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HTML ABSTRACT • LINKS

Surface-diffusion-controlled incorporation of nanosized voids during hydrogenated amorphous silicon film growth

A. H. M. Smets, W. M. M. Kessels, and M. C. M. van de Sanden[a)]
Department of Applied Physics, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands

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The incorporation of nanosized voids during hydrogenated amorphous silicon film growth is studied by measurements of the film mass density and the hydrogen present at the void surfaces. The observed dependence of the density of nanosized voids on the growth flux and substrate temperature is explained in terms of a surface-diffusion-controlled void incorporation model. From this analysis, an activation energy for surface diffusion in the range of 0.77–1.05 eV has been found, a value which is in agreement with the activation energy obtained from the analysis of the surface roughness evolution during growth in a previous study. © *2005 American Institute of Physics*.
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Nanosized voids are important in the morphology of optoelectronic materials as these voids are related to electronic defects, while they also enhance optical losses. The void-related properties have therefore negative effects on the performance of these materials in devices such as solar cells[1] and photonic waveguide structures.[2,3] Since the incorporation of nanosized voids depends on the growth technique employed, a good understanding of the film growth mechanism and more specifically the incorporation of these nanosized voids is essential for manufacturing improved device structures. A possible incorporation mechanism of nanosized voids has been revealed by two-dimensional molecular dynamic (MD) simulations in which it was observed that surface valleys or film roughness can finally evolve into nanosized voids in the bulk during film growth.[4,5] This incorporation mechanism of nanosized voids is illustrated schematically in Fig. 1. The main outcome of the MD studies is that void incorporation is controlled by the competition between the diffusivity of surface species and the arrival rate of the growth precursor at the surface. The importance of these observations will be demonstrated by the growth of hydrogenated amorphous silicon (a-Si:H) for which typical nanosized voids with a diameter of approximately 4 nm[6,7] (corresponding to $>10^3$ "missing" silicon atoms) have been reported. The void surfaces are covered by silicon-hydride species.[8] In this letter we will report on the study of the void incorporation during a-Si:H growth and its dependence on substrate temperature T and growth flux. In close analogy with the aforementioned MD calculations,[4,5] the experimental results will be analyzed by a model based upon the competition between surface diffusion and growth flux.

The a-Si:H films have been deposited using the expanding thermal plasma deposition technique[9] under conditions where the SiH_3 radical is the key growth precursor. This growth can be considered as purely chemical in nature, i.e., the surface processes control the growth process in the absence of high-energy ion-bombardment. The growth of a-Si:H under these conditions is well characterized in previous studies, which have revealed the T-independent SiH_3 surface reaction probability and the T-dependent surface hydride composition.[10] Furthermore, the existence of a thermally activated surface diffusion process during a-Si:H growth has been proven under these conditions by the study of the T dependence of the scaling behavior of the surface roughness evolution during film growth.[11] An activation energy of the surface diffusion process of ~1.0 eV has been found.[11] The mechanism of surface diffusion and/or the mobile surface species or features have not been identified.

Two methods have been employed to study nanosized void incorporation during a-Si:H growth. In the first method the hydrogen at void surfaces has been used as a measure of the void density. The silicon hydrides Si-H_x ($x=1$ or 2) at void surfaces has been determined by means of the high stretching mode (HSM, 2070–2100 cm^{-1}) in infrared spectroscopy data as described in Ref. 8. For a hydrogen content $c_H > 14$ at. %, hydrogen is dominantly located on void surfaces, whereas for $c_H < 14$ at. % hydrogen resides predominantly in divacancies as monohydrides, which contribute to the low stretching mode (LSM, 1980–2010 cm^{-1} in the infrared spectrum). In the second method the void fraction has been determined from the film mass deficiency defined as $f_m = (1 - \rho_{a\text{-Si:H}}/\rho_{a\text{-Si}})$ with $\rho_{a\text{-Si:H}}$ and $\rho_{a\text{-Si}}$ the mass density of a-Si:H and a-Si, respectively, as discussed in Ref. 8. The

