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Universal dopant and defect equilibration kinetics in *n*-type *a*-Si:H

K. Winer and W. B. Jackson

Xerox Palo Alto Research Center, Palo Alto, California 94304

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The time dependences of the reversible decay of the dc conductivity of single-layer doped *a*-Si:H films following thermal quenching and the reversible increase of the threshold voltage in metal–insulator–*a*-Si:H structures during voltage biasing were measured to determine the kinetics of dopant and defect equilibration, respectively, in *n*-type *a*-Si:H. The equilibration time constants were measured as a function of temperature for different dopant-gas ratios (3×10^{-7} to 1×10^{-2}), different dopant atoms (Li, P, As, and Sb), and different voltage biases (3.5 to 20 V) in the absence of dopants. In all cases, the time constants were thermally activated with activation energies between 0.7 and 1.0 eV, and were inversely proportional to the two-thirds power of the electron concentration. This universal behavior suggests that the rate-limiting step of the two distinct chemical reactions describing dopant deactivation and defect creation in *a*-Si:H are the same. We propose that this step is the dispersive diffusion of hydrogen from bond-terminating to weak-bond-trapping sites.

The equilibrium concentrations of species that participate in chemical reactions depend on external system parameters such as temperature and pressure. If these external parameters are varied more rapidly than the system can respond, nonequilibrium concentrations can be "frozen-in" and the time dependence of their equilibration is characteristic of the kinetics of the reaction. The active-dopant[1] and deep-defect[2–4] concentrations in hydrogenated amorphous silicon (*a*-Si:H) have been discovered recently to behave in exactly this manner. The corresponding chemical reactions can be approximately described for *n*-type (say, P-doped) *a*-Si:H as follows:

$$P_4^{+}+e^{-}\leftrightarrows P_3\,, \tag{1}$$

$$Si_4+e^{-}\leftrightarrows Si_3^{-}\,, \tag{2}$$

where the subscript refers to the atom coordination. The reactions are independent but are linked by their dependence on electron concentration. However, they also incompletely specify how the coordination changes of silicon and dopant atoms occur. The mechanism by which these changes take place will determine the reaction kinetics. We studied the forward kinetics of these reactions in *n*-type *a*-Si:H as a function of electron concentration to investigate this mechanism: reaction (1) for a variety of substitutional and interstitial dopants at different dopant concentrations in single-layer films, and reaction (2) in the absence of dopants using metal–insulator–*a*-Si:H (MIS) structures at different applied bias voltages. These two systems are comparable because the reactions take place in *a*-Si:H with an excess of electrons (i.e., *n* type). The forward kinetics of these reactions display universal behavior suggesting a common rate-limiting step, which we propose is the dispersive diffusion of hydrogen.

The forward kinetics of reaction (1) was studied in 1-μm-thick, single-layer *a*-Si:H films doped with either P, As, Sb, or Li. The P- and As-doped films were deposited at 2 W and 230 °C by the standard glow-discharge method. The Sb-doped films were deposited from a solid source in a remote hydrogen plasma reactor.[5] The Li doping was accomplished by in-diffusion into nominally undoped films.[6] In the case of P doping, the electron concentration at equilibrium is proportional to the square root of the gas-phase mole fraction of P (X_{PH_3}).[7] The films were water quenched from 250 °C and the decay of the dark dc conductivity σ was measured as a function of time for different temperatures. Assuming that the mobility is constant, and given that the defect concentration does not change significantly in *n*-type-doped *a*-Si:H films undergoing this procedure,[8] the change in the concentration of active dopants (e.g., $\Delta[P_4^{+}]\approx\Delta[e^{-}]$ for P doping) during equilibration is proportional to the change in σ.

The forward kinetics of reaction (2) in undoped *a*-Si:H was studied in MIS capacitors fabricated with gate dielectrics of 300 nm of silicon nitride. Similar kinetics were observed for thermal oxide gate dielectrics indicating that trapping within the nitride dielectric is not significant. The undoped *a*-Si:H layer was 500-nm thick followed by a 30-nm n^{+} layer and Al forming the Ohmic contact. Defects were generated by the application of a gate bias voltage V_s to form an electron accumulation layer in the undoped *a*-Si:H. The electron concentration in the accumulation layer at equilibrium is approximately proportional to V_s above threshold ($V_T\sim0.5$ V). During biasing, shifts in the threshold voltage ΔV_T of the 100-kHz capacitance-voltage curve were measured as a function of time for different temperatures and gate biases. Since the curves were nearly parallel, the change in the defect concentration $\Delta[Si_3^{-}]$ during equilibration is given by $C_i\Delta V_T$, where C_i is the insulator capacitance.[9]

