Theory of defect formation in the glow-discharge deposition of phosphorus-doped hydrogenated amorphous silicon

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A quantitative theory (with no fitted parameters) of the doping of n-type hydrogenated amorphous silicon deposited by glow discharge from phosphine-silane mixtures is presented. Film growth results from the reaction of neutral Si dangling bonds on the film surface with SiH_3 radicals. Fourfold-coordinated P donors are produced by the reaction of PH_3 with positively charged Si dangling bonds. This theory explains the dependence of the donor concentration, the dangling-bond concentration, and the Fermi level of the film on the phosphine concentration in the discharge.

INTRODUCTION

The discovery that glow-discharge-deposited hydrogenated amorphous silicon (a-Si:H) can be doped by addition of phosphine or diborane to the silane[1-3] was somewhat surprising since it had been expected that dopant atoms could not be forced into fourfold coordination by the amorphous network.[4] However, the technological importance of a-Si:H would be severely limited if it could not be doped. Not surprisingly, doping of a-Si:H is different from doping of crystalline silicon. For example, the addition of 1 ppm phosphine to the silane can shift the Fermi level of the a-Si:H by 0.2 eV or more, but 10 000 ppm of phosphine results in an additional shift of only about 0.1 eV. This example of the "law of diminishing returns" has important consequences for the fabrication of a-Si:H p-i-n photovoltaic devices. The p and n layers must be heavily doped using dopant-gas concentrations of the order of 1%, but the residual traces of those gases present during the deposition of the i layer must be much less than 1 ppm, in order to keep the Fermi level near midgap. Many researchers are resorting to multichamber deposition systems to achieve this level of control of dopant concentrations.[5-8]

In order to explain how doping occurs in a-Si:H, Adler has suggested that the formation of dopant-defect pairs would require only a small amount of energy.[9] Street[10] has argued that doping can be understood by considering the role of charged states in the deposition process. For example, a neutral phosphorus atom should have threefold coordination, according to Mott's "$8-N$" rule.[11] However, a positively charged phosphorus, having four valence electrons, should be fourfold coordinated and act as a donor. Street also stated that the position of the Fermi level during deposition controls the doping process and defect formation. Consequently the threefold-coordinated P atoms are in equilibrium with the fourfold-coordinated donors plus defects: $P_3^0 \leftrightarrow P_4^+ + D^-$. As a result, the concentrations of P_4^+ and of D^- should be proportional to the square root of the total phosphorus concentration. Street and co-workers[12] have determined dangling-bond concentrations in P- and B-doped films and found them

to be approximately proportional to the gas-phase dopant concentrations. Wronski et al.[13] have used photoconductivity to measure the optical absorption of P-doped films and calculated the concentration, energy, and energy spread of the dangling bonds. They also found a square-root dependence of dangling-bond concentration on phosphine concentration.

Street's model also explains why compensated films have lower defect densities than films grown with one dopant[12] since it is the position of the Fermi level that controls defect formation. However, Street's model does not explain the observed dependence of the Fermi level on dopant gas-phase concentration. In this paper we shall expand Street's ideas on doping into a quantitative model which does explain this dependence. In this model the charge on the dangling bonds at the growing film surface controls the rate of formation of donors which self-consistently determines the surface charge states.

EXPERIMENTAL RESULTS

The dependence of the a-Si:H film Fermi energy E_F on gas-phase phosphine concentration is shown in Fig. 1 for films deposited from 0.1-Torr SiH_4-PH_3 mixtures by rf glow discharge at two different substrate temperatures. Details of the deposition system and the conductivity measurements have been published elsewhere.[14] The position of the Fermi level relative to the conduction-band edge $E_C - E_F = k_B(300 \text{ K})\ln(\sigma_0/\sigma)$, where σ_0 is taken as 200 $(\Omega \text{ cm})^{-1}$ and k_B is the Boltzmann constant. This method was used since the value obtained from the slope of the Arrhenius plot is inaccurate due to statistical shifts.[14-16]

MODEL

In this section we propose a set of surface reactions for film growth and donor formation. The relative rates of these reactions, which depend upon the charges on the surface dangling bonds, determine the donor concentration in the film. The surface-dangling-bond charge is self-consistently related to the donor concentration by charge neutrality. We assume that the film surface is neu-
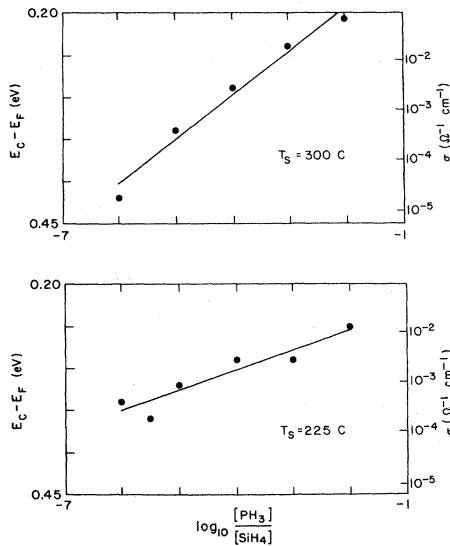
FIG. 1. Fermi-level position and conductivity of phosphorus-doped a-Si:H prepared at two different substrate temperatures T_s. See text for other deposition conditions.

tral and that the dangling-bond charge states are in equilibrium.

