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Inherently area-selective hot-wire assisted atomic layer deposition of tungsten films

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Abstract. This work demonstrates area-selective growth of tungsten (W) films by hot-wire assisted atomic layer deposition (HWALD). With this recently developed technique, low-resistivity alpha-phase W films can be deposited by using sequential pulses of atomic hydrogen (at-H) and WF_6 at a substrate temperature of 275 °C. As reported in this article, the deposition is highly selective. HWALD tungsten grows with little to no incubation time on W, Co and Si surfaces. On the other hand, no growth is observed on TiN, Al_2O_3 and SiO_2 surfaces. The interfaces of W and various substrates are examined by transmission electron microscopy. The absence of oxygen in the interfaces indicates that the atomic-hydrogen not only serves as a suitable ALD precursor for W, but is here shown to effectively reduce the native oxides of W and Co at the ALD process conditions, enabling in situ surface preparation before starting the deposition sequence.

Keywords: Hot-wire atomic layer deposition; Inherently selective growth; Tungsten; transmission electron microscopy

1. Introduction

Atomic layer deposition (ALD) [1] is known to form conformal and highly uniform (ultra) thin films with thickness control precision on a sub-monolayer scale due to its self-limiting reaction mechanisms. Modern ultra-large-scale integration requires downscaling of devices and circuits with less than 10 nm feature sizes [2]. Conventional etch or deposition/lift-off processes in combination with various lithography techniques, which are employed to achieve film patterning, become increasingly challenging due to the ever-shrinking alignment requirements [3,4]. In this light, area-selective ALD (AS-ALD) increasingly attracts attention over the past several years. AS-ALD enables nanoscale patterning and further downscaling of device dimensions [5,6].

The most common approach to AS-ALD is to provide a molecular mask as a “resist” layer disabling deposition over selected areas. Such masks include self-assembled monolayer (SAM) materials [7-10] and polymers [3,11]. However, SAMs typically have long assembly times in the order of hours and must be removed after deposition [12]. An alternative approach to AS-ALD is to take advantage of differences in nucleation rates on different surfaces for a given ALD process. This offers a cost-effective approach to form patterned layers at low material budget. Recently, a few results have been reported on the area-selective ALD using the inherent substrate-dependent growth initiation based on nucleation delay, or ‘inherent AS-ALD’ processes [13-15]. However, there is more work need to be done to overcome the difficulty in finding and combining the required chemical properties of ALD precursors and deposition substrates.

In this work, we demonstrate an inherent AS-ALD of tungsten (W) films by utilizing a technique called hot-wire (HW) assisted ALD (HWALD) [16-18]. In the mentioned references, we have demonstrated high-purity alpha-phase HWALD W films, grown by employing a

filament heated to 1300-2000 °C to dissociate molecular hydrogen (H_2) into atomic hydrogen (at-H) as one of the precursors. WF_6 was adopted as a second (tungsten) precursor.

Many studies about selective growth of W by chemical vapor deposition (CVD) on Si/SiO₂ substrates were reported in the last decade [19-22]; only very little work has however been published on AS-ALD of W [12]. In all these reports, H_2 and silane (SiH_4) were the two main precursors adopted as reductants. Although area-selective CVD and ALD of W were established for a given processing time or number of ALD cycles, extending these parameters to a longer time or a larger number of cycles generally led to undesirable nucleation on all exposed surfaces, thereby losing the selectivity.

The loss of selectivity in silane- WF_6 based ALD was attributed to the occurrence of Si-H terminations on SiO₂ surfaces caused by the dissociative adsorption of silane [12,23,24]. For selective ALD based on H_2 - WF_6 , articles proposed the by-product hydrogen fluoride (HF) as the culprit [20], which was later claimed not to be the main reason causing the loss of selectivity [25]. Instead, the partial decomposition of WF_6 into tungsten subfluorides (WF_x , $x < 6$) was confirmed to be the cause [22,25,26].

The HWALD process we use employs no silane. Further, introducing separate precursor pulses with a sufficient purge time in between prevents the mixing of WF_6 and hydrogen in the gas phase. This may well suppress the influence of tungsten subfluorides. Our HWALD process therefore bears the promise to remain selective.

In this work, we demonstrate the retarded nucleation of HWALD W on SiO₂, Al₂O₃ and TiN surfaces in contrast to its readily-occurring deposition on W and cobalt (Co) surfaces. The HWALD experiments were monitored in situ by a spectroscopic ellipsometer (SE). Further sample characterization was performed ex situ with the assistance of a high resolution transmission electron microscope (HRTEM). Finally, we studied the effect of the amorphous

silicon (a-Si) seed layer thickness on the incubation time and growth rate for HWALD on the substrates showing the retarded nucleation.

