

# Upper limit on room-temperature diffusion of metal impurities interstitially dissolved in amorphous Si

O. Diop and S. Roorda

**Abstract:** Impurity profiles of Cu and Ag in amorphous silicon were studied before and after one year storage at room temperature and found to be indistinguishable. Since just before storage, hydrogen had been ion implanted into the uniformly metal doped layer, a diffusivity in excess of  $3 \times 10^{-24} \text{ m}^2/\text{s}$  would have led to an observable change in the impurity profile. Therefore the room-temperature diffusivity must be less than that ( $3 \times 10^{-24} \text{ m}^2/\text{s}$ ), which in turn implies one of two possibilities: either the interstitial diffusivity is much lower than previously determined, or the metal impurities were not fully detrapped by the implanted hydrogen. A subsequent thermal anneal at  $450^\circ\text{C}$  confirmed that the detrapping and diffusion of Ag and Cu in H-implanted amorphous Si conforms to its normal behaviour. The low value of the room-temperature diffusivity is important for the interpretation of forthcoming measurements on high-energy ion tracks in amorphous Si.

PACS Nos.: 66.30.J-, 71.55.Jv, 61.72.uf, 81.05.Gc.

**Résumé :** Nous avons étudié les profils d'impureté de Cu et de Ag dans du silicium amorphe, avant et après remisage d'un an à la température de la pièce et nous observons qu'ils sont indiscernables. L'implantation ionique d'hydrogène dans la couche dopée métalliquement aurait causé un changement observable dans les profils d'impureté si le coefficient de diffusion avait été plus grand que  $3 \times 10^{-24} \text{ m}^2/\text{s}$ . Ce coefficient est donc plus petit que  $3 \times 10^{-24} \text{ m}^2/\text{s}$ , ce qui implique deux possibilités. Soit que la diffusivité est plus faible que déterminée précédemment, soit que les impuretés métalliques n'ont pas été libérées de leur piège par l'hydrogène. Un recuit subséquent à  $450^\circ\text{C}$  confirme que la libération et la diffusion de Ag et Cu dans du Si amorphe avec implantation de H sont conformes au comportement normal. La basse valeur du coefficient de diffusion à la température de la pièce est importante dans l'interprétation de mesures à venir de trajectoires d'ions de haute énergie dans du Si amorphe. [Traduit par la Rédaction]

## Introduction

Metals such as Cu, Ag, and Au are known to be very fast diffusers in crystalline (c-) Si [1] and Ge [2]. In the study of amorphous silicon (a-Si), the solubility, diffusivity, and interaction with hydrogen of these metals have contributed significantly to the understanding of the defect structure of the random network [3–5]. In the present study, we again use the behaviour of Cu and Ag in a-Si to put an experimental limit on the room-temperature diffusivity of the metal impurities. The solubility of those metals is very low but can be increased if the host Si contains vacancy-type defects that act as traps for the metal atoms. Trapping by such defects slows down the diffusion, which must now be thought of as a combination of detrapping and interstitial diffusion. The much (more than five orders of magnitude) larger solubility and lower diffusivity of many metals in a-Si compared to c-Si [3, 4] is understood as being indicative of a large number (on the order of an atomic percent) of vacancy-type sites in the a-Si network. Metal atoms can be in the interstitial state, and diffuse fast and far, or trapped at vacancies or vacancy-type defects where they are immobile until they are detrapped, either thermally or otherwise. In a-Si, the trapping sites are also known to correspond to the location of dangling bonds, because it has been observed that metal atoms, trapped in a-Si, can be dislodged after hydrogen is introduced and has passivated the dangling bonds [5].

The possibility of dislodging metal atoms from vacancy sites in a-Si creates a unique experimental opportunity. Suppose that one has a piece of a-Si with metal atoms uniformly distributed and trapped in vacancy-type defects. Then, if hydrogen is added by ion

implantation, a fraction of the metal atoms will be detrapped and become part of the fast-diffusing, interstitially dissolved atoms. In this paper, we describe an experiment where we attempted to observe the low-temperature diffusion of the interstitial fraction of Cu and Ag dissolved in a-Si, obtained by detrapping using hydrogen ion implantation. We found no measurable change in the depth profile after one year at room temperature, putting an upper limit on the diffusivity of the detrapped interstitial metal atoms. This result is important for forthcoming measurements of the density profile of latent tracks made by swift heavy ions (e.g., 75 MeV Ag) in a-Si.