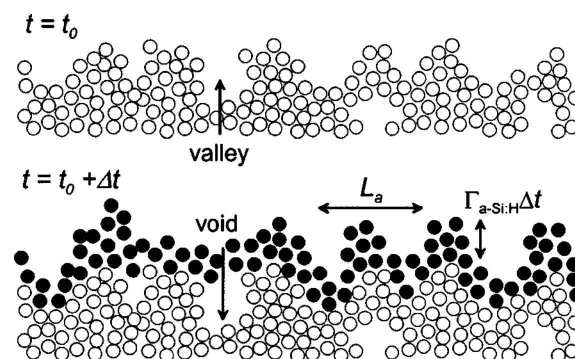

FIG. 1. Schematic two-dimensional representation of an amorphous surface during deposition at times t_0 and $t_0+\Delta t$. The atoms deposited in the period Δt are indicated as solid dots. A valley is incorporated as a nano-sized void in the period Δt by overhangs that overgrow. The nano-sized voids in a-Si:H are typically 4 nm in diameter corresponding to approximately $>10^3$ missing silicon atoms.

[a)]Author to whom correspondence should be addressed; electronic mail: m.c.m.v.d.sanden@tue.nl

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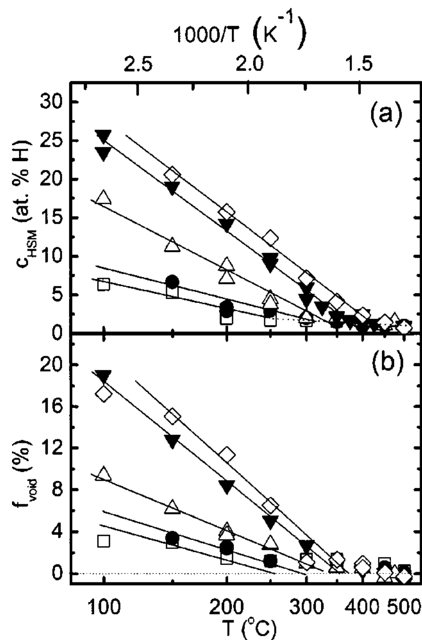

FIG. 2. (a) The hydrogen content at nano-sized void surfaces c_{HSM} and (b) the void fraction $f_{\mathrm{void}}=f_m-f_{\mathrm{vac}}$ vs the substrate temperature T. Data are given for five mass growth fluxes [0.049 μg cm^{-2} s^{-1} (□), 0.11 μg cm^{-2} s^{-1} (●), 0.48 μg cm^{-2} s^{-1} (△), 1.5 μg cm^{-2} s^{-1} (▼) and 2.7 μg cm^{-2} s^{-1} (◇)] while $f_{\mathrm{vac}}=0.015$. The lines are fits from which the critical temperature T_c is deduced from the intercept with the temperature axis.

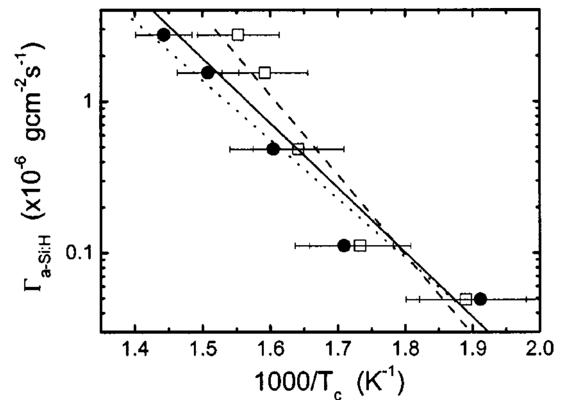

FIG. 3. The mass growth flux $\Gamma_{a\text{-Si:H}}$ vs $1000/T_c$, with T_c the critical temperature as determined from c_{HSM} (●) and f_{void} (□) in Fig. 2. The lines represent fits of Eq. (2) on the HSM data (dotted line), f_{void} data (dashed line), and the combination of the HSM and f_{void} data (solid line), respectively. The activation energies obtained are $E_{\mathrm{dif}}=0.77\pm0.11$ eV, $E_{\mathrm{dif}}=1.05\pm0.13$ eV, and $E_{\mathrm{dif}}=0.85\pm0.11$ eV, respectively.

