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Determination of diffusion mechanisms in amorphous silicon

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We have established experimentally and theoretically that transition metals in amorphous Si undergo direct interstitial diffusion that is retarded by temporary trapping at the defects intrinsic to the amorphous structure. The diffusion of Cu, Zn, Pd, Ag, Pt, and Au has been investigated by means of Rutherford-backscattering spectrometry and that of Au tracer atoms by neutron-activation and sputter-sectioning analysis. The data can be fitted using the foreign-atom interstitial diffusion coefficients in crystalline Si modified due to the presence of traps with concentrations between 0.2 and 1 at. % and trapping enthalpies of about 0.9 eV.

The study of diffusion in crystalline solids has been a powerful tool in establishing defect structures and mass transport mechanisms. A comparable state of understanding has not yet been reached for amorphous solids. A classic example is Si, where diffusion in the crystalline phase is rather well understood, but little is known about fundamental diffusion mechanisms in amorphous Si (*a*-Si).[1,2] In this paper we show that transition metals are useful probes for clarifying diffusion in *a*-Si. Indeed, we demonstrate that transition-metal diffusion can be quantitatively understood in terms of diffusion mechanisms pertinent to crystalline Si (*c*-Si). Diffusion in *c*-Si can be classified as follows.[3]

(i) The slow diffusion of self-atoms and substitutional solutes that takes place by indirect mechanisms, where self-interstitials and vacancies act as diffusion vehicles.

(ii) Most of the transition metals (e.g., Mn, Fe, Co, Ni, Cu, and Pd) behave as fast diffusers that reside in interstices and diffuse by hopping from interstitial site to interstitial site. In this direct interstitial mechanism, the diffusion coefficient obeys an Arrhenius law

$$D_i = D_{i,0}\exp(-H_i^M/kT) , \quad (1)$$

where H_i^M is the migration enthalpy of the interstitials (e.g., 0.2 eV for Pd[3]) and the preexponential factor $D_{i,0}$ and kT have their usual meanings.

(iii) A few transition metals (Zn, Pt, and Au) diffuse at intermediate rates via the kick-out mechanism.[3] This mechanism results from the hybrid nature of these solutes, which spend most of their time sitting on substitutional sites (A_s). However, self-interstitials (I) may kick them out from the A_s sites according to the reaction

$$A_s + I \rightarrow A_i . \quad (2)$$

In this way the hybrids become interstitials (A_i) which undergo fast long-range diffusion by the direct interstitial mechanism until reaction (2) is spontaneously reversed. In dislocation-free *c*-Si, without internal sinks for I, the outflux to the specimen surface of I produced in this reverse reaction is the rate-controlling step for the in-diffusion of the substitutional fraction of a hybrid solute. Therefore, in thermal equilibrium, the effective diffusion coefficient D_s^{eff} of A_s is given by[3]

$$D_s^{\text{eff}} = \frac{C_I^{\text{eq}} D_I}{C_s^{\text{eq}}} , \quad (3)$$

and the corresponding effective activation enthalpy by

$$H_s^{M,\text{eff}} = H_I^F + H_I^M - H_s^{\text{sol}} , \quad (4)$$

where C_I^{eq}, D_I, H_I^F, and H_I^M are the equilibrium concentration, diffusivity, formation enthalpy, and migration enthalpy of I, respectively, while C_s^{eq} and H_s^{sol} are the solubility and solution enthalpy of A_s, respectively. The effective activation enthalpies for Au and Pt are 2.8 and 3.2 eV, respectively.[4,5] In highly dislocated *c*-Si, which contains a high concentration of internal sinks for I, the effective diffusivity of hybrids is higher than in dislocation-free *c*-Si because the rate-limiting step is the in-diffusion of A_i and the effective diffusion coefficient is given by[3]

$$\tilde{D}_s^{\text{eff}} = \frac{D_i C_i^{\text{eq}}}{C_s^{\text{eq}}} , \quad (5)$$

where D_i and C_i^{eq} are the diffusivity and the solubility of A_i, respectively.