## Specimen preparation

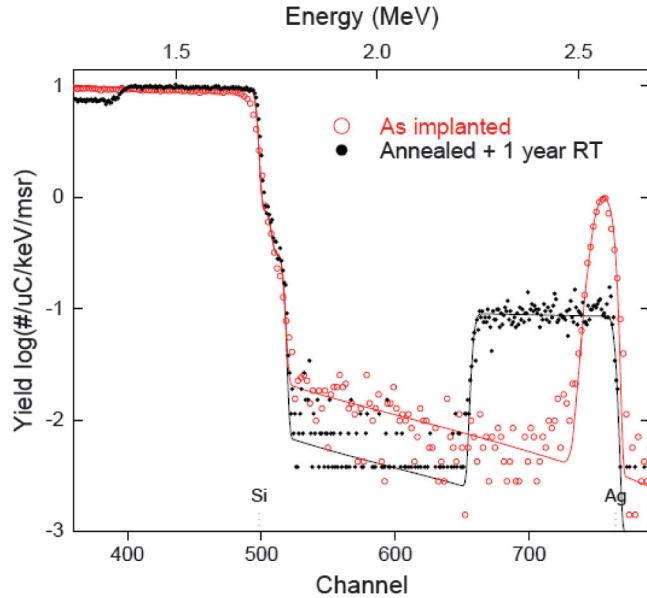
Pure a-Si was made by self-implantation of  $5 \times 10^{15} \text{ ions/cm}^2$  at 500 keV and 1 MeV into a c-Si wafer clamped to a sample holder held at liquid nitrogen temperature. This treatment leads to the formation of a pure a-Si layer of about  $1 \mu\text{m}$  thickness. Next, either Ag or Cu was ion implanted to a nominal fluence of  $4 \times 10^{15} \text{ ions/cm}^2$  and at an energy of 90 keV. The projected range (average penetration depth) for 90 keV is 73 nm for Cu and 50 nm for Ag, much less than the thickness of the a-Si layer. The implantation treatment was followed by a vacuum (better than  $10^{-6} \text{ mbar}$ ) anneal at  $350^\circ\text{C}$  for 6 h and at  $450^\circ\text{C}$  for 8 h. During the anneal treatment, the metal impurities redistribute evenly throughout the a-Si layer, as was confirmed by Rutherford backscattering spectrometry (RBS, see next section). In view of the large difference in solubility in c-Si and a-Si, the impurities are not expected to significantly penetrate into the underlying c-Si and this was

Received 11 January 2013. Accepted 29 July 2013.

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**Fig. 1.** Rutherford backscattering spectra of amorphous Si implanted with Ag (open red circles), measured at 2 MeV and plotted against channel number (bottom axis). Black dots: The same samples after subsequent thermal anneal H implantation, and one year storage at room temperature. This spectrum was measured at 3 MeV and is plotted against the top axis. The lines correspond to calculated spectra using parameters described in the text.

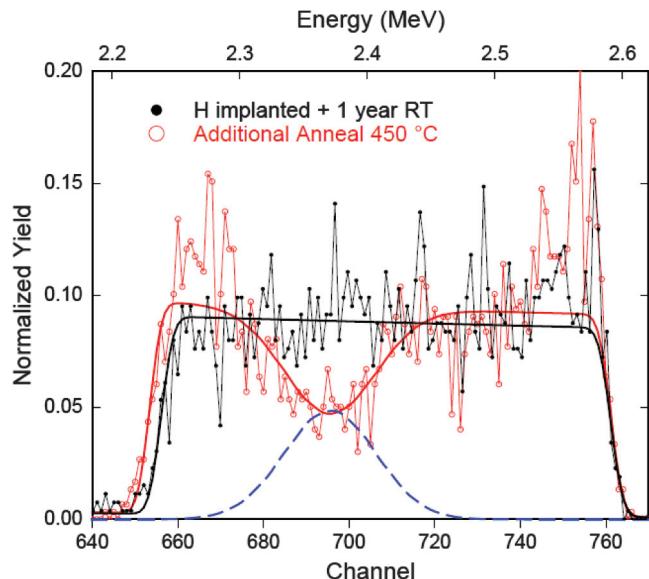


also confirmed by RBS. The third ion implantation consisted of 45 keV,  $2 \times 10^{16}$  ions/cm<sup>2</sup> H ions, which is expected to give rise to a nearly Gaussian hydrogen profile at a depth of about 430 nm, with a width of 50 nm and a peak concentration well in excess of the local defect density. The samples were kept at room temperature for one year and were subjected to one final thermal anneal (450 °C for 1 h) under vacuum.

