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Hydrogen chemical potential and structure of *a*-Si:H

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It is proposed that the chemical equilibrium of hydrogen is an important factor in determining the structure of thin films deposited from silane-hydrogen plasmas. Hydrogen interacts with the silicon network to optimize the local bonding configurations. Raising the effective hydrogen chemical potential reduces the disorder of hydrogenated amorphous silicon films and eventually induces a transition to crystallinity.

The effects of hydrogen in *a*-Si:H are complex and varied. For example, hydrogen termination of silicon dangling bonds improves the electronic properties; H dilution of SiH_4 in the plasma induces the growing film to be crystalline rather than amorphous;[1] and defects in *a*-Si:H reach thermal equilibrium at elevated temperatures through the diffusion of bonded hydrogen.[2] This paper addresses the role of hydrogen in determining the structure of *a*-Si:H films during growth, and proposes that equilibrium chemical reactions involving hydrogen are a major influence. The variations in structure are usually attributed to different mixtures of gas radicals.[3,4] SiH_3 is generally considered to be an important precursor to growth of good quality material, while SiH_2 or SiH are thought to result in poor material, largely due to differences in their reactivity, sticking coefficient, and surface mobility.[4]

Considerations of thermodynamic equilibrium and chemical bonding provide a different viewpoint. The equilibrium structure of a material is determined by a minimum of the free energy, independent of the growth process. The attention given to the growth process of amorphous semiconductors is largely because the amorphous structure is not the equilibrium solid phase. Nevertheless, the structure of *a*-Si:H can adopt many alternative bonding configurations, and it is reasonable to suppose that the structure in any small volume may represent a minimum free energy, subject to the constraints imposed by the long-range disorder of the network. The equilibrium of defects and dopants at temperatures near the normal growth temperatures (200–300 °C) is modeled with this assumption.[2,5]

Equilibration of the structure requires sufficient atomic motion to allow changes in the bonding configurations. Hydrogen in *a*-Si:H is mobile at the normal deposition temperature and has the property of terminating silicon dangling bonds and breaking weak Si—Si bonds. Thus hydrogen motion promotes structural change, and has frequently been proposed as the underlying mechanism of defect equilibration (e.g., the hydrogen glass model).[2,6] The thermodynamic approach has been applied to the incorporation of impurities during growth,[7] and more recently to the growth of *a*-Si:H.[8]

This paper extends the equilibrium model by considering the role of hydrogen in the growth of films from silane plasmas. It is proposed that the chemical potential, μ_H, of atomic hydrogen in the plasma is a determining factor in the structure of the deposited *a*-Si:H and microcrystalline films. We suppose that the hydrogen reactions at the growth surface promote an equilibrium film structure, subject to other constraints on the network. The model relates μ_H to the disorder of the film and explains the conditions for optimum film growth, the transition to crystallinity and the structure dependence of the equilibration rates. The model is broadly based on the sequence of growth proposed by Gallagher in which SiH_x radicals attach to the growing surface.[4] Since the hydrogen concentration of the radicals is much larger than of the resulting film, Gallagher envisions a subsurface region (with thickness, d_S, of order 10 Å at usual growth temperatures) from which the excess hydrogen is eliminated. The model focuses on hydrogen because it can diffuse into the film and induce structural changes.

In plasma-assisted chemical vapor deposition, the plasma creates radicals which are not present in large quantity in the unexcited gas. These metastable radicals react with the surface to cause growth, but the plasma is believed to have a minimal direct role in the surface growth. Aside from silicon-containing radicals, the plasma creates atomic hydrogen whose concentration we describe by a chemical potential,

$$\mu_H = E_H + kT \ln(N_H/N_{H0}) , \tag{1}$$

where E_H is the energy of atomic H in vacuum (see Fig. 2), N_H is the concentration in the plasma, and N_{H0} is the effective density of states (2.5×10^{24} cm^{-3} at 550 K, the inverse of the quantum volume). The steady-state hydrogen concentration is a balance between its creation by the plasma and its loss to various chemical reactions. The chemical potential in this situation is analogous to the quasi-Fermi energy defined for electrons in a photoconductor under illumination.

At the normal growth temperature, hydrogen diffuses within *a*-Si:H and redistributes between alternative bonding sites. Consequently, the hydrogen distribution is close to equilibrium and can also be described by a chemical potential. The interchange of hydrogen across the growing surface implies that the hydrogen chemical potentials in the plasma and the film tend to equalize; the main assumption of the model is that this process causes the hydrogen in the plasma to determine the atomic structure of the growing film.

