Model for the amorphous roughening transition in amorphous semiconductor deposition

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Abstract

The evolution of surface roughness on hydrogenated amorphous silicon (a-Si:H) films prepared by plasma-enhanced chemical vapor deposition exhibits initial smoothening due to nuclei coalescence, a region of surface stability, and finally a prominent roughening transition (designated $a \rightarrow a'$) at a critical thickness. The thickness at which the $a \rightarrow a'$ transition occurs, as measured by real time spectroscopic ellipsometry (SE), is found to correlate closely with the electronic properties of the film. Thus, the transition has been incorporated into deposition phase diagrams that have been applied successfully to optimize solar cell performance and stability. A simple continuum model for the evolution of the 1D surface profile using an initial condition designed to be consistent with the nucleation characteristics measured by real time SE is sufficient for insights into the correlation between the roughness evolution and film properties. Good agreement between the experimental results and model calculations support the concept that optimum electronic properties of the films are associated with weakly reactive surfaces and long lifetime radicals that lead to adsorbed precursors with large surface diffusion lengths.

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1. Introduction

Real time spectroscopic ellipsometry (SE) results have demonstrated the existence of three regimes of surface roughness evolution during amorphous semiconductor thin film growth by plasma-enhanced chemical vapor deposition (PECVD) [1]:

(i) smoothening (or coalescence) of initial nucleation-generated clusters;
(ii) stable surface until a critical thickness; and
(iii) roughening of the film beyond the critical thickness.

It should be emphasized that the films remain fully amorphous throughout these regimes.

Hydrogenated amorphous silicon (a-Si:H) thin films exhibiting the highest electronic performance also reveal in regime (i) the largest surface smoothening magnitudes and rates during coalescence, as well as in regime (ii) the smoothest, most stable surfaces throughout the growth of thick films [1]. In fact, for these highest quality films, the transition between regimes (ii) and (iii), denoted the $a \rightarrow a'$ roughening transition, is not observed, presumably because it occurs at thicknesses greater than the final film thickness (typically at thicknesses $> 0.5 \mu$m). Deterioration of electronic quality is correlated with a reduction in the magnitude and rate of smoothening in regime (i) and an increase in the roughness thickness in regime (ii). Deterioration is also accompanied by a shift in the $a \rightarrow a'$ transition to lower thicknesses. In fact, regimes (i) and (ii) may
disappear when the electronic quality is sufficiently poor, e.g., under conditions combining high plasma power, little or no H$_2$-dilution, and low temperatures. In this article, insights into the three regimes listed above and their correlations with the electronic performance will be obtained by applying a simple, one-dimensional (1D) continuum model of film growth.

2. Results

2.1. Experimental data

Real time SE has been performed using a rotating-compensator multichannel ellipsometer [2] in order to study the evolution of the surface roughness thickness for Si:H films fabricated by PECVD on crystalline silicon (c-Si) wafer substrates. Fig. 1 (main part) depicts examples from a high-pressure, high-rate PECVD series for which all films remain amorphous throughout growth [3]. The substrate temperature $T$, rf plasma power $P$, and total pressure $p$ were fixed at the following values: $T = 200^\circ$C, $P = 0.72$ W/cm$^2$, and $p = 3$ Torr. The H$_2$-dilution ratio $R = [\text{H}_2]/[\text{SiH}_4]$, was set at four different values ranging from 15 to 60, leading to deposition rates ranging from 18 Å/s ($R = 15$) to 6.6 Å/s ($R = 60$). These data demonstrate significant changes in the surface roughness evolution with $R$ and clearly exhibit all three regimes described above. The $a \to a$ roughening transition thickness as a function of $R$ is included in the deposition phase diagram shown in the inset. This diagram also includes the amorphous-to-(mixed-phase microcrystalline) transition thickness obtained from depositions with $R$ set from 70 to 100.

Because similar characteristics in the surface roughness evolution have been observed for widely different semiconductor deposition processes from PECVD to sputtering (see, e.g., [4]), generic models (i.e., those that do not depend on the specific surface chemical mechanisms of the growth process) have been considered in this research. Connections can then be made between the generic model that is supported by the data and the specific mechanisms elucidated in the extensive literature on this topic. In this way, the three regimes in Fig. 1 can be understood through a relatively simple model to be discussed briefly in the next subsection.

