Defect states of amorphous Si probed by the diffusion and solubility of Cu

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The diffusivity and solubility of Cu impurities have been measured in different structural states of amorphous Si (a-Si) formed by MeV Si implantation. The 2.2-μm-thick a-Si layers were first annealed (structurally relaxed) at 500 °C and then implanted with 200 keV Cu ions, returning a 300-nm-thick surface layer to the as-implanted state. After diffusion at temperatures in the range 150–270 °C, we observe solute partitioning at a sharp phase boundary between the annealed and Cu-implanted layers, the partition coefficient being as large as 8.2 ± 1.3. The diffusion coefficient in annealed a-Si is 2–5 times larger than in as-implanted a-Si, with activation energies of 1.39 ± 0.15 and 1.25 ± 0.04 eV, respectively. The data show quite strikingly the role which defects can play in the a-Si structure.

Amorphous silicon (a-Si) is an important material in present day semiconductor technology, yet many of its fundamental properties are poorly understood.[1] Low-temperature calorimetry and optical scattering[2–7] have shown that a-Si exhibits a continuous range of structural configurations, depending on the thermal history of the material. These experiments show that thermal annealing can relax a-Si, with typical relaxation times of 100 s.[3–5] Our recent calorimetry studies of ion beam damaged single crystal (c-Si) and annealed a-Si (Ref. 8) have shown that the relaxation process can be understood in terms of annealing of defect complexes with concomitant changes in the bond angle distributions.

In the present letter we use the diffusivity and solubility of Cu in a-Si as a probe of the defect complexes. In crystalline Si (c-Si) it is known that fast diffusing impurities such as Cu can be trapped at defects ("gettering"). In an amorphous solid the concept of defects obviously is more complicated. There are only few measurements of diffusion in a-Si, principally because of the low-temperature boundary condition. The a-Si crystallizes at temperatures typically 500 °C and above. The best characterized data besides those for hydrogen are for Cu, Ag, and Au which are fast diffusers in a-Si as well as in c-Si.[9–11] In these experiments, however, the dependence on the structural state of the a-Si was not studied. In this letter we show that both the diffusivity and effective solubility of Cu are very sensitive to the defect state of the a-Si network.

Implantation of 0.5, 1, and 2 MeV Si ions was used to create an a-Si surface layer of 2.2 μm thickness in a single-crystal Si(100) substrate. Silicon implantation into c-Si is known to produce pure a-Si without macroscopic voids and impurities. At each energy, the implantation dose was 5×10^{15} ions/cm^2 and the beam current was kept low in order to maintain the total power on target below 15 W. All implants were done with the target holder cooled using liquid nitrogen. The implanted Si sample was cut into three pieces, two of which were annealed in vacuum at a base pressure below 10^{-7} Torr, for 1 h at 500 °C. This annealing treatment relaxes the a-Si network as has been shown before.[2–8] One of the annealed samples was then implanted with 5.5 MeV Si ions to a total fluence of 1.6×10^{15} ions/cm^2. For this irradiation the damage resulting from nuclear collisions is estimated to range from 0.1–0.2 displacement per atom (dpa) over a 1-μm-thick surface layer.[12] As has been shown before, this returns the a-Si to a state similar to the as-implanted, unannealed state.[13] All three samples (i.e., unannealed, annealed, and annealed irradiated) were then implanted with 200 keV Cu ions to a dose of 5.5×10^{15} ions/cm^2. The estimated maximum damage resulting from this implant amounts to approximately 20 dpa at ~ 80 nm depth; for larger depths the displacement profile is a rapidly decreasing function of depth. The diffusion of Cu in all samples was then studied following thermal treatment in vacuum at a base presure below 10^{-7} Torr, at various temperatures ranging from 150 to 270 °C, for times between 10 min and 104 h (note that hereafter we will refer to "annealing" as the treatment of the a-Si at 500 °C for 1 h, and to "thermal treatment" as the subsequent process used to induce the Cu diffusion). The Cu concentration profiles were measured using 4 MeV ^{4}He backscattering (BS) using a scattering angle of 125°. All BS measurements were performed using a beam current of 60 ± 3 nA He^{++}, yielding the same pileup background signal for all spectra.

