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On the solid phase crystallization of $\text{In}_2\text{O}_3\text{:H}$ transparent conductive oxide films prepared by atomic layer deposition

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ABSTRACT

Hydrogen-doped indium oxide ($\text{In}_2\text{O}_3\text{:H}$) has emerged as a highly transparent and conductive oxide, finding its application in a multitude of optoelectronic devices. Recently, we have reported on an atomic layer deposition (ALD) process to prepare high quality $\text{In}_2\text{O}_3\text{:H}$. This process consists of ALD of $\text{In}_2\text{O}_3\text{:H}$ films at 100 °C, followed by a solid phase crystallization step at 150-200 °C. In this work, we report on a detailed electron microscopy study of this crystallization process which reveals new insights into the crucial aspects for achieving the large grain size and associated excellent properties of the material. The key finding is that the best optoelectronic properties are obtained by preparing the films at the lowest possible temperature prior to post-deposition annealing. Electron microscopy imaging shows that such films are mostly amorphous, but feature a very low density of embedded crystallites. Upon post-deposition annealing, crystallization proceeds merely from isotropic crystal grain growth of these embedded crystallites rather than by the formation of additional crystallites. The

relatively high hydrogen content of 4.2 at. % in these films is thought to cause the absence of additional nucleation, and thereby rendering the final grain size and optoelectronic properties solely dependent on the density of embedded crystallites. The temperature-dependent grain growth rate has been determined, from which an activation energy of (1.39 ± 0.04) eV has been extracted. Finally, on the basis of the observed crystallization mechanism, a simple model to fully describe the crystallization process has been developed. This model has been validated with a numerical implementation thereof, which accurately predicts the observed temperature-dependent crystallization behaviour.

I. INTRODUCTION

Optoelectronic devices such as displays and solar cells often employ thin films of transparent conductive oxides (TCOs) as conductive window layers. Historically, Sn-doped indium oxide (ITO) made by sputtering has been the TCO of choice for such purposes. This can mainly be attributed to its relatively high electron mobility μ ($20\text{-}40 \text{ cm}^2/\text{Vs}$)¹, which mitigates the need for a high carrier density N_e while still yielding a low resistivity ρ . Due to a lower required N_e , optical losses in the infrared (IR) due to free carrier effects are reduced. In recent years, new In_2O_3 -based TCOs with a higher carrier mobility of $>50 \text{ cm}^2/\text{Vs}$ have gained significant interest, examples include Zn-doped indium oxide (IZO)², W-doped indium oxide (IWO)³, Mo-doped indium oxide (IMO)⁴ and H-doped indium oxide ($\text{In}_2\text{O}_3\text{:H}$, also referred to as IO:H or IOH)⁵⁻⁷. Due to the greatly-reduced IR-losses in such TCOs, they have found direct application in various solar cell devices, mainly leading to increased short-circuit current densities J_{sc} when compared to conventional ITO. For example, these high-mobility TCOs have played a key role in achieving the record conversion efficiencies for silicon heterojunction (SHJ) solar cells^{8,9}, and are also being explored for CIGS¹⁰⁻¹² and perovskite tandem cells.^{13,14,15}

Among these high-mobility TCOs, $\text{In}_2\text{O}_3\text{:H}$ is capable of achieving the highest mobility with values even up to $138 \text{ cm}^2/\text{Vs}$.⁷ This material was originally developed by Koida *et al.*, using reactive magnetron sputtering at room temperature from an In_2O_3 target with the addition of H_2O vapour, which resulted in mostly amorphous $\text{In}_2\text{O}_3\text{:H}$ films. The crucial step for achieving high μ values $>100 \text{ cm}^2/\text{Vs}$ is a solid phase crystallization (SPC) step by thermal annealing at $160\text{-}400 \text{ }^\circ\text{C}$.⁵ Recently we have demonstrated a similar approach to prepare high-mobility $\text{In}_2\text{O}_3\text{:H}$ using an atomic layer deposition (ALD) process instead of sputtering. After deposition at $100 \text{ }^\circ\text{C}$, the ALD film is almost entirely amorphous. Also here, a crystallization step at $150\text{-}200 \text{ }^\circ\text{C}$ is key to get μ values up to $138 \text{ cm}^2/\text{Vs}$.^{7,16} Besides achieving such high mobility values, the main advantages of the ALD process are the low temperature processing (post-crystallization can take place at temperatures as low as $150 \text{ }^\circ\text{C}$), the ability to conformally deposit on non-planar surfaces, and the fact that plasma-induced damage, typically encountered during sputtering (“sputter damage”)¹⁷, is absent during ALD.^{18,19}

