Impurity trapping and gettering in amorphous silicon

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Palladium atoms have been gettered from the bulk of an amorphous Si (a-Si) layer to an ion-implanted surface region. The 2.2-μm-thick a-Si layers, formed by MeV Si implantation, were implanted with 500 keV Pd and then annealed at 500 °C. This produces a complete redistribution of Pd within the layer and relaxation or substantial defect annihilation in the a-Si. Subsequently, defects were introduced into the surface region ($\sim$4000 Å) by 200 keV Si implantation at various doses. After low-temperature diffusion at 250 °C, Pd atoms are gettered in the Si-implanted region. At low Si fluences, Pd decorates the Gaussian depth distribution of the ion-induced damage, while at higher a saturation is reached in the gettering profile. The ion damage is calculated to saturate when 2% of the target Si atoms are displaced by atomic recoils. Below saturation, the displacement of two Si atoms is calculated to produce one Pd trapping site.

The properties and structure of amorphous (a)-Si depend on its thermal history.[1–4] Upon thermal annealing, as-implanted a-Si prepared by ion implantation exhibits a continuous transformation to a relaxed state, with the release of heat.[3,4] Recent calorimetry and Raman investigations of ion-implanted crystalline (c)-Si and a-Si demonstrate the important role which defects in the amorphous structure play in this structural relaxation process and suggest that structural relaxation in a-Si is, in fact, defect annealing.[5] In this letter the presence and the density of defects produced in a-Si by ion implantation is determined by the trapping or gettering of an impurity species, Pd.

Palladium diffuses interstitially in c-Si.[6] It exhibits a large and measurable diffusivity in a-Si but with a higher activation energy and lower extrapolated diffusivity than in c-Si.[7] Moreover, the diffusivity of Pd in a-Si depends on the thermal history of the material in a similar fashion as to that of Cu:[8] the value is a factor of 5 higher in 500 °C-annealed a-Si than in 200 °C-annealed a-Si.[7] Furthermore, Pd shows solute partitioning between as-implanted and annealed a-Si, similar to Cu.[7,8] These phenomena are interpreted by assuming that the diffusion mechanisms in c and a-Si are similar and that the defects in the a-Si structure act as traps for the fast moving interstitials, thus reducing the effective diffusivity.[7] The relaxation process, involving defect annealing, therefore enhances the diffusivity. The calorimetry and Raman studies showed that ion bombardment will return annealed a-Si to the as-implanted, defective state when the number of ion-induced displacements per atom (dpa) is greater than about 0.02 dpa.[5] As Pd diffusion and solubility are strongly influenced by the defect concentration, this element is ideal to study the damage production by ion beams in a-Si.

The 2.2-μm-thick a-Si layers were produced by implanting c-Si(100) with Si ions at three different energies: 0.5, 1.0, and 2.0 MeV. Implantation fluences were 5×10^{15} ions/cm^2 at each energy, and the samples were kept at 77 K during implantation. The as-produced a-Si was then implanted at 77 K with 2×10^{15} Pd ions/cm^2 at 500 keV. Heating at 500 °C in vacuum (10^{-6} mbar) causes the redistribution of the Pd atoms within the layer, and anneals out a considerable fraction of the defects in the amorphous structure.[3–5] In this way, a thermally annealed amorphous silicon layer with a uniform concentration of 1×10^{19} Pd/cm^3 is generated. Figures 1(a)–1(c) show a schematic illustration of this sample preparation sequence.

The near-surface region of the a-Si layer was then implanted at 77 K with 200 keV Si at fluences ranging from 1×10^{12} to 5×10^{15} ions/cm^2. This Si implantation induces a Gaussian distribution of damage in the first 4000 Å of the material, leaving the remaining amorphous layer in the annealed state [Fig. 1(d)]. The estimated maximum ion beam damage for this energy, calculated using a Monte Carlo simulation (TRIM[9]), is about 4×10^{-4} dpa and 2.0 dpa for the lowest and the highest fluence, respectively. The damage distribution peaks at about 2000 Å depth. The samples were then annealed at 250 °C for 36 h to enable a redistribution of the impurity atoms [Fig. 1(e)]. Such a low temperature is employed to produce Pd diffusion without substantial annealing of the Si bombardment-induced defects.