Figure 1 shows Cu backscattering spectra of the unannealed and annealed samples, before and after thermal treatment for 4 h at 221 °C. As can be seen, the as-implanted Cu profile peaks at approximately 100 nm below the surface. The peak Cu concentration amounts to 0.7 at. %. After thermal treatment of the unannealed sample, significant in-diffusion of Cu is observed [Fig. 1(a)]. The typical diffusion distance is in agreement with parameters found in our earlier study.[9]

An entirely different diffusion behavior is observed in the annealed sample [Fig. 1(b)]. A uniform Cu concentration is observed in an approximately 300-nm-thick surface layer, and a low-concentration Cu tail is observed in the deeper lying annealed layer. The interface between the two concentration regions coincides with the end-of-range of

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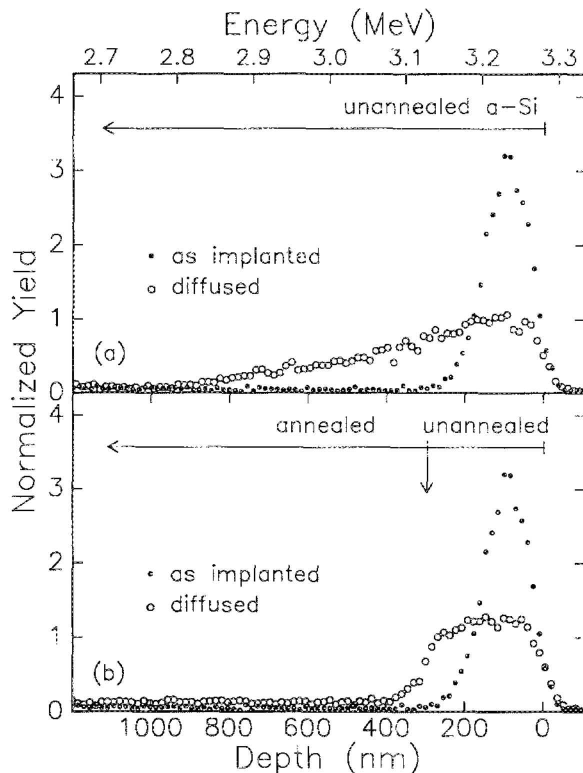

FIG. 1. Backscattering spectra of two types of Cu-implanted *a*-Si samples before and after thermal treatment at 221 °C for 4 h. (a) unannealed *a*-Si, (b) double layer of annealed and unannealed *a*-Si.

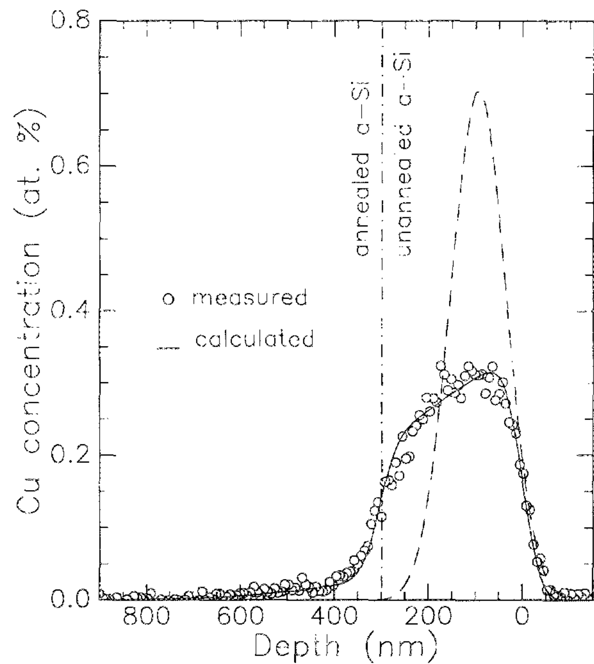

FIG. 2. Cu concentration as a function of depth in an unannealed/annealed double layer structure after thermal treatment at 170 °C for 20.5 h (circles). The dashed line is the as-implanted profile, the drawn line is a fit using numerical simulation of diffusion and solute partitioning.

