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Amorphization Processes in Ion Implanted Si: Temperature Dependence

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Temperature dependence of amorphization processes in ion-implanted Si has been investigated using Raman spectroscopy together with cross-sectional transmission microscopy. The crystal Si Raman peak decreased and the amorphous Si (a-Si) peak became predominant as the substrate temperture was decreased from 23°C to -200°C. Based on the analysis of bond angle deviations derived from the a-Si peaks, we have proposed a model in which an accumulation of small vacancies induces amorphization at low temperatures, while larger vacancy complexes play an important role

1. INTRODUCTION

Ion implantation is a key technology for fabrication of doped layers in semiconductor microelectronic devices. Since defects formation is associated with ion implantation, it is essential to anneal out these defects for device applications. Recently, it has been reported that amorphization and annealing characteristics of ion implanted Si were strongly dependent on substrate temperature during ion implantation and that low temperature (-200°C) implantation of B (200 keV, 10^{15} cm^{-2}) led to complete amorphization resulting in a remarkable reduction of extended defects after annealing at 900°C for 30 minutes.[1] Although the temperature dependence of ion-beam-induced amorphization has been generally considered to be due to competition between defect accumulation in an energetic collision cascade and outdiffusion of the defects from the cascade,[2] the amorphization mechanism is still contraversial and not yet fully understood.[3]

In this paper, we have investigated substrate temperature effects on amorphization processes of Si during self-ion implantation using Raman spectroscopy and cross-sectional transmission electron microscopy (TEM).

2. EXPERIMENTAL PROCEDURE

The substrates used in these experiments were optically flat Czochralski-grown n-type Si(100) wafers with a resistivity of 10 Ω-cm. The substrate temperature was varied from room temperature (23°C) to -200°C using a temperature-controlled Cu block with an accuracy of ±2°C. Si^+ ion implantations were performed with the substrates oriented 4° off-normal to the incident ion beam for suppression of channeling effects. The ion energy, dose, and current density were 200 keV, $5x10^{14}$ cm^{-2}, and 0.11 μA/cm^2, respectively.

Raman measurements were carried out at room temperature using a Spex Triplemate 1877. An argon-ion laser beam tuned to 488 nm was grazingly incident on the sample surfaces and scattered light was observed in the direction normal to the surface through a f/1 lens and dispersed in a f=600 mm single-monochromator with a 1800 l/mm grating. The optical signal was then detected by a photomultiplier and processed by a SPEX DM 3000 photon counting system. The monochromator scanning step was 1 cm^{-1} with a 10 cm^{-1} spectral slit width and the integration time was 5 seconds for each step.

3. RESULTS AND DISCUSSIONS

Figure 1 shows Raman spectra from ion implanted Si at various substrate temperatures Ts=23~-200°C. The spectrum from undamaged crystal Si (c-Si) is also shown for reference. The c-Si Raman peak at 521 cm^{-1} corresponds to the triply degenerate k≈0 transverse optical (TO) phonon modes and a weak peak at 305 cm^{-1} is due to two-phonon transitions.[4] The spectrum for Ts=23°C is similar to that of the undamaged Si, although the c-Si peak intensity markedly decreases due to ion-induced defects. As Ts is decreased, the sharp c-Si peak decreases and a broad peak centered at ~480 cm^{-1} corresponding to the amorphous Si (a-Si) peak contributed from the all TO phonon modes becomes predominant for Ts=-50, -125, and -200°C. The centers and widths of these peaks were determined based on a curve fitting using a Voight function for the c-Si peak and a Gaussian function for the a-Si TO peak. Since the lower energy part of the a-Si peak includes other phonon modes such as longitudinal optical modes, the high-energy side of the a-Si peak was taken for the fitting. As shown in Fugure 1, the c-Si peak centers shift to the low energies as Ts is decreased, which can be attributed to an increase of plasticity in the Si lattice due to a formation of buried amorphous layer. However, the observed peak shifts are smaller than those obtained in the previous study on the dose dependence of amorphization where shifts up to ≈ 6 cm^{-1} were observed for the 100 keV Si^+ ion-implanted samples with various doses (0.8-8.5x10^{14} cm^{-2}) at room temperature.[5]

