

# LIGHT EMISSION from SILICON NANOCRYSTALS EMBEDDED in ALD-ALUMINA at LOW TEMPERATURES

I. Brunets, R.V.A. van Loon, R.J. Walters, A. Polman, A. Boogaard, A.A.I. Aarnink,  
A.Y. Kovalgin, R.A.M. Wolters, J. Holleman, J. Schmitz

**Abstract** — In this work, we realize light emitting functional multilayer ( $\text{Al}_2\text{O}_3/\text{Si}$ -nanocrystals (Si-NC)) stacks at low temperatures (300-325 °C) by a combination of ALD and CVD techniques. The multilayer structure was obtained by a sequential deposition of a 20 nm-thick ALD  $\text{Al}_2\text{O}_3$  film, followed by LPCVD of a Si-NC layer, without vacuum break. A high nanocrystal density was achieved through an enhanced nucleation rate by using trisilane ( $\text{Si}_3\text{H}_8$ , known as Silcore®) as precursors for LPCVD of Si-NC layers. The photoluminescence and electroluminescence of the functional multilayer stacks were measured. A decrease of the Si-NC deposition time (i.e. smaller size of Si-NC's) provided a gradual shift of the photoluminescence peak to higher photon energies, indicating exciton confinement in the nanocrystals.

**Index Terms** — 3-D integration, ALD, CVD, nanocrystal, photoluminescence, electroluminescence.

## I. INTRODUCTION

The prospective implementation of optical data transfer within IC's requires efficient, CMOS-compatible light sources. The integration of light emitting devices further demands process flows with very low thermal budgets, in order to prevent thermal degradation in the underlying device layers. Silicon based light emitters have the potential to meet these process requirements, but often emit light with low quantum efficiency due to the indirect band gap of silicon. Increasing the quantum efficiency of light emission from silicon is a topic that has received much attention in the past years. An enhanced emission can be obtained from silicon nanocrystals (Si-NC) in comparison to bulk silicon [1]-[4]. However, the problem of sufficient size control in combination with low-temperature CMOS back-end compatible processing needs further investigations.

In this paper, we explore the fabrication of the low-

Manuscript received October 1, 2008. This work is supported by the Dutch Technology Foundation (STW). Project number STW-TEL 6358.

I. Brunets, A. Boogaard, A.A.I. Aarnink, A.I. Kovalgin, R.A.M. Wolters, J. Holleman and J. Schmitz are with MESA+ Institute for Nanotechnology, Chair of Semiconductor Components, University of Twente, Hogekamp, P.O. Box 217, 7500 AE Enschede, The Netherlands. Phone: +31 (0)53 489 4394; fax: +31 (0)53 489 1034; e-mail: [i.brunets@utwente.nl](mailto:i.brunets@utwente.nl)

R.J. Walters, R.V.A. van Loon and A. Polman are with Photonic Materials Group, FOM Institute for Atomic and Molecular Physics, Kruislaan 407, 1098SJ Amsterdam, The Netherlands

temperature multilayer stack with Si-NC embedded in ALD- $\text{Al}_2\text{O}_3$  matrix and its light emitting and electrical characteristics. The encapsulating  $\text{Al}_2\text{O}_3$ -matrix, realized without vacuum break, provided a sufficient protection against further oxidation of the Si-NC layers during the next processing steps. Therefore, the size of silicon nanocrystals was determined by their deposition parameters, eliminating any need for further high temperature processing steps.

## II. EXPERIMENTAL

We investigated both the photoluminescence (PL) and the electroluminescence (EL) from the silicon nanocrystals in metal-insulator-semiconductor structures fabricated entirely through low temperature processing. The optically active insulating layer is a multilayer stack of  $\text{Al}_2\text{O}_3$  films with embedded silicon nanocrystals.