The profiles of Pd were then measured using Rutherford backscattering spectrometry of 4 MeV He ions. Figure 2 shows the Pd depth profiles in unimplanted and Si-implanted samples. It can be seen that the Pd is gettered from the bulk of the material to the Si-implanted surface region. As can be seen, the amount of trapped impurity increases with Si fluence up to 5×10^{12} ions/cm^2 [Fig. 2(a)]. For higher fluences [Fig. 2(b)] a saturation is observed, characterized by the same heights for the Pd signal but with a progressive sharpening of the interface between the annealed and Si-implanted regions.

It appears from Fig. 2(a) that the low-fluence Pd profiles can be identified with the Pd decoration of defects produced by the Si beam. These profiles can be compared with damage profiles calculated using TRIM. A 15 eV displacement threshold energy in a-Si has been assumed and displacements by recoiled atoms have been taken into account. Figure 3 shows the calculated profiles of the concentration of displaced atoms (solid lines) compared with the measured profiles of gettered atoms for the lower Si fluences. The latter were obtained by subtracting the con-

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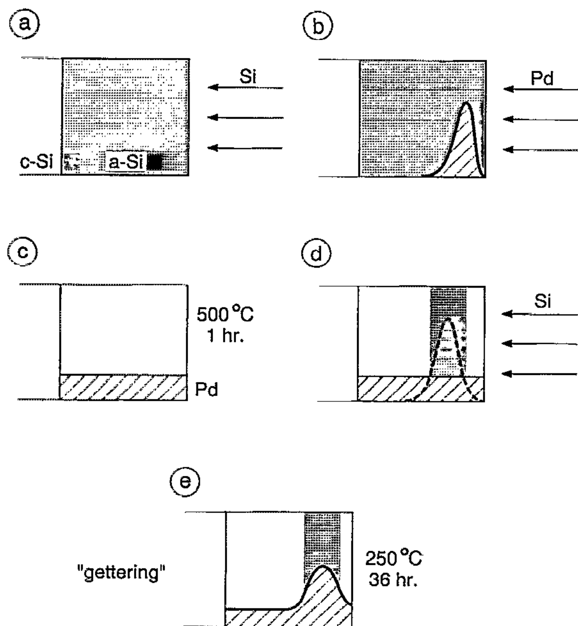

FIG. 1. Schematic of sample preparation procedure.

stant background of the annealed, unimplanted region from each profile. The agreement between experimental data and the simulations is striking and strongly supports the idea that Pd is gettered at beam-induced traps.

To allow for a direct comparison, the calculated damage profiles in Fig. 3 have been normalized by a factor of 3.0×10^{-2} (lower fluence) and 1.8×10^{-2} (higher fluence). In order to explain the physical meaning and the difference between these normalization factors, it is necessary to derive the relation between the concentration of trapped atoms and the concentration of ion-induced traps. We can do this by assuming that the defects act as traps for the impurity and that local thermodynamic equilibrium is realized between free and trapped atoms due to the trapping process. The ratio of the concentration profile of Pd atoms trapped at beam-induced defects (C_t) and the background Pd level in the annealed, unimplanted a-Si (C_{bulk}) then reflects the ratio of the defect densities in the two regions:

$$\frac{C_t(x,\phi)}{C_{\text{bulk}}}=\frac{tN_d(x,\phi)}{b}, \tag{1}$$

where x is the depth; $N_d(x,\phi)$ is the concentration profile of displaced atoms (according to TRIM) for the particular fluence ϕ; t is the number of traps generated for each displaced atom; and b is the density of traps present in the annealed a-Si. The concentration C_{bulk} is determined by the normalization condition $\int_0^d [C_{\text{bulk}}+C_t(x,\phi)]dx=\phi_{\text{Pd}}$, where ϕ_{Pd} is the total amount of Pd atoms per cm^2 and d is the total thickness of the amorphous layer. By substituting in Eq. (1):

$$C_t(x,\phi)=\phi_{\text{Pd}}\frac{tN_d(x,\phi)}{\int_0^d[b+tN_d(x,\phi)]dx}. \tag{2}$$