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The relation between the hydrogen chemical potential and the network structure of a-Si:H is developed next. One of the enduring concepts of amorphous semiconductors is that each atom in the network tends to satisfy its local chemical-bonding requirements.[9] Mott's $8-N$ rule applies broadly to amorphous semiconductors, and in a modified form is the basis of the equilibrium models of doping in a-Si:H.[10] The $8-N$ rule follows from the formation of chemical bonds which minimize the electronic energy. Singly occupied electronic states are not the lowest-energy structural configurations (they do not obey the $8-N$ rule), and are unstable with respect to a structural change which forms pairs of electrons in bonding states and leaves antibonding states empty. This reactivity tends to open a gap in the electronic density of states at the Fermi energy, as illustrated in Fig. 1. It follows that an ideal undoped amorphous semiconductor has few paramagnetic dangling bonds, and doped a-Si:H has a minimum density of states between the charged dopants and defects (both of which obey the $8-N$ rule by virtue of their extra charge).

An analogous argument applies to hydrogen in a-Si:H. Atomic H forms a strong bond to silicon and the optimum structure is one which minimizes the hydrogen which is not strongly bonded to silicon. Thus, ideal bonding in a-Si:H consists of Si—Si and Si—H bonds, but not dangling silicon bonds or interstitial hydrogen. The bond-angle and bond-length disorder cause a distribution of Si—Si (and possibly Si—H) bond strengths. Figure 1 illustrates the hydrogen density-of-states distribution in a-Si:H.[2] The energy is that of the hydrogen bonding to different structural configurations. The Si—H bonds lie below the hydrogen chemical potential, since they are occupied by hydrogen. The energy needed for hydrogen to insert into a Si—Si bond is larger, so that these states lie above μ_H and are mostly unoccupied by hydrogen. The weakest Si—Si bonds are closest to μ_H, since these are most easily broken by hydrogen through a reaction of the general type,

$$\text{weak bond} + \text{H} \leftrightarrows \text{broken bond} + \text{Si—H} . \quad (2)$$

An Si—H bond which loses its hydrogen becomes a dangling bond, and a weak bond which gains a hydrogen atom results in a similar defect. A high density of both types of states at μ_H is therefore incompatible with the $8-N$ rule for chemical bonding. The immediate conclusion is that an ideal amorphous structure is formed when the hydrogen density-of-states distribution has a minimum at μ_H (see Fig. 1, right). The similar electron and hydrogen distributions illustrate a general principle that any reactive species causes a gap in the distribution of bonding states to open at its chemical potential, because the lowest-energy structures contain strong covalent bonds.

The minimization of the density of states at μ_H induces an interaction between the hydrogen and the silicon network structure. Accordingly, the growth reactions determine the structure by inducing a low weak-bond density at μ_H. If the growth conditions are such that μ_H is raised, the bonding structure is no longer in a stable state and there is a tendency to change the distribution of Si—Si bonds by breaking weak bonds and reconstructing the network to give either Si—H bonds or stronger Si—Si bonds. The different network structures which follow from a change in μ_H are shown in Fig. 2.

The weak-bond model assumes an exponential distribution of weak Si—Si bonds,[7,11,12]

$$N_{WB}(E) = N_0 \exp[-(E_S - E)/E_0]; \; E < E_S \quad (3)$$

where E_S is indicated in Fig. 2 and is approximately the energy of hydrogen in a normal Si—Si bond, and E_0 is the slope of the distribution. A density of weak-bond states, N_{min}, at μ_H then gives

$$E_0 = (E_S - \mu_H)/\beta, \text{ where } \beta = \ln(N_0/N_{min}) . \quad (4)$$

E_0 is a measure of the structural disorder of the material

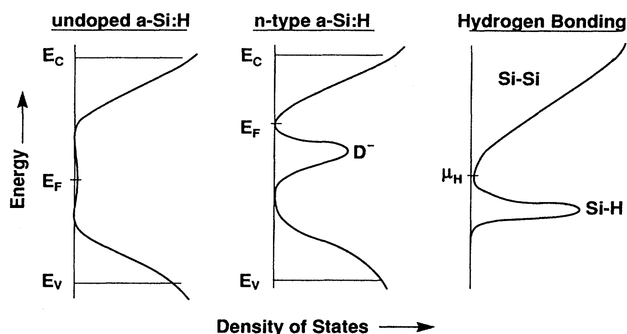

FIG. 1. Illustration of the electronic density of states (left and center), and the hydrogen density of states (right), showing a gap opening at the chemical potential (Fermi energy) as a result of the interaction with the silicon network structure.