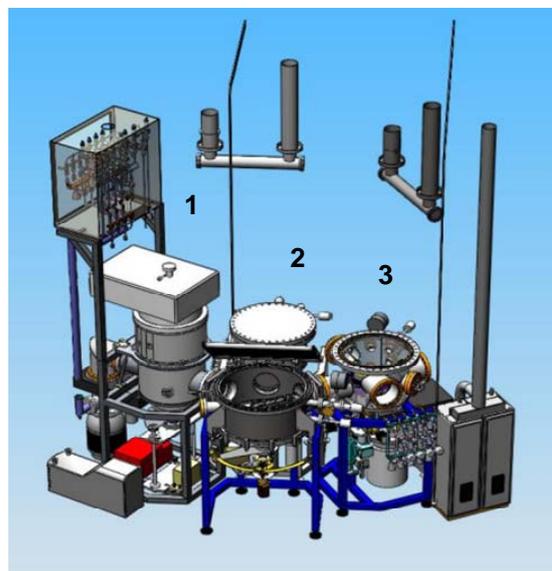


Fig. 1. Cluster System.

Reactor 1: ICPECVD for low-temperature deposition.

Reactor 2: Deposition of metals and silicon in ALD and CVD modes.

Reactor 3: Deposition of high-k dielectrics.

### A. Formation of the multilayer structure

The multilayer stack was deposited on p-type silicon wafers

with (100) orientation. First, the standard cleaning procedure was applied. Afterwards, to etch the native oxide and to avoid the metal contaminations, the wafers were briefly (around 1.5 minutes) dipped in a solution of 0.3% HF and 0.3% HCl.

Immediately after this dip, the wafers were placed into the loadlock of the cluster system (shown in Fig. 1). Further, the deposition of the functional multilayer stack ( $\text{Al}_2\text{O}_3/\text{Si-NC}/\dots/\text{Si-NC}/\text{Al}_2\text{O}_3$ ) was done at temperatures ranging from 300 to 325 °C, without vacuum break. The thicknesses of deposited layers were measured after each deposition step with a Spectroscopic Ellipsometer Woolam M2000DI ( $\lambda = 245 - 1688 \text{ nm}$ ).

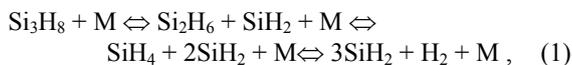
#### 1) ALD of $\text{Al}_2\text{O}_3$

The 20-nm thick  $\text{Al}_2\text{O}_3$  layers were grown by atomic layer deposition at a temperature of 300 °C in reactor 3 of the cluster system. The wafer was sequentially exposed to  $\text{Al}(\text{CH}_3)_3$  (Trimethylaluminum, or TMA) and  $\text{H}_2\text{O}$ , with a  $\text{N}_2$  purge cycle in between [5], [6]. The deposition rate of alumina was 0.08 nm per cycle. After the deposition, the wafer was transferred without vacuum break to reactor 1 to perform the film thickness measurements using spectroscopic ellipsometry.

#### 2) LPCVD of Si-nanocrystals

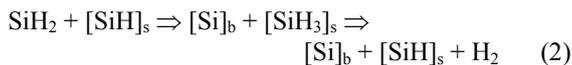
The layer with silicon nanocrystals (approximately 3-5 nm thick) was formed during LPCVD (in reactor 2) at 325 °C, using trisilane ( $\text{Si}_3\text{H}_8$ , known as Silcore®) as the source gas. The deposition pressure was set to 1 mbar and deposition time was between 10 and 30 minutes. We expected to obtain a significantly higher Si-nanocrystal density using  $\text{Si}_3\text{H}_8$  in comparison with depositions where disilane ( $\text{Si}_2\text{H}_6$ ) or silane ( $\text{SiH}_4$ ) was used especially at low temperatures, as reported previously [7]. The dramatic increase of silicon nucleation and growth rate, when using  $\text{Si}_3\text{H}_8$  as a precursor, was also reported for deposition temperatures between 410-500 °C [8] and higher.