There are several reasons why it has not been possible to classify diffusion in *a*-Si in such a systematic fashion. There is, for example, the experimental problem that one has to measure low-temperature diffusion coefficients, as *a*-Si crystallizes at temperatures greater than 500 °C. The overriding problem, however, lies in the lack of detailed knowledge of the structure of *a*-Si. This structure has been modeled[6] in terms of a continuous random network where local order is maintained by the directional covalent Si bonding and long-range order is suppressed by

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bond bending. As the local order in a- and c-Si is basically the same, it is tempting to predict that similar diffusion mechanisms are operative in the two phases. However, it has not been possible to test this assumption because of the lack of knowledge of the defect structure in a-Si. Recently we have shown that defects introduced in a-Si by ion bombardment exhibit close similarities to defects introduced in c-Si under equivalent bombardment conditions.[7] So far, there is no information on the atomic structure of these defects, but their concentration in as-implanted a-Si saturates at 1–2 at. %,[7,8] and, as in c-Si, thermal annealing reduces the concentration of defects.[8,9] However, this reduction is limited, as only low-temperature annealing ($T \leq 500\,°C$) is possible before the onset of crystallization. This large density of defects in a-Si, which has been demonstrated directly by the trapping and gettering of Cu (Ref. 9) and Pd,[8] leads to an extremely high solubility of transition metals. For example, at 400 °C, the solubility of Cu in a-Si (Ref. 10) is 0.02 at. % and thus exceeds the corresponding solubility in c-Si (Ref. 11) by about six orders of magnitude.

In earlier studies[1,12] we showed that Cu, Ag, and Au diffuse rapidly in a-Si with activation enthalpies of about 1.5 eV. Here we extend the measurements for these species and demonstrate that Zn, Pd, and Pt are also rapid diffusers in a-Si. The 2.1-μm-thick a-Si layers, used in this work, were produced by self-ion implantation in c-Si at 77 K at different energies (500 keV, 1 MeV, and 2 MeV) for a total fluence of 1.5×10^{20} ions /m^2. This procedure is known to produce pure a-Si without macroscopic voids and impurities. Subsequently, these layers were implanted with the particular diffusers to be studied (500 keV, 10^{17}–10^{20} ions /m^2). Diffusion annealings were performed in vacuum at temperatures between 150 and 600 °C. The as-implanted Gaussian-shaped profiles and the diffusion profiles were measured by Rutherford-backscattering spectrometry (RBS) using 4-MeV He ions and a scattering angle of 170° [Fig. 1(a)]. Fitting numerical solutions of the diffusion equation, which was computed under the assumption of total reflection at both the surface and the a-Si/c-Si interface, to the measured profiles yielded estimates of the diffusion coefficients (full circles in Fig. 2) and the corresponding activation enthalpies (caption of Fig. 2). A constant-diffusion coefficient was assumed because the impurity concentrations employed here are below the value ($\sim$1 at. %) where concentration-dependent phenomena occur.[1]

It should be noted that we searched for other fast diffusers in a-Si and, guided by the expected similarity to c-Si, checked Mn, Fe, Co, and Ni. However, no measurable diffusion of these elements was observed within the 20-nm-depth resolution and the 10^{18} atoms/m^2 detectability of RBS. We do not believe, on the basis of these negative results, that these species should be ruled out as fast diffusers in a-Si. Rather, at the peak concentration of about 0.02 at. %, necessary to study diffusion with RBS, these elements may have precipitated. This assumption is supported by the fact that they have solubilities in c-Si (Ref. 11) which are orders of magnitude lower than those of Cu (Ref. 11) and Pd.[4]

The measurements of the Au diffusivity were extended to temperatures as low as 250 °C by a tracer-profiling technique. The diffusion coefficients obtained in this way are represented by closed squares in Fig. 2. By means of sputter deposition an approximately 150-nm-thick layer of amorphous Si containing 0.66 at. % Au was deposited on a glass substrate and, in a subsequent sputtering process, covered by an a-Si layer of about the same thick-

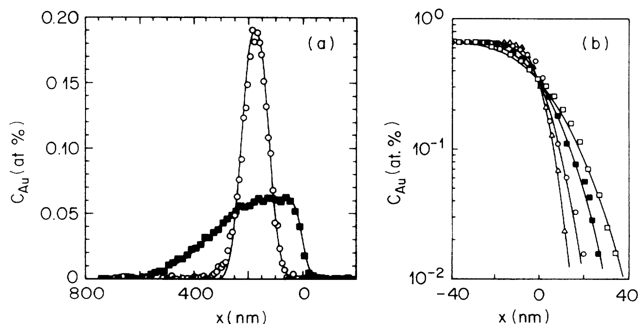

FIG. 1. (a) RBS-measured Au concentration profiles $C_{Au}(x)$ of as-implanted Au, 1×10^{19}/m^2,500 keV (○), and after subsequent annealing for 1 h at 500 °C (■) in an a-Si layer ($x>0$). The surface is at $x=0$. The solid curves are fits of a Gaussian distribution to the as-implanted profile and solution of the diffusion equation to the diffusion profile. (b) Neutron-activation and sputter-sectioning Au concentration profiles $C_{Au}(x)$ in a-Si ($x>0$) and a-Si–0.66 at. % Au ($x<0$) in the as-deposited state (Δ) and after subsequent annealing at 430 °C for 0.05 h (○), 0.1 h (■), and 0.15 h (□).