$\rho_{a\text{-Si:H}}$ is obtained from the Clausius–Mossoti relation[8,12] using the infrared spectroscopy data. Since f_m includes the vacancy fraction f_{vac} as well, we define the void fraction as $f_{\mathrm{void}}=f_m-f_{\mathrm{vac}}$. For compact film growth we find $f_{\mathrm{vac}}\sim0.015$, in line with the reported values of $f_{\mathrm{vac}}=0.01-0.03$ using other deposition methods and which have no HSM signature.[7]

The void fraction has been studied for a large set of samples, by varying the deposition rate R_d from 2 up to 120 Å/s and the T from 100 up to 500 °C resulting in five mass growth fluxes $\Gamma_{a\text{-Si:H}}=0.045$, 0.11, 0.48, 1.5, and 2.7 μg cm^{-2} s^{-1}, which are found to be independent of T.[13] Both the hydrogen content c_{HSM} contributing to HSM and f_{void} as a function of the substrate temperature are shown in Fig. 2. Both parameters show that at high temperatures almost no voids are incorporated in the material. In these compact films, H resides mainly at divacancies.[8] A critical temperature T_c can be defined, above which the growth can be considered as compact. The T_c has been determined for the five different mass growth fluxes and the results are shown in an Arrhenius-type plot of $\Gamma_{a\text{-Si:H}}$ vs T_c in Fig. 3. The T_c increases for increasing $\Gamma_{a\text{-Si:H}}$ reflecting that a higher T_c is required at higher growth rates. The relation between both parameters corresponds to an Arrhenius dependence and the slope in Fig. 3 can be regarded as a measure of the activation energy of the process responsible for the void incorporation.

A hypothesis that can explain Fig. 3 and which is in agreement with the void incorporation observed in the MD calculations[4,5] is that surface diffusion is the process that controls the incorporation of voids during film growth. A similar incorporation mechanism has been suggested by Thornton[14] to describe the void incorporation in metallic films deposited by sputtering in $T/T_m<0.3$ range, with T_m the metal melting point. In other words for $T_{\mathrm{sub}}>T_c$ the diffusion is effective, valleys (when generated) are filled and less or no voids are incorporated, whereas if the diffusion is ineffective ($T_{\mathrm{sub}}<T_c$) voids can be incorporated (cf. Fig. 1). T_c can be considered as a measure of the activation of the surface diffusion at a certain growth flux. The dependence in Fig. 3 therefore implies that the surface diffusion process is thermally activated. In analogy with the MD simulations, this means that two competitive time scales determine T_c: one time scale related to the surface diffusion τ_D and one time scale related to the arrival rate of the growing species τ_R, with τ_R the characteristic time to grow one monolayer with thickness t_m: $\tau_R=t_m/R_d=t_m\rho_{a\text{-Si:H}}/\Gamma_{a\text{-Si:H}}$ with $\Gamma_{a\text{-Si:H}}$ the mass growth flux. The time scale for diffusion is $\tau_D=L_a^2/D$, with $D=D_0\exp(-E_{\mathrm{dif}}/kT)$ the diffusion coefficient of the diffusing surface species, and with L_a the lateral diffusion length. At the critical temperature T_c we assume that the two time scales are equal, which result in

$$\Gamma_{a\text{-Si:H}}=\frac{D_0 t_m \rho_{a\text{-Si:H}}}{L_a^2}\exp\left(-\frac{E_{\mathrm{dif}}}{kT_c}\right). \tag{1}$$

The lateral diffusion length L_a in Eq. (1) also depends on both $\Gamma_{a\text{-Si:H}}$ and T_{sub}. Das Sarma *et al.*[15] showed that in general the diffusion length L_a scales with D and the growth flux Γ (for a-Si:H growth $\Gamma=\Gamma_{a\text{-Si:H}}$) according to $L_a=\alpha(D/\Gamma)^\gamma$ for compact solid on solid growth, where α is a constant and γ a scaling exponent which can have the values $1/6\leqslant\gamma\leqslant1/4$ for surface diffusion on a two-dimensional surface.[15] Note that on the basis of this scaling L_a is much more weakly activated than D. Substitution of L_a in Eq. (1) results in an Arrhenius-type relation:

$$\Gamma_{a\text{-Si:H}}=D_0\left(\frac{t_m\rho_{a\text{-Si:H}}}{\alpha^2}\right)^{1/(1-2\gamma)}\exp\left(-\frac{E_{\mathrm{dif}}}{kT_c}\right). \tag{2}$$

If we apply Eq. (2) exclusively to the data based upon the c_{HSM} or f_{void} results we obtain an activation energy for diffusion of $E_{\mathrm{dif}}=0.77\pm0.11$ eV and $E_{\mathrm{dif}}=1.05\pm0.13$ eV, respectively, whereas if we apply Eq. (2) to both data sets in Fig. 3, we obtain $E_{\mathrm{dif}}=0.85\pm0.11$ eV.