Though the direct surface reactions from  $\text{Si}_3\text{H}_8$  are limited by rather slow surface dehydrogenation, at sufficient gas pressures the following bimolecular gas-phase reactions sequences can occur [9] during CVD from silcore (1):



where M denotes any other gas molecule.

As a result, highly reactive species such as  $\text{SiH}_2$  (i.e., silylene) with a reactive sticking coefficient close to unity are generated [9]-[12]. These reactive species can react with the surface  $[\text{SiH}]_s$  sites according to the reaction (2).



The use of trisilane, according to (1), assures a higher concentration of silylene. Due to the very high reactivity of silylene, it is expected that a higher concentration of silylene will result in a higher nucleation rate, providing a higher number of silicon nanocrystals. This expectation is confirmed by the AFM measurements (see Fig. 2), where the

concentration on nanocrystals deposited from Silcore ( $\sim 1.9 \times 10^{12} \text{ cm}^{-2}$ ) is higher in contrast to that deposited from disilane ( $\sim 0.2 \times 10^{12} \text{ cm}^{-2}$ ).

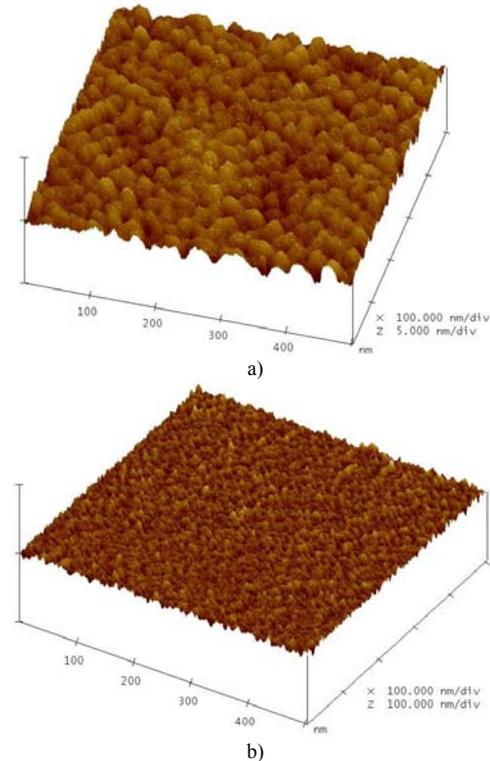


Fig. 2. AFM images of oxidized Si-NC layers deposited at 325°C from disilane at 10 mbar (a) and from trisilane at 1 mbar (b). To enable the observation of the nano-crystals, no upper protection layer was deposited.

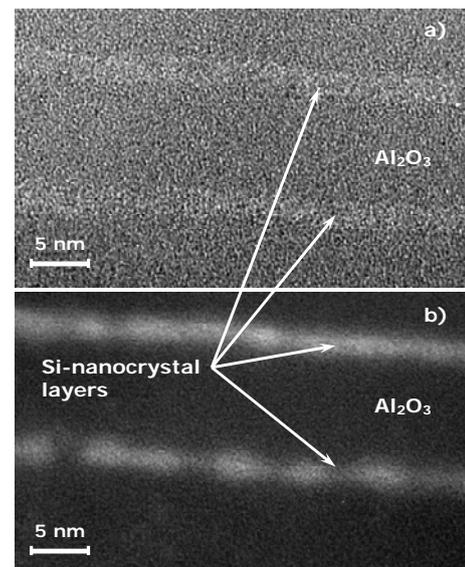


Fig. 3. High Resolution (a) and Energy Filtered TEM images (b) depicting the cross-section of multilayer stack with Si-nanocrystals embedded in  $\text{Al}_2\text{O}_3$  matrix. In the EFTEM image the Si-containing areas appear bright, whereas oxides – dark. It is clearly visible from EFTEM that the Si-NC layers are discontinuous.