the Cu implant, which has returned a 300-nm-thick surface region to the as-implanted, unannealed state. This depth has been determined using channeling in a *c*-Si sample which was implanted with Cu under the same conditions, and is indicated by an arrow in Fig. 1(b). The diffused Cu concentration in the 300 nm surface layer in Fig. 1(b) is higher than in the corresponding region in Fig. 1(a). This indicates that during diffusion, Cu is partially reflected at the interface between annealed and unannealed *a*-Si. This is characteristic for solute partitioning at a phase boundary. The ratio between the Cu levels in the two *a*-Si phases can then be interpreted as a partition coefficient (k), and amounts to $k = 9 \pm 1$ in this case. The discontinuity in the Cu profile is quite abrupt. This can be understood from the face that at the end-of-range the damage (dpa) profile of the Cu implant is a rapidly decreasing function of depth, resulting in a sharp phase boundary between unannealed and annealed *a*-Si.

The Cu diffusion profile in the annealed-implanted sample (500 °C anneal + Si implant) is not shown, but could not be distinguished from that in the unannealed sample in Fig. 1(a). This indicates that ion beam damage of 0.1 dpa is sufficient to return annealed *a*-Si to a state which equals that of as-implanted *a*-Si as far as diffusion properties are concerned. Moreover, this shows that the partitioning effects shown in Fig. 1(b) are not an artefact, for example, of the annealing treatment. We have also performed a diffusion experiment in a similar structure as in Fig. 1(b) produced by half the Cu implantation fluence. This yielded a value of $k = 10 \pm 2$. Therefore, the measured partition coefficient appears to be independent of Cu concentration.

Additional studies were performed to determine diffusion and partition coefficients over a wide temperature range (150–270 °C). Figure 2 shows a Cu concentration profile in the annealed/unnannealed layer structure after thermal treatment at 170 °C for 20.5 h. In this spectrum, pileup background subtraction was applied. Again, a discontinuity in the Cu concentration is observed at the interface between the two regions. In addition, a decreasing Cu tail can be seen in the annealed region. Figure 2 also shows results of numerical calculations of the Cu profile taking into account total reflection at the surface and partitioning at the annealed/unannealed interface and convoluted with the depth resolution of 50 nm. In the simulations the diffusion coefficients in both layers and the partition coefficient were varied. The drawn line represents a best fit, obtained using $k = 7$ and a ratio of 2 between the diffusion coefficients in annealed and unannealed *a*-Si. In additional experiments it was found that, within the error bars, the partition coefficient was not very sensitive to the diffusion time and temperature in the temperature range betwen 150 and 270 °C; an average of $k = 8.2 \pm 1.3$ was obtained. Also, it was found that the partition coefficient is smaller for samples in which the *a*-Si is preannealed at a lower temperature than the 500 °C as used in the present study.[14]

Figure 3 summarizes the measured Cu diffusion coefficients in annealed *a*-Si in the temperature range 150–270 °C in an Arrhenius fashion. In addition, data from our earlier study on diffusion in unannealed *a*-Si are shown.[9]

