power available.

Chapter 3 and 4 focused on thermal annealing by ultra-short laser pulses of SnO₂ thin films (thickness $\approx 1 \mu\text{m}$). In chapter 3, the effect of the laser annealing on the electrical and optical properties was studied. In this chapter research question Q2 was answered, which is: how the optical and electrical properties of the films change after the laser process? That is, a marked increased optical transmittance of light in the visible-UV range and a simultaneous modest decrease of the electrical properties of the laser treated films were found. Combining these two contributions via the so-called Figure of Merit, an overall improvement of the performance of the films after the laser treatment was observed. At high laser fluence levels, modification of the surface texture of the films was also observed. Chapter 4 focused on the explanation, at a microscopic level, of the observed changes in the SnO₂ thin films, which answered question Q3. That is, it explained, at a microscopic level, the origin of the measured macroscopic changes. The increased optical transmittance

was mainly attributed to the removal of the thin interfacial carbon-rich layer present in the as-deposited samples and to the new surface morphology, while the small decrease of the electrical performance was ascribed to the generation of laser-induced defects, upon laser processing, especially in the molten-resolidified region.

In chapter 5, ultra-short pulsed laser annealing of Al:ZnO thin films (thickness $\approx$ 130-800 nm) was studied. A remarkable improvement of the electrical properties was observed, while the optical properties did not show a significant change. This result answers question Q2 for this process. In the same chapter, also research question Q3 was answered, explaining the observed changes, at a microscopic level, with a local atomic reorganization at the nm-scale.

In chapter 6, thin molybdenum films (thickness $\approx$ 150-400 nm) deposited on glass were textured by ultra-short laser pulses. On the surface of the films, nano-sized gratings formed which are known as Laser-Induced Periodic Surface Structures (LIPSSs). These structures modify the optical properties of the films by increasing the scattering of light in the near infra-red part of the spectrum. This result answers questions Q2 and Q3. Focusing on the technical side of laser nano-fabrication of long regular LIPSSs on thin brittle molybdenum films, the aim of this work was also to give an understanding of the correct laser parameters to apply during laser texturing of these thin films, in order to avoid or minimize thermal damage. It was found that the brittle-ductile transition must be taken into account when optimizing the laser parameters during laser processing. This answers question Q4, i.e. how the optimal laser parameters can be chosen in order to avoid any thermally related damage of the films?

In summary, it was experimentally shown that the extremely short heating-cooling cycle time, induced by ultra-short laser pulses in the studied materials, were still long enough to produce changes on the microscopic scale, which resulted in effective changes on the macroscopic properties (i.e. electrical and optical properties). This was demonstrated even in the case the materials remain in the solid state during laser processing. This new result also shows that heat treatments with ultra-short pulsed lasers can limit the thermally induced reorganization of the microstructure down to few nanometers, hence avoiding unwanted diffusion of specific atomic species over a longer distance. This peculiar characteristic can be potentially exploited for reducing atomic contamination in multi-layered structures during heat treatments, when compared to processing using longer pulse durations or other conventional techniques, such as furnaces, lamps, or cw and ns-pulsed lasers.

Based on the obtained results, it is concluded that the main question of this thesis (*can ultra-short laser pulses be exploited for thermal processing of thin films?*) can be answered. That is, indeed ultra-short pulsed lasers can be used for thermal processing of thin films.

7.2 Recommendations

This work is intended to represent a first step to research in the development of thermal processing using ultrafast lasers in order to increase the yield of thin film-based devices. Although any kind of thermal process can be studied using ultrafast lasers, here some recommendations for future research are presented in the same direction of the applications studied in this work.

The first recommendation is to investigate the effect of the ultra-short laser annealing on other, but similar materials than SnO_2 , Al:ZnO and Mo , which are interesting for photovoltaic as well as for microelectronic applications, such as ITO , thin film Si , etc.

In this thesis, n-type doped TCOs were considered. Another recommendation for future study is to investigate the effect of ultra-short laser pulses for the fabrication of p-type TCOs. The latter would be of both technological and scientific relevance. That is because the extreme briefness of the laser process can be exploited to generate and freeze particular defects in the lattice, which are necessary for p-conductivity, i.e. p-type defects, such as Zn vacancies in intrinsic ZnO , or activation of p-type dopants.

One last recommendation, of practical interest, would be to demonstrate the applicability of selective thermal processes using ultra-short laser pulses on fully functional thin film devices.

Publications

In the framework of this thesis, the following articles have been published.
D. Scorticati was the main contributor to all of these publications.

Journal articles

D. Scorticati, G.R.B.E. Römer, D.F. de Lange, and A.J. Huis in't Veld, Ultra-short-pulsed laser-machined nanogratings of laser-induced periodic surface structures on thin molybdenum layers, *Journal of nanophotonics*, 6 (1), 1-11, ISSN 1934-2608 (2012).

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D. Scorticati, A. Illiberi, T. Bor, S.W.H. Eijt, H. Schut, G.R.B.E. Römer, M. Klein Gunnewiek, A.T.M. Lenferink, M.W.G.M. Verhoeven, B.J. Kniknie, M.R. Joy, M.S. Dorenkamper, D.F. de Lange, C. Otto, D. Borsa, W.J. Soppe, A.J. Huis in 't Veld, Thermal annealing using ultra-short laser pulses to improve the electrical properties of Al:ZnO thin films, *submitted to Acta Materialia* (2015).

D. Scorticati, G.R.B.E. Römer, D.F. de Lange, A.J. Huis in 't Veld, Modeling of temperature cycles induced by pico- and nanosecond laser pulses in ZnO and Mo thin films, *submitted* (2015)

Conference articles

D. Scorticati, J. Z. P. Skolski, G. R. B. E. Römer, A. J. Huis in 't Veld, M. Workum, M. Theelen, and M. Zeman. Thin film surface processing by ultrashort laser pulses (USLP). *Proceedings of SPIE - The International Society for Optical Engineering*. 8438:84380T-1-8 (2012).

D. Scorticati, A. Illiberi, G. R. B. E. Römer, T. Bor, W. Ogieglo, M. Klein Gunnewiek, A. Lenferink, C. Otto, J. Z. P. Skolski, F. Grob, D. F. de Lange, and A. J. Huis in 't Veld, Optical and electrical properties of SnO₂ thin films after ultra-short pulsed laser annealing. *Proceedings of SPIE - The International Society for Optical Engineering*. 8826:88260I-1-12 (2013).

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