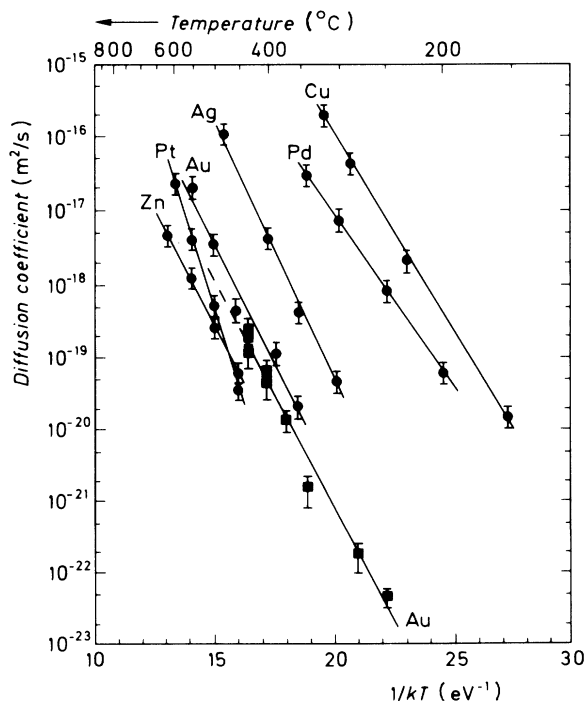

FIG. 2. Diffusion coefficients for several transition metals in a-Si (●, RBS data; ■, tracer-diffusion data). With an accuracy of ±0.1 eV the diffusion enthalpies amount to 1.4 eV for Zn, 2.2 eV for Pt, 1.4 [● (Ref. 1)] and 1.5 eV (■) for Au, 1.6 eV for Ag, 1.1 eV for Pd, and 1.2 eV for Cu.

ness. After diffusion annealing and neutron activation the penetration profile of Au in the a-Si layer was determined by sectioning and radioactive counting.[13] The diffusivity at a given temperature was determined by fitting measured Au concentration profiles to the appropriate solution of the diffusion equation [Fig. 1(b)]. It should be noted that the shape of the diffusion profiles of Figs. 1(a) and 1(b) are very different from those of corresponding Au profiles in dislocation-free c-Si,[4] which are more complex due to the dominance of the kick-out mechanism.

Figure 2 demonstrates that in a-Si Cu and Pd exhibit considerably higher diffusivities than Zn, Ag, Pt, and Au. This finding supports the assumption that the diffusion mechanisms in a- and c-Si are similar. In c-Si, Cu and Pd are rapid interstitial diffusers, whereas Zn, Pt, and Au are hybrids diffusing at intermediate rates via the kick-out mechanism.[3] Although the diffusion mechanism of Ag in c-Si has not been completely clarified, it has been classified[14] as "between hybridlike and fast-interstitial-like," in striking correspondence with the fact that in a-Si Ag diffuses slower than Cu and Pd but faster than Zn, Pt, and Au (Fig. 2). The diffusion of specific transition metals in a-Si will now be examined starting with Cu and Pd, which are interstitial diffusers in c-Si.

We have measured the diffusion of Pd in as-implanted (unrelaxed) a-Si and in thermally annealed (relaxed) a-Si. The relaxed a-Si was prepared by annealing at 500 °C for 1 h the 2.1-μm-thick a-Si before implanting Pd in the surface region. As shown in Fig. 3 the diffusivity in relaxed a-Si ($D_{i,r}^*$) is higher (by about a factor of 5) than in unrelaxed a-Si ($D_{i,u}^*$). Both $D_{i,u}^*$ and $D_{i,r}^*$, however, are considerably lower than the extrapolation of the Pd diffusivity in c-Si (D_i, dashed line in Fig. 3) and exhibit a considerably higher activation enthalpy [1.1 eV vs 0.2 eV in c-Si (Ref. 3)]. At 350 °C the diffusivity in a-Si is approximately seven orders of magnitude smaller than in c-Si. The same behavior has been also observed for Cu,[9] and we explain these phenomena in the following fashion.

