On the effect of the underlying ZnO : Al layer on the crystallization kinetics of hydrogenated amorphous silicon

Citation for published version (APA):

DOI:
10.1063/1.4809517
101.1063/1.4809517

Document status and date:
Published: 01/01/2013

Document Version:
Publisher’s PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:
• A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher’s website.
• The final author version and the galley proof are versions of the publication after peer review.
• The final published version features the final layout of the paper including the volume, issue and page numbers.

Link to publication

General rights
Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

• Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
• You may not further distribute the material or use it for any profit-making activity or commercial gain
• You may freely distribute the URL identifying the publication in the public portal.

If the publication is distributed under the terms of Article 25fa of the Dutch Copyright Act, indicated by the “Taverne” license above, please follow below link for the End User Agreement:
www.tue.nl/taverne

Take down policy
If you believe that this document breaches copyright please contact us at:
openaccess@tue.nl
providing details and we will investigate your claim.

Download date: 05. May. 2019
On the effect of the underlying ZnO:Al layer on the crystallization kinetics of hydrogenated amorphous silicon

K. Sharma, M. V. Ponomarev, M. C. M. van de Sanden, and M. Creatore

Citation: Appl. Phys. Lett. 102, 212107 (2013); doi: 10.1063/1.4809517

View online: http://dx.doi.org/10.1063/1.4809517

View Table of Contents: http://apl.aip.org/resource/1/APPLAB/v102/i21

Published by the American Institute of Physics.
On the effect of the underlying ZnO:Al layer on the crystallization kinetics of hydrogenated amorphous silicon

K. Sharma,1,a) M. V. Ponomarev,2 M. C. M. van de Sanden,1,2 and M. Creatore1,3

1Department of Applied Physics, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands
2DIFFER (Dutch Institute For Fundamental Energy Research), P.O. Box 1207, 3430 BE Nieuwegein, The Netherlands
3Solliance, High Tech Campus 5, 5656 AE Eindhoven, The Netherlands

(Received 12 April 2013; accepted 17 May 2013; published online 31 May 2013)

In this contribution, we analyze the thickness effect of the underlying aluminum doped-zinc oxide (ZnO:Al) layers on the structural properties and crystallization kinetics of hydrogenated amorphous silicon (a-Si:H) thin films. It is shown that the disorder in as-deposited a-Si:H films, as probed by Raman spectroscopy, decreased with increasing ZnO:Al roughness. This caused an earlier nucleation upon crystallization when compared to a-Si:H layers directly grown on SiNₓ-coated glass. © 2013 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4809517]

Thin-film polycrystalline silicon (poly-Si) solar cells are an appealing alternative to wafer-based technology as they combine the low cost production typical of thin-film technologies with the superior opto-electronic properties of crystalline silicon. Poly-Si thin films for photovoltaic applications have already been achieved in the past two decades by solid phase crystallization (SPC) of hydrogenated amorphous silicon (a-Si:H).1–5 CSG Solar has developed a solar cell technology where poly-Si is fabricated on glass by SPC of a-Si:H with a conversion efficiency up to 10.4%.2 Poly-Si thin films on foreign supporting materials are particularly appealing. One of the most promising substrates for low cost photovoltaics is glass, as it is inexpensive, transparent (enabling the superstrate configuration and/or bifacial modules), long-term stable, and readily available on large scale. Light trapping can be enhanced by the implementation of a transparent conductive oxide layer such as ZnO:Al. An important aspect of poly-Si solar cell technology is the deposition of a-Si:H on the ZnO:Al followed by a thermal annealing step to induce the transition from amorphous to crystalline phase. The kinetics of the crystallization process (incubation-nucleation-grain development)6 in a-Si:H controls the grain size evolution and, thus, significantly influences the material quality. Sontheimer et al.7,8 have reported on the crystallization of amorphous silicon (a-Si) deposited on ZnO:Al and SiNₓ-coated glass. They have demonstrated that the crystallization of a-Si/ZnO:Al is faster than in a-Si/SiNₓ and the former contained smaller crystals than the latter. This difference in crystallization kinetics was attributed to the roughness of ZnO:Al, although no further studies have been specifically reported on the influence of the ZnO:Al roughness on the a-Si:H microstructure, in terms of SiHₓ bond distribution and short-to-medium range order.

Therefore, the present contribution aims to address the influence of the ZnO:Al texturing on the microstructure of a-Si:H by following its crystallization kinetics upon SPC treatment.

