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Chemical-equilibrium model of optimal *a*-Si:H growth from SiH_4

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A model of optimal hydrogenated-amorphous-silicon growth based on bulk chemical reactions involving Si—Si and Si—H bonds is proposed. The optimal growth temperature is determined by the balance between the rate of hydrogen diffusion and the rate of film growth.

The complexity of plasma-enhanced chemical-vapor deposition (PECVD) of hydrogenated amorphous silicon (*a*-Si:H) has frustrated efforts to describe this growth process simply. This is partly due to the difficulty of distinguishing the importance of such attendant effects as uv light exposure, charged-particle bombardment, plasma-gas reactions, and solid-state chemical reactions on the material properties of the resultant films. The recent success of chemical modeling to describe defect formation[1,2] in *a*-Si:H suggests that a similar chemical approach might lead to new progress in understanding the PECVD process.

The key idea for this approach is to view the role of the plasma as a supplier of chemically reactive species, with the *a*-Si:H material properties being determined mostly by chemical reactions that take place at or *below* the growth surface. This solid-state chemical approach is radically different from most previous attempts to describe *a*-Si:H growth,[3] which have emphasized plasma-gas processes and the kinematics of surface accumulation. However, the fact that *a*-Si:H films produced in remote-hydrogen-plasma reactors, in the absence of uv light and charged-particle bombardment, are indistinguishable from those produced in rf glow-discharge reactors[4] suggests that plasma-related effects do not necessarily determine *a*-Si:H material properties. The success of the forthcoming analysis supports this view.

The analysis of *a*-Si:H growth requires identifying and relating the important chemical species in the growth process through one or more chemical reactions. We consider only undoped *a*-Si:H growth from silane (SiH_4) and treat *a*-Si:H as a homogeneous ensemble of Si—Si and Si—H bonds. We identify neutral defects (D^0's) as Si—H bonds lacking a terminating H; the defect concentration $[D^0]$ serves as the measure of material quality. The growth model consists of the following reactions.

(i) Si-Si and Si-H incorporation. SiH_3 has been demonstrated to be one important gaseous precursor for *a*-Si:H growth.[5] Therefore, Si-H and Si-Si incorporation during growth may be described stoichiometrically by the following reaction:[6]

$$SiH_3(g)+Si_3Si-(s)\rightarrow Si_3Si-SiH(s)+H_2(g)\,, \qquad (1)$$

where $Si_3Si-(s)$ is a surface dangling bond (D^0), (g) and (s) refer to gas- and solid-phase species, and the subscript refers to the number of atoms in the species (i.e., Si_3Si-SiH is a Si atom bonded to three Si atoms and one SiH unit). The reaction proceeds at a rate proportional to the plasma power P.

(ii) Neutral-defect formation. Defect formation occurs in a manner analogous to Frenkel defect formation in crystals,[1,2]

$$SiH+SiSi\leftrightharpoons D^0+SiHSi\,, \qquad (2)$$

where H is transferred from an isolated Si—H bond to a weak Si—Si bond to form an isolated neutral defect D^0 and a weak bond occupied by hydrogen SiHSi. Both the forward and reverse reaction rates depend on the rate of dispersive hydrogen diffusion and, therefore, on the substrate temperature T_s. The law of mass action can be used to solve for $[D^0]$ at equilibrium,[1,2]

$$[D^0]=\int_0^\infty \frac{N_{v0}\exp(-E/E_0)dE}{1+([D^0]/[SiH])\exp[2(E_{D^0}-E)/kT]}\,. \qquad (3)$$

The integral expresses the defect density at E_{D^0} as the total concentration of weak bond states in the exponential valence-band tail of slope E_0 occupied (i.e., removed) by hydrogen, in analogy with Fermi occupation statistics where the neutral-defect chemical potential

$$\mu_{D^0}\equiv E_{D^0}+(kT/2)\ln([D^0]/[SiH])$$

plays the role of the Fermi level. Equation (3) can be integrated to yield $[D^0]$ as a simple function of the temperature T and valence-band tail slope E_0,

$$[D^0]\simeq\left[\frac{N_{v0}E_0kT}{(2E_0-kT)}\right]\left[\frac{2E_0}{kT}\exp(-\mu_{D^0}/E_0)-\exp(-2\mu_{D^0}/kT)\right], \qquad (4)$$

where E_{D^0} is the defect state energy relative to, and N_{v0} is the density of states at, the top of the valence-band tail ($E\equiv0$). The greater E_0 is, the greater $[D^0]$ is.