The forward kinetics of both reactions (1) and (2) displayed a stretched-exponential time dependence.[10] The stretched-exponential time constants τ for (a) the decay of active P donors for various dopant concentrations; (b) the decay of active P, As, Sb, and Li donors; and (c) the creation of defects in the electron accumulation layer of an MIS capacitor for various gate biases are plotted as a function of inverse temperature in Fig. 1. The time con-

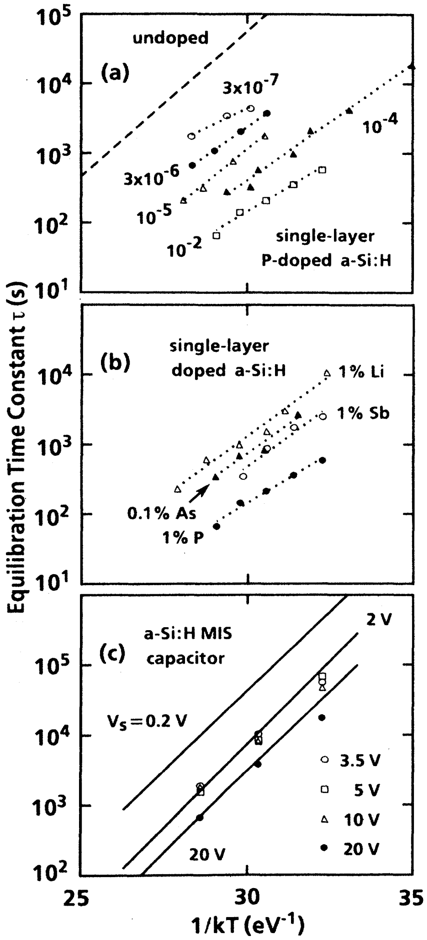

FIG. 1. Stretched-exponential time constants as a function of $1/kT$ for (a) the decay of active P donors for various dopant concentrations; (b) the decay of active P, As, Sb, and Li donors in single-layer a-Si:H doped films; and (c) the creation of charged defects in a-Si:H MIS capacitors for various applied gate bias voltages. The dotted lines in (a) and (b) are least-squares fits to the data points. The solid lines in (c) are from the calculation described in the text. The time constant behavior for the decay of neutral defects in undoped single-layer a-Si:H films (Ref. 4) is shown in (a) for comparison (dashed line).

stants for all the data exhibit thermally activated behavior with activation energies between (a) and (b) 0.72 and 0.90 eV, and (c) 0.87 and 0.98 eV. The activation energies are independent of doping level or bias voltage within the experimental error. The activation energies are also essentially the same for all n-type dopants, including interstitial Li whose bonding chemistry is substantially different from the substitutional group-V dopants.

The time constants decrease with increasing doping [Fig. 1(a)] and increasing gate bias voltage [Fig. 1(c)]. The corresponding change in the prefactors we ascribe to the increase in electron concentration with doping in the single-layer films and with applied bias in the MIS capacitors. The longer time constants for a-Si:H doped by impurities other than P [Fig. 1(b)] may be due to the lower doping efficiencies of these impurities. The dependence of τ on electron concentration $[e^-]$ is more apparent in Fig. 2, where τ is plotted versus (a) $X_{\mathrm{PH}_3}^{1/2}\propto[e^-]$ and (b) $V_s\propto[e^-]$. For a given temperature, τ is proportional to $[e^-]^{-\epsilon}$ over this narrow range of $[e^-]$, where ϵ is between 0.6 and 0.7 in the P-doped a-Si:H films and between 0.5 and 0.7 in the MIS capacitors with the exponent increasing with decreasing temperature. This is in excellent agreement with the predicted $\epsilon=0.7$ dependence.[11] This power-law dependence is only approximate; there is a slight upward curvature to the data which is particularly apparent in Fig. 2(a). The model discussed below predicts a similar curvature [solid lines in Fig. 2(b)].

In summary, the forward kinetics of both reaction (1) observed through the decay of active dopants in single-layer doped films and reaction (2) observed through defect creation in MIS capacitors have a number of features in common: The same stretched-exponential time dependence, a similar range of activation energies and prefactors of the equilibration time constants, and a similar power-law dependence on electron concentration. These features of the forward kinetics are independent of the chemical identity or even the presence of dopant atoms. This universal behavior suggests that the forward kinetics of reactions (1) and (2) are rate limited by the same step.

