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COHERENT-PRECIPITATE FORMATION IN TI-IMPLANTED Si

B. R. Appleton, J. Narayan and C. W. White
J. S. Williams and K. T. Short

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COHERENT PRECIPITATE FORMATION IN Tl IMPLANTED Si*

B. R. Appleton, J. Narayan and C. W. White
Solid State Division, Oak Ridge National Laboratory
Oak Ridge, Tennessee 37830

and

J. S. Williams and K. T. Short
RMIT
Melbourne, Australia

ABSTRACT

Ion scattering, ion channeling, and cross-section electron microscopy were used to investigate Si single crystals implanted with $^{205}\text{Tl}^+$ ($0.29 - 1 \times 10^{16} \text{ Tl/cm}^2$, 90 keV) and annealed with pulses (1.6 J/cm^2 , 15 ns) from a ruby laser. Coherent precipitates of Tl were found to form as a result of laser processing. The systematics of the effect are presented and a formation mechanism proposed.

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1. INTRODUCTION

The initial motivation for this work was to investigate the effects of pulsed laser annealing on the acquired lattice sites of Tl implanted into Si at various temperatures. Investigations of a wide range of group III and V dopants implanted in Si have shown that pulsed laser processing can lead to the formation of supersaturated substitutional alloys [1,2], unique lattice alterations [1,3], and even amorphous layers [1,4] as a consequence of the extremely rapid laser melt quenching process. Previous studies of the Si(Tl) system have shown that room temperature as well as elevated temperature implantations, and thermal annealing in some cases, can result in substantial amounts of interstitial Tl [5-9]. Consequently, an investigation of the effects of pulsed laser annealing of the ion implanted Si(Tl) system was expected to provide additional insights into the solute interactions which occur during rapid recrystallization. A careful analysis by ion scattering/channeling and transmission electron microscopy showed that the laser melting and rapid recrystallization led to the formation of Tl precipitates which were coherent with the Si host. This paper presents the results of this coherent precipitate study and suggests a formation mechanism. The results of implantations at higher temperatures will be presented elsewhere.

2. RESULTS AND ANALYSIS

The samples investigated were p-type Si {100} single crystals implanted near room temperature with $^{205}\text{Tl}^+$ to doses of $2.9 \times 10^{15} \text{ cm}^{-2}$ and $1 \times 10^{16} \text{ cm}^{-2}$ at 90 keV. Portions of the implanted samples were annealed using a Q-switched ruby laser (15 ns pulse duration). The samples were

then analyzed with ion scattering/channeling techniques and transmission electron microscopy.

Typical ion scattering/channeling results are shown in Fig. 1 for a Si single crystal implanted with 1×10^{16} $^{205}\text{Tl}/\text{cm}^2$ and annealed with a single $1.6 \text{ J}/\text{cm}^2$, 15 ns pulse from the ruby laser. The channeling spectrum in Fig. 1 (open triangles) was obtained with the 1.5 MeV He^+ beam incident parallel to $\langle 111 \rangle$, while the reference random spectrum (open circles) was obtained by continuously rotating the crystal to average over many crystallographic orientations. Comparison of the implanted impurity profiles in Fig. 1 shows that the fraction of Tl which is substitutional along $\langle 111 \rangle$ following pulsed laser annealing is quite small. Despite this, and the fact that the implanted Tl concentration is quite large, comparison of the channeled and random Si spectra shows that the silicon host is relatively good, unstrained, single crystalline material since the minimum yield ($\chi_{\min} \lesssim 0.06$) is comparable to that measured from the unimplanted silicon ($\chi_{\min} \lesssim 0.03$). Analysis of the $\langle 110 \rangle$ axial direction of this crystal showed similar results with a slightly lower $\chi_{\min}$ and a larger fraction of Tl on substitutional lattice sites. Annealing this sample with a second $1.6 \text{ J}/\text{cm}^2$ laser pulse resulted in no significant changes. However, the residual disorder and substitutional Tl concentration did change near the edge of the laser spot.