### Observations from RBS

The samples were analyzed by RSB [6] using 2 or 3 MeV He ions backscattered through 165°. An example of some complete spectra is shown in Fig. 1, using a log scale so as to be able to distinguish the signal both from the Si and from the metal (in this case, Ag) impurity. The open circles correspond to the signal measured on an as-implanted sample; this spectrum was measured with 2 MeV He ions and is plotted as a function of channel number (bottom axis). The markers “Si” and “Ag” near the channels 500 and 770 indicate the surface channels for backscattering of those elements. The nearly Gaussian peak near the right of the figure corresponds to the implantation profile, the rectangular signal to the left of channel 500 comes from the Si substrate (the “shoulder” is due to the presence of the <sup>29</sup>Si and <sup>30</sup>Si isotopes) and the noisy signal between the Si bulk and the Ag peak is due to “pile-up”. Pile-up happens when two or more ions hit the detector nearly simultaneously and are accidentally counted as one event, with the total energy of both backscattered ions. The black closed circles were measured after the sample was first annealed and then allowed to sit for one whole year at room temperature. This spectrum was measured using 3 MeV He ions and is plotted as a function of backscattered ion energy (top axis), allowing a direct comparison to the as-implanted spectrum. For the spectrum shown in black dots, the main crystallographic axis was aligned with the direction of the ion beam (known as “channeling”). The channeling effect leads to a drop in intensity from the Si substrate near channel 400 and this position can be used to determine the

**Fig. 2.** Rutherford backscattering signal from the Ag in a-Si. Black dots: after one year storage at room temperature. Red circles: after an additional anneal (1 h at 450 °C). Solid lines: theoretical fits to the spectra assuming a profile that is the sum of a constant box-type profile + a missing fraction. The missing fraction is described using a Gaussian distribution with parameters corresponding to the H implantation profile. The dashed line shows the expected spectrum if Ag atoms were distributed according to the H implantation profile, that is, illustrates the missing fraction.

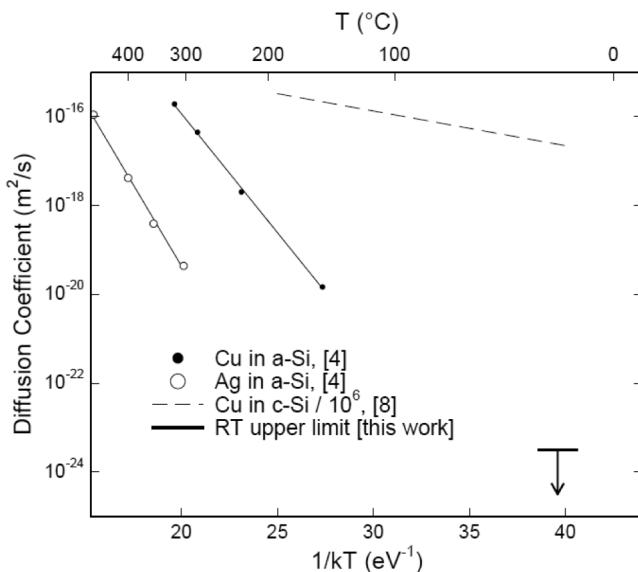


thickness of the a-Si layer (in the a-Si, channeling cannot occur and therefore the signal is as high as in the random case). The Gaussian peak is no longer observed and instead one can see a rectangular signal between channels 655 and 764 indicating that the Ag has redistributed throughout the a-Si layer without penetrating significantly into the underlying c-Si. This spectrum was measured at a lower beam current, resulting in a reduced pile-up in the channel range 500–650.

The RBS signals were simulated [7] and the calculated curves are shown as solid lines in Fig. 1. From these simulations, one can extract several numerical values. The Gaussian profile shown corresponds to  $(3.7 \pm 0.3) \times 10^{15}$  Ag/cm<sup>2</sup> atoms at an average depth of  $460 \pm 10$  Å. The rectangular signal from Ag corresponds to a uniform concentration of  $0.078 \pm 0.002$  at % over the entire depth of the a-Si layer ( $929 \pm 7$ ) nm for a total Ag areal concentration of  $3.6 \pm 0.1$  at/cm<sup>2</sup> confirming that indeed very little Ag was lost to the substrate.