Polycrystalline ZnO:Al films were deposited using an expanding thermal plasma chemical vapor deposition (ETP-CVD) technique.9–12 An argon (Ar) plasma was generated in a high pressure (360 mbar) cascaded arc and expanded into a low pressure deposition chamber (0.3–1.5 mbar). The precursors for film deposition, i.e., diethylzinc (DEZ), oxygen, and trimethylaluminum (TMA), were injected downstream via injection rings. More details about this deposition tool have been reported elsewhere.9–12 Thin (130 nm) and thick (800 nm) ZnO:Al films were deposited on glass at 200 °C. As roughness scales with thickness for ETP deposited ZnO:Al films,9,12 thin and thick films were used to obtain two extreme values of surface roughness.

NT-MDT Solver P47 was used to perform atomic force microscopy (AFM) measurements on ZnO:Al films. 200 nm and 1000 nm thick ETP-CVD a-Si:H films were deposited on ZnO:Al layers at 400 °C. The Ar-H₂ thermal plasma was generated in a cascaded arc at typical pressures of 0.2–0.6 mbar. Silane, which was injected downstream, was dissociated by atomic hydrogen mainly into SiHₓ radicals for relatively high H₂ flow rates through the arc (>5 sccs).9,12 200 nm thick a-Si:H films were analyzed by Raman spectroscopy using a Renishaw Raman system. Thin (200 nm) a-Si:H films ensure that the Raman laser wavelength (514.5 nm) penetrates through the whole layer thickness. a-Si:H layers deposited on ZnO:Al and SiNₓ coated glass substrates were annealed up to 600 °C: the ramp started at room temperature and developed up to 400 °C at 10 °C/min and from 400 °C to 600 °C at 1 °C/min. The incubation time (time before the onset of crystallinity) was defined as the time needed to observe the c-Si (111) XRD peak rise to 1/10 of its final intensity.15–17 To study the crystallization kinetics, an Anton Paar DHA 1100 heating unit attached to a PANalytical XRD instrument was used to anneal the samples in an argon atmosphere. 1000 nm thick a-Si:H films were used for in situ XRD measurements as thick films led to high intensity signal (low signal-to-noise ratio). It is worth mentioning here that no microstructural differences were observed between thin (200 nm) and thick (1000 nm) a-Si:H films. Finally, crystallized film

---

a)Authors to whom correspondence should be addressed. Electronic addresses: k.sharma@tue.nl and m.creatore@tue.nl
composition was measured by time of flight secondary ion mass spectrometry (TOF-SIMS).

The surface roughness of ZnO:Al films is found to increase with film thickness, as earlier reported \cite{11,12}. AFM measurements showed that thin (130 nm) and thick (800 nm) ZnO:Al films have rms roughness ($\delta_{\rm rms}$) values of 8.5 and 41 nm, respectively. In order to understand the effect of the underlying ZnO:Al layer, the structural analysis of a-Si:H layers was performed by Raman spectroscopy where the stretching mode of a-Si:H centered around 2000 cm$^{-1}$ was measured and deconvoluted into a low stretching mode (LSM, 1980–2010 cm$^{-1}$) \cite{18} and a high stretching mode (HSM, 2070–2100 cm$^{-1}$) \cite{18}, as shown in Figure 1. Monohydrides in divacancies contribute dominantly to the LSM, whereas hydrides on the nano-size void surface contribute to the HSM. \cite{18} The area of the HSM peak ($A_{\rm HSM}$) decreased with increasing ZnO:Al thickness, indicating a decrease in nano-size void density (Figure 1). Furthermore, due to the decrease in nano-size voids, the $R^*$ ($= A_{\rm HSM}/(A_{\rm LSM} + A_{\rm HSM})^{19,20}$) parameter was also found to decrease with increasing ZnO:Al thickness. As $R^*$ represents the degree of disorder in the material, the observed decrease in $R^*$ reflects the reducing disorder in the as-deposited a-Si:H with increasing ZnO:Al thickness. A similar effect was observed from the peak position ($\omega$) and full-width-at-half-maximum (FWHM) of the TO mode (480 cm$^{-1}$) of a-Si:H (Fig. 2(a)). A shift in $\omega$ towards higher wave number values and a decreasing FWHM with increasing ZnO:Al thickness indicate the improvement of the silicon network order at short range \cite{21-24}. Furthermore, the ratios of $I_{\rm TA}/I_{\rm TO}$ and $I_{\rm LO}/I_{\rm TO}$, which represent the medium range order (MRO), \cite{25-27} were computed from Raman analysis \cite{8,28,29} and represent the silicon network (3–25 Å) surrounding the vacancies. \cite{16,30} The $I_{\rm TA}/I_{\rm TO}$ ratio decreased and the $I_{\rm LO}/I_{\rm TO}$ ratio increased with increasing ZnO:Al thickness. This was due to the improvement in MRO \cite{21,22,24,28,29} caused by the underlying ZnO:Al. To summarize, the nano-size void content decreased with increasing ZnO:Al thickness (i.e., increasing roughness), which further led to the improvement in structural order at short- and medium range scales. Smets et al. \cite{31} have reported that the reduction of nano-size voids in a-Si:H is caused by enhanced surface diffusion. The experimental results here reported point out to the cause of the improved structural order in a-Si:H films, i.e., the surface roughness of the underlying ZnO:Al films. Therefore, besides experimental parameters such as deposition temperature and gas flow rates, the structural properties (specifically, short- and medium range order) of a-Si:H are also affected by the surface roughness of underlying ZnO:Al. However, the relationship between the surface roughness of ZnO:Al films and the enhanced surface diffusion of growth radicals during a-Si:H deposition requires further investigation.