2. Experimental

HWALD alpha-phase W films of low resistivity were grown using sequential pulses of WF_6 and HW-generated at-H, as described in our previous work, utilizing a home-built **hot-wall** reactor [27-29]. Briefly, the process conditions were fixed at a substrate temperature of 275 °C and a total pressure of 50 Pa. A standard HWALD cycle consisted of an at-H (50 sccm) pulse of 7 s, a post-at-H purge of 7 s, and a WF_6 (3 sccm) pulse of 0.5 s followed by a post- WF_6 purge of 7 s. The hot-wire temperature was 1750 °C. The standard growth rate varied between 0.01 and 0.02 nm/cycle for different deposition experiments, depending on the amount of residual fluorine-containing species remaining in the reactor. The reactor was equipped with an in-situ SE (Woollam M-2000) operating in the wavelength range between 245 and 1688 nm; this enabled monitoring of the deposition process in real time.

Non-patterned substrates were utilized to investigate the nucleation and growth behavior of HWALD W on SiO_2 , Al_2O_3 , TiN, W and Co. SiO_2 was thermally grown to a thickness of 100 nm on p-type Si (100) wafers. Prior to metal depositions, the SiO_2 -covered wafers were cleaned in fuming (99%) HNO_3 and boiling 69% HNO_3 to remove organic and metallic contaminations. W films used as the substrates were deposited by a standard HWALD process on top of thermal SiO_2 , using a pre-formed W seed layer of 5 nm (see ref. [16,17] for details). Cobalt layers of 10 nm in thickness were sputtered directly on SiO_2 . Al_2O_3 was formed by thermal ALD in a separate Picosun ALD reactor; TiN was however deposited in the same HWALD reactor, without vacuum break and prior to the W deposition.

After the depositions, the W- and Co-covered wafers were exposed to air for up to 360 hrs, leading to native oxide formation. Prior to starting each HWALD-W process, this native oxide was reduced by a 20-min continuous exposure to at-H at 275 °C (see further discussion), leaving a clean W or Co surface. The reduction step additionally ensures a good conductivity between the two layers of metal in applications. Except for a constant flow of H₂ via the hot-wire, the same conditions were used for the at-H reduction process as for the HWALD process.

Patterned W/SiO₂ substrates were provided by ASM International, with trenches in SiO₂ filled by CVD W and then planarized by chemical mechanical polishing. The Co/SiO₂ substrates were fabricated at the Nanolab Twente by Co sputtering and lift-off. Importantly, before sputtering of 10 nm Co upon SiO₂, an approximately 3 nm thick titanium (Ti) layer was pre-sputtered for better Co adhesion.

The thickness of the a-Si seed layer was varied from 0.01 nm to 5 nm to find out the thinnest seed layer enabling HWALD of W on SiO₂, TiN and Al₂O₃. The film thickness at the wafer center was measured real-time by SE during corresponding experiments. The thicknesses were earlier verified by high-resolution scanning electron microscopy and HRTEM for 10- and 12-nm-thick layers [16,29]. Further, X-ray reflectivity measurements showed a very good agreement with SE for a 14-nm HWALD W film [17]. The optical functions of HWALD W were obtained by SE and parameterized using a Drude-Lorentz description [30,31], as earlier documented in Ref. [17]. Importantly, the sub-nanometer thickness values shown in Figures 1 and 4 fall beyond the accuracy of SE. The plotted thickness ranges are in other words hardly physical and are only shown to indicate the lack of a measurable thickness change during the corresponding experiments. The larger but still few-nm thickness variations (see Figures 2b and 3) solely indicate a qualitative trend (i.e., increase, decrease or little change) in thickness behavior and do *not* provide quantitative information. The sub-monolayer numbers given in

Table 1 can at best be interpreted as the average thickness over the mm-scale area probed by SE; this area features discrete nm-scale film islands on an otherwise uncovered surface. The HRTEM was executed on a Philips CM300ST-FEG model with GATAN cameras at 300 kV. The samples were prepared by dimple grinding/polishing and Argon ion sputtering.

