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Fundamentals of Film Growth: Amorphous and Microcrystalline

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ON THE SURFACE ROUGHNESS EVOLUTION DURING a-Si:H GROWTH

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ABSTRACT

The surface roughness evolution during a-Si:H film growth from a SiH_3 beam under purely chemical deposition conditions is discussed. The data is explained in terms of the different universality classes proposed in literature. It is argued that roughness evolution during a-Si:H growth shows great similarity with MBE growth, which belongs to a universality class studied extensively by Das Sarma and coworkers. The activation energy for surface diffusion extracted from simulating the growth exponent β vs. temperature reveals an activation energy of about 1 eV. This result suggests that the surface roughness evolution is not controlled by the weakly adsorbed SiH_3 radical.

INTRODUCTION

The surface roughness evolution during thin film growth is an extensively studied subject because of its interesting scaling and fractal properties [1,2]. This makes these studies of fundamental interest. On the other hand, the roughness development also relates to the different surface processes occurring during deposition [1,2]. For example, physical processes such as ion bombardment leads to smoother films whereas reactive radicals impinging the film surface results in rough films if surface diffusion is absent. Therefore the study of the roughness development of thin film growth gives insight into the details of the different surface processes provided the study is well conducted and interpreted. It is important to note that the mechanisms are determined from the roughness development in time, meaning that the actual value of the film roughness is unimportant.

Many studies have been devoted to the surface roughness development during the growth of a-Si:H using various surface topography techniques [3-7]. Originally the studies were concentrated on the initial growth and substrate effects [8,9], later the studies were aimed at proving the correlation between roughness development and the species responsible for growth [4,5,7]. It has been firmly established by many investigations that a-Si:H films as grown from SiH_4 containing plasmas are extremely smooth [10]. Moreover, the roughness evolution revealed a clear scaling behavior. In most cases it was concluded that a surface smoothening process during a-Si:H growth should be present, resulting in a so called *valley filling mechanism* [3-7]. For example, Kondo *et al.* [5] and Bray *et al.* [7] have argued that this valley filling mechanism is ruled by the weakly adsorbed or physisorbed SiH_3 radical. This was concluded from the lateral correlation length of the roughness as function of substrate temperature. In contrast Tanenbaum *et al.* [3] have discussed their results in terms of the preferential presence of dangling bonds in valleys where the SiH_3 radicals can stick. This speculation is confirmed by calculations of Ramalingham *et al.* [11] who actually observed dangling bonds to be present in the lower parts of the film surface. An alternative explanation was given by Flewitt *et al.* [4] who speculated that SiH_3 radicals preferentially abstract atomic hydrogen in surface valleys.

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Most of the studies are performed on films as deposited from RF-PECVD. A disturbing effect in these plasmas is the presence of ion bombardment, the influence of other high sticking radicals or the influence of atomic hydrogen. All these effects could have an influence on the roughness development. In this paper we will investigate the roughness development of hydrogenated amorphous silicon from a well defined flux of silyl radicals, as generated from an expanding thermal plasma (ETP) [12,13]. Under the deposition conditions studied in this paper the growth can be characterized as being fully chemical in origin [14]. In the remainder of this paper we will refer to this as purely chemical deposition. The roughness evolution in time will be studied as function of growth rate and substrate temperature.

Universality classes of of thin film growth

The various universality classes of thin film growth concerning the roughness development are well described by Barabási and Stanley [1]. We will repeat here the main universality classes as necessary for the understanding of the growth of a-Si:H. Family and Vicsek [15] introduced a general scaling law for self-affine surfaces ($\boldsymbol{x} \rightarrow b\boldsymbol{x}$, $h(\boldsymbol{r}) \rightarrow b^{\alpha}h(\boldsymbol{r})$, $\boldsymbol{r} = (x,y)$), which describes the evolution of the root mean square (rms) of the film height distribution of a film during deposition. This width, i.e. the root mean square (rms) surface roughness $W(L,d)$ of a so-called self-affine surface obeys the so-called Family-Vicsek scaling law [15]:

$$W(L,d) \propto L^{\alpha} F(d/L^{\alpha/\beta}) \tag{1}$$

The scaling function $F(u)$ has the properties

$$F(u) \propto u^{\beta} \qquad \text{for } u \ll 1 \tag{2a}$$

and

$$F(u) = \text{constant} \qquad \text{for } u \gg 1 \tag{2b}$$

In Eq. (1) $W(L,d)$ is defined by $W(L,d)^2 = \langle (h(x,y) - \langle h(x',y') \rangle_{x',y'})^2 \rangle_{x,y}$ where $h(x,y)$ is the surface height profile of the film and the brackets indicate an average over the entire (x',y') and (x,y) plane respectively. L is the lateral size of the growing surface in D-1 dimensions, d is the mean film thickness, α the roughness exponent and β the growth exponent [1]. For thin films $W(L,d)$ scales as d^{β} whereas for thick films the saturated roughness $W_{\mathrm{sat}}(L,d)$ scales as L^{α}. Thus the exponent β characterizes the time dependent dynamics of the roughening process and α characterizes the roughness of the saturated roughness in terms of the system lateral size L [1,2,5,15].

Every self-affine growth process can be classified according to its scaling exponents α and β by a so called universality classes. Three universality classes have been widely used to explain the surface growth of thin films. The most simple class is Random Deposition (RD, cf. Fig. 1a), a class of deposition processes in which the growth species arrive randomly on the surface and no surface relaxation occurs. The scaling exponents can be easily derived from the stochastic differential equation for the surface height variable $h(\boldsymbol{r},t)$ valid in the continuum coarse grained limit [1]

$$\partial h(\boldsymbol{r},t)/\partial t = R + \eta(\boldsymbol{r},t) \tag{3}$$

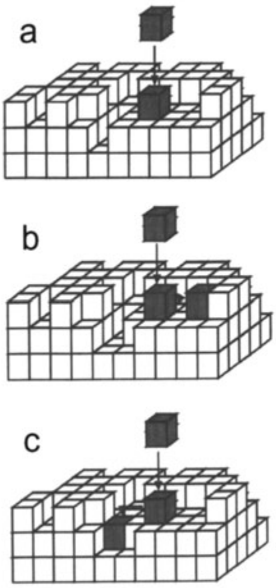

Figure 1 The growth models for the three different universality classes a) Random Deposition (RD), b) Random Deposition with Diffusion (RDD), c) Random Deposition with Relaxation (RDR).

where R is the deposition rate and $\eta(\boldsymbol{r},t)$ reflects the random fluctuations in the deposition process. The average of $\eta(\boldsymbol{r},t)$ is equal to zero, whereas the second moment reflects the Gaussian character of the randomly arriving species. For RD α is undefined and $\beta = ½$. A closely related universality class is the class in which the species are allowed to diffuse before they incorporate into the growing film, Random Deposition with Diffusion (RDD, cf. Fig. 1b). In the continuum coarse grained limit, the stochastic differential equation describing this universality class is given by

$$\partial h(\boldsymbol{r},t)/\partial t = R - K\nabla^4 h(\boldsymbol{r},t) + \eta(\boldsymbol{r},t) \qquad (4)$$

with K proportional to the surface diffusion coefficient. The surface diffusion term was originally derived in classical papers by Mullins [16] and Herring [17]. It can be proven straightforwardly that the scaling exponents in $D = 2+1$ are given by $\alpha = 1$ and $\beta = ¼$. Note that this means that the film surface topography reveals a self-similar character, *i.e.* lateral and normal coordinates scale in an identical way. Also it should be noted that the scaling is substrate temperature independent although the surface diffusion itself depends explicitly on the substrate temperature. As a last example of a universality class, we discuss Random Deposition with diffusion and full Relaxation (RDR, cf. Fig. 1c). The coarse grained differential equation for this class is given by an Edward-Wilkinson type equation [18]

$$\partial h(\boldsymbol{r},t)/\partial t = R + \nu\nabla^2 h(\boldsymbol{r},t) + \eta(\boldsymbol{r},t) \qquad (5)$$

with ν a substrate temperature dependent constant related to the surface tension of the film surface or proportional to desorption-adsorption processes [1,18]. Also for this differential equation the scaling exponents can be analogously derived as for Eq. (4). The result in $D = 2+1$ is that both α and β are equal to zero, *i.e.* there is no roughness development of the film during growth. Again this scaling property is independent of substrate temperature.