The fitting results for the a-Si TO peaks are shown

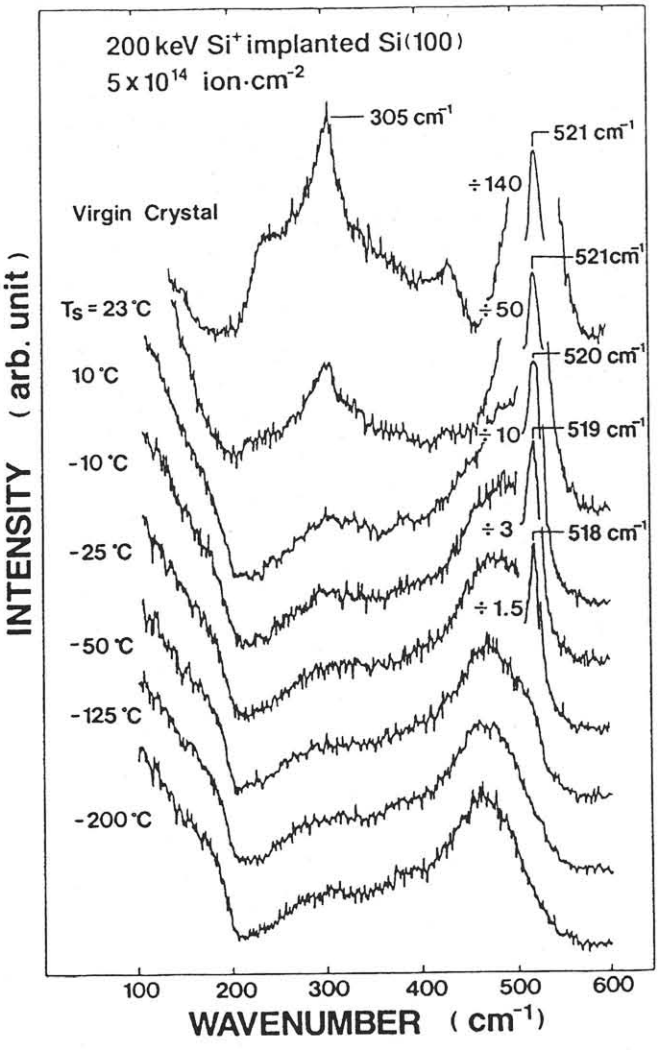

Fig.1 Raman spectra for self-ion implanted Si(100) at various T_s

in Figure 2. Both the peak centers and widths drastically change between Ts=10 and -50°C suggesting that there is a large structural change in this temperature range. It should be noted that as all Raman measurements were carried out at room temperature, all the samples implanted at lower Ts were in effect annealed at room temperature. The optical extinction coefficients were determined as a

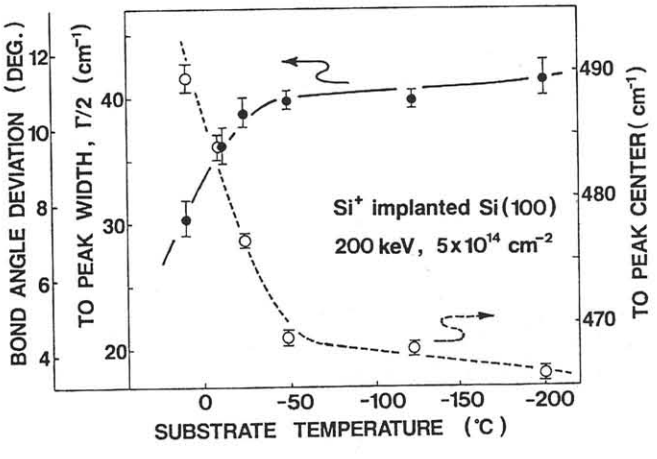

Fig.2 Fitting results for the a-Si TO peak centers and widths together with the calculated bond angle deviations.

function of the substrate temperature using *in-situ* ellipsometry measurements and indicated that substantial structural changes occured at ~ -100°C. [1)]

Figure 3 shows the cross-sectional TEM micrographs from the same samples. No amorphization can be seen at Ts=23°C, while as Ts is decreased amorphization occurs around the most heavily damaged region centered at a depth of ~270 nm (Ts=10°C). The amorphous region proceeds to the surface (Ts=-10, -25, and -50°C) and finally the whole implanted layers are amorphized at Ts=-125 and -200°C. These results are consistent with the Raman spectra described in Figure 1.