3. Results and discussions

3.1. Nucleation of HWALD W on substrates of various materials

The nucleation behavior of HWALD W on a thermally-grown 100 nm thick SiO_2 layer is shown in Figure 1. The figure presents the development of the W thickness with or without a pre-treatment with at-H. Without the pre-exposure, 850 HWALD cycles resulted in a negligible change in the W thickness, indicating nearly no growth. The same occurs when applying a 20 min at-H pre-exposure step: no deposition of W occurs for at least 1000 HWALD cycles. Therefore, it can be concluded that W can hardly nucleate by the HWALD process up to 1000 cycles on a SiO_2 surface. Additionally, there is no effective at-H reduction of SiO_2 to Si at this substrate temperature (otherwise W deposition would start). Based on the measured growth rate of 0.01 to 0.02 nm/cycle for the HWALD W [29], this retarded nucleation on SiO_2 implies growing at least 10 to 20 nm of W on a suitable substrate, with no deposition on SiO_2 .

Although HWALD W can barely nucleate directly on SiO_2 , it can readily grow on W. Clarifying the actual growth mechanism remains outside the scope of this manuscript. In our recently submitted work [32] we explore several factors which might influence the HWALD W process. In previous works [16-18], it has been shown that HWALD W could nucleate without an incubation time upon a W seed layer with an average thickness of 5 nm. The seed layer was pre-formed in the same reactor without a vacuum break, aiming to limit the oxidation process and to

provide a clean metal surface for the subsequent HWALD of W. To note, this seed layer was not continuous and formed in islands, as proven earlier by HRTEM [29].

In this work, we extended the experiments to perform HWALD on natively oxidized W layers, given a sufficient at-H reduction of the native oxide before starting the actual deposition. The reduction process is presented in figure 2 (a). Delta, an optical parameter directly measured by SE and representing the phase difference of light induced by the reflection, changed during the at-H reduction. The SE technique is sufficiently sensitive to quantify such a small increase of delta, so we witness a significant change of the W surface when it is exposed to at-H. However, the thicknesses of W and W-oxide in the optical model could hardly be extracted with this tiny change of delta, which also implied that the native oxide layer was very thin. Nevertheless, the change of delta revealed a measurable influence of at-H upon a 20 min exposure.

Figure 2 (b) shows the growth behavior of HWALD W on a standard 5-nm thick (discontinuous) seed layer of W, pre-exposed to air for 91 hrs. Before starting the deposition, the native oxide was reduced by at-H for 20 min (not shown), as described above. After an incubation period of roughly 150 cycles, the growth rate reached a steady value of 0.017 nm/cycle, which was comparable to that of our standard HWALD process. Separately, a 10-nm W film was pre-deposited by HWALD and kept in air for 900 hrs. Figure 2 (c) demonstrates that after a 20-min reduction by at-H (not shown), HWALD W growth restarted on this air-exposed and then reduced surface after an incubation time of approx. 100 cycles, reaching a standard growth rate of 0.011 nm/cycle. In contrast, growth of HWALD W on a standard W seed layer, pre-formed in-situ without vacuum break using a-Si and WF_6 (see Experimental), resulted in zero incubation time. As the latter approach minimizes the chance of formation of interfacial oxide, the former (i.e., the occurrence of 100-150 cycles of incubation) indicates interface deterioration

upon exposure to air. The interface can however be made suitable for the subsequent deposition of W (presumably by reducing native oxide) by an appropriate exposure to at-H.

Apart from tungsten, cobalt (Co) was also examined as a substrate material for HWALD W. First, a 15-nm Co layer was sputtered on top of a SiO₂ film and then exposed to air for 360 hrs. Prior to starting the HWALD process, the native Co-oxide was reduced by at-H; the SE monitoring is demonstrated in figure 3 (a). The at-H exposure started at 2 min. The thickness of Co and its native oxide were measured by SE with a model consisting of a cobalt oxide/Co/SiO₂/Si layer stack. To be specific, the cobalt oxide was modelled using a Tauc-Lorentz formulation with 1 oscillator [33] whereas Co was modelled by the Drude-Lorentz approach with a Drude term and two Lorentz oscillators [31]. The dramatic coherent thickness change of Co and the native oxide at 3-4 min of the at-H exposure indicated an effective oxide reduction. Although the reduction time was fixed at 20 min to be consistent with the at-H exposure applied to W, the cobalt oxide was easier to reduce as a 2-3 min exposure appeared sufficient to remove the entire ~1.3 nm of native oxide at 275 °C. The slight thickness increase of cobalt oxide after 4 min of reduction can be related to the accuracy of SE measurements (see Experimental) or the substrate temperature change. Figure 3 (b) shows the HWALD growth of W on the as-prepared Co surface. Comparable with W layers, the incubation time was around 120 cycles before achieving a linear growth regime with a stable growth rate of 0.017 nm/cycle.