The charges of the threefold silicon T_3, threefold phosphorus P_3, and fourfold phosphorus P_4 structures as a function of the position of the Fermi level are shown in Fig. 2. The dividing line between T_3^+ and T_3^0 is 1.25 eV below the conduction band; the line between T_3^0 and T_3^- is 0.9 eV below the conduction band according to photo-thermal-deflection spectroscopy.[17] The level for P_4 was placed near the conduction band since fourfold-coordinated phosphorus atoms should form shallow donors in a-Si:H as they do in crystalline silicon. The energy level for P_3 has been placed near the valence band
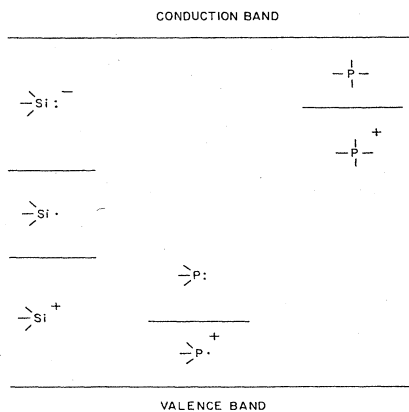
since P_3 is the expected bonding configuration for phosphorus atoms.

There is now strong evidence that SiH_3 is the species responsible for the growth of a-Si:H films in SiH_4 discharges.[18,19] Film growth probably proceeds through the reaction of the SiH_3 radicals with neutral dangling bonds $\equiv Si$ on the film surface, as shown in Eq. (1).[19] We have

$$\equiv Si + SiH_3 \rightarrow \equiv Si\text{-}SiH_3 . \tag{1}$$

Subsequent reactions will replace the hydrogens with silicons. The dangling bonds on the film surface are produced by removal of hydrogen from the surface[20] by SiH_3:

$$\equiv SiH + SiH_3 \leftrightarrow \equiv Si + SiH_4 . \tag{2}$$
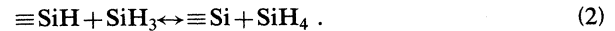
We expect that the concentration of dangling bonds at the film surface N_{RS} will be much larger than the concentration in the bulk (N_R). This is because reaction 2 creates dangling bonds at the growing surface. Consequently there will be band bending in the growing film and the Fermi level at the film surface will be such that most of the dangling bonds will be neutral. This is shown in Fig. 3.

We now focus on the mechanisms responsible for incorporation of phosphorus donors in the a-Si:H film. The model should be applicable to arsenic doping as well. Boron doping will not be covered since the chemistry of bo-
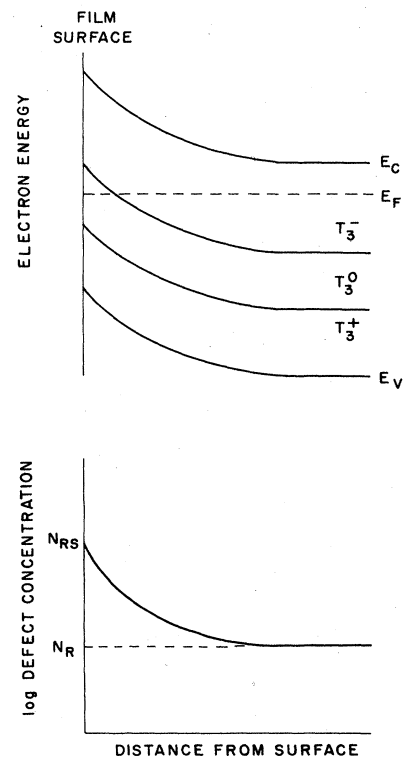

FIG. 3. Qualitative illustration of band bending and dangling-bond concentration in n-type a-Si:H films during deposition.

FIG. 2. Charge state of threefold-Si, threefold-P, and fourfold-P atoms as a function of Fermi-level position.

ron is considerably more complicated. Street has suggested that positively charged sites are involved in the formation of phosphorus donors.[10] Two possibilities are the positively charged dangling bond (T_3^+) and the positively charged threefold-coordinated phosphorus (P_3^+). The positively charged dangling bond should be able to accept an electron pair from a PH_3 molecule to form a bond:

$$\equiv Si^+ + :PH_3 \rightarrow \equiv Si\text{-}P^+H_3 . \tag{3}$$
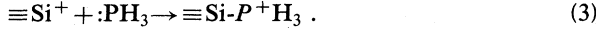
The reaction of P_3^+ sites with SiH_3 is another possibility. However, the concentration of P_3^+ sites on the surface will be much smaller than the concentration of positive dangling bonds because the P_3 level is lower in the gap. Therefore, reactions of P_3^+ will not be included in the model.