Furthermore, to investigate the influence of the underlying ZnO:Al film on the crystallization kinetics of a-Si:H, annealing was performed at 600 °C for 10 h. A resistivity improvement in the underlying ZnO:Al films was observed after SPC, as reported in a previous work from our group, by Ponomarev et al. \cite{32} This is in agreement with the experimental observation from Lee et al. \cite{33} and Ruske et al. \cite{34} Figure 3 shows the crystallization kinetics results, where the crystallization content ($X_c$) \cite{35} was plotted as a function of the annealing time. The nucleation took place earlier in glass/ZnO:Al (130 nm and 800 nm)/a-Si:H than in glass/SiNx/a-Si:H in agreement with the results earlier reported. \cite{7,8} This is due to the fact that former was characterized by a better MRO than the latter one. It was reported in the literature that MRO controls the incubation time ($t_{i}$): smaller MRO leads to longer $t_{i}$, while a higher MRO results in a shorter $t_{i}$ \cite{16,30}. As the MRO in a-Si:H increased with an increasing ZnO:Al thickness, a shorter $t_{i}$ was observed (inset Fig. 3). As reported earlier, the grain size in poly-Si decreased with decreasing $R^*$. \cite{20} Therefore, the decrease in $R^*$ in a-Si:H layers upon increase in ZnO:Al roughness is expected to deliver smaller grains in poly-Si films upon SPC. No impurities (signal counts for B, Na, Ca, Ba, Al, and Zn were below 5, matching the noise.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure1.png}
\caption{Variation of $A_{\rm HSM}$ and $R^*$ as a function of the ZnO:Al thickness. The inset shows the stretching mode of a-Si:H deconvoluted in the LSM and HSM contributions by two Gaussians. The glass/SiNx/a-Si:H data point is also reported in the graph. Top x-axis shows the rms roughness ($\delta_{\rm rms}$) values.}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure2.png}
\caption{Variation of (a) peak position, $\omega$ (cm$^{-1}$) and FWHM (b) $I_{\rm TA}/I_{\rm TO}$ and $I_{\rm LO}/I_{\rm TO}$ in a-Si:H films, as a function of the ZnO:Al thickness.}
\end{figure}
FIG. 3. Crystallization content ($X_c$) in poly-Si layers as a function of the annealing time. The solid lines are fits to the data using the methodology of Iverson and Reif. The variation of $X_c$ as a function of ZnO:Al thickness is shown in the inset.

level) were found in the glass/ZnO:Al/poly-Si layers, as indicated by TOF-SIMS measurements. Therefore, we can conclude that the observed difference in crystallization between glass/ZnO:Al/a-Si:H and glass/SiN$_x$/a-Si:H is due to the improvement in structural order caused by the underlying ZnO:Al layer.

In conclusion, the analysis of the influence of the underlying ZnO:Al layer on the microstructure ($R^*$, short- and medium-range order) of the as-grown a-Si:H and on its crystallization kinetics has been presented. The results have shown that the decrease in nano-size void density with increasing thickness of the underlying ZnO:Al led to the improvement in the structural order of the as-grown a-Si:H, and resulted in a faster nucleation in the a-Si:H layer during annealing. The understanding of the crystallization kinetics of a-Si:H on ZnO:Al is expected to play an essential role not only in poly-Si solar cell technology but also in other technologies such as a-Si:H and tandem a-Si:H/microcrystalline-Si:H solar cells.

This work was carried out with a subsidy of the Dutch Ministry of Economic Affairs under the EOS-LT program (project number EOSLT06029). The authors acknowledge M. J. F. van de Sande, W. Keuning, J. J. L. M. Meulendijks, and J. J. A. Zeebregts for their technical support. This research has been made possible within the project NOVASIL founded by Agentschap.nl (former SenterNovem).