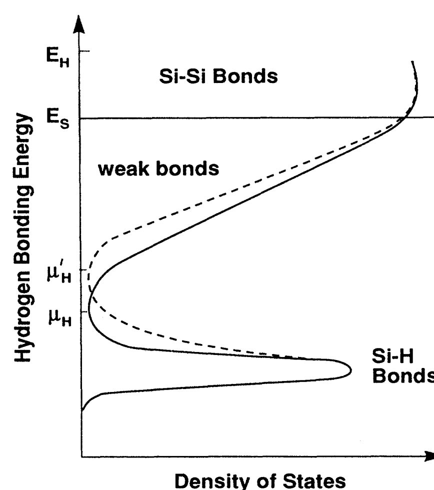

FIG. 2. The hydrogen density-of-states distribution, showing the Si—H bonds below μ_H and Si—Si bond above μ_H which are mostly unoccupied by hydrogen, and the minimum at the hydrogen chemical potential. The dashed line shows the modified density of states for a higher μ_H, with a narrower distribution of weak bonds. E_S is the energy of H in a strong Si—Si bond, and E_H at rest in vacuum.

and in the weak-bond model is related to the slope, E_V, of the exponential valence-band tail, which has a density of states proportional to $\exp[-E/E_V]$.[7,11] Equation (3) is doubtless approximate, but illustrates the nature of the relation between structural order and μ_H—i.e., an increase in the hydrogen chemical potential reduces the disorder, as measured by the weak-bond distribution (see Fig. 2). From Eq. (1), it is expected that E_0 increases with temperature, and is reduced with increased hydrogen concentration in the plasma.

The position of the H chemical potential is not the only constraint on the structural disorder. An unhydrogenated amorphous silicon network has a high bonding disorder, because a fourfold coordinated network is overconstrained. The inclusion of hydrogen relaxes the network and reduces the disorder. Many measurements show that the band-tail slope, E_V, can be reduced to 45–50 meV, but no *a*-Si:H films exist with substantially smaller values.[11] We infer that there is a minimum disorder in *a*-Si:H. Figure 3 illustrates the region of allowed *a*-Si:H structures based on this reasoning. The boundary line limits the possible structures, which are constrained to have a higher disorder at very low hydrogen concentrations (and possibly also at high hydrogen levels). Hydrogenated crystalline silicon lies in a separate region of the space, characterized by a high structural order and generally a low hydrogen content. Following the arguments used to obtain Eqs. (3) and (4), we associate the structural order with the energy of μ_H, such that a high order corresponds to a high chemical potential of H, as shown in Fig. 3.

The growing film surface is assumed to have a high hydrogen concentration and a high disorder, both originating from the attachment of SiH_x radicals; this starting point is illustrated by the circle in Figs. 3 and 4. During the subsurface reactions, the structure follows a trajectory of H concentration and structural order, towards a stable structure determined by the position of μ_H. The model does not consider the specific reactions, but there is evidence that bonded hydrogen in the film is removed by reaction with hydrogen from the plasma.[13] The hydrogen reactions create Si dangling bonds which may bond to

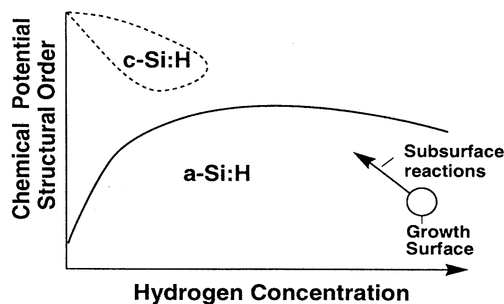

FIG. 3. Illustration of the range of allowed structural order and hydrogen concentration of *a*-Si:H and crystalline silicon (*c*-Si:H). The position marked by the circle corresponds to the surface structure during growth, and the dashed line illustrates the change in structure induced during the subsurface reactions. The H chemical potential is an equivalent measure of order, as described in the text.

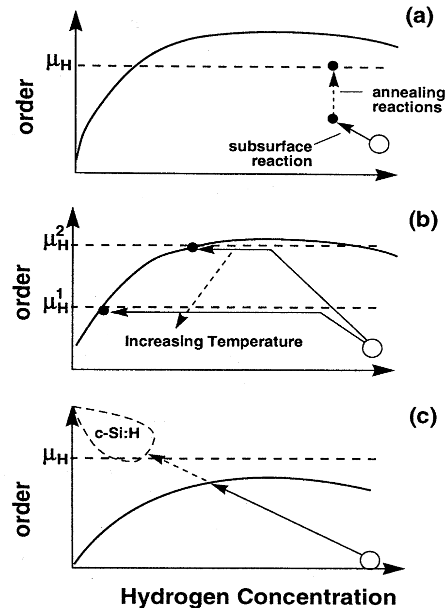

FIG. 4. Illustrations of the various hydrogen-induced structural reactions, showing three types of growth, as described in the text.

each other or may acquire another hydrogen. Similarly, weak Si—Si bonds are broken by the hydrogen and may be reformed as different stronger bonds.[8] These processes change the hydrogen content and modify the local structural order of the silicon network.