Despite the importance of the crystallization step in realizing high-mobility $\text{In}_2\text{O}_3\text{:H}$, little is known about the crystallization process itself. Therefore, in this contribution, the crystallization process of ALD $\text{In}_2\text{O}_3\text{:H}$ is studied in detail by electron microscopy to gain a deeper understanding of the physical origin of the very high mobility. The study provides new insights into the crystal growth both during deposition and post-annealing, and explains why films should be prepared at the lowest possible deposition temperature in order to obtain the largest grain size and associated excellent optoelectronic properties after post-annealing. In addition, the temperature-dependent kinetics of the crystallization process is studied. Given the high sensitivity to elevated temperatures of the aforementioned solar cell concepts, knowledge of the temperature-dependent grain growth rate and crystallization kinetics is of direct interest for the optimization of the anneal temperature and time (i.e. thermal budget) when implementing such layers in these cells. As will be shown, the grain growth rate is strongly

thermally activated with an activation energy of (1.39 ± 0.04) eV. Based on the observations from electron microscopy, a model to fully describe the crystallization process is proposed. The validity of this model is corroborated by a numerical implementation thereof, which is capable of accurately reproducing the experimentally observed crystallization kinetics. Finally, it is shown that our ALD approach works on silicon nanowires as well, yet subtle differences with respect to the case of planar substrates will be highlighted.

II. EXPERIMENTAL DETAILS

A. Sample preparation.

The $\text{In}_2\text{O}_3\text{:H}$ films studied in this contribution were prepared in the same way as in our earlier work.¹⁶ Si(100) wafers with a 430 nm thermal oxide were covered with a seed layer of 20 cycles of ALD aluminum oxide (Al_2O_3) using trimethylaluminum (TMA, $\text{Al}(\text{CH}_3)_3$) and H_2O . $\text{In}_2\text{O}_3\text{:H}$ films of 75 nm thickness were prepared using an ALD process that is based on the work of Libera *et al.*⁶, i.e. using cyclopentadienyl indium (InCp) as the indium source and a combination of O_2 and H_2O as oxidant. All depositions were carried out in an Oxford Instruments OpAL ALD reactor. Depositions were performed at 100, 130 or 200 °C. Note that 100 °C is the lowest deposition temperature at which growth was achieved for this ALD process. Subsequently, separate $\sim 1 \times 1 \text{ cm}^2$ samples were cut from the wafers, and the films were annealed separately for various durations and at temperatures ranging from 150 °C to 200 °C. Post-deposition annealing was performed in a Jipelec rapid thermal anneal (RTA) furnace in an inert N_2 atmosphere.

B. Film analysis.

The films were investigated by TEM (JEOL ARM 200 probe corrected TEM, operated at 200 kV) in cross section using Focused Ion Beam made lamella. An FEI Helios 650 Dualbeam

system was used for SEM imaging. Details on the X-ray diffraction and spectroscopic ellipsometry measurements can be found in previous reports.¹⁶ Hall measurements were performed using a Europa HMS-3500 Hall Effect Measurement System in the Van der Pauw configuration. A combination of Rutherford backscattering (RBS) and elastic recoil detection (ERD) was employed to obtain absolute atomic densities of indium, oxygen and hydrogen in the film. Atomic force microscopy (AFM) scans were performed using a NT-MDT Solver P47 microscope in tapping mode using TiN-coated Si tips (NSG10/TiN, NT-MDT).