We further examined the nucleation of HWALD W on ALD-formed TiN and Al₂O₃. Specifically, TiN was deposited in the same reactor as HWALD W without vacuum break and Al₂O₃ was fabricated in a commercial ALD tool. The HWALD W failed to nucleate on these substrates up to 1000 HWALD cycles. Figure 4 displays the growth of HWALD W on both materials and no at-H exposure was applied to them before HWALD of W. The negative thickness is not physical; it occurs because the used model does not account for the surface

roughness. Both materials were modelled by the Cauchy SE model. Figure 4 confirms that only very little surface modifications occur after 600 HWALD cycles. However, even a lesser change of the surface state was observed on Al_2O_3 up to 1000 cycles. Therefore, selective growth of HWALD W can also be expected on surfaces containing a suitable nucleation layer (e.g., W or Co) in combination with TiN and/or Al_2O_3 patterns.

3.2. Selective growth of HWALD W

3.2.1. W/ SiO_2 substrates

Based on the results above, we expect HWALD W to selectively grow on patterned W/ SiO_2 and Co/ SiO_2 substrates. To investigate this, 2200 HWALD cycles were applied to a substrate with CVD W deposited into trenches formed in SiO_2 . Namely, 85-nm-deep and 160-nm-wide SiO_2 trenches were filled with W, with a 200 nm spacing, see figure 5 (a). Before the deposition, the standard at-H pre-exposure was executed to reduce the native tungsten oxide. Figure 5 presents the cross-sectional HRTEM images of the W/ SiO_2 substrates before and after HWALD of W. After executing 2200 HWALD cycles, a 19-nm thick W layer was obtained, selectively covering the CVD-W trenches. Importantly, after the first 1200 HWALD cycles, the grown W film was taken out of the reactor and exposed to air for 10 hrs. Then, the sample was placed back into the reactor, followed by at-H reduction and the remaining 1000 cycles. The intermediate exposure to air can explain the lower-than-standard growth rate per cycle (GPC) of <0.009 nm/cycle; one should keep in mind that standard GPC can be as high as 0.02 nm/cycle.

The HRTEM image of figure 5 (b) clearly demonstrates the presence of HWALD W only on top of the W, with no measurable deposition on the SiO_2 surface. Close-ups are shown in figure 6. Noticeably, triangular-shaped “ears” appear at the edges between CVD W and SiO_2 ,

indicating lateral overgrowth of HWALD W at the edges. All these observations confirm the selective growth of HWALD W on CVD W without nucleation on SiO₂.

HRTEM images in figure 6 visualize the interfaces between the HWALD- and CVD-W, as well as the atomic arrangements. Noticeably, the HWALD W film thickness of 18 nm as indicated in figure 6 (a) corresponds with the lateral width of the “ear”, being 15 nm. This implies a comparable growth rate of HWALD W in both vertical and lateral directions. Moreover, the triangular-shaped feature confirms the growth on CVD W but not on SiO₂. Figures 6 (b) and (c) show the interfaces between the two layers of W. The interface in (b) can hardly be observed; the atomic arrangements continue from the CVD W to the HWALD W formed on top, indicating an epitaxial growth. However, there is an obvious change of crystal orientation at the interface depicted in figure 6 (c). Therefore, HWALD W can grow on CVD W either epitaxially or in a polycrystalline form. Applying the Fast Fourier Transform (FFT) method to the observed periodicity in the image yields the d-spacing of all W layers, solely revealing alpha-phase W. Noticeably, the interruption of the HWALD process half-way with the subsequent exposure of the layer to air, followed by the at-H reduction step and the remaining deposition cycles resulted in no (measurable) oxygen contamination at the interface or through the entire HWALD W film. This reconfirmed the efficient interface reduction by at-H.

3.2.2. Co/SiO₂ substrates

We further investigated the selective growth of W using HWALD on patterned Co/SiO₂ surfaces. Figure 7 (a) shows these Co/Ti/SiO₂/Si substrates. The W has only been formed on Co, leaving the SiO₂ surfaces blank and thus affirming the selectivity. Figure 7 (b) shows a close-up of the Co/SiO₂ sample; note the commonly observed feature formed at the Co edge due to the lift-off process. Prominently, a uniform and conformal layer of W covering both sides of this

feature highlights the advantages of the HWALD technique in terms of its uniformity and step coverage. Moreover, single crystal grains are imaged in figure 7 (c). The thickness of the W layer varies between 9 and 13 nm due to the surface roughness, consistent with the expectations for 1100 HWALD cycles. Importantly, the d-spacing obtained from the crystals after an FFT analysis again revealed pure alpha-phase W, the lowest-resistivity phase of tungsten [34].