2.2. Model for surface roughness evolution

Continuum models have been applied to study both physical and chemical vapor deposition processes [5–8]. In such studies, the dynamics of the surface roughness are often investigated by means of linear stability analysis. In this analysis, the surface roughness is considered to be a small perturbation from a perfectly flat surface (or from a straight line profile in a 1D simulation), allowing one to linearize the differential equation that describes the surface profile evolution. Then the time evolution of the amplitude $h(\lambda, t)$ of a surface perturbation with spatial period $\lambda$ in the in-plane direction can be described simply as

$$h(\lambda, t) = h_0 \exp[\omega(\lambda)t],$$

(1)

where $\omega$ is a decay rate that depends on the pertinent physical mechanisms of growth. In fact, the relevance of this approach has been tested in real time SE studies of a-Si:H growth on microscopically rough transparent conducting oxide surfaces having well defined in-plane periods [9]. In depositions on such surfaces, the substrate-induced roughness is observed to decay exponentially with time in accordance with Eq. (1). In general, the decay rate $\omega$ in Eq. (1) can be described as a polynomial function of spatial frequency $k = 2\pi/\lambda$ [10]

$$\omega(\lambda) = \sum_{m} (a_m/\lambda^m).$$

(2)

In this analysis, the physical mechanisms that impact the evolutionary development of the surface determine the polynomial terms present as well as the polynomial coefficients $a_m$. The three regimes listed above can be understood qualitatively from Eqs. (1) and (2) in the following general way. Low amplitude surface modulations of period $\lambda$ less than a critical length scale $\lambda_0$ are unstable and decay versus time $t$ (or thickness) according to Eq. (1), where $\omega(\lambda) < 0$ for $\lambda < \lambda_0$. This behavior applies to short period surface modulations associated with the coalescence of initial nuclei as is evident in Fig. 1. Features with $\lambda > \lambda_0$, such that $\omega(\lambda) > 0$, are enhanced. This behavior applies to the later stage characteristics of growth in Fig. 1, i.e., the $a \to a$ transition, in which case statistical fluctuations in nuclei height and radius ultimately lead to larger scale structures through space-filling competition among neighboring columns [11].
In one model [5,9], smoothening can be attributed to capillarity-driven surface diffusion that exhibits a negative term in \( \omega(\lambda) \) given by \( \omega(\lambda) = -16\pi^2D_x\lambda^{-4} \), where \( D_x = \Omega^2\sigma_xD_s/k_BT \), and \( \Omega, \sigma, D_s, \) and \( k_BT \) are the atomic volume, number of atoms per area, surface energy density, surface diffusivity, and thermal energy, respectively. The roughening is an atomic size effect that exhibits a positive term in \( \omega(\lambda) \) given by \( \omega(\lambda) = 4\pi^2\rhoJ^{-2} \), where \( \rho \) is the atomic radius and \( J \) is the deposition flux. For this effect, regions where the surface exhibits positive or negative curvature receive a deposition flux greater than or less than \( J \), respectively, as in a shadowing effect. In this two-term model, the critical length scale \( \lambda_0 = (4\pi^2D_x\rho J)^{1/2} \) corresponds to the specific period that is stable. Since this is the shortest period that cannot be damped by diffusion, it can be interpreted as a surface diffusion length. Additional useful features of this model have been described previously [5,9].

### 2.3. Simulations of surface roughness evolution

In applying the model of the previous subsection, the surface perturbation is associated with the initial nucleation process. An appropriate 1D model for the surface profile at nuclei contact consists of a series of contacting semicircles that simulate clusters, with radii determined by one Gaussian distribution, and the elevation of the semicircle diameter from the surface determined by a second Gaussian distribution [9]. This one-dimensional surface profile is then allowed to evolve during film growth using the approach described in the previous subsection, as shown in Fig. 2. As is evident in the figure, the short-period perturbations in the initial surface profile arising from nuclei contact smoothen out during film growth in the initial stages. Generally with time (or thickness), however, the surface profile coarsens as can be seen by the disappearance of the smallest cluster in Fig. 2 and the development of superclusters encompassing many smaller clusters. The superclusters evolve from the statistical distribution of initial cluster heights and spacings, and control the roughness amplitude associated with the roughening transition. From the surface profile extracted at any point during film growth as in Fig. 2, the root-mean-square value of the surface roughness layer thickness, \( d_{\text{rms}} \), can be deduced and converted to the surface roughness layer thickness, \( d_s \), determined from real time SE using the expression \( d_s = 3\AA + 1.5d_{\text{rms}}(\AA) \). This expression has been obtained from a correlation of real time SE and atomic force microscopy (AFM) of the same surfaces [12].

As an example of the final results, Fig. 3 shows a fit (solid line) to the surface roughness evolution determined by real time SE for the \( R = 40 \) a-Si:H film from the series of Fig. 1. Also shown are the simulated roughness evolution curves obtained using the same initial nucleation profile, but assigning different values to the surface diffusion length \( \lambda_0 \) from 12 to 160 \( \AA \), above and below the best fit value of 45 \( \AA \). Fig. 4 summarizes the best simulation results plotted versus \( R \) for all four depositions of the series of Fig. 1. The simulations suggest that all the films in this series have a mean cluster radius \( \sim 20 \AA \) which describes the contact thickness; however, \( \lambda_0 \), ranges from 28 \( \AA \) for \( R = 15 \) to 50 \( \AA \) for \( R = 60 \), which accounts for the significant variations with \( R \). As shown in the figure, a linear correlation is found between the best fit surface diffusion length in the simulation, and the observed \( a \) \( \rightarrow \) \( a \) transition thickness. The amorphous roughening transition is only sensitive to diffusion lengths above a certain value, however; below this value the roughening begins almost immediately in the deposition process.
related. Fig. 1. Over this range of experimentally in AFM studies [16].