III. RESULTS AND DISCUSSION

A. Influence of the deposition temperature on film crystallinity

In order to first establish the effect of the deposition temperature and post-annealing on the electrical properties of the $\text{In}_2\text{O}_3\text{:H}$ films, Hall measurements are performed on samples prepared at 100, 130 and 200 °C, both before and after annealing at 200 °C for 10 minutes. As can be seen from Table 1, by far the best optoelectronic properties are obtained by annealing the sample prepared at 100 °C. Under these conditions a very high mobility μ of 138 cm^2/Vs and the lowest resistivity ρ of 0.27 $\text{m}\Omega\text{cm}$ are achieved. As reported in earlier work, the crystallization process improves the optical properties by leading to a strong reduction in the Drude contribution at low photon energies and to an increase in the optical bandgap.⁷ For a sample prepared at 130 °C the electrical properties improve to a lesser extent after annealing, whereas expectedly annealing a sample at its deposition temperature of 200 °C does not significantly improve its electrical properties.

Table 1 Electrical properties of In₂O₃:H films prepared at various deposition temperatures, as determined from Hall measurements. Values for samples both as-deposited (as-dep) and after annealing at 200 °C for 10 minutes are shown.

Deposition temperature (°C)	Mobility μ (cm ² /Vs)		Carrier density N_e (10 ²⁰ cm ⁻³)		Resistivity ρ (mΩcm)	
	As-dep	Annealed	As-dep	Annealed	As-dep	Annealed
100	35	138	5.0	1.8	0.35	0.27
130	57	103	1.9	1.3	0.58	0.46
200	48	50	1.8	1.7	0.72	0.73

In order to explain why the best optoelectronic properties are obtained for films prepared at the lowest deposition temperature, top-view SEM and cross-sectional TEM imaging are employed to study the crystal morphology of both as-deposited and post-crystallized samples. In Figure 1 (a-e), top-view SEM images of the samples deposited at 100, 130 and 200 °C are shown, both before and after post-crystallization. As can be seen, the as-deposited film (Figure 1 (a)) is not purely amorphous, but contains small embedded crystallites which appear in bright. The presence of such crystallites in as-deposited In₂O₃:H has also previously been observed in In₂O₃:H prepared by sputtering⁵ and ALD²⁰. Also, the fact that the as-deposited film contains a very small crystalline fraction is in line with our earlier observation that XRD spectra of our as-deposited ALD In₂O₃:H films contain a dim feature of (111)-oriented grains.^{7,16} High magnification SEM images (inset of Figure 1(a)) and AFM images (Figures S1 and S2 in the supplementary material) show that the crystallites protrude from the surface. The higher brightness for the crystallites observed in the SEM images is the result of a higher secondary electron yield due to the presence of this additional surface roughness. After crystallization (Figure 1(b)) the top-view SEM imaging shows a very large grain size of a few hundred nm, in line with our previous results.^{7,16}

FIG. 1. Top-view SEM images of $\text{In}_2\text{O}_3\text{:H}$ films grown at (a) 100, (c) 130 and (e) 200 °C, respectively. (b and d) For the samples prepared at 100 and 130 °C, also images after post-annealing for 10 minutes at 200 °C are shown. The films have a thickness of 75 nm. Image (a) has an inset with an image at higher magnification, showing the morphology of the crystallites protruding from the surface. Except for the inset all images have the same scale.

Figure 1(c) shows that the film prepared at 130 °C is mostly crystalline. Also here the dark areas are thought to be amorphous $\text{In}_2\text{O}_3\text{:H}$, since they disappear upon post-annealing (Figure 1 (d)). Clearly, the crystallite density for a film prepared at 130 °C is much higher than for a film prepared at 100 °C, which leads to a much smaller grain size after post-annealing. The sample prepared at 200 °C (Figure 1(e)) is observed to be fully crystalline, with a smaller grain size and with a rougher morphology. Therefore, the better electronic properties after crystallization of films prepared at the lowest deposition temperature of 100 °C can be attributed to the fact that that such films have the largest grain size.