The purpose of roughness development studies is to determine the scaling properties of the surface topography by determining the scaling exponents α and β. This enables the assignement of a universality class for the particular growth process belongs. This is not a straightforward procedure, as we will show below, and in many cases it is impossible to determine the universality class experimentally.

EXPERIMENTAL DETAILS AND DATA ANALYSIS

Films are grown with varying thickness, deposited at growth rates ranging from 2 Å/s up to 70 Å/s and at different substrate temperatures (100 – 500 °C) using the expanding thermal plasma (ETP) technique [12,19]. The ETP technique is based on generation of an Ar-H_2 plasma in a

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thermal plasma source (cascaded arc), which is subsequently expanded in a low pressure chamber where it dissociates SiH_4 [12,19]. The SiH_4 is admixed in the low pressure chamber (12 to 21 Pa) just behind the source exit via an injection ring. The remote like character of the ETP leads to a substrate self-biasing smaller than 2 eV, which means that the influence of ions on the growth process is marginal in comparison to conventional RF-PECVD. The electron temperature downstream of the arc exit is low (typically 0.3 eV). The silane is therefore mainly dissociated by atomic hydrogen into SiH_3. An advantage of this technique is the fact that the plasma is very pure, i.e. the SiH_3 radical is the dominant radical and is responsible for 90 % of the a-Si:H growth under the conditions presented [14]. The growth flux is only weakly temperature dependent [12] and the atomic hydrogen flux is small in comparison with the silyl flux arriving on the substrate [14]. This leads to a growth process that is purely chemical: silyl radicals arrive on the surface and form the film by eliminating hydrogen from the surface and sub-surface regions. A substrate holder with accurate substrate control (100 °C – 500 °C) is positioned at 38 cm from the plasma source exit. Deposition experiments are performed on atomically flat c-Si<111>. All films studied were amorphous even at the highest substrate temperature of 500 °C as proven by the absence of any crystalline peak in Raman spectra [19].

The AFM measurements are performed on as-deposited films, meaning that a-Si:H surface is covered with native oxide, as observed by XPS analysis on some samples. Comparison of *in situ* STM measurements with *ex situ* AFM measurements on the same a-Si:H sample, as reported in [7], showed that ambient exposure does not significantly affect the surface topography. AFM measurements are performed using a Nanoscoop IIIa with NCR-12 tips. The measured AFM images consists of 256 × 256 pixels. Every a-Si:H film has been measured at various scan sizes ranging from 10 nm up to 10 μm. The AFM scans are used to deduce the roughness exponent α. Since in practice the α value can vary from method to method, three methods were used to determine α, as described elsewhere extensively [20]. The values for α as obtained from the three methods differed significantly but where all in the range 0.4 – 0.7, and showed a weak temperature dependence. Although not explicitly explained here, the main reason we believe that the determination of α is difficult is the limited availability of thick films (> 3 μm). Important for the discussion below is that $0.4 < \alpha < 0.7$, from which we conclude that a surface smoothening process is active during the growth of a-Si:H. Other investigations have obtained similar unsatisfying results as we have concerning the establishment of the universality class to which the surface roughness evolution of a-Si:H growth belongs [3].

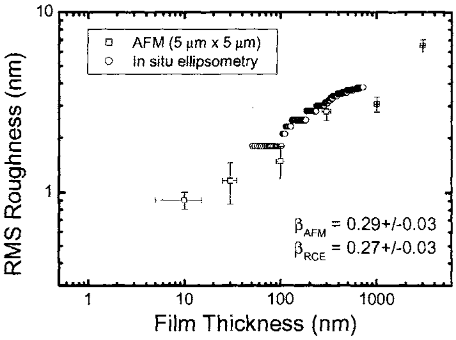

Figure 2 The RMS roughness as function of film thickness as determined from *in situ* ellipsometry and AFM