In these models, the average diffusion length, is consistent with previous atomic scale models for under conditions that yield the largest surface diffusion the highest electronic quality a-Si:H materials are prepared the smoothness of a-Si:H arises from a valley filling mechanism. In the early stage when clusters are making contact, the surface is more disordered with higher defect density, and this will limit the diffusion length. After the coalescence process and even in the later growth stages, the diffusion length may increase with thickness as the surface defect density decreases and as valley regions cover a smaller fraction of the surface. As a result, any simple model of the full roughness evolution from thin film coalescence to thick film roughening is unlikely to be sufficiently complete for detailed quantitative purposes.

3. Discussion

The full set of roughness evolution simulations reproduce the trends of the experimental data in Fig. 1, revealing all three characteristics, namely, coalescence of initial nucleation-generated clusters; a stable surface until a critical thickness; and roughening of the film beyond the critical thickness. Here it is of interest to address whether such a simple model includes a sufficiently strong physical basis to account for the complex growth process of a-Si:H [13].

In support of this simple approach, molecular dynamics (MD) studies of surface roughness evolution suggest that the smoothness of a-Si:H arises from a valley filling mechanism [14]. This mechanism involves adsorbed SiH₃ precursors that diffuse over the surface via over-coordination defects and relaxation of bond strain. The precursors incorporate preferentially in valleys where dangling bonds exist in greater numbers. Making connection to the simple continuum model, this process is analogous to the valley filling mechanism that serves to reduce the surface free energy. The roughening mechanism in the simple model is similarly reasonable based on simple geometric constraints of film growth at the atomic level [15]. The critical length scale identifiable as the diffusion length in Fig. 4 lies between that identified in the MD studies, and that established experimentally in AFM studies [16].

The ultimate conclusion of the present study, namely that the highest electronic quality a-Si:H materials are prepared under conditions that yield the largest surface diffusion length, is consistent with previous atomic scale models for growth [17,18]. In these models, the average diffusion length is limited either by short lifetime radicals that impinge on the surface from the plasma or by surface defects such as dangling bonds, both of which can lead to bulk defects that degrade electronic properties and stability. Additionally, surface diffusion may be limited by the reaction of two or more diffusing precursors. This is likely to be an important process at high deposition rates and may also lead to continuous renucleation and its associated bulk defects.

Finally, it is important to note the drawbacks of the simple model. First of all, the simulation is 1D and should be extended to 2D for closer quantitative comparisons. Given the complexity of the surface processes, however, it is likely that one can say with confidence only that the surface roughness evolution is reflective of a competition between smoothing driven by diffusion and a roughening process that drives columnar growth in thin films. It is less likely, however, that the mathematical forms of these competing terms are so simply described as in the continuum model. As a result, the greatest confidence should be placed in the trends reported here, rather than the numerical values. One of the complexities of real surfaces is that the diffusivity and hence the diffusion length may depend on the stage of film evolution. In the early stage when clusters are making contact, the surface is more disordered with higher defect density, and this will limit the diffusion length. After the coalescence process and even in the later growth stages, the diffusion length may increase with thickness as the surface defect density decreases and as valley regions cover a smaller fraction of the surface. As a result, any simple model of the full roughness evolution from thin film coalescence to thick film roughening is unlikely to be sufficiently complete for detailed quantitative purposes.

4. Summary

A 1D continuum model of surface profile evolution with an initial condition designed to be consistent with nucleation characteristics measured by real time SE has been used in order to better understand the surface roughness evolution of Si:H films that remain amorphous throughout growth. The surface roughness evolution of such films as measured by real time SE exhibits a prominent roughening transition (designated \( a \rightarrow a \)) at a critical thickness, and this critical thickness is found to correlate with the electronic properties of the film. In fact, for materials with the best electronic quality, the \( a \rightarrow a \) transition occurs at thicknesses beyond that typically deposited for devices. Because of the importance of the \( a \rightarrow a \) transition, it has been incorporated into deposition phase diagrams that have been applied successfully to optimize solar cell performance and stability. A key feature of modeling performed here is that the \( a \rightarrow a \) transition thickness scales linearly with the precursor diffusion length. As a result such modeling supports previous proposals that optimum electronic film qualities are associated with weakly reactive surfaces, long lifetime precursors, and large precursor surface diffusion lengths.

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