It should be noted that the protrusion of the crystallites from the surface in Figure 1(a) shows that the growth per cycle (GPC) is enhanced on the crystalline surfaces. This is not uncommon for ALD, and enhanced GPC values on crystalline surfaces have for example also been observed for MoO_x and TiO_2 .^{21–23} In fact, from AFM (Figures S1 and S2 in the supplementary material) it is deduced that the crystallites can protrude up to ~25 nm from the surface. Since the film is 75 nm thick, this suggests an enhancement in GPC of at least 33% on the crystalline surface, if the crystallites were to nucleate directly at the start of the film deposition. As will be shown later, the crystallites are observed to not nucleate directly at the start of the film deposition, and therefore the GPC enhancement on crystalline surfaces should even exceed 33%. Interestingly, in the aforementioned work of Libera *et al.* using the same ALD process, an increase in GPC of almost 50% was observed when going from amorphous growth at a deposition temperature of 100 °C to purely crystalline growth at a deposition temperature of 140 °C.⁶ Therefore, the increase in GPC at elevated temperatures for this ALD process can be mainly attributed to the change from amorphous to polycrystalline growth.

B. Electron microscopy imaging of the crystallization process

Since the samples deposited at 100 °C feature the highest mobility and lowest resistivity after crystallization, the crystallization process of these samples is studied in more detail. To this end, top-view SEM imaging is performed on a large set of samples prepared at 100 °C and annealed for various times at 150, 165, 175, 185 or 200 °C. Figure 2 shows two exemplary top-view SEM images of samples annealed at 150 °C for 60 minutes and at 175 °C for 10 minutes, respectively. Interestingly, both images show that upon annealing grain growth occurs from the embedded crystallites (as seen in Figure 1 (a)). Note that this is observed for all the samples studied and a larger set of top-view SEM images can be found in the supplementary material.

FIG. 2 Top-view SEM images of $\text{In}_2\text{O}_3\text{:H}$ films prepared at $100\text{ }^\circ\text{C}$ and post-annealed at (a) $150\text{ }^\circ\text{C}$ for 60 minutes and at (b) $175\text{ }^\circ\text{C}$ for 10 minutes.

The grain growth from the embedded crystallites has been studied by cross-sectional TEM images for films annealed at $175\text{ }^\circ\text{C}$ for 5, 10 and 120 minutes, as shown in Figure 3. As can be seen in (a) and (b), the crystals exhibit a hemispherical growth front, implying that grain growth proceeds in an isotropic manner from the embedded crystallites residing at the top surface. This shows that the crystallites in the SEM images of Figure 1(a) are indeed located near and/or at the surface and act as the seeds for further crystallization. Therefore, it is most likely that ALD film growth starts out amorphous, up to a certain thickness where nucleation of crystallites occurs that subsequently grow along with the film.

FIG. 3. Cross-sectional TEM images of separate $\text{In}_2\text{O}_3\text{:H}$ films at various stages of crystallization. The samples were annealed for (a) 5, (b) 10 and (c) 120 minutes at 175 °C. Note that only a few of the embedded crystallites protruding from the surface were captured within these images due to the limited thickness of the TEM lamella.

Upon close inspection of the top-view SEM images, it appears that crystallization occurs solely by grain growth from the embedded crystallites and that additional nucleation is absent or of very minor importance. In order to quantitatively determine whether additional nucleation occurs during annealing, the surface crystallite density n_s has been determined from the SEM images as a function of the film crystalline fraction X_c for all the investigated annealing temperatures. The crystalline fraction X_c of the film has been determined from the fraction of the bright parts of the $\text{In}_2\text{O}_3\text{:H}$ surface using image analysis software (ImageJ). The result is shown in Figure 4. Interestingly, there is no clear dependence of n_s on the crystallinity for all annealing temperatures in the range 150-200 °C. This confirms that additional nucleation of crystallites during the annealing process is indeed absent or at least of very minor

importance. In other words, the time scale for full crystallization of the film by grain growth from the embedded crystallites is much smaller than the typical timescale for crystallite nucleation for the investigated temperature range of 150-200 °C. This has the important consequence that the final grain size is independent of the annealing temperature, in line with our earlier observation that identical properties are obtained for fully crystallized films irrespective of annealing temperature in the range of 150-200 °C.¹⁶ Note that the independence of the electrical quality on the annealing temperature also implies that, besides the grain size, also the ingrain crystal quality is independent of the annealing temperature.