The redistribution of Ag in the a-Si layer can be observed in detail in Fig. 2, which shows the channel range of interest and compares the Ag distribution after the hydrogen implantation and one year at room temperature with that after a subsequent thermal anneal. Again, symbols represent measured counts and the solid lines represent simulated curves used to extract numerical values. The large dip in the annealed Ag signal (red open circles) is well described by a Gaussian with negative amplitude, which indicates that Ag diffuses away from that part of the a-Si where hydrogen has passivated dangling bonds [5]. The position and width of the Gaussian dip were  $430 \pm 10$  and  $50 \pm 5$  nm for Ag and  $400 \pm 15$  and  $110 \pm 20$  nm for Cu. These values are close to the values expected from the implanted H profile. The position and width of the dip thus confirm that after one year, the hydrogen is still present and still dislodges the Ag atoms from their trap sites. The absence of such a dip in the signal from the “room temperature” sample shows that no measurable diffusion took place in

**Fig. 3.** Arrhenius plot of reported values for Ag and Cu diffusion in a-Si according to ref. 4. Also shown is the purely interstitial diffusivity of Cu in dislocation-free c-Si, reduced by six orders of magnitude (dashed line, after ref. 8). The horizontal bar and arrow indicate the upper limit and range of possible values for the room temperature diffusion of Cu and Ag in a-Si deduced from our work.



the course of one year at room temperature even though the hydrogen was there all the time.

### Discussion: limit on the diffusivity of interstitially dissolved impurities in a-Si

Because the Ag distribution depicted by the red circles essentially follows the profile in the chemical potential imposed by the localized hydrogen passivation of dangling bonds, the diffusion length during the short (1 h at 450 °C) thermal anneal must be at least 5 times the thickness of the as-Si layer (i.e.,  $\geq 5 \mu\text{m}$ ). Conversely, the complete absence of measurable diffusion during the one year storage at room temperature implies that the diffusion length in that case can be conservatively estimated as less than one-fifth of the width of the dip visible in the annealed sample (i.e.,  $\leq 10 \text{ nm}$ ). To put this latter value into context, we compare it in Fig. 3 with the literature values for the Ag and Cu diffusivities in a-Si [4] and c-Si [1, 8]. While our measurements can only put an upper limit on the actual diffusivity value, it is clear that our data falls close to values for Ag and Cu diffusion in defected, unpassivated a-Si and are much smaller (by many orders of magnitude) than those for purely interstitial diffusion species.

Several studies have shown that hydrogen implanted into Si, either amorphous or crystalline, is initially mobile, forms bonds with Si, and passivates dangling bonds, even at temperatures well

below room temperature [9–12]. Near the peak of the proton implantation profile, the hydrogen concentration is nearly 10 at. %, well in excess of the defect concentration and therefore any vacancy-type site available for metal retrapping would have been passivated by hydrogen. Therefore, one would expect any metal impurities trapped in a vacancy associated with such a dangling bond to become detrapped or at least competing with a hydrogen atom for the trapping site. The observed absence of enhanced diffusion implies that either the detrapping has not been completed (the metal atoms have not been fully “kicked out” of the trapping sites), or detrapped metal atoms are immediately re-trapped in the close vicinity of their original trapping sites, which requires a defect density in excess of the peak hydrogen concentration (10%).

The attempted measurement reported here is important for the interpretation of a recent experiment involving tracks of swift heavy ions in a-Si containing metal impurities<sup>1</sup>. Small angle X-ray scattering appeared to show impurity redistribution during the ion implantation, and for this interpretation to be valid, it is required that the impurities do not diffuse at room temperature, not even over a small distance. Our present measurement thus will be important for the interpretation of the small angle X-ray scattering measurement.

### Conclusion

The room-temperature diffusivity of Cu and Ag in amorphous silicon was studied and found to be below  $3 \times 10^{-24} \text{ m}^2/\text{s}$ , which was the limit of detection after one year of storage. The low value of the room-temperature diffusivity is important for the interpretation of forthcoming measurements on high-energy ion tracks in amorphous Si.

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<sup>1</sup>Xie et al. Unpublished.