Although selective growth of W has been achieved in both CVD and ALD earlier [2,19-22,35], extended process times or cycle numbers generally lead to nucleation on all surfaces. Hence, the selectivity window (i.e., the process range where growth only occurs on dedicated surfaces) is crucial and efforts are made to broaden it. In a recent publication, it has been reported that the selectivity window of ALD W on Si/SiO₂ patterns, using WF₆ and SiH₄, could be broadened from 10 nm to 16 nm [12]. The loss of selectivity beyond 16 nm was attributed to Si-H bonds on SiO₂ surfaces due to the action of SiH₄ [12,24]. Moreover, Lemaire *et al.* [2] have claimed that the surface hydroxyls on SiO₂ surfaces are a key factor for SiH₄ adsorption, causing the loss of selectivity after 10-35 ALD cycles using WF₆ and SiH₄. However, in our case neither WF₆ nor at-H could efficiently provide nucleation sites on SiO₂. As for the established selective CVD W using WF₆ and hydrogen at 250-350 °C [35], the loss of selectivity up to 200 nm was attributed to the adsorption and incorporation of the by-product tungsten subfluorides (WF_x), on SiO₂ [25,26]. In our HWALD process, the loss of selectivity was not observed at a substrate temperature of 275 °C up to 2200 cycles, excluding the possible role of subfluorides.

To summarize, under the optimized process conditions, HWALD W can be selectively grown during at least 1100 cycles tried so far on patterned Co/SiO₂ substrates and at least for 2200 cycles tried so far on W/SiO₂ substrates. Besides, no nucleation was visible on TiN and Al₂O₃ surfaces after an exposure up to 1000 HWALD cycles.

3.3. Nucleation of HWALD W on a-Si seed layers of various thicknesses

Surfaces on which the HWALD W growth is inhibited, such as SiO₂, TiN and Al₂O₃, can be modified to allow tungsten to deposit. In previous works, we have reported on a method of forming a W seed layer with an average thickness from 2 to 5 nm at a substrate temperature of 325 °C. This seed layer was formed in two steps: (i) growing a 5-nm-thin amorphous Si (a-Si) layer using Si₃H₈ gas and (ii) consequently exposing the a-Si to WF₆ gas, forming a solid W film and volatile silicon fluorides [16,17]. Here, we report on experiments to reduce the a-Si layer thickness in order to determine the thinnest layer still acting as a nucleation seed layer for W.

Dealing with few-nm-thick layers requires a reliable thickness measurement method. SE can provide reliable data for continuous (closed) layers, still requiring a few thickness verification points by other (ex-situ) techniques. However, for very thin films, one should bear in mind the earlier notice: the values can only be used to compare qualitative trends. We have additionally demonstrated that a W seed layer, obtained from converting a 5-nm a-Si film (measured by SE), was actually in a form of discontinuous clusters with the height ranging from 1 to 7 nm, instead of being a continuous layer [29]. The average thickness of 3-4 nm was in agreement with that given by SE (3.5 nm), assuming a continuous layer.

Figure 8 depicts a cross-sectional HRTEM image of a W seed layer pre-formed from a roughly 0.8-nm a-Si seed layer, measured by SE. From figure 8, the resulting W seed layer (of ~1.6 nm as measured by SE) consists of separated clusters with a thickness varying between 1 and 3.5 nm. Again, one can see that SE gives roughly average thickness values. Therefore, SE can still provide a meaningful indication of film thickness, even for discontinuous ultra-thin W seed layers.

Table 1 presents the experimental results clarifying the seed layer thickness influence. In all the experiments, the W seed layers were further exposed to 500 HWALD cycles. Noticeably, an a-Si layer of less than 0.2 nm already resulted in normal ALD growth, as evidenced by the standard (0.014-0.016 nm/cycle) GPC, after roughly 100 incubation cycles. With thinner a-Si layers, the growth failed to reach the linear regime. Using an a-Si (indicative) thickness of around 0.5 nm, a HWALD W layer of 10 nm was deposited on SiO₂ with hardly any incubation time. The average resistivity of this film, measured by four-point-probe, was 15.6 $\mu\Omega\cdot\text{cm}$. This is comparable to the resistivity (15 $\mu\Omega\cdot\text{cm}$) of a 10-nm HWALD W layer deposited on a W seed layer of 5 nm. We conclude that even ultra-thin a-Si seed layers can effectively work to enable HWALD of alpha-phase W on SiO₂ surfaces.