Consider a chemical reaction between two species A and B (i.e., $A\leftrightarrows B$) characterized by states a and b whose

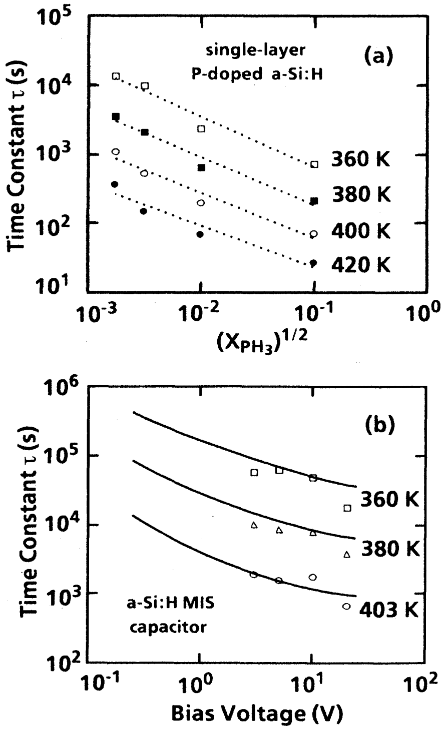

FIG. 2. Stretched-exponential time constants as a function of (a) the square root of the gas-phase P mole fraction in single-layer P-doped a-Si:H films and (b) the applied gate bias voltage in a-Si:H MIS capacitors, both of which are proportional to the electron concentration. The dotted lines in (a) are least-squares fits to the data points. The solid lines in (b) are from the calculation described in the text.

energy difference is $\Delta E = E_b - E_a$ and which are separated by an energy barrier E^*. At equilibrium, the concentration of B is given by

$$[B]_{\mathrm{eq}} = [A]_{\mathrm{eq}} \exp(-\Delta E/kT) . \tag{3}$$

When the system equilibrium is perturbed, simple reaction rate theory predicts that the concentration of B will equilibrate exponentially fast, i.e.,

$$[B](t) - [B]_{\mathrm{eq}} = \{[B](0) - [B]_{\mathrm{eq}}\} \exp(-t/\tau) , \tag{4}$$

where the equilibration time constant $\tau = \tau_0 \exp[(E^* - E_b)kT]$. If the single barrier is replaced by an exponential distribution of barriers, the equilibrium concentrations given by Eq. (3) do not change, but the equilibration kinetics of $[B]$ will approximately follow a stretched-exponential form,

$$[B](t) - [B]_{\mathrm{eq}} \simeq \{[B](0) - [B]_{\mathrm{eq}}\} \exp[-(t/\tau)^{\beta}] , \tag{5}$$

where $\beta = kT/E_0$ and E_0 is the width of the exponential distribution of barriers.

In fact, as shown previously,[9,11] the kinetics of any reaction in which (i) there is an exponential distribution of barrier heights, (ii) the energy difference between the initial and final states depends on the Fermi level, and (iii) the maximum barrier height depends on carrier concentration, will be characterized by stretched-exponential time decays, thermally activated time constants, and a power-law dependence on carrier concentration. The results of modeling an ensemble of reaction centers with the above three properties are depicted by the solid lines in Figs. 1(c) and 2(b).[11] These curves were generated by considering two states separated by an exponential distribution of barriers with a maximum barrier height of 0.95 eV, an attempt frequency $(1/\tau_0)$ of 3×10^8 Hz, and a distribution width E_0 of 0.05 eV.[11] The agreement between the theory and the data in Fig. 2 suggests that the observed dependence of τ on temperature, doping level, and gate bias voltage is consistent with reactions whose kinetics conform to the above three criteria.

While this phenomenology can account for the data, a microscopic understanding of this behavior based on the diffusion of a particular species is desirable. Dopant diffusion can immediately be excluded. There are two obvious remaining possibilities, native defect diffusion and hydrogen diffusion. *A priori*, both are equally likely. However, reversible equilibration below 200 °C has not yet been demonstrated in unhydrogenated *a*-Si. Also, it has recently been shown that the spin (neutral defect) diffusion rate is less than half the H diffusion rate in undoped *a*-Si:H.[12] These facts, coupled with the much larger concentration of H ($\sim 10^{22}$ cm^{-3}) compared to defects ($\sim 10^{16}$ cm^{-3}) typical in this material and the observation that the defect creation rate is proportional to the H diffusion rate over 5 orders of magnitude,[9] argue for H rather than defect diffusion as the rate-limiting step in reactions (1) and (2). Of course, the diffusion of an as yet undetected species cannot be completely ruled out, but the case for H-diffusion-mediated reactions is strong. A similar exponential distribution of barrier heights is required to account for the dispersive nature of H diffusion in *a*-Si:H, while criteria (ii) and (iii) above lead to the observed Fermi-level dependence of the H diffusion coefficient.[11] Clearly, any reaction whose rate-limiting step is the dispersive diffusion of hydrogen will exhibit the kinetic behavior shown in Figs. 1 and 2 regardless of the nature of the reaction.