This equation shows that the relation between the concentration of trapped atoms $C_t(x,\phi)$ and the concentration of ion-induced traps $tN_d(x,\phi)$ becomes nonlinear when tN_d is of the same order as the background defect level b.

Equation (2) has two free parameters: b and t. The defect density in the annealed a-Si, b, is still a parameter of debate, and estimates are in the order of 1 at.%.[5,8,10] In fact, from our diffusion model in a-Si, in which it is assumed that diffusion in a-Si can be described by the same interstitial diffusion rate as in c-Si, but including trapping at defect sites, we have derived a value of $b=0.3$ at.%.[7] Using this estimate of b we can derive a value of t such that

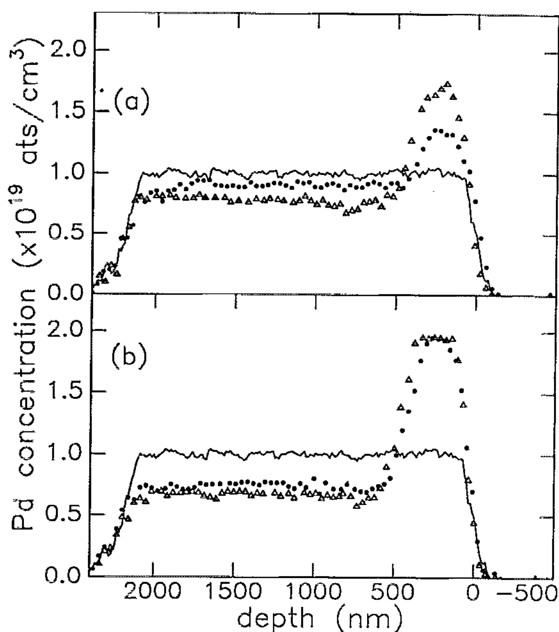

FIG. 2. Depth profiles for palladium inside the amorphous layer following silicon implantation in the surface region and diffusion at 250 °C for 36 h: (a) low Si fluences: 1×10^{12} ions/cm^2 (points), 5×10^{12} ions/cm^2 (triangles), (b) high Si fluences: 1×10^{13} ions/cm^2 (points), 5×10^{15} ions/cm^2 (triangles). The solid line gives the Pd profile before diffusion.

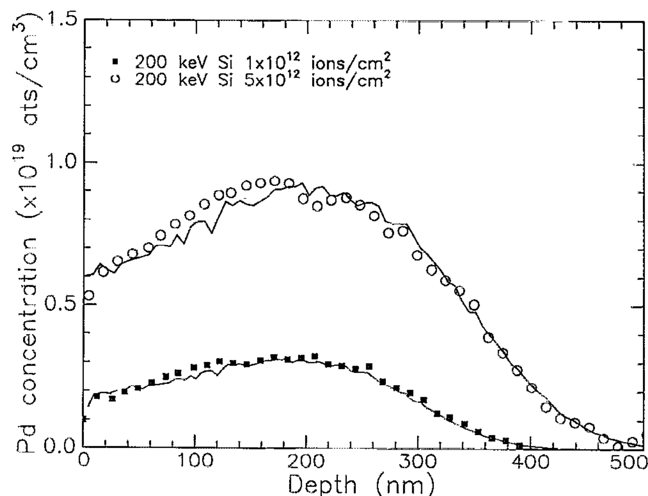

FIG. 3. Comparison of the concentrations of gettered atoms with those of displaced atoms calculated according to TRIM (solid lines). Calculated TRIM profiles are scaled with a factor 3.0×10^{-2} (bottom curve) and 1.8×10^{-2} (top curve).

