Transient diffusion of Ga in amorphous silicon

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The redistribution of Ga in amorphous silicon (a-Si) in the temperature range of 560–830 K by means of medium-energy ion scattering has been studied. During the initial 10 s of the annealing the diffusivity shows a transient behavior that is attributed to the change in the relaxation state of the amorphous matrix. From 560 to 830 K the diffusivity during relaxation is enhanced by seven to two orders of magnitude compared to the value for bulk a-Si. Possible models that show the observed transient diffusion behavior are discussed.

INTRODUCTION

The diffusion of dopants is an important parameter in the fabrication of delta-doping layers in crystalline Si (c-Si). In conventional Si molecular beam epitaxy (MBE) it has proved impossible to confine dopants like Ga or Sb to a few atomic layers.[1] In this article a solid phase epitaxy growth (SPEG) method is used to overcome the strong tendency of the dopant atoms to float on the surface at typical growth temperatures of 900–1000 K. The dopant atoms are buried underneath an amorphous layer that is subsequently crystallized *in situ* by heating to 830 K.[2] Recently we have grown Ga delta-doping layers with a full width at half-maximum (FWHM) of less than 1 nm and with almost all the dopants residing on substitutional sites.[3]

When using SPEG, one of the limiting factors in obtaining sharp doping profiles is the diffusion of the dopants into amorphous Si (a-Si) at the regrowth temperature. The structure of a-Si is a covalently bonded continuous random network, where the angles between bonds are distorted with respect to the ideal tetrahedral angle in c-Si. Upon thermal annealing defect complexes in the amorphous structure are annealed out and are accompanied by a decrease in the average bond angle distortion.[4] This process is known as structural relaxation.[5] Amorphous Si exhibits a continuous range of structural configurations in the temperature range of 300–1070 K.[6,7]

In order to obtain more insight into the redistribution of Ga during the preparation of delta-doping layers in c-Si,[8] we have investigated the diffusion of Ga in a-Si. We have found that the redistribution of Ga in *unrelaxed* a-Si in the temperature range of 560–830 K shows a transient by which the diffusion is enhanced by several orders of magnitude with respect to relaxed a-Si.

EXPERIMENT

For the Ga diffusion experiments three identical a-Si/Ga/a-Si sandwiches were grown on the native oxide of Si(001) substrates. The Si(001) samples ($16\times6\times0.4$ mm^3) were cut from a phosphor doped wafer with a resistivity of 5–10 Ω cm. The silicon oxide layer at the interface between the crystalline substrate and the amorphous film prevented the a-Si from regrowing epitaxially. Each sample was annealed at a different temperature and subsequently analyzed *in situ* using medium-energy ion scattering (MEIS).[9] The depositions were done in an ultrahigh vacuum system for MBE that is connected to the ion scattering chamber.[10] All the layers were grown at room temperature. First, an a-Si layer of ~15 nm was deposited onto the native oxide of the substrate using an electron-beam evaporator at a deposition rate of 0.2 nm/s. Next, a submonolayer of elemental Ga was deposited from a Knudsen cell containing a graphite crucible. The cell was used at a temperature of 1160 K, which resulted in a flux of 7×10^{12} atoms/cm^2 s. Finally, a top layer of ~3 nm of a-Si was grown at a rate of 0.05 nm/s. Reflection high-energy electron diffraction showed no diffraction spots or rings, which indicate an amorphous structure. After the samples had been transferred to the scattering chamber, Auger-electron spectroscopy indicated clean surfaces with C and O contamination only below the detection limit of 1% of a monolayer (ML). [One ML is defined as the number of atoms in the Si(001) plane and equals 6.78×10^{14} atoms/cm^2.] Temperatures were measured using an optical pyrometer. The temperature scale was calibrated to within an accuracy of ±30 K for temperatures below ~750 K and to within an accuracy of ±10 K in the range of 750–950 K.[3]

MEIS, in combination with ion shadowing and blocking effects, was used to determine the morphology of the grown structures after each of the annealing stages. The incident beam of 100 keV protons was aligned with the $[11\bar{1}]$ direction of the c-Si substrate. The direction of detection was along the [111] axis. In this doubly aligned geometry the deeper layers of the c-Si hardly contributed to the backscattering signal. Since the energy loss of H ions is well known in the energy range from 50 to 200 keV, the backscattering energy range can be converted into a depth scale in the sample. For the experiments described here, the depth conversion corresponded to 450 eV/nm. The energy resolution was limited by thickness variations of the overlying a-Si layer and energy straggling of the backscattered ions. The corresponding depth resolution was ~1.0 nm (FWHM) in this experiment.[3]