Table 1. Growth behavior of HWALD W on different-thickness^a seed layers.

a-Si thickness by SE [nm]	W seed layer thickness by SE [nm]	Number of incubation cycles preceding standard GPC	GPC [nm/cycle]
< 0.1	< 0.1	>500	0.0005 ^b
< 0.2	< 0.2	~100	0.014
~ 0.5	~ 1	<5	0.019
~ 5	~ 7	<5	0.017

^a An indication of film thickness is given, as measured by SE; see the text for further clarification.

^b Growth rate failed to reach standard values after 500 cycles; even no trend to approaching standard GPC was noticed.

4. Conclusions

In this work, we characterized and compared the nucleation and growth of tungsten films deposited by hot-wire assisted ALD (HWALD W) using atomic hydrogen and WF₆ on various substrates. No nucleation was found on a thermally-grown SiO₂ surfaces nor on (ALD-grown)

TiN and Al₂O₃ surfaces. On the contrary, HWALD W could be deposited on properly cleaned W and Co surfaces, with an incubation during approximately 100 cycles. The native oxides of these metals were effectively reduced by at-H under the same process conditions as used in the ALD recipe. An area-selective HWALD W process was achieved on W/SiO₂ and Co/SiO₂ patterned surfaces. Furthermore, ultra-thin a-Si seed layers were explored in order to start HWALD of W on surfaces which were inert to the process. Applying an a-Si seed layer far below 1 nm in thickness appeared sufficient to support the effective nucleation, enabling the standard GPC with little to no incubation time.

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References

- [1] S. M. George, Atomic layer deposition: an overview, *Chem. Rev.* 110 (2010) 111.
- [2] P. C. Lemaire, M. King, and G. N. Parsons, Understanding inherent substrate selectivity during atomic layer deposition: effect of surface preparation, hydroxyl density, and metal oxide composition on nucleation mechanisms during tungsten ALD, *J. Chem. Phys.* 146 (2017) 052811.
- [3] M. Biercuk, D. Monsma, C. Marcus, J. Becker, and R. Gordon, Low-temperature atomic-layer-deposition lift-off method for microelectronic and nanoelectronic applications, *Appl. Phys. Lett.* 83 (2003) 2405-2407.
- [4] J. Goldberger, A. I. Hochbaum, R. Fan, and P. Yang, Silicon vertically integrated nanowire field effect transistors, *Nano Lett.* 6 (2006) 973-977.
- [5] M. Fang and J. C. Ho, Area-Selective atomic layer deposition: conformal coating, subnanometer thickness control, and smart positioning, *ACS Nano* 9 (2015) 8651-8654.
- [6] A. Haider, M. Yilmaz, P. Deminskyi, H. Eren, and N. Biyikli, Nanoscale selective area atomic layer deposition of TiO₂ using e-beam patterned polymers, *RSC Adv.* 6 (2016) 106109-106119.