FIG. 4. Surface crystallite density n_s as obtained from analysis of top-view SEM images as a function of the film crystalline fraction X_c . No dependence of n_s on X_c can be observed, indicating that additional nucleation during post-annealing is negligible. The average crystallite density $\langle n_s \rangle$ as and the standard deviation therein σ_{n_s} are shown as well. The annealing times of the samples are the same as reported in Figure 6.

In the absence of additional nucleation, the determined average n_s of $6.3 \mu\text{m}^{-2}$ predicts an average lateral final grain size of 400 nm, in good agreement with the top-view SEM image of Figure 2(b) and the cross-sectional TEM images of Figure 3. Additionally, since no nucleation from the amorphous phase is observed, it can be concluded that nucleation during post-deposition annealing requires annealing temperatures exceeding the investigated temperature range of 150-200 °C. More importantly, this also implies that the inclusion of a low density of crystallites during the deposition of the film is necessary to enable post-crystallization at low annealing temperatures. Fortunately for our ALD process this inclusion of a small density of crystallites occurs exactly at the lowest end of the ALD temperature window, i.e. 100 °C, although this could be different for other ALD processes or deposition methods.

On the basis of the presented observations, a model is proposed to describe the crystallization process of the ALD $\text{In}_2\text{O}_3\text{:H}$ films. The model is schematically shown in Figure 5. During the ALD process, initially an amorphous incubation layer develops (A.1) up to a certain thickness. Subsequently, crystallites nucleate at the surface (A.2). During the following ALD cycles these crystallites grow in size and new crystallites nucleate (A.3). Due to the enhanced local growth rate on the crystalline surface, the crystallites protrude from the surface.

FIG. 5. Schematic of the proposed model for the nucleation and growth of crystallites in ALD $\text{In}_2\text{O}_3\text{:H}$ (A) during the ALD process and (B) during subsequent solid phase crystallization.

During subsequent solid phase crystallization, isotropic growth of the crystallites occurs without the formation of new crystallites, as concluded from cross-sectional TEM and top-view SEM, respectively (B.1). The grain growth proceeds until the crystallites coalesce (B.2.) and finally the film is fully crystallized (B.3). The embedded crystallites can still be distinguished on the surface.

C. Temperature-dependent crystallization kinetics

In addition to the crystallization mechanism, the temperature-dependent kinetics of the crystallization process is studied. From top-view SEM images, the crystalline fraction X_c of the film is measured as a function of annealing temperature and time. The result is shown in Figure 6 (crossed symbols), in conjunction with the results from previous work based on X-ray diffraction (XRD, closed symbols) and spectroscopic ellipsometry (SE) modelling using an effective medium approximation (EMA, open symbols).¹⁶ Note that the dashed and dotted lines in Figure 6 are the result of the model that will be addressed later in this paper. As can be seen, the crystallization occurs more rapidly at higher annealing temperatures, clearly indicating thermally activated behaviour, as expected. Also, there is a good agreement between the X_c values obtained from SEM with those obtained from the XRD and SE EMA approaches¹⁶, albeit that the SEM values are slightly higher. This can likely be attributed to the fact that the crystalline fraction determined by SEM is a *surface* projection of the crystallites, whereas the values determined by XRD and SE are *bulk* crystalline fractions. Given the shape of the crystallites during crystallization (as can be seen in Figure 3(b) and in the model of Figure 5), it is evident that the *surface* crystalline fraction exceeds the *bulk* crystalline fraction for partially crystallized films.

FIG. 6. Crystalline fraction of the $\text{In}_2\text{O}_3\text{:H}$ films as a function of annealing time for various annealing temperatures. The crystallinity has been deduced from XRD (closed symbols), SE modelling using an effective medium approximation (EMA, open symbols) of fully crystalline and amorphous $\text{In}_2\text{O}_3\text{:H}$, and from image analysis of top-view SEM images (crossed symbols). The lines represent the result of a model, where the dashed lines denote the *bulk* crystallinity, $X_{c,bulk}$, and the dotted lines correspond to the *surface* crystallinity $X_{c,surface}$. The XRD and SE data are replotted from our previous work.¹⁶

From top-view SEM imaging, the grain growth rate v_g is determined as a function of the crystallization temperature. This is done by tracking the increase of the crystallite radius of non-coalesced crystallites as a function of crystallization time. The result is shown in Figure 7. A thermally activated behaviour can clearly be observed, with v_g varying from 2 nm/min at 150 °C to 119 nm/min at 200 °C.