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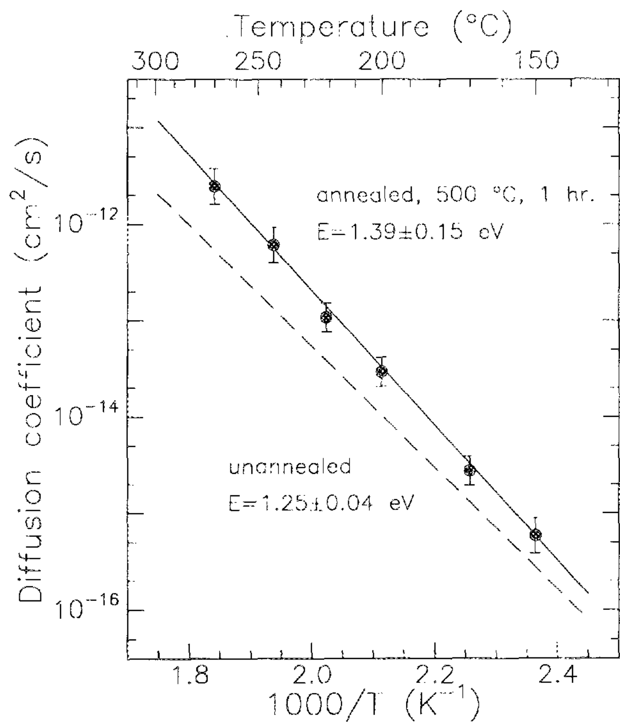

FIG. 3. Cu diffusion coefficients in *a*-Si annealed at 500 °C for 1 h (circles). The drawn line is an Arrhenius fit to the data. Data from our earlier study for unannealed *a*-Si are also indicated (dashed line).

These data are in agreement with coefficients found for the unannealed layer in the simulations described above. As can be seen, in the temperature range studied, the diffusion rate in annealed *a*-Si is a factor 2–5 higher than in unannealed *a*-Si. The diffusion activation energy (E) in annealed *a*-Si is not significantly different than in unannealed *a*-Si ($E = 1.39 \pm 0.15$ eV vs $E = 1.25 \pm 0.04$ eV, respectively).

The present Cu solute partitioning and diffusion data show quite strikingly the role which defects can play in the *a*-Si structure. To first order, if we assume that Cu concentrations are correlated with defect concentrations, the data would imply that the defect concentration in the annealed material is considerably lower than that in the as-implanted, unannealed material. These defects influence the diffusion rate: assuming that Cu is an interstitial diffuser in *a*-Si and is trapped at defect sites, then the diffusion coefficient will increase for lower defect concentrations, as is observed. It should be pointed out that this observation is opposite to that seen in the annealing of metallic glasses where the diffusivity decreases with annealing.[15,16] However, the diffusion and defect annealing process in *a*-Si would apear to be quite different from that of a metallic glass. The fact that the activation energies for diffusion in the annealed and as-implanted *a*-Si are identical within experimental error indicates that the annealed state is still highly defective and that diffusion in both cases is defect dominated.

It should be noted that the measured Cu concentrations are not necessarily related to the equilibrium solid solubilities in the two *a*-Si phases. It cannot be excluded that our experiments are performed in the regime of supersaturation. However, no anomalous diffusion behavior, indicative of precipitation, was observed. The typical Cu concentrations observed in the present experiments are at least ten orders of magnitude higher than the (extrapolated) equilibrium solubility in *c*-Si at 221 °C.[17]

In conclusion, we have found that the diffusion and solubility of Cu in *a*-Si are strongly dependent on the defect state of the amorphous matrix. As-implanted *a*-Si contains a large concentration of defects (point defects or larger defect agglomerates). Thermal annealing at 500 °C for 1 h reduces the density of Cu trapping defects and hence the Cu solubility. As a result, solute partitioning is observed at a phase boundary between as-implanted and annealed *a*-Si, the partition coefficient being 8.2 ± 1.3. Due to the reduced defect concentration, the diffusion coefficient in annealed *a*-Si is a factor 2–5 higher than in as-implanted *a*-Si. Since the Cu solubility is extremely sensitive to the defect density, these measurements can be extended to study structural changes and defect phase boundaries in *a*-Si in more detail.

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