In Ref. [20] it is shown that the growth exponent β can be obtained more reliable from the measurement of $W(L,d)$ as a function of sample thickness d in the $x << \gamma$ range (cf. Fig. 2). In practice the accuracy of the determination of β is limited by the number of different film thicknesses that can be deposited (over some thickness orders) and the number of

AFM measurements required for reasonable statistics. Overall this is a time consuming experiment. A less time consuming method to monitor the roughness evolution is by means of *in situ* (spectroscopic) ellipsometry [9,21]. Notice, that from the ellipsometry data no lateral information about the surface topography can be obtained in contrast to the AFM technique. However, an advantage of ellipsometry is the fact that it determines the roughness evolution during growth and is not affected by oxidation of the samples when exposed to air. In this study we have used the rotating compensator ellipsometer (RCE) with a HeNe laser ($\lambda = 632$ nm) as light source [21]. The ellipsometry data is modeled by a top layer consisting of a 50 % voids [9,21]. The refractive index of the top layer is calculated according to Bruggeman approximation using the refractive index of the bulk film. The thickness of the top layer is assumed to correspond to $W(L,d)$. Since the used laser spot size is at least a couple of mm^2, the obtained $W(L,d)$ corresponds to the β dominated scaling regime, *i.e.* $u \ll 1$ in Eqs. (2). The multi-film modeling of the ellipsometry data is validated by comparison with the results of AFM measurements (cf. Fig. 2) [21].

Drevillon *et al.* [8] and Collins *et al.* [9] showed that the growth initially starts with a substrate dependent nucleation until the nuclides coalesce. This growth phase of some nm's is followed by homogeneous deposition. In this phase the kinetic surface processes on the a-Si:H film surface are in equilibrium. In this paper the roughness development is studied in this post initial growth phase ($d > 100$ nm), to exclude possible substrate dependent nucleation phenomena.

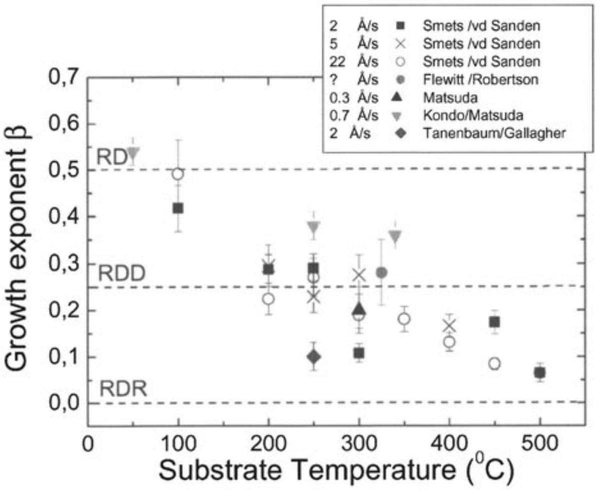

Figure 3 The roughness exponent β as function of substrate temperature for three different growth rates [20]. Data from Refs. [3-6] are also shown for comparison.

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RESULTS

In Fig. 3 we have plotted the β values obtained from both AFM as well as RCE roughness data, together with values as reported in the literature using various surface topography techniques [3-6]. As can be seen β depends on the substrate temperature meaning that none of the stochastic differential equations discussed above (Eq. (3)-(5)) describe the roughness evolution of the a-Si:H film growth under purely chemical conditions. Furthermore, it should be noticed that considering the wide range of deposition rates in Fig. 3, the surface roughness evolution weakly depends on the growth rate. Figure 3 displays the fact that the surface roughness evolution crosses over from an RD type of growth at low substrate temperature, through a phase of RDD scaling ending finally at high substrate temperature in a RDR type of scaling. Since the result in Fig. 3 reveals that the common growth models usually employed and described by the stochastic differential equations Eq. (3)-(5) do not hold in our case, a valid question is what universality class describes a-Si:H growth under purely chemical deposition conditions. Notice that our β values as a function of the substrate temperature correspond very well with the results reported in literature [3-6], although our growth rates are much higher. This clearly shows the generality of our observed β trend with substrate temperature.