In total, five layers of 20-nm thick  $\text{Al}_2\text{O}_3$  and 4 layers of silicon nanocrystals (3.5 nm-thick) were deposited sequentially one after the other and the multilayer stack was formed. Fig. 3 shows a transmission electron microscope (TEM) image of a cross-section of a similar structure where the thicknesses of  $\text{Al}_2\text{O}_3$  layers were 10 nm. The energy filtered TEM analyses confirmed a discontinuous character of the silicon layers.

### 3) Metallization

Finally, the wafer was removed from the cluster system and both the front- and back-side metallization were done by sputtering gold layers. To enable the electroluminescence measurements of Si-nanocrystals embedded in  $\text{Al}_2\text{O}_3$  functional layer, a 20-nm thick semi-transparent layer of gold was additionally sputtered on the top surface (i.e. directly on the  $\text{Al}_2\text{O}_3/\text{Si-NC}$  layer stack). A schematic cross-sectional overview of the realized structure is shown in Fig. 4.

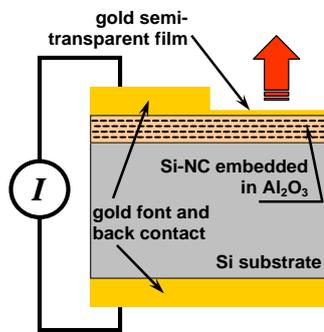


Fig. 4. Schematic overview of the electroluminescence measurement set-up.

## III. RESULTS AND DISCUSSION

The PL emission spectrum of the silicon nanocrystals embedded in alumina matrix was measured using the  $\text{Ar}^+$  laser line at a 488 nm for excitation. The spectra were measured with a grating spectrometer and a CCD camera. The excitation power was typically  $1 \text{ W/cm}^2$ . For the electroluminescence measurements, the metal-insulator-silicon capacitor structures shown in Fig. 4 were used.

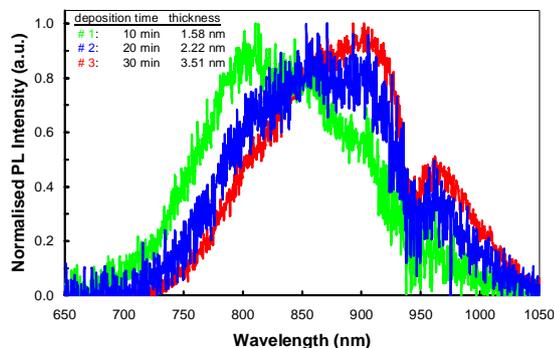


Fig. 5. Photoluminescence spectra measured for layers with different thicknesses (excited using the 488 nm line of an  $\text{Ar}^+$  laser).

The photoluminescence of layers containing silicon nanocrystals with different thicknesses/sizes (i.e., deposited

during 10, 20 or 30 min from trisilane at  $300^\circ\text{C}$ ) was investigated. The measured spectra show broad peaks centered at approximately 800 nm, 850 nm and 900 nm for 1.6 nm-, 2.2 nm- and 3.5 nm-thick Si-NC layers, respectively. A “blue-shift” is observed with decreasing the layer thickness (shown in Fig. 5).

The multilayer stack containing 3.5 nm-thick Si-NC layers in alumina matrix was further annealed in forming gas (10%  $\text{H}_2/\text{N}_2$ ) at  $500^\circ\text{C}$  for 10 minutes. This resulted in an increase in the photoluminescence spectra maximum of up to 400% of the initial intensity, as shown in Fig. 6.

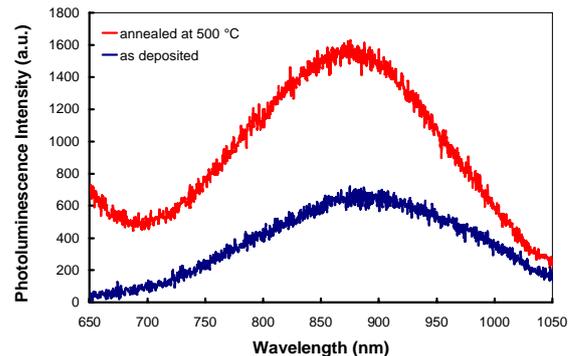


Fig. 6. Photoluminescence spectra showing the enhancement of the luminescence after annealing in a hydrogen-rich forming gas atmosphere.