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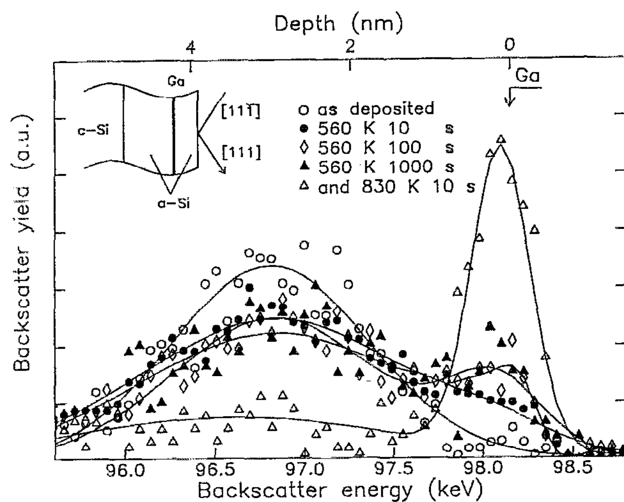

FIG. 1. High resolution MEIS spectra obtained for the as-deposited and annealed Ga profiles of an a-Si/Ga/a-Si sandwich. The sample contained 0.66 ML of Ga. The scattering geometry is shown in the inset. The arrow indicates the energy expected for the elastic backscattering of Ga surface atoms. The solid curves are to guide the eye.

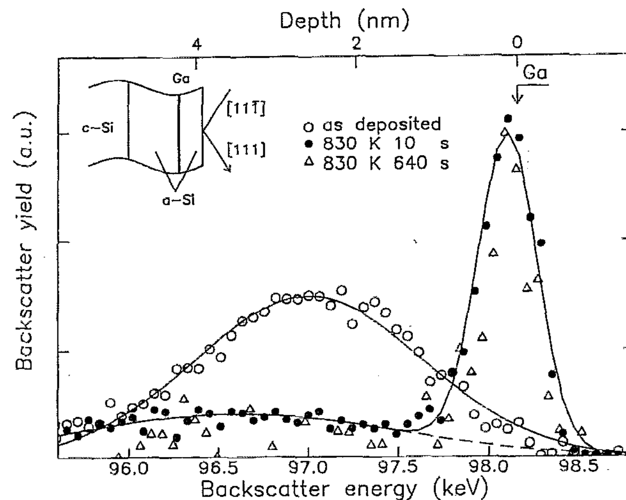

FIG. 2. High resolution MEIS spectra of Ga after different annealings at 830 K. The fraction of Ga atoms at the surface is 0.34 ML. The scattering geometry is shown in the inset. The solid curves serve to guide the eye. The dashed line is a Gaussian fit to the buried Ga profile.

RESULTS

The three a-Si/Ga/a-Si sandwiches were annealed at 560, 670, and 830 K, respectively, for different periods of time each. After each annealing, MEIS spectra were recorded. Figure 1 shows the backscattering peak of 0.66 ML of Ga buried in the a-Si sandwich. At the surface about 0.03 ML of Ga atoms is visible. The as-deposited FWHM of the Ga profile was 3.4±0.2 nm in the case of all three samples. In the case of the first sample, the width of this profile broadened to 3.9±0.2 nm upon annealing to 560 K for 10 s. Annealing for an additional 10 s at 560 K resulted in a slight increase of the amount of Ga atoms at the surface from 0.03 to 0.07 ML (not shown). Further annealing for a total of 100 and 1000 s did not change the profile. The second sample was annealed to 670 K. After 10 s at this temperature the as-deposited profile broadened from 3.4 to 4.2±0.3 nm, and 0.25 ML of the deposited Ga atoms became detectable at the surface (also not shown). Longer annealing at this temperature did not cause the Ga to redistribute any further. Figure 2 shows the depth distribution of Ga in the third sample, which was annealed to 830 K. After a first annealing of 10 s the profile broadened from 3.4 to 5.3±0.4 nm, and 0.34 ML of the Ga atoms was detected at the surface. Additional annealing to a total of 640 s left the Ga atoms immobile as far as could be detected by ion scattering.