- [7] R. Chen, H. Kim, P. C. McIntyre, and S. F. Bent, Self-assembled monolayer resist for atomic layer deposition of HfO_2 and ZrO_2 high- κ gate dielectrics, *Appl. Phys. Lett.* 84 (2004) 4017-4019.
- [8] M. Yan, Y. Koide, J. Babcock, P. Markworth, J. Belot, T. Marks, and R. Chang, Selective-area atomic layer epitaxy growth of ZnO features on soft lithography-patterned substrates, *Appl. Phys. Lett.* 79 (2001) 1709-1711.
- [9] J. P. Lee and M. M. Sung, A new patterning method using photocatalytic lithography and selective atomic layer deposition, *J. Am. Chem. Soc.* 126 (2004) 28-29.
- [10] M. H. Park, Y. J. Jang, H. M. Sung-Suh, and M. M. Sung, Selective atomic layer deposition of titanium oxide on patterned self-assembled monolayers formed by microcontact printing, *Langmuir* 20 (2004) 2257-2260.
- [11] A. Sinha, D. W. Hess, and C. L. Henderson, A top surface imaging method using area selective ALD on chemically amplified polymer photoresist films, *Electrochem. Solid-State Lett.* 9 (2006) G330-G333.
- [12] B. Kalanyan, P. C. Lemaire, S. E. Atanasov, M. J. Ritz, and G. N. Parsons, Using hydrogen to expand the inherent substrate selectivity window during tungsten atomic layer deposition, *Chem. Mater.* 28 (2016) 117-126.
- [13] H.-B.-R. Lee and S. F. Bent, Microstructure-dependent nucleation in atomic layer deposition of Pt on TiO_2 , *Chem. Mater.* 24 (2011) 279-286.
- [14] S. E. Atanasov, B. Kalanyan, and G. N. Parsons, Inherent substrate-dependent growth initiation and selective-area atomic layer deposition of TiO_2 using “water-free” metal-halide/metal alkoxide reactants, *J. Vac. Sci. Technol. A* 34 (2016) 01A148.
- [15] M. M. Kerrigan, J. P. Klesko, and C. H. Winter, Low temperature, selective atomic layer deposition of cobalt metal films using bis (1, 4-di-tert-butyl-1, 3-diazadienyl) cobalt and alkylamine precursors, *Chem. Mater.* 29 (2017) 7458-7466.
- [16] M. Yang, A. A. Aarnink, A. Y. Kovalgin, R. A. Wolters, and J. Schmitz, Hot-wire assisted ALD of tungsten films: in-situ study of the interplay between CVD, etching, and ALD modes, *Phys. Status Solidi A* 212 (2015) 1607-1614.
- [17] M. Yang, A. A. Aarnink, A. Y. Kovalgin, D. J. Gravesteijn, R. A. Wolters, and J. Schmitz, Comparison of tungsten films grown by CVD and hot-wire assisted atomic layer deposition in a cold-wall reactor, *J. Vac. Sci. Technol. A* 34 (2016) 01A129.
- [18] A. Y. Kovalgin, M. Yang, S. Banerjee, R. O. Apaydin, A. A. Aarnink, S. Kinge, and R. A. M. Wolters, Hot-Wire assisted ALD: a study powered by in situ spectroscopic ellipsometry, *Adv. Mater. Interfaces* 4 (2017) 1700058.
- [19] T. Tsutsumi, H. Kotani, J. Komori, and S. Nagao, A selective LPCVD tungsten process using silane reduction for VLSI applications, *IEEE Trans. Electron Devices* 37 (1990) 569-576.
- [20] Y. Pauleau and P. Lami, Kinetics and mechanism of selective tungsten deposition by LPCVD, *J. Electrochem. Soc.* 132 (1985) 2779-2784.
- [21] R. Wilson and A. Williams, New insights on nucleation of tungsten on insulators during selective chemical vapor deposition, *Appl. Phys. Lett.* 50 (1987) 965-967.
- [22] E. Broadbent and C. Ramiller, Selective low pressure chemical vapor deposition of tungsten, *J. Electrochem. Soc.* 131 (1984) 1427-1433.
- [23] S. Dana, M. Liehr, M. Anderle, and G. Rubloff, Kinetics of nucleation and growth of Si on SiO_2 in very low pressure SiH_4 chemical vapor deposition, *Appl. Phys. Lett.* 61 (1992) 3035-3037.