(iii) Strain reduction. A mechanism of strain reduction is required for equilibration of the film to proceed. This can be accomplished by the following reaction:[7]

$$SiHSi+SiSi\ (weaker)\leftrightharpoons SiSi\ (stronger)\ +SiHSi\,, \qquad (5)$$

which is exothermic in the forward direction. The forward reaction proceeds until the valence-band tail is sufficiently narrowed to reach equilibrium if there is sufficient time to do so near the surface during growth. Below the surface, bulk constraints increase the kinetic barrier(s) of the reaction. The equilibration rate depends on the rate of H diffusion and, therefore, on T_s. Both reactions (2) and (5) (at least in the forward direction for the latter) can proceed after deposition; in this case, their rates depend on T. When reaction (5) can reach equilibrium during growth, the concentration of weak Si—Si bonds between an energy E and $E+dE$ should be approximately given by

$$[\mathrm{SiSi}] \approx N_{v0}\exp(-E/kT_s)dE , \qquad (6)$$

where E is the weak bond formation enthalpy and $kT_s = E_0$ is the valence-band tail slope. In this case, the greater T_s is, the greater E_0 should be and, therefore, $[D_0]$.

Reaction (1) describes transport of Si—Si and Si—H bonds into the growing a-Si:H film at a rate proportional to the plasma power P. Reactions (2) and (5) describe bulk chemical reactions between these species whose kinetics depend only on temperature. The material properties of a-Si:H depend on the relative rates of these reactions, which are determined by the growth parameters P and T_s. We now apply this model to interpret the conditions of optimal a-Si:H growth.

In undoped a-Si:H films grown under the empirically determined "optimal" conditions of $P \sim 2$ W and $T_s \sim 230\,°\mathrm{C}$, $[D^0]$ and E_0 attain their minimum values of $\sim 10^{16}$ cm^{-3} and 45 meV, respectively. Post-deposition thermal annealing of optimally grown a-Si:H at, say, 300 °C leads to the reversible increase of $[D^0]$ according to Eq. (4) as the equilibrium point of reaction (2) is momentarily pushed to the right,[2] while E_0 is essentially unchanged. When conditions deviate from the optimal situation and a-Si:H is grown at low temperature and high plasma power, $[D^0]$ and E_0 are much larger (up to 10^{18} cm^{-3} and 100 meV, respectively) and sufficient post-deposition annealing at 300 °C can lead to the irreversible decrease of both $[D^0]$ and E_0 to near their optimal values.[7,8]

The effect of plasma power P and substrate temperature T_s on $[D^0]$ and E_0 can be cast in terms of a competition between the rate of H diffusion in the film, which controls the rates of reactions (2) and (5) and increases with T_s, and the rate of film growth R, which increases with P. Because Eq. (4) is found to hold even in films grown far from equilibrium,[9] reaction (5) is most likely the rate-limiting step for equilibrium a-Si:H growth. If R is high or T_s low, then H diffusion will not be able to equilibrate the near surface fast enough to keep up with the deposition rate. Inhomogeneous equilibration will result. Upon thermal annealing after deposition, reaction (5) will continue in the forward direction and the equilibrium point of reaction (2) will correspondingly move to the left (i.e., $[D^0]$ will decrease as E_0 decreases). A similar optimal growth model which relates material quality to the surface diffusion length of SiH_3 precursors has been proposed by Tanaka and Matsuda.[10]

In order for "optimal" growth to occur, the average rate of H diffusion v_H in the time interval Δt should be roughly equal to the growth rate R,

$$v_H \equiv (4D_H/\Delta t)^{1/2} \approx R \approx 4D_H/L , \qquad (7)$$

where D_H is the H diffusion constant in a-Si:H (Ref. 11) and $L \equiv R\Delta t$, such that the time available for equilibration in the less-constrained near-surface layer of thickness L decreases as R increases. Agreement with the data is obtained with $L = 1$ Å, which suggests a surface-limited equilibrium growth process. Of course, Eq. (7) is approximate and does not take into account the dispersive nature of H diffusion.[11] Under condition (7), reactions (2) and (5) can achieve equilibrium during deposition, which we take as the definition of optimal a-Si:H growth. This definition is quantified in Fig. 1, where the a-Si:H growth rate is plotted as a function of rf plasma power P and compared to v_H ($L = 1$ Å) at various T_s. For a given P,

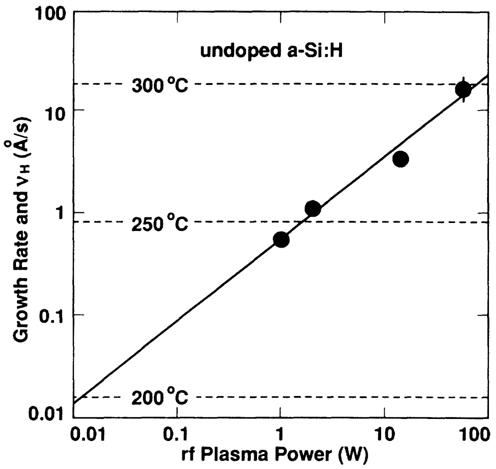

FIG. 1. a-Si:H growth rate vs rf plasma power (filled circles and solid line). Also plotted are the H diffusion rates v_H (dashed lines), whose intersection with the growth-rate curve denotes the optimal growth condition.