Thus for all three samples we observed a rapid Ga redistribution that stopped within ~10 s at each temperature. In addition, the first sample was subjected to extra annealing to 830 K for 10 s, i.e., it was given the same treatment as the third sample. This caused a further transient redistribution of the Ga, and the resulting profile (open triangles in Fig. 1) matches that of the third sample (closed circles in Fig. 2) to within 5%.

The diffusion transients occurred in the temperature and time ranges in which the a-Si is known to exhibit structural relaxation. In order to verify whether there is a relationship between the two phenomena, a fourth sample was made in which the underlying a-Si layer was *relaxed* by thermal annealing to 750 K for 3 min prior to the deposition of 0.40 ML Ga. After the deposition of the top layer of Si at room temperature the as-deposited profile had a width of 2.5±0.2 nm. This is significantly less than the 3.4 nm width obtained for the unrelaxed samples and is equal to that observed in earlier studies for c-Si/Ga/a-Si sandwiches.[3] Next, the sample with the relaxed a-Si layer was isochronally annealed for 60 s in a sequence of four different temperatures (see Fig. 3). The broadening of the Ga profiles was significantly less than that observed in the case of the unrelaxed samples (see Figs. 1 and 2). At the highest annealing temperature of 800 K the Ga profile broadened to 3.4±0.4 nm (Fig. 3).

Figure 4(a) summarizes the measured "final" profile widths as a function of the annealing temperature for the three unrelaxed samples and for the sample with the relaxed/unrelaxed a-Si layers. We conclude that both the starting width and the rate at which the width increases were smaller in the case of the sample with the relaxed a-Si layer. The difference in Ga redistribution is also demonstrated by the number of Ga atoms found on the surface after annealing. A larger fraction of the Ga atoms was found on the surface in the case of the sample with the relaxed layer [Fig. 4(b)]. The observed transient diffusion is thus clearly related to the relaxation state of the a-Si.

For our study to be relevant, it is important that the film indeed stays amorphous during thermal annealing. The Si trailing edge of the four samples was checked to ascertain that the a-Si had not epitaxially crystallized upon annealing. Indeed, in the case of all annealed samples the native oxide

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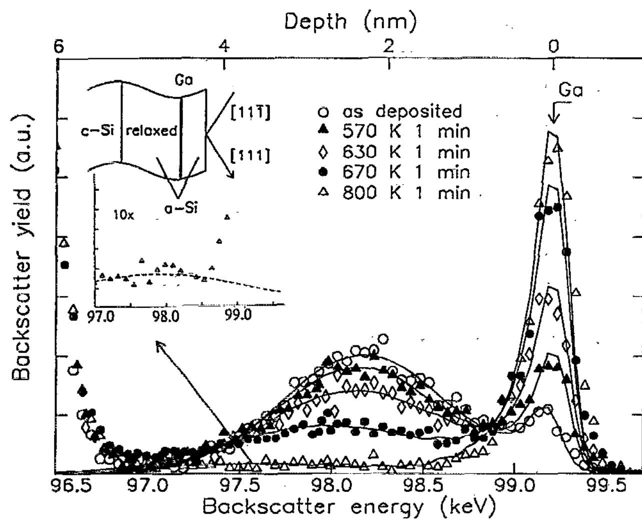

FIG. 3. High resolution MEIS spectra of 0.40 ML of Ga in an a-Si/Ga/a-Si sandwich. The first layer of Si was deposited onto the native oxide of the substrate at room temperature and was relaxed by annealing at 770 K for 60 s. Subsequently, the Ga and Si layers were deposited at room temperature. After the final annealing at 800 K 0.35 ML of Ga atoms was at the surface. The arrow indicates the backscatter energy for the surface Ga atoms. On the low energy side of the spectrum the leading edge of the Si backscatter peak is just visible. The solid curves are to guide the eye. The dashed line in the inset is a Gaussian fit to the buried Ga profile.