- [24] S. Miyazaki, Y. Hamamoto, E. Yoshida, M. Ikeda, and M. Hirose, Control of self-assembling formation of nanometer silicon dots by low pressure chemical vapor deposition, *Thin Solid Films* 369 (2000) 55-59.
- [25] J. Creighton, A mechanism for selectivity loss during tungsten CVD, *J. Electrochem. Soc.* 136 (1989) 271-276.
- [26] J. Creighton, Selectivity loss during tungsten chemical vapor deposition: The role of tungsten pentafluoride, *J. Vac. Sci. Technol. A* 7 (1989) 621-624.
- [27] S. Bystrova, A. Aarnink, J. Holleman, and R. Wolters, Atomic layer deposition of $W_{1.5}N$ barrier films for Cu metallization process and characterization, *J. Electrochem. Soc.* 152 (2005) G522-G527.
- [28] H. Van Bui, A. Y. Kovalgin, A. A. I. Aarnink, and R. A. M. Wolters, Hot-Wire generated atomic hydrogen and its impact on thermal ALD in $TiCl_4/NH_3$ system, *J. Solid State Sci. Technol.* 2 (2013) P149-P155.
- [29] M. Yang, A. A. I. Aarnink, J. Schmitz, and A. Y. Kovalgin, Low-resistivity α -phase tungsten films grown by hot-wire assisted ALD in high-aspect-ratio structures, *Thin Solid Films* 646 (2018) 199-208.
- [30] G. Jellison and F. Modine, Optical functions of silicon between 1.7 and 4.7 eV at elevated temperatures, *Phys. Rev. B* 27 (1983) 7466.
- [31] F. Wooten, *Optical Properties of Solids* Academic Press, New York, 1972.
- [32] M. Yang, A. A. Aarnink, R. A. Wolters, J. Schmitz, and A. Y. Kovalgin, Effects of oxygen, nitrogen and fluorine on the crystallinity of tungsten by hot-wire assisted ALD, *J. Solid State Sci. Technol.* 6 (2017) P839-P844.
- [33] J. Tauc, R. Grigorovici, and A. Vancu, Optical properties and electronic structure of amorphous germanium, *Phys. Status Solidi B* 15 (1966) 627-637.
- [34] E. Lassner and W. D. Schubert, *Tungsten: properties, chemistry, technology of the elements, alloys, and chemical compounds*, Springer Science & Business Media, New York, 1999.
- [35] J. O. Carlsson and M. Boman, Selective deposition of tungsten-prediction of selectivity, *J. Vac. Sci. Technol. A* 3 (1985) 2298-2302.

Figure 1. HWALD of W on 100 nm thick thermally-grown SiO₂. The black line depicts the growth for 850 HWALD cycles without preceding at-H exposure. The red line corresponds to a 20 min in situ pre-exposure to at-H followed by 1000 HWALD cycles. During the at-H exposure, all process conditions were the same as those used in the following HWALD step; the H₂ flow rate was 50 sccm. Note: the plotted thickness values fall beyond the accuracy of SE measurements and are only shown to indicate no measurable change of the W thickness after 1000 cycles on a SiO₂ surface.

Figure 2. (a) The change of optical parameter delta during at-H reduction of native tungsten oxide. The growth behavior of HWALD W on (b) standard 5-nm-thick W seed layer, pre-exposed to air for 91 hrs, and (c) a layer of HWALD W (10 nm) pre-exposed to air for 900 hrs. Before the deposition, a 20-min reduction by at-H was applied to samples (b) and (c), to remove the native oxide.

Figure 3. (a) Reduction of native cobalt oxide, grown on a 15-nm Co layer formed by sputtering and then exposed to air for 360 hrs, by at-H; the at-H exposure started at 2 min. (b) Kinetics of HWALD of W subsequently carried out on the same Co layer.

Figure 4. An attempt to grow HWALD W on TiN and Al₂O₃ substrates: no deposition has been observed under standard conditions. No pre-exposure to at-H was applied. Note: the plotted thickness values fall beyond the accuracy of SE measurements and are only shown to indicate no measurable change of the W thickness after the given number of HWALD cycles.

Figure 5. Cross-sectional HRTEM images of patterned substrates with CVD W and SiO₂: (a) reference sample before deposition and (b) after an exposure to 2200 HWALD cycles; the newly-appeared triangular-shaped extensions (“ears”) can be seen at the edges between CVD W and SiO₂.

Figure 6. Cross-sectional HRTEM images of the interfaces between HWALD W and substrate CVD W, visualizing (a) film thickness, the triangular-shaped “ears” and the interface, (b) epitaxial growth, and (c) change of crystal orientation between the two W layers.

Figure 7. HRTEM images of W grown by HWALD (1100 cycles) on patterned Co/Ti/SiO₂ substrates. (a) Selective growth of W on Co without nucleation on SiO₂; (b) close-up showing the lateral growth at the Co/SiO₂ edge (similar to the triangular-shaped features of the W/SiO₂ substrates); and (c) individual W and Co crystal grains.

Figure 8. HRTEM images of a W seed layer, obtained from converting an a-Si layer of approximately 0.5 nm, as measured by SE.

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Highlights

- Area-selective growth of tungsten (W) films
- Hot-wire assisted ALD (HWALD) using sequential pulses of atomic hydrogen (at-H) and WF_6 .
- Highly selective on W/SiO_2 and Co/SiO_2 due to the different nucleation time.
- At-H can efficiently reduce native oxide of the substrates, leaving no oxygen in the interfaces

Figure 1

Figure 2

Figure 3

Figure 4

a

b

Figure 5

a **b** **c**

Figure 6

Figure 7

Figure 8