To find the relative concentrations of the various charge states we consider the equilibrium

$$2T_3^0 \leftrightarrow T_3^+ + T_3^- . \tag{4}$$

In order to find the dangling bond and donor concentrations as a function of discharge phosphine concentration, we write equations based on reactions (1)–(4). The concentration of neutral dangling bonds at the growing film surface N_{RS}^0 (where RS represents reaction surface) will be determined by the equilibrium in reaction (2),

$$N_{RS}^0[SiH_4]/(N_S[SiH_3]) = K_2 , \tag{5}$$

where $N_S = [\equiv SiH]$, the concentration of surface sites (around $10^{15} cm^{-2}$). The value of K_2 should be near 1 since there is no enthalpy change in reaction (2) because the reaction breaks and forms a Si-H bond. The relative concentration of donors N_D/N_{Si} in the film will be determined by the ratio of the rates of reactions (3) and (1)

$$N_D/N_{Si} = R_3/R_1 , \tag{6}$$

and

$$R_1 = k_1 N_{RS}^0[SiH_3] , \tag{7}$$

$$R_3 = k_3 N_{RS}^+[PH_3] . \tag{8}$$

The equilibrium in reaction (4) gives the following relationship:

$$N_{RS}^+ N_{RS}^-/(N_{RS}^0)^2 = K_4 . \tag{9}$$

The energy difference between the left- and the right-hand side of Eq. (4) is the correlation energy of the dangling bond U [about 0.4 eV (Ref. 17)]. To estimate the value of K_4 we note that the spread of the energy of the dangling bond is 0.1 eV.[13] Using the density of states assumed by Wronski et al.[13] [see Eq. (17)] and writing $N_{RS}^- = \int_{-\infty}^{E_F} N_{RS}(E)dE$ and $N_{RS}^+ = \int_{E_F+U}^{\infty} N_{RS}(E)dE$ gives $K_4 = (4/\pi^2)e^{(-4)}$. See Fig. 4.

Combining Eqs. (5)–(9) gives the following:

$$N_D N_{RS}^- = C[PH_3]/[SiH_4] , \tag{10}$$

$$C = N_{Si}N_S(k_3/k_1)K_4K_1 , \tag{11}$$

which is similar to Street's result but contains the gas-phase phosphine concentration rather than the P concentration in the film. This is an important distinction since
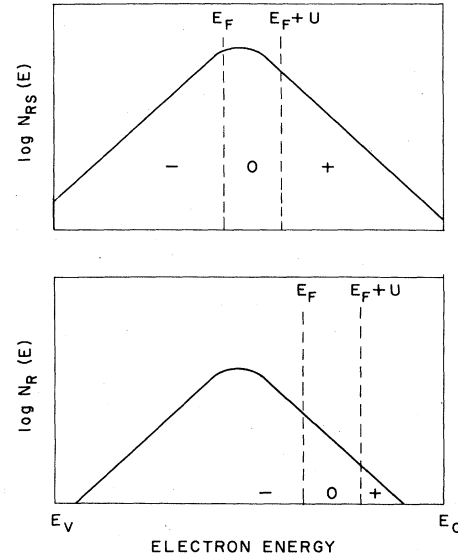

FIG. 4. Charge of dangling bonds at growing film surface and in the bulk.

the P concentration in the film goes as the 0.8 power of the phosphine concentration.[21]

Charge neutrality requires that

$$N_D^+ + N_{RS}^+ = N_{RS}^- . \tag{12}$$

Neutral donors have not been detected by electron-spin resonance in a-Si:H.[10] Therefore $N_D^+ = N_D$. If the doping level is high enough so the $N_{RS}^+ \ll N_D^+$, then $N_D = N_{RS}^-$. In that case Eq. (10) becomes

$$N_{RS}^- = C^{1/2}([PH_3]/[SiH_4])^{1/2} . \tag{13}$$

Using 5×10^{22} cm^{-3} for N_{Si}, 10^{15} cm^{-2} for N_S, estimating k_3/k_1 as 10^3 (a typical value for the rate constant of an ion molecule reaction divided by the rate constant for a radical molecule reaction[22-24]), using $(4/\pi^2)e^{-4}$ for K_4 (see above), and estimating K_1 as 1 (as discussed earlier) gives a value of $C^{1/2}$ of about 1.2×10^{19} cm^{-3}. This agrees quite well with the observed value of 2.6×10^{19} cm^{-3}.[13]