FIG. 7. The grain growth rate v_g as a function of annealing temperature as extracted from the SEM images.

From the temperature-dependent grain growth rate the activation energy E_A for grain growth in $\text{In}_2\text{O}_3\text{:H}$ can be determined through an Arrhenius plot, as has been done in Figure 8. From the fit, an activation energy E_A of (1.39 ± 0.04) eV has been determined. The activation energy for the crystallization process has also been determined by fitting the crystallization curves of Figure 6 with the so-called Avrami equation:

$$X_c = 1 - e^{-(Kt)^n} \quad (3)$$

with K a temperature-dependent rate constant and n an exponent that reflects the geometry of the transformation.²⁴ The exponents n of all fitted curves lie in the range of 1.3-1.6. Being close to 3/2, this suggests site-saturated growth²⁵ (i.e. all nuclei are present at $t=0$) with a grain growth dimensionality in between 1D and 2D, in line with the observations obtained from SEM and TEM. From the temperature-dependent Avrami rate constant K an activation energy E_A of

(1.31 ± 0.04) eV has been determined as shown in Figure 8. This activation energy is similar to the value obtained from the temperature-dependent growth rate analysis.

FIG. 8. Arrhenius plot of the grain growth rate as obtained from analysis of the SEM images and of the Avrami rate constant. The activation energies are determined from the slopes.

It is instructive to compare these results to the work of Wang *et al.*, who reported an activation energy of 0.83 eV for sputtered Sn-doped In_2O_3 , which increased to 1.20 eV when adding H-doping.²⁵ It should be noted that in that work the activation energy was determined from the crystallization rate, and therefore encompasses both nucleation and grain growth, whereas in our case the activation energy purely represents grain growth. Interestingly, they showed that nucleation occurs continuously during the entire annealing process in In_2O_3 without H-doping, whereas the addition of H-doping reduces further nucleation, thereby leading to a larger final grain size (54 to 93 nm). Also, in their work the addition of H-doping led to a decrease of the Avrami exponent from $\sim 5/2$ to $\sim 3/2$, further evidencing a transition from continuous nucleation to site-saturated growth. Although the hydrogen content in their H-doped films was not reported, it can be speculated that the hydrogen content of 4.2 at. % in our as-deposited ALD

films grown at 100 °C¹⁶ is the reason for the observed complete absence of additional nucleation during annealing, for the high activation energy for grain growth and for the large final grain size of ~400 nm. In that respect, the presence of a substantial hydrogen content in the film is highly beneficial for the final film properties. This also favors deposition at the low end of the ALD temperature window, as the hydrogen content in the film is the highest at low deposition temperatures. For example, when increasing the deposition temperature from 100 °C to 130 °C, the hydrogen content decreases from 4.2 to 3.3 at. %. Interestingly, it has previously been observed that almost all the atomic H in the film is retained even after crystallization at 200 °C.¹⁶ The observed reduction in film crystallinity upon the introduction of dopants is not uncommon. For example, the presence of Zn in IZO has been observed to completely hamper crystallization, as an IZO film sputtered from a 90 wt.% In₂O₃ and 10 wt.% ZnO target remains fully amorphous even after a 20 minute anneal at 190 °C.²

D. A numerical simulation of the crystallization process

In the foregoing, a model of the crystallization process has been proposed (Figure 5). Under the assumptions of the model, the crystallization curves of Figure 6 can be calculated, provided the density of embedded crystallites and the temperature-dependent grain growth rate are known. Since these have been determined from the SEM analysis, a numerical implementation of the growth model has been made in an attempt to reproduce the crystallization curves of Figure 6 and thereby to verify its validity.