Finally, we propose how reactions (1) and (2) might be completed to explicitly take the role of H motion into account. Consider the modified reactions

$$\mathrm{Si_3PH^+} + e^- \leftrightarrows \mathrm{Si_3PH} , \tag{6a}$$

$$\mathrm{SiSi} + \mathrm{Si_3PH} \leftrightarrows \mathrm{Si_3P} + \mathrm{SiHSi} , \tag{6b}$$

$$\mathrm{SiSi} + \mathrm{SiH} \leftrightarrows \mathrm{Si_3Si} + \mathrm{SiHSi} , \tag{7a}$$

$$\mathrm{Si_3Si} + e^- \leftrightarrows \mathrm{Si_3Si^-} , \tag{7b}$$

where SiSi are weak Si—Si bonds, SiHSi is an H atom trapped at a weak-bond site, the SiH are H trapped at bond-terminating sites, and the subscripts now refer to numbers of neighbor atoms (i.e., Si$_3$PH is a P atom bonded to three Si and one H atoms). Reactions (6a) and (6b) describe active-dopant neutralization and deactivation, respectively. Reactions (7a) and (7b) describe neutral defect creation and defect ionization, respectively. These reactions could quantitatively account for the equilibrium concentrations of all species if the reaction enthalpies were known.[4] An interesting feature of reaction (6b) is that dopant activation can occur without the direct creation of compensating defects in accord with experimental observation.[8] Also, enhanced defect creation by reaction (7b) is a result of the presence of excess electrons which is not necessarily dependent on the presence of dopants.

The important aspect of reactions (6) and (7) for this discussion is their explicit dependence on H diffusion from bond terminating to weak-bond-trapping sites. Hydrogen moves interstitially through the disordered *a*-Si:H network of weak Si—Si bonds whose potentials are distributed exponentially in energy. The corresponding exponential distribution of diffusion barriers gives rise to the dispersive nature of H diffusion and to the stretched-exponential equilibration kinetics of any *a*-Si:H process limited by a H diffusion step.[10,11] The identical role of H in reactions (6b) and (7a) is exactly what is required to account for the identical equilibration kinetics displayed in all measurements.

In summary, we have experimentally determined that the kinetics of the dopant deactivation and defect reactions in *n*-type *a*-Si:H is essentially identical. This universal behavior suggests that the rate-limiting step in both reactions is the same. We have proposed that this step is the dispersive diffusion of H.

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[1] R. A. Street, J. Kakalios, and T. M. Hayes, Phys. Rev. B **34**, 3030 (1986).

[2] Z. E. Smith, S. Aljishi, D. Slobodin, V. Chu, S. Wagner, P. M. Lenahan, R. R. Arya, and M. S. Bennett, Phys. Rev. Lett. **57**, 2450 (1986).

[3] X. Xu, A. Okumura, A. Morimoto, M. Kumeda, and T. Shimizu, Phys. Rev. B **38**, 8371 (1988).

[4] R. A. Street and K. Winer, Phys. Rev. B **40**, 6236 (1989).

[5] R. A. Street, N. M. Johnson, J. Walker, and K. Winer, Philos. Mag. Lett. **60**, 177 (1989).

[6] K. Winer and R. A. Street, Appl. Phys. Lett. **53**, 505 (1988); J. Appl. Phys. **65**, 2272 (1989).

[7] R. A. Street, Phys. Rev. Lett. **49**, 1187 (1982).

[8] R. A. Street, M. Hack, and W. B. Jackson, Phys. Rev. B **37**, 4209 (1988).

[9] W. B. Jackson, J. M. Marshall, and M. D. Moyer, Phys. Rev. B **39**, 1164 (1989).

[10] J. Kakalios, R. A. Street, and W. B. Jackson, Phys. Rev. Lett. **59**, 1037 (1987).

[11] W. B. Jackson, Phys. Rev. B (to be published).

[12] W. B. Jackson, J. Non-Cryst. Solids (to be published).