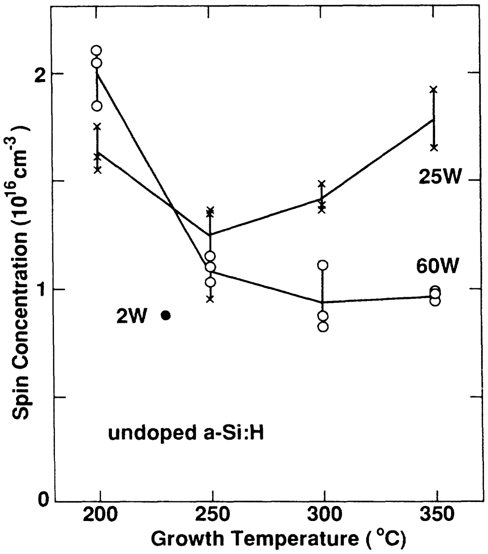

FIG. 2. Spin (neutral defect) concentration measured by ESR as a function of growth temperature with no H_2 dilution, which shows the increase in the optimal growth temperature with increasing rf power expected from the growth model. Gas-flow rate was 100 cm^3/min, gas pressure 0.1 Torr.

the optimal T_s should be approximately given by the temperature at which v_H equals R. Thus, at $P=2$ W, R is ≈ 1 Å/s and the temperature at which v_H equals R is ≈ 250 °C. This is the growth temperature at which $[D^0]$ and E_0 are minimum for $P=2$ W.[3] At higher P, a higher T_s should be required to achieve optimal growth.

The dependence of $[D^0]$ on growth temperature T_s should follow a "U"-shaped curve whose minimum corresponds to the optimal T_s. The low-temperature part of the curve corresponds to the premature arrest of reaction (5), while the high-temperature part results from the increased valence-band tail slope $E_0=kT_s$. When T_s is low, reaction (5) cannot proceed appreciably and a large density of weak bonds is "frozen" into the amorphous network. Although post-deposition annealing above the low T_s will remove the weakest bonds via reaction (5), bulk constraints will prevent the achievement of material properties as good as those in films grown under optimal conditions. When T_s is high, reactions (2) and (5) can achieve equilibrium at and below the growth surface. At equilibrium, [SiSi] and $[D^0]$ will be determined by T_s and higher values than the optimal will be frozen into the film during growth. The optimal growth temperature should be reduced under hydrogen dilution due to the reduced growth rates.

The optimal growth temperature T_s should, in general, increase with rf power P and decrease with H_2 dilution. Electron-spin-resonance (ESR) measurements of the spin (neutral defect) concentration of undoped *a*-Si:H grown with no H_2 dilution as a function of T_s partially support this expectation (Fig. 2). The optimal T_s for pure silane growth increases from ≈ 230 °C at $P=2$ W to >300 °C at $P=60$ W, which is in reasonable agreement with Eq. (7) and Fig. 1. Also, a reduction in optimal growth temperature at reduced *a*-Si:H growth rates has been observed in remote plasma reactors.[12] Although the T_s dependence is relatively weak, it is clear from the data available that solid-state chemical equilibrium models of optimal *a*-Si:H growth are worthy of further consideration.

Finally, we note that other aspects of *a*-Si:H growth might be successfully treated within a similar chemical equilibrium framework. For example, *a*-Si:H usually results from the PECVD of silane and hydrogen gas mixtures because the deposition rate is fast enough to frustrate network organization, which requires the collective rearrangements of many atoms and the destruction of a great deal of entropy. This results in a large free-energy barrier being formed between the crystalline and all amorphous Si:H phases which can only be surmounted at high (~600 °C) temperatures. If the H_2 dilution is increased sufficiently, the growth rate may become so low that the probability of locally tunneling through (or hopping over) this barrier via H-mediated crystallite nucleation [reaction (5) taken to completion in the forward direction] at the growth surface is greatly increased. This might correspond to the onset of microcrystalline growth.

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