The ideal structure only occurs when there is sufficient hydrogen mobility to complete the reactions. The subsurface zone of interaction, d_S, is defined by the balance between hydrogen diffusion D_H and growth rate g,[8]

$$d_S = D_H/g\,. \tag{5}$$

At depths below d_S, the bonded hydrogen is not in communication with the plasma hydrogen, although some bulk structural changes may still occur. The thermally activated H diffusion gives a strong temperature dependence to d_S.

The present model identifies three broad regions of growth, illustrated in Fig. 4, as follows:

a. Kinetically limited growth [Fig. 4(a)]. Low-temperature growth results in defective material because hydrogen is not properly equilibrated due to its low diffusion coefficient. The interaction depth defined by Eq. (5) has essentially zero width. The H content and the disorder are higher than for an ideal *a*-Si:H film because the equilibration reactions cannot occur. Subsequent annealing of the film improves the structural order and reduces the defect density, without changing the hydrogen concentration [see Fig. 4(a)]. The annealing effect is a well-known phenomenon in films deposited below about 200 °C.

b. Amorphous structures determined by μ_H [Fig. 4(b)]. At higher temperatures, the H diffusion is fast enough to allow the film structure and H content to be determined by the chemical potential. We expect that the

surface reactions first establish a structural order determined by μ_H, and then continue to remove hydrogen until constrained by the inability of very-low-hydrogen-concentration films to maintain the same structural order; these two processes are illustrated in Fig. 4(b). Optimum films require a sufficiently high μ_H so that the structure reaches the limits imposed by the network disorder. A higher temperature reduces μ_H, and therefore induces a more disordered film and a lower hydrogen concentration. Optimum films are therefore grown at the lowest temperature at which the kinetic limitation can be avoided. Our model further predicts that high-temperature growth (> 300 °C) benefits from a high hydrogen concentration in the plasma gas and increased rf power. In contrast, at deposition temperatures of 250 °C or below, the increased growth rate of a high rf power reduces d_S and causes kinetically limited growth.

c. Instabilities at high μ_H [Fig. 4(c)]. A sufficiently high hydrogen chemical potential leads to an unstable situation, because the degree of structural order determined by μ_H greatly exceeds that available in the amorphous network. As shown in Fig. 4(c), μ_H does not intersect the range of structures available to *a*-Si:H material. We propose that this is the condition necessary for a transition to growth of crystalline silicon. The model suggests that the transition to crystalline growth is enhanced by high H concentration in the plasma, high rf power, and low temperature, since all three raise the chemical potential. These are indeed the observed conditions, although the films revert to being amorphous at low temperature because the H diffusion rate is too low to allow equilibration. The predicted suppression of microcrystallinity at high deposition temperature is observed.[1]

The model accounts for many of the observed trends in the growth of *a*-Si:H, and also gives some insights into the growth-dependent bulk properties of *a*-Si:H. For example, the most ordered *a*-Si:H films have the highest μ_H, and these structures have the lowest defect density due to the equilibration between defects and weak bonds. Since the H diffusion also depends on the position of μ_H, the model predicts that the material with the best electronic properties has the fastest equilibration rate; this effect is observed.[14]

Only a very approximate quantitative evaluation of the model can be made. The proposed equalization of μ_H in the plasma and the film applies best at high deposition temperatures, above 700 K,[12] where the structural order is not limited by the network. Equation (1) places μ_H in the plasma at roughly $E_H - 1.7$ eV for this temperature, with an estimated H concentration of 10^{12} cm^{-3}. Equating the minimum density of weak bonds, N_{min}, with the equilibrium defect density of about 10^{16} cm^{-3}, and assuming $E_0 \approx 2E_V \approx 90$ meV, as suggested by the weak-bond model,[7] then μ_H in the film is at $E_S - 1.1$ eV. The energy E_S is estimated to be about 1 eV below E_H,[15] thus placing μ_H at $E_H - 2.1$ eV. The difference of 0.4 eV between the two values of μ_H is within the accuracy of the various estimates. Much more information is needed about the hydrogen bonding and the interaction of the plasma with the growing surface to obtain acurate energies.

Combining Eqs. (1) and (4) gives

$$2E_V \approx E_0 = \frac{E_S}{\ln(N_0/N_{min})} + kT\frac{\ln(N_{H0}/N_H)}{\ln(N_0/N_{min})} . \quad (6)$$

The parameters used above predict that the valence-band slope increases roughly as kT in the high-deposition-temperature regime, which is in reasonable agreement with experiment.[12] The effect of plasma hydrogen concentration on the slope of the absorption tail should be an interesting test of the model.

In summary, hydrogen promotes structural change through chemical reactions with the silicon. The lowest-energy structure has a minimum bonding energy, subject to the long-range topological constraints of the structure. The hydrogen chemical potential is proposed to be the important parameter determining the network disorder of *a*-Si:H and the transition to microcrystalline growth.

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