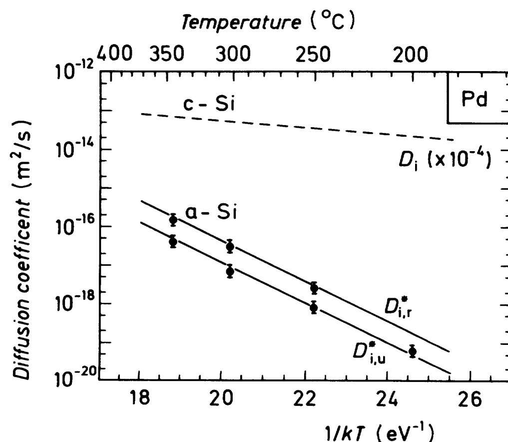

FIG. 3. Comparison of the diffusion coefficients of Pd in c-Si (D_i, low-temperature extrapolation of data reported in Ref. 3 multiplied by a factor of 10^{-4}), thermally relaxed a-Si ($D_{i,r}^*$), and unrelaxed a-Si ($D_{i,u}^*$).

Transition-metal elements, which undergo fast interstitial diffusion in c-Si, diffuse interstitially in a-Si, too. However, in a-Si they become trapped temporarily by the defects intrinsic to the amorphous structure. Thus their effective diffusivity is reduced to[15]

$$D_i^* = \frac{D_i}{1+\alpha C_t \exp(H_{it}^B/kT)} \tag{6}$$

with

$$\alpha = Z_i \frac{\theta_0}{\bar{\theta}_0} \exp(-S_{it}^B/kT) \ . \tag{7}$$

In Eq. (6), which is valid exclusively for a small occupancy of the traps, D_i is the interstitial diffusivity in a hypothetical trap-free a-Si and is assumed to be equal to D_i in c-Si [Eq. (1)]. The quantities C_t, H_{it}^B (S_{it}^B), Z_i, and θ_0 ($\bar{\theta}_0$) are the atomic fraction of traps, the positively defined binding enthalpy (entropy) that is released when an interstitial associates with a trap, the number of interstitial trapping sites available around a trap, and the attempt frequency for a free (trapped) interstitial, respectively. For high trap concentrations and high binding enthalpies at low temperatures (i.e., prerequisites which are expected to be fulfilled for interstitial diffusion in a-Si), Eq. (6) reduces to

$$D_i^* = D_{i,0}^* \exp[-(H_i^M + H_{it}^B)/kT] \tag{8}$$

with the preexponential factor

$$D_{i,0}^* = \frac{D_{i,0}}{\alpha C_t} \ . \tag{9}$$

The model explains why the activation enthalpy and the preexponential factor are larger in a-Si [Eqs. (8) and (9)] than in c-Si [Eq. (1)] for the same interstitial diffuser. In fact, the effective activation enthalpy (1.1 eV for Pd in a-Si) is the sum of the migration enthalpy for the interstitial atoms ($H_i^M=0.2$ eV for Pd), which we assume to be the same in a- and c-Si, and the binding enthalpy ($H_{it}^B=0.9$ eV for Pd). Moreover, the model shows why thermal relaxation of a-Si results in an increase in the preexponential factor while the activation enthalpy remains unchanged (Fig. 3). According to Eqs. (8) and (9), if thermal relaxation reduces the trap concentration C_t without changing the nature (i.e., H_{it}^B) of the traps, the only effect on diffusion can be an increase in the preexponential factor $D_{i,0}^*$. Fitting these equations to the $D_{i,u}^*$ and $D_{i,r}^*$ data in Fig. 3 and assuming $\alpha=1$, we obtain a trap concentration of 1 and 0.2 at. % in unrelaxed and relaxed a-Si, respectively. This is in agreement with the estimated concentration of defects derived by a comparison of defect annealing in a- and c-Si.[7] This value has to be compared with a typical density of 0.01–1 at. % ppm for thermal-equilibrium defects in c-Si.[3] Further evidence for trap-retarded diffusion of transition metals in a-Si is the observation[1] that their diffusivities increase when their concentrations become comparable to the trap concentration C_t. This is so since filled traps are ineffective on the still untrapped diffusers.