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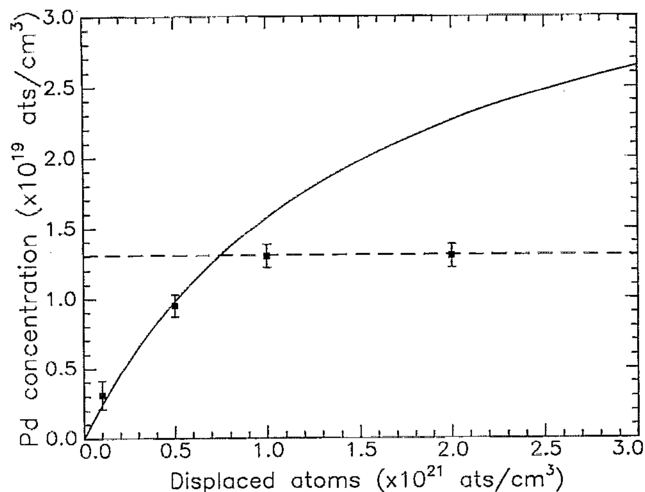

FIG. 4. Peak concentration of trapped Pd atoms as a function of Si fluence: experimental points (squares) and theoretical calculation (solid line). The dashed line shows the saturation level.

the calculated curve for C_t fits the gettered Pd profiles for the two low-fluence implants. This is shown in Fig. 4 which shows the two data points for the peak Pd concentration of the gettered profiles from Fig. 3, together with the curve for C_t. A best fit for C_t was obtained for $t = 0.5$. Indeed, the calculated curve shows the nonlinear increase of Pd peak concentration with ion damage. This nonlinearity explains the difference in the normalization factors used in Fig. 3. The obtained value of t indicates that on average a displacement of two atoms will result in the formation of one trapping site. It should be noted that this value of t depends on the particular value chosen for b. However, for any choice of b in the order of 1 at.%, a value of t in the order of 1 is obtained.

Figure 4 also includes the measured Pd peak concentration for the two high-fluence Si implants. It is evident that for these high fluences the amount of trapping does not further increase with fluence. Instead, a saturation is observed in the concentration of trapped atoms, which implies a saturation in the ion-induced damage. The damage saturation level can be directly determined from Fig. 4 and amounts to $\sim 1 \times 10^{21}$ atoms/cm^3, i.e., ~ 0.02 dpa, in agreement with calorimetry and Raman results.[5] This behavior must be a manifestation of the way in which a-Si accommodates these defects in its structure. While the absolute defect density in the 500 °C annealed sample is not known accurately, the experimental data show directly [Fig. 2(b)] that the intrinsic saturation level of defects in the bombarded region is a factor 3 higher. In other words, annealing at 500 °C reduces the density of defects compared to the defect density at 250 °C by only a factor 3. It should be noted that the fluence at which saturation is observed (1×10^{13} ions/cm^2) is about one order of magnitude lower than the fluence required to reach amorphization of c-Si which is $\sim 2 \times 10^{14}$ ions/cm^2 for 200 keV Si at 77 K.

In conclusion, we have shown that Pd atoms can be gettered from the bulk of a thermally annealed amorphous Si layer to an ion-implanted surface region. The resulting profiles can be accounted for by a model which assumes trapping of the fast moving interstitials at defects in the amorphous structure. At low fluences the impurity decorates the ion-induced damage and the concentration of gettered impurity atoms increases with fluence. At higher fluences a saturation is observed in the Pd profile which reflects a saturation in the ion-induced defect concentration. The saturation occurs above about 0.02 displacements per atom. This damage level is in good agreement with the value obtained for the transition from the annealed to the as-implanted state of a-Si as measured by calorimetry and Raman spectroscopy. Thermal annealing at 500 °C reduces the defect density in a-Si by a factor 3. Assuming a defect density of ~ 0.3 at.% in a-Si annealed at 500 °C, an atomic displacement of two atoms will result in the formation of one trapping site.

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