As the film grows, already-deposited a-Si:H will anneal if the substrate temperature is sufficiently high, resulting in a decrease in the dangling-bond concentration. All neutral dangling bonds will reconstruct pairwise, as will all pairs consisting of positive and negative dangling bonds ($T_3^0 + T_3^0 \rightarrow Si\text{-}Si$ and $T_3^+ + T_3^- \rightarrow Si\text{-}Si$). Therefore the total dangling-bond concentration after annealing N_R will be given by $|N_{RS}^- - N_{RS}^+|$. Using Eq. (12) and the fact that all donors are ionized ($N_D = N_D^+$) gives

$$N_R = N_{RS}^- - N_{RS}^+ = N_D . \tag{14}$$

Most, but not all, of these remaining dangling bonds will be negative. Charge neutrality in the deposited film implies that

$$N_D = N_R^- + n_C \qquad (15)$$

where n_C is the number of electrons in the conduction band. We neglect the conduction-band tail since it is steep.[13] Combining Eqs. (14) and (15) gives the result

$$N_R - N_R^- = n_C . \qquad (16)$$

In Fig. 2 the energy level separating T_3^0 from T_3^- was depicted as a discrete level for simplicity. However, Wronski *et al.* found a range of energies[13] and used a density of states which can be written

$$N_R(E) = (\pi E_{R0})^{-1} N_R \, \mathrm{sech}[(E - E_R)/E_{R0}] . \qquad (17)$$

Since the value of E_{R0}, about 0.1 eV, is considerably larger than $k_B T$ for room temperature, the left-hand side of Eq. (16) can be approximated by replacing the Fermi function with a step function. This gives the expression

$$N_R - N_R^- = \int_{E_F}^{\infty} N_R(E) dE$$

$$= (2N_R/\pi) \exp[(E_R - E_F)/E_{R0}] . \qquad (18)$$

See Fig. 4. The value of n_C is calculated using the conduction-band density of states[13]

$$N_C(E) = (6.7 \times 10^{21} \ \mathrm{cm}^{-3} \ \mathrm{eV}^{-3/2})(E - E_C)^{1/2} .$$

Multiplying by the Fermi function and integrating gives

$$n_C = N_C \exp[(E_F - E_C)/k_B T] \qquad (19)$$

where $N_C = 2.47 \times 10^{19} \ \mathrm{cm}^{-3}$ at room temperature. Combining Eqs. (16), (18), and (19) gives the result

$$E_F - E_C = \frac{k_B T}{k_B T + E_{R0}} \left[E_R - E_C + E_{R0} \ln\left(\frac{2N_R}{\pi N_C} \right) \right] . \qquad (20)$$

Wronski *et al.* used their photoconductivity-derived absorption spectra to find values of E_R, E_{R0}, and N_R at values of $[PH_3]/[SiH_4]$ of 0, 10^{-5}, 10^{-4}, 10^{-3}, and

5×10^{-3}, for films deposited at 240 °C. The values of N_R were fitted to the expression $N_R = (2.6 \times 10^{19} \ \mathrm{cm}^{-3}) p^{1/2}$, where $p = [PH_3]/[SiH_4]$. Using that expression, the values of E_R and E_{R0} found for $p = 10^{-4}$ (1.02 and 0.10 eV, respectively), and using Eq. (20) gives the result $E_C - E_F = (0.239 \ \mathrm{eV}) - (1.03 \times 10^{-2} \ \mathrm{eV}) \ln(p)$. The line fitted to the $T_s = 225 \, °C$ data in Fig. 1 has the form $E_C - E_F = (0.205 \ \mathrm{eV}) - (1.05 \times 10^{-2} \ \mathrm{eV}) \ln(p)$, in close agreement with the expression calculated using Eq. (20). It is obvious, however, that the dependence of E_F on p is different in Fig. 1 for the films deposited at 300 °C. This can be explained by making the quite reasonable assumption that films deposited at 300 °C have a broader conduction-band tail. In that case, the characteristic temperature corresponding to the width of the band tail would appear in Eq. (20) in place of room temperature, increasing the slope E_F versus $\ln(p)$ plot, as observed.

CONCLUSIONS

The dependence of dangling-bond concentrations in phosphorus-doped *a*-Si:H films deposited by glow discharge from silane-phosphine mixtures can be understood quantitatively in terms of a model of the surface reactions responsible for film growth and donor formation, charge neutrality, and complete annealing of neutral dangling bonds. The dependence of the film Fermi level on gas-phase phosphine concentration used during deposition is consistent with the density of states of films deposited under similar conditions, as determined by absorption spectra derived from photoconductivity.

ACKNOWLEDGMENTS

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