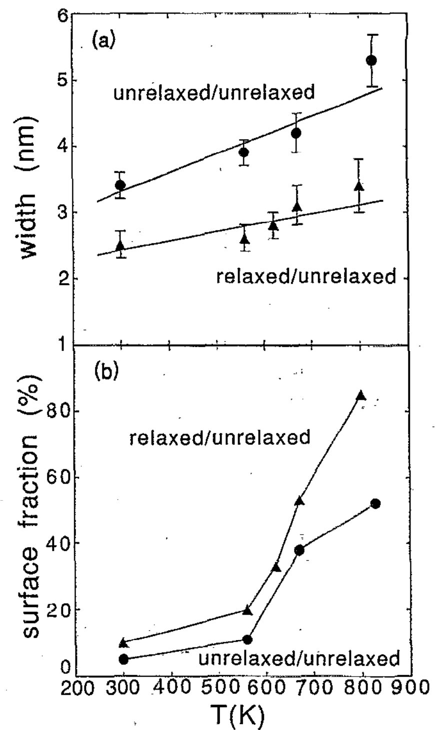

FIG. 4. (a) Observed widths of the Ga backscatter profile as a function of the annealing temperature. (λ) 0.66 ML Ga buried in an unrelaxed a-Si/Ga/a-Si sandwich. (σ) 0.40 ML Ga buried in an a-Si/Ga/a-Si sandwich with a relaxed a-Si layer grown prior to Ga deposition. (b) Ga surface fractions as a function of the annealing temperature. The symbols correspond to the results of measurements performed on the samples described in (a).

in the samples was checked to ascertain that the a-Si had not epitaxially crystallized upon annealing. In all cases in the annealed samples the native oxide inhibited epitaxial crystallization. At temperatures up to 830 K random nucleation is unlikely because 70 h are required for random crystallization at this temperature.[11] However, in the case of high dopant concentrations (>0.5 at %), several ion implanted dopant systems in Si show an amorphous to polycrystalline transformation after annealing at temperatures much lower than the 770 K usually required for SPEG.[12,13] Crystallization may occur in the amorphous film away from the c-Si/a-Si interface, as in the case of In in Si.[14] We performed some additional experiments to check this possibility for the samples with Ga. First, we followed by ion scattering the crystallization of an a-Si/Ga/a-Si sandwich that had been grown on a *clean* Si(001) surface and had subsequently been annealed at 830 K in time intervals of 10 s. The moving c-Si/a-Si interface and the low minimum yield behind the Si surface peak indicated that the amorphous layer became progressively monocrystalline.[8] This observation excludes the possibility of the formation of polycrystalline Si through the nucleation of Si at the Ga spike. High-resolution transmission electron microscopy (HTREM) was also performed on a sample consisting of a sandwich of a-Si/Ga/a-Si layers deposited onto the native oxide of a Si(001) substrate at room temperature. After annealing at 470 K for 60 s and then at 570 K for 60 s cross-sectional micrographs showed that the matrix is still amorphous.[15]

DISCUSSION

Our data show that the diffusion of Ga exhibits *transient* behavior in the temperature range studied, i.e., the redistribution takes place in a relatively short period (~10 s), after which the Ga atoms are practically immobile.

From the broadening of the widths of the Ga backscatter energy spectra the transient diffusion coefficients were derived. Starting from the FWHM values of the as-deposited Ga profiles (3.4 nm) the diffusion length L after annealing was calculated. Hereafter L^2 (at temperature T) is defined as the difference between the square of the width (FWHM) of the Ga profile at temperature T minus the square of the width of the as-deposited Ga profile. Since the annealing time t is known, the diffusion coefficient D follows from

$$D=\frac{L^2}{t}. \quad (1)$$

We have found lower limits for the transient diffusion coefficients of 3.7×10^{-15} cm^2/s at 560 K, 6.0×10^{-15} cm^2/s at 670 K, and 1.7×10^{-15} cm^2/s at 830 K. These are lower limits because the redistribution takes place very rapidly in a period that may be less than 10 s and therefore the actual diffusivity may be higher.

In the temperature range from 830 to 950 K the diffusion of Ga into a-Si has been found to exhibit an Arrhenius type of behavior with an activation energy of 1.9 eV.[16] Extrapolation of this diffusion coefficient to lower temperatures gives 7×10^{-22} cm^2/s at 560 K, 5×10^{-19} cm^2/s at 670 K, and 3×10^{-16} cm^2/s at 830 K. The observed transient diffusion is thus several orders of magnitude higher than expected for

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bulk amorphous material. Clearly, changes in the structure of the a-Si have a great effect on the redistribution of Ga in a-Si. It is known that the a-Si structurally relaxes over the whole temperature range we used.[6,7] It has been shown that the random network reaches a pseudosaturated level of relaxation after annealing at each temperature with a $1/e$ relaxation time of 10–100 s.[17]

In principle, three possible explanations exist for the transient observed, namely: (1) concentration-enhanced diffusion, (2) trapping and detrapping at defects present in a-Si, and (3) kick-out by Si interstitials released during relaxation. We will now discuss these three possibilities.