FIG. 9. Visualization of the model used to describe the crystallization process. The grid points corresponding to the crystalline state are transparent in this visualization, and the film has a crystalline fraction X_c of 45%. For clarity, a smaller grid of $1 \times 1 \times 0.075 \mu\text{m}^3$ and fewer nuclei (8) are used in this particular visualization compared to the model used for the calculations. Note that the nuclei are randomly distributed and that the grid has periodic boundaries in the xy -directions.

In line with the proposed crystallization mechanism, the basic assumptions of the simulation are that randomly-distributed hemispherical crystallites with surface density n_s are present on the surface, which grow isotropically upon annealing with a certain grain growth rate v_g . A visualization of a grid generated by the implemented model can be seen in Figure 9. Details on the numerical implementation of the model can be found in the supplementary material.

Using the film thickness, crystallite density and temperature-dependent grain growth rate as input parameters, the model can calculate both the *bulk* crystalline fraction $X_{c,bulk}$ and the *surface* crystalline fraction $X_{c,surf}$ as a function of time. These input parameters are all known from the SEM analysis and have been used to calculate the evolution of the crystalline fraction for our studied films. The resulting crystallization curves have been plotted in Figure 6 for the various annealing temperatures. As can be seen, despite the simple assumptions and

limited number of input parameters, the model accurately predicts the observed crystallization kinetics and thereby corroborates the model proposed in Figure 5.

E. ALD of $\text{In}_2\text{O}_3\text{:H}$ on non-planar geometries

The discussion in this paper so far has dealt with depositions on planar surfaces. Nonetheless, one of the strengths of the ALD approach is the ability to conformally deposit on more complex 3-dimensional topologies, which are nowadays becoming ubiquitous in many high-end semiconductor device applications. Therefore, here we would like to briefly highlight that our ALD approach can also be successfully extended to non-planar substrate geometries, i.e. silicon nanowires in this specific case. Although similar results are obtained, subtle differences occur on such a geometry.

Figure 10(a) shows a TEM image of a silicon nanowire which has been covered with a layer of ~ 30 nm of $\text{In}_2\text{O}_3\text{:H}$, deposited at 100°C . Note that this film is thinner than the 75 nm used in the study on planar substrates. As can be seen, the silicon nanowire is conformally covered with ALD $\text{In}_2\text{O}_3\text{:H}$. Strikingly, already at this lower film thickness the film consists of an amorphous phase with relatively large embedded crystallites. This might point to enhanced nucleation of crystallites during deposition on the nanowire geometry. Nonetheless, a fully crystalline shell with large grains is obtained around the nanowire after post-annealing for 10 minutes at 200°C , as shown in Figure 10(b).

FIG. 10. TEM images of silicon nanowires covered with ~ 30 nm of ALD $\text{In}_2\text{O}_3\text{:H}$ prepared at 100°C , both (a) as-deposited and (b) after annealing for 10 minutes at 200°C .

IV. CONCLUSIONS

In this work, the crystallization mechanism and crystallization kinetics of $\text{In}_2\text{O}_3\text{:H}$ films have been investigated by a combined structural and optoelectronic characterization approach involving scanning and transmission electron microscopy, XRD and SE. In order to obtain the best optoelectronic properties it is shown that for the ALD films it is prerequisite to prepare the $\text{In}_2\text{O}_3\text{:H}$ at the lowest possible temperature prior to post-deposition annealing, since such films reveal the highest grain size after crystallization. This is attributed to their low density of embedded crystallites that act as seeds for further crystallization, and the substantial hydrogen content in those films which likely hampers additional nucleation from the amorphous phase. The temperature-dependent grain growth rate has been determined, from which a thermal activation energy of (1.39 ± 0.04) eV has been found. Based on the observations from SEM and TEM, a growth model for the crystallization of $\text{In}_2\text{O}_3\text{:H}$ has been proposed. This model has been implemented numerically, and the close match between the experimental and predicted crystallization curves corroborates its validity. Finally, similar results have been observed on

non-planar substrates, although subtle differences have been observed which require further research.

SUPPLEMENTARY MATERIAL

See supplementary material for AFM images of an $\text{In}_2\text{O}_3\text{:H}$ film prepared at 100 °C, top-view SEM images of $\text{In}_2\text{O}_3\text{:H}$ films at various stages of crystallization and for further details on the numerical implementation of the model.

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