The value range of the activation energy for surface diffusion found, which is within the range 0.77–1.05 eV, is very close to the ~1.0 eV activation energy found from the temperature-dependent scaling of the roughness evolution under the same deposition conditions.[11] Since the proposed

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model that void incorporation is controlled by diffusion results indeed in an activation energy that matches with the activation energy of the surface diffusion and since the model is in line with the void incorporation mechanism as observed in MD calculations,[4,5] we conclude that the void incorporation is surface diffusion controlled.

Another study has also reported the empirical value of an activation energy for surface diffusion on *a*-Si:H surface.[16] Bray *et al.* found a lower activation energy of 0.2 eV by means of the temperature dependence of L_a^2, with L_a deduced from surface morphology scans measured by atomic force microscopy. Note that this activation energy of L_a^2 is an underestimation of the activation of D, due to the scaling relation between both parameters $L_a \sim (D/\Gamma)^{\gamma}$[15] as mentioned earlier. Furthermore, Bray's results are hard to compare with the activation energy for diffusion found in this letter since in contrast to the deposition conditions used by Bray *et al.*[16] our deposition conditions are without high ion bombardment and therefore any ion bombardment induced enhancement of surface diffusion is absent.[17]

The relatively "high" activation energy values ($\sim$1.0 eV) found are intriguing in the sense that it contradicts the hypothesis, often proposed in *a*-Si:H literature, that the *a*-Si:H surface diffusion is controlled by weakly adsorbed radicals.[16,18–21] The activation energies found (0.77–1.05 eV) imply that the surface diffusing species during *a*-Si:H growth may be chemical bounded or that for an unknown reason the energy barrier to a diffusional state on an amorphous surface is higher.

The fit in Fig. 3 also provides a prefactor $\Gamma_0 = D_0(t_m \rho_{a\text{-Si:H}}/\alpha^2)^{1/(1-2\gamma)}$, from which the absolute value for the lateral diffusion length at $T = T_c$ can be estimated. Using $L_a = \alpha(D/\Gamma_{a\text{-Si:H}})^{\gamma} = \alpha(D_0/\Gamma_0)^{\gamma}$ we can substitute out α and get

$$L_a = \left(\frac{D_0 t_m \rho_{a\text{-Si:H}}}{\Gamma_0}\right)^{1/2}. \tag{3}$$

From Fig. 3 we obtain a prefactor Γ_0 on the order of 10^4-10^6 μg cm^{-2} s^{-1}. The prefactor of the diffusion coefficient is estimated by $D_0 = \Lambda^2/\tau_{\text{hop}}$, with Λ the lattice site distance ($\sim t_m$) and τ_{hop} the "hopping time" ($\sim h/2kT_c$). Applying Eq. (3) on the experimentally determined Γ_0 value and the assumed D_0 value, we find that the lateral diffusion length L_a is in the range of 20–200 nm at $T_c = 250$ °C, implying about 500–5000 hops for random walk diffusion. The found L_a is roughly related with the averaged distance between the valleys L_v, which ends up as voids in the material. If we assume that the voids have a typical diameter of 4 nm and use $c_{\text{HSM}} \approx 1$ at. % H at $T = T_c$ (see Fig. 2), we can estimated that $L_v \sim 22$ nm, a value on the same order as the L_a values obtained.

Above T_c ($c_{\text{H}} < 14$ at. %) compact films are grown in which the hydrogen resides predominantly in divacancies.[8] Therefore we would like to stress that the hydrogen incorporation of compact films is only ruled by the vacancy incorporation mechanism, whereas the hydrogen incorporation below T_c is ruled by both the void and vacancy incorporation mechanism. It is noteworthy that most hydrogen incorporation models are based upon random incorporation of Si–H bonds in the matrix,[21,22] and therefore not in agreement with the observation that H is located at vacancies or voids.[8]

In summary, in this letter we have demonstrated that nanosized voids are incorporated in the absence of sufficient surface diffusion during SiH_3 dominated *a*-Si:H growth with negligible surface ion bombardment. The void incorporation is explained in terms of a model in which the surface diffusion competes with growth flux. This model has been applied to the observed dependence of the void fraction on growth flux $\Gamma_{a\text{-Si:H}}$ and T and an activation energy for surface diffusion of 0.77–1.05 eV is deduced, a value in agreement with previous results from Ref. 11.

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