Bray et al. have argued that the roughness evolution obtained for their a-Si:H films deposited using PECVD scaled according to the RDD universality class with a corresponding roughness α and growth exponents β of close to 1 and 0.25, respectively [7]. This result is not necessarily in conflict with our result since the presence of ion bombardment and reactive species (atomic hydrogen, metastable He or Ar) can not be excluded in their experiment. These species could influence the surface processes considerably. A possible confirmation of this conjecture can be found in their observation that the scaling exponents α and β depend on the gas in which SiH_4 is diluted [7].

In reality, during deposition of thin films more than one type of relaxation process will occur at the surface. Therefore the universality class to which the roughness evolution of a-Si:H growth belongs will contain a multiple of surface kinetic processes than described by Eq. (3)-(5) and cross-over effects between universality classes should be expected. In particular, if we look at the roughness development of a-Si:H growth, not one single activated diffusion process takes place due to the surface's amorphous character. In contrast, since the silyl radical can adsorb in multiple ways, optimizing the number of chemical bonds to the film surface more than one activation energy is most probably involved. This is corroborated by the fact that both α and β depend on temperature and are not constant as one would expect from RD, RDD or RDR universalities. In this respect we invoke that the universality class for growth under Molecular Beam Epitaxy conditions is more representative for the roughness development of a-Si:H growth under purely chemical deposition conditions [1,22-24].

The universality class describing MBE growth was studied extensively by Das Sarma and co-workers [22,23]. Although Das Sarma and co-workers established a nonlinear stochastic differential equation for MBE growth (note that Eq. (3)-(5) are linear equations) this leaves the stochastic differential equation for a-Si:H under ETP condition still an open issue since real steps and kinks are absent on an amorphous surface [22-24]. Analogously to Das Sarma and co-workers, we will assume that the cross-over phenomena as observed in Fig. 3 is caused by a multiple diffusion process of species adsorbing on the film surface. We will use a solid-on-solid (SOS) model that includes multiple hopping rates for the growing species [1]. This leaves the question of which coarse grained continuum differential equation represents a-Si:H growth under

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the mentioned purely chemical conditions and whether the answer to this question could be a combination of Eq. (4) and (5), *i.e* without any nonlinear terms, open to theoreticians.

The SOS model is based upon nearest neighbor diffusion of growth units having a site dependent hopping rate. The hopping rate of surface diffusing species is given by $R = R_0\exp(-E_A/kT_{sub})$ where $R_0 = 2kT_{sub}/h$ and E_A the activation energy for a growth specie to hop from one site to another neighboring site. For an atom on the surface which has n-1 neighbor atoms, so n bonds, the hopping activation energy will be $E_0 + nE_1$, where E_0 is the activation energy to bring an atom in a mobile diffusion state and E_1 the binding energy per bond [25]. Details of the SOS-model will be reported elsewhere, here we will mainly discuss the results in terms of the surface processes occurring during the growth of a-Si:H under purely chemical deposition conditions.

It is not straightforward to apply an SOS model for MBE growth to a-Si:H growth. During MBE growth, the surface is covered with dangling bonds (DB), whereas during a-Si:H growth the surface is almost fully hydrogen passivated [10,26,27]. This complicating issue will be addressed below, for the moment we will assume that growth species arrive on the film surface and can relax to a surface site where growth occurs. The relaxation process we consider is of the diffusional nature discussed above, *i.e.* multiple activation energies exist on the surface.

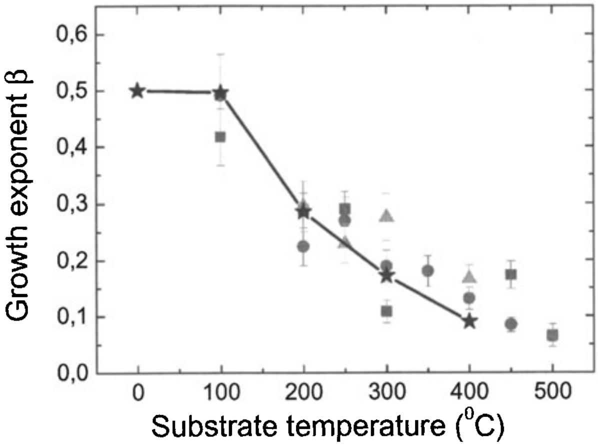

Figure 4 The results of the SOS simulation together with the roughness exponent β as function of substrate temperature obtained under purely chemical deposition conditions. The activation energy obtained from the SOS simulation is about $E_0 + E_1 = 0.7 + 0.3$ eV with an accuracy in both values of about 0.1 eV [20].