The typical electroluminescence spectrum (shown in Fig. 7) shows a slight red-shift in comparison to the PL spectrum.

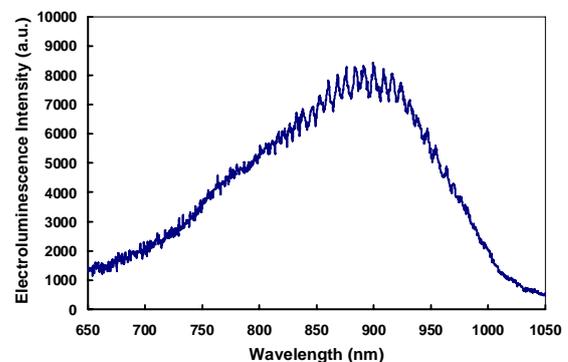


Fig. 7. Electroluminescence spectrum ( $\sim 2 \mu\text{A/cm}^2$  at 100 V).

## IV. CONCLUSION

Optically active multilayer stacks consisting of silicon nanocrystals embedded in alumina were realized using low-temperature (below  $400^\circ\text{C}$ ) CMOS-compatible processing. The multilayer stacks exhibited near-infrared photoluminescence and electroluminescence. Annealing in hydrogen-rich atmosphere led to a 400% increase of the luminescence intensity.

The demonstrated optical activity of the realized structures can lead to their further integration into silicon-based IC's using the low-temperature CMOS post-processing technology.

#### ACKNOWLEDGMENT

This work is supported by the Dutch Technology Foundation (STW). Project number STW-TEL 6358.

#### REFERENCES

- [1] L.T. Canham, *Appl. Phys. Lett.*, 57 (1990) 1046.
- [2] L.S. Liao, X.M. Bao, X.Q. Zheng, N.S. Li, N.B. Min, *Appl. Phys. Lett.*, 68 (1996) 850.
- [3] M.V. Wolkin, J. Jorne, P.M. Fauchet, G. Allan, C. Delerue, *Phys. Rev. Lett.* 82 (1999) 197.
- [4] R.J. Walters, J. Kalkman, A. Polman, H.A. Atwater, and M. J. A. de Dood, *Phys. Rev. B, Condens. Matter*, 73 (2006) 132302-1.
- [5] D.S. Tsai, T.C. Chang, W.C. Hsin, H. Hamamura, Y. Shimogaki, *Thin Solid Films*, 411 (2002) 177.
- [6] R. Bankras, J. Holleman, J. Schmitz, M. Sturm, A. Zinine, H. Wormeester, B. Poelsema, *Chem. Vap. Deposition*, 12 (2006) 275.
- [7] I. Brunets, A.A.I. Aarnink, A. Boogaard, A.Y. Kovalgin, R.A.M. Wolters, J. Holleman, J. Schmitz, *Surface & Coatings Technology*, 201 (2007) 9209.
- [8] P.R. Fischer, S.R.A. Van Aerde, T.G.M. Oosterlaken, B. Bozon, P.M. Zagwijn, *ECS Trans.* 3 (2006) 203.
- [9] A.C. Dillon, A.W. Ott, J.D. Way, S.M. George, *Surface Science*, 322 (1995) 230.
- [10] M. Juppo, A. Rahtu, M. Ritala, *Chemistry of Materials*, 14 (2002) 281.
- [11] M.Q. Snyder, B.A. McCool, J. DiCarlo, C.P. Tripp, W.J. DeSisto, *Thin Solid Films*, 514 (2006) 97.
- [12] C.R. Kleijn, *J. Electrochem. Soc.*, 138 (1991) 2190.