One possible explanation is concentration-enhanced diffusion. This could lead to a transient since the diffusion could be enhanced until the concentration drops below a certain level. The unrelaxed samples, which showed the strongest transient, had a Ga coverage of 0.66 ML, whereas the relaxed/unrelaxed sandwich, which showed less broadening, had smaller coverage of 0.40 ML. However, we observed that the broadening of the unrelaxed samples (all with 0.66 ML Ga coverage) depended on temperature only, not on time. If the diffusion were enhanced by the concentration, then the same end state should have been reached (at different rates) for each temperature. However, at each temperature broadening was observable (which showed that the Ga was mobile), and therefore each temperature clearly had its own final Ga distribution. Thus the transient cannot be explained by concentration-enhanced diffusion.

A second possibility is that trapping at defects in the a-Si is important. Coffa *et al.*[18] have proposed this mechanism to explain their data on the diffusion of transition metals in a-Si. These transition metals undergo direct interstitial diffusion and are temporarily trapped at defects.[18] Assuming that Ga is also trapped at defects in the a-Si, at each temperature, Ga atoms would be released when the associated defects are annealed out. The Ga atoms then undergo a fast diffusion until they are trapped again, either at intrinsic defects or at the surface. This model does indeed explain the transient behavior, but predicts that the diffusion in relaxed a-Si is *higher* than that in the unrelaxed material, as the latter material has a higher trap density. We found that the diffusion in relaxed material is *lower* than that in unrelaxed material and, therefore, the trapping model does not explain our observations.

The third possible mechanism involves Si interstitials in the a-Si. For many impurities it has been found that there are similarities in the diffusion mechanism in c-Si and a-Si.[18–20] This is probably caused by the fact that the local order in a-Si and c-Si is basically the same.[18] In c-Si Ga diffuses through a substitutional/interstitial interchange mechanism (interstitialcy mechanism).[21] Our observations of transient-enhanced diffusion in a-Si can be explained by the same mechanism in which kick-out reactions occur between *substitutional* Ga atoms and Si *interstitials*. Fast diffusion may occur because Si interstitials are released into the unrelaxed a-Si during thermal annealing. At a given temperature the structural relaxation reaches a pseudosaturation level, and the subsequent drop in the concentration of Si interstitials leaves the Ga atoms practically immobile after the high-mobility transient. At a higher temperature, the process repeats itself for a new range of structural defects. The difference in Ga diffusion between the unrelaxed samples and the sample with the relaxed a-Si layer is then caused by the lower concentration of Si interstitials present in the latter material during annealing. Thus the broadening is less in the case of the Ga sandwiched between the relaxed and unrelaxed materials [Fig. 4(a)], whereas more Ga reaches the surface since the Ga is reflected at the interface with the relaxed material [Fig. 4(b)]. This model assumes the existence of Si interstitials in a-Si during structural relaxation. The existance of such interstitials has not been demonstrated, but models assuming Si interstitials have been proposed to explain the transient behavior of dopant diffusors in Si.[20]

The second (trapping) and third (interstitial) models are, of course, related. In both models the structural relaxation of a-Si during annealing leads to a diffusion transient. The difference is related to the importance of traps for the impurity of interest. The transition metals studied by Coffa *et al.*[18] underwent long-range interstitial diffusion that was retarded by traps. Ga, on the other hand, diffuses only from one substitutional site to the next: essentially the entire material acts as a trap and, therefore, the additional defects in unrelaxed a-Si are not important as traps, but are very important as sources of interstitials.

CONCLUSIONS

We have found that the diffusion of Ga in a-Si is strongly enhanced during the structural relaxation of the amorphous matrix. In an unrelaxed material the diffusion is enhanced by many orders of magnitude in the temperature range studied (560–830 K). The redistribution mechanism shows transient behavior. After the initially enhanced diffusion, the diffusion of the Ga atoms becomes negligibly low. The observed redistribution can be explained by a substitutional/interstitial interchange mechanism during the thermal relaxation of the a-Si.

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