In Fig. 4 the best fit from our SOS simulation is compared with the growth exponent β. As can be seen we obtain relatively high values for the activation energies of $E_0 \approx 0.7$ eV and $E_1 = 0.3$ eV (with accuracies in the range of 0.1 eV). These high values explain in a natural way the

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weak growth rate dependence observed in Fig. 3, *i.e.* only a little increase of substrate temperature is needed to increase the diffusion rates on the surface and thus to compensate for the increased arrival rate of growth species. Also the model predicts that $\beta \rightarrow 0$ for high substrate temperatures, in accordance with both experiment as well as with Eq. (5) for the case of full relaxation of the surface roughness (RDR regime). The roughness exponent α obtained from the SOS simulations vary between 0.40 – 0.65 in agreement with the measured values obtained by the three different methods to determine α [20].

DISCUSSION

The widely accepted model for the growth of a-Si:H, the so called Matsuda, Gallagher and Perrin model (MGP), assumes the presence of a weakly adsorbed silyl radical on a hydrogenated surface [28,29,31]. The silyl radical diffuses over the surface with a small activation energy (0.1-0.4 eV) and abstracts atomic hydrogen from the surface to create a dangling bond. Another weakly adsorbed silyl radical attaches to this dangling and growth occurs. In previous work we have argued that the creation of dangling bonds on the surface is a direct hydrogen abstraction process by silyl radicals from the gas phase, as suggested by MD calculations [30] and the weak temperature dependence of the growth flux [12,31]. In addition, the high value found for the activation energy $E_0 + E_1 \approx 1.0$ eV from the SOS simulation is incompatible with a diffusion process of the weakly adsorbed state. Both arguments lead us to the conclusion that the weakly adsorbed state is *not* responsible for the surface smoothening mechanism of the a-Si:H films grown using a purely chemical process. This was also concluded from MD calculations [11].

Our measurements do not rule out the presence of a weakly adsorbed state. In fact surface dangling bond measurements under growth conditions indicate a low value (coverage $10^{-2} - 10^{-4}$) [32,33]. This low value is incompatible with the reported sticking probability of the silyl radical [28,34]. Therefore we still think that a weakly adsorbed state is necessary to explain the low dangling bond coverage by a Kisliuk type of adsorption process [35]. The weakly adsorbed state samples the available surface sites quickly to find a dangling bond which is created by a gas phase abstraction reaction with a probability much higher than the surface dangling bond coverage.

So the remaining question which needs to be answered is: Which diffusion process is responsible for the surface smoothening mechanism during a-Si:H growth under purely chemical conditions. We will consider two possibilities which are based on the dangling bond as the growth site: 1) surface diffusion of a dangling bond to a valley and 2) the surface diffusion of a chemisorbed SiH_3 configuration to a valley. An alternative growth model for a-Si:H was recently proposed by von Keudell *et al.* [36] based on the direct insertion of silyl radicals in strained bonds. Since the proposed surface diffusion in this model is very similar to possibility 2), we do not consider it here separately as a way to explain the roughness data [36].

The diffusion of dangling bonds, after creation by a gas phase process, to a surface valley was first suggested by Tanenbaum *et al.* [3] and later also considered by us to explain the roughness development [25,31]. However, if the weakly adsorbed state is present, the lifetime of a dangling bond is too short to reach the valley on the film surface within the growth time of a monolayer τ_{growth}. The lifetime of a dangling bond τ_{DB} on the surface is given by

$$\tau_{DB} \approx \tau_{SiH3}/\theta_{DB} \qquad (6)$$