A different picture emerges for Au and Pt. As shown

in Fig. 4 for Au, their diffusion coefficients in a-Si lie between the extrapolations to lower temperatures of the diffusion coefficients in dislocation-free and highly dislocated c-Si.[4] In c-Si Au and Pt are hybrids and diffuse interstitially until they become substitutional and thus sessile by replacing Si atoms in kick-out reactions (see above). In the following it will be demonstrated that, as a result of the fact that structural defects act as traps for the A_i atoms and as sinks for I, Au and Pt undergo trap-retarded direct interstitial diffusion in a-Si. If Γ is the average number of jumps an A_i performs in a trap-free matrix before it spontaneously undergoes a kick-out reaction [Eq. (2)], then $C_t\Gamma$ is a measure of the probability of a trapping event compared to a kick-out event.

Due to the high concentration of defects in a-Si, the situation $C_t\Gamma \gg 1$ normally prevails. Therefore, trapping at defects completely overwhelms the kick-out reaction and the effective diffusion coefficient is given by Eqs. (8) and (9). The measured activation enthalpy, 1.5 eV for Au, is given by the sum of the Au_i diffusion enthalpy H_i^M and the binding enthalpy H_{it}, and is lower than the effective activation enthalpy, 2.8 eV, for diffusion in dislocation-free c-Si [Eq. (4)]. In Fig. 4 the experimental data for a-Si cover the range of temperatures from 250 °C–700 °C and exhibit the same activation enthalpy over about eight orders of magnitude. In accordance with Eq. (9) the preexponential factor gradually increases at higher temperatures due to the effect of partial trap annealing.

If C_t decreases to a value such that $C_t\Gamma \lesssim 1$ the kick-out reaction [Eq. (2)] becomes more important than trapping, but the traps can still act as internal sinks for I generated in this reaction. Therefore, the diffusion coefficient approximates the value characteristic of highly dislocated c-Si [Eq. (5)]. A further reduction of C_t ($C_t\Gamma \ll 1$) will result in the situation prevailing in c-Si without internal sinks and thus in a decrease of the diffusivity to the value D_s^{eff} of Eq. (3) characteristic of dislocation-free c-Si.

In conclusion, we have demonstrated that in a-Si, transition metals undergo direct interstitial diffusion that is retarded by temporary trapping at defects intrinsic to the a-Si structure. While mass transport through interstitial movement is a common feature for the diffusion of these elements in both a- and c-Si, the high density of defects in the a-Si network (0.2–1 at. %, compared to 0.01–1 at. % ppm in c-Si) determines the differences in the effective diffusion coefficients in the two Si phases. Pure interstitial diffusers in c-Si, such as Pd, exhibit lower effective diffusivities in a-Si due to the trap-induced retardation. For hybrids, such as Au, whose interstitial diffusion in c-Si is interrupted by temporary conversion to the sessile substitutional configuration, trapping at defects in a-Si completely overwhelms this kick-out reaction, thus giving rise to higher diffusion coefficients.

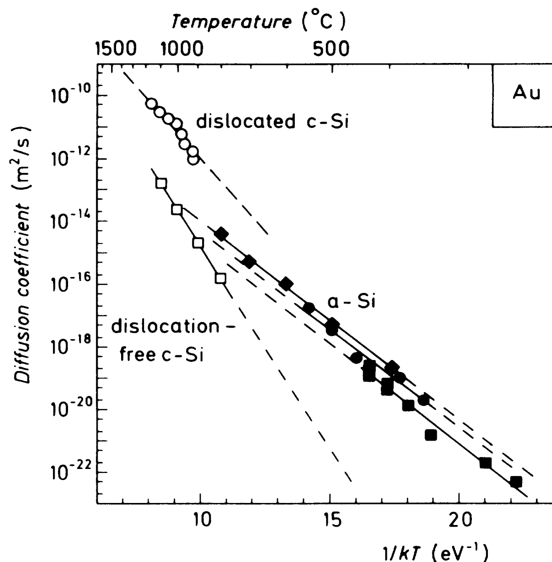

FIG. 4. Comparison of the diffusion coefficients of Au in dislocation-free c-Si (Ref. 4) (□), dislocated c-Si (Ref. 4) (○) and a-Si [◆ (Ref. 12); ●, RBS data; ■, tracer-diffusion data].

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