The Si crystal implanted with 2.9×10^{15} $^{205}\text{Tl}/\text{cm}^2$ and annealed ($1.6 \text{ J}/\text{cm}^2$, 15 ns) showed features similar to those for the sample of Fig. 1. Detailed angular scans were made across the major axial and planar directions of both samples to determine the relative Tl lattice sites. Measurements from the 2.9×10^{15} $^{205}\text{Tl}/\text{cm}^2$ sample are shown in Fig. 2 for

scans across $\langle 110 \rangle$ tracking in the $\{100\}$ planes and across $\langle 111 \rangle$ tracking in the $\{110\}$ planes. The $\langle 110 \rangle$ scan clearly shows that Tl atoms are aligned with the Si lattice along this direction, but the Tl minimum yield is much higher and its angular half width much narrower than Si. Although not as pronounced, the $\langle 111 \rangle$ data in Fig. 2 also show a preferential alignment with Si. Scans taken along the $\langle 100 \rangle$ axial direction were comparable to the $\langle 110 \rangle$ results in Fig. 2, and $\{100\}$ planar scans also showed Tl alignment. Angular scans for the higher dose sample were qualitatively the same. Analysis of the as-implanted portions of both samples showed that the near surface regions had been made amorphous by the Tl implantations and consequently no preferential lattice sites could be detected. This is not inconsistent with early results where large interstitial Tl concentrations were reported since these results were either obtained from lower dose implantations (10^{13} - 10^{15} cm $^{-2}$), or were made on crystals that were heated during implantation and/or annealed afterwards [5-9].

These ion channeling results show that large concentrations of Tl have been incorporated into the Si host in a relatively strain-free environment, and although the detailed angular scans show alignment between the Tl and host Si atoms the widths and minimum yields are not consistent with expectations for substitutional Tl. This suggested that the Tl might be present as coherent precipitates. To verify this cross-section microscopy was performed on the sample implanted with 2.9×10^{15} Tl/cm 2 and annealed with a 1.6 J/cm 2 laser pulse. Figure 3(a) shows a cross-section electron micrograph taken under bright-field, kinematical diffraction conditions. Thallium precipitates exhibit black contrast under these diffraction conditions. The average size of the precipitates was determined to be 100 Å with the precipitate distribution extending up to 600 Å from the surface. The same area

of a specimen imaged under dynamical conditions is shown in Fig. 3(b). The precipitates exhibit black-white contrast indicating the presence of unrelaxed strains around the precipitates. This contrast behavior under dynamical diffraction conditions, is consistent with the precipitates being coherent with the silicon matrix. Additional studies are planned to determine the relative orientation of the coherent precipitates.

4. DISCUSSION

The ion scattering/channeling and TEM results show that Tl precipitates form coherently with the Si host lattice as a result of pulsed laser annealing. The mechanism by which this occurs is probably as follows. The laser pulse leads to near-surface melting beyond the range of the implanted Tl distribution. The near surface remains molten for times $\tau \sim 200$ ns and as the heat is conducted away to the substrate the molten silicon crystallizes very rapidly by liquid-phase-epitaxial regrowth [1,2]. During the time the silicon is molten, assuming a diffusion constant for Tl in molten silicon $D_l \sim 5 \times 10^{-4}$ cm²/s [10], the Tl can move distances $\sim \sqrt{D_l \tau} \sim 10^3$ Å. Calculations show that such mobility is sufficient to nucleate precipitates of the dimensions observed while the surface is molten. This process is favored because Tl is immiscible in liquid silicon [11]. Solid state diffusion of Tl ($D_s = 8 \times 10^{-14}$ cm²/s at 1100°C) [12] results in mobilities much too low ($\sqrt{D_s \tau} \sim 10^{-2}$ Å) to nucleate such precipitates. However, because of the much lower melting temperature of Tl (303°C) compared to Si (1410°C) coherence may be established when the still-molten Tl precipitates solidify in the crystalline Si matrix.

These results illustrate the utility of ion implantation doping and pulsed laser processing for studying the formation mechanisms and kinetics

of precipitate growth. By controlling the species and concentration of the implanted impurity and the time the surface is molten a systematic evaluation of the process can be made. Recently coherent precipitate formation has been investigated during solid-phase-epitaxial growth using ion channeling and TEM techniques [13]. These studies provide additional dimensions for investigating the precipitation process.

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FIGURE CAPTIONS

- Fig. 1 1.5 MeV He ion scattering/channeling spectra from a Si {100} single crystal ion implanted (1×10^{16} Tl cm^2) and laser annealed (1 pulse, 1.6 J/cm^2), for incidence-parallel to $\langle 111 \rangle$ (open triangles) and in a random (open circles orientation).
- Fig. 2 Detailed angular scans showing the near-surface yields from Tl and Si for 1.5 MeV He ions incident near $\langle 110 \rangle$ and $\langle 111 \rangle$ of a Tl implanted and laser annealed Si single crystal.
- Fig. 3 Cross section electron micrographs of a Tl implanted ($2.9 \times 10^{15}/\text{cm}^2$) pulse laser annealed (1.6 J/cm^2) Si single crystal.

Fig. 1

Fig. 2

Fig. 3