Beeman et al. proposed the following linear relationship between the TO peak full width of the half maximum Γ (cm^{-1}) and bond angle deviation $\Delta\theta$ (degree) in a-Si, [6)]

$$\Gamma/2 = 7.5 + 3\,\Delta\theta. \qquad (1)$$

Based on Eq. (1), $\Delta\theta$ was calculated and is shown in Figure 2. The bond angle deviation $\Delta\theta$ increases from 8° to 11° as Ts is decreased. These $\Delta\theta$ values are similar to those of as-implanted a-Si, 12° and annealed a-Si, 11° (200 °C for 3 hours) and 10° (400 °C for 3 hours). [7)] The results suggest that free energies can be described as a funciton of $\Delta\theta$ as schematically illustrated in Figure 4. It is known that, based on computer simulations and Raman spectroscopy measurements, [8)] that there is no amorphous phase with $\Delta\theta$ < 7°. On the other hand, there exist various kinds of amorphous phases between ~7° and 12°. Since bond angle distortion energies are propotional to $(\Delta\theta)^2$, the free energy increases with increasing $\Delta\theta$. The typical energy difference was estimated to be 0.04 eV/atom using differential scanning calorimetry measurements. [9)] The $\Delta\theta$ values corresponding to the local minima may well depend on the details of the amorphization processes and it is possible that various kinds of amorphous states correspond to the same $\Delta\theta$.

According to the cystallization data of deposited a-Si films, it is suggested that the cohesive energy difference between the a- and c-Si phases is 0.14 eV/atom. [10)] The large activation barrier between the amorphous and crystalline ($\Delta\theta$=0) phases is due to existence of 5- or 7-membered rings in a-Si. These rings do not exist in c-Si and it is necessary to break Si-Si bonds and transform the wrong rings to the correct ones, 6- or 8-membered rings, in order to form c-Si. The activation barrier was estimated at ≈3.7 eV [11)] which may correspond to the single-vacancy formation energy. For the defect laden crystal, $\Delta\theta$ is small and the free energies will be in the region illustrated in Figure 4.

Based on the schematic diagram described above, we propose the following model for the temperature effects on amorphization. Single vacancies generated by ion bombardment are frozen at Ts ~-200°C, while at Ts ~-100°C they can move and form divacancies. [12)] Interstitial Si may recombine with another single vacancy (Frenkel pair annihilation) or is trapped at some impurity even at low temperature. [12)] An accumulation of these small defects primarily composed of divacancies increases the free energy and it finally exceeds the activation barrier for crystalline-to-amorphous (c/a) phase transition. [13)] On the other hand, for higher Ts, in addition to more frequent defect annihilation, the small vacancies are mobile to form larger vacancy complexes which are more stable and thus the free energy decreases below the barrier for the c/a phase transition and the lattice is essentially crystalline,

although it is defective due to the larger vacancy complexes such as quadravacancies or P_3 centers.[14] These defected crystals are ultimately amorphized when densities of the larger vacancy complexes increase and the free energies exceed the activation barrier for the c/a transition. Although more complicated defects including interstitial atoms may be involved, the present model suggests that a-Si formed at higher Ts includes larger vacancy complexes which may well result in formation of extended defects such as dislocations after further high temperature annealing. This is consistent with the experimental results obtained for B and P ion-implanted Si.[1]

4. CONCLUSION

Substrate temperature effects on amorphization processes in self-ion implanted Si have been investigated using Raman spectroscopy and cross-sectional TEM. The sharp c-Si peak at 521 cm-1 decreased and the broad a-Si peak centered at ~480 cm^{-1} became predominant as the substrate temperatures of 200 keV Si^+ ion-implanted Si with a dose of $5x10^{14}$ cm^{-2} were decreased from 23°C to -200°C. The cross-sectional TEM micrographs also indicated that amorphization initially occured around the most heavily damaged region centered at a depth of ~270 nm and the amorphous region extended to throughout the implanted layer with decreasing temperature. Based on the analysis of bond angle deviations derived from the a-Si Raman peaks, the following model for the temperature effects on amorphization has been proposed. When Ts is low, single vacancies generated by ion bombardment are frozen or some of them can form divacancies and an accumulation of these small defects induces amorphization. For higher Ts, vacancies and divacancies may well gather together and form more stable vacancy complexes which gives rise to a defected crystal rather than amorphized Si resulting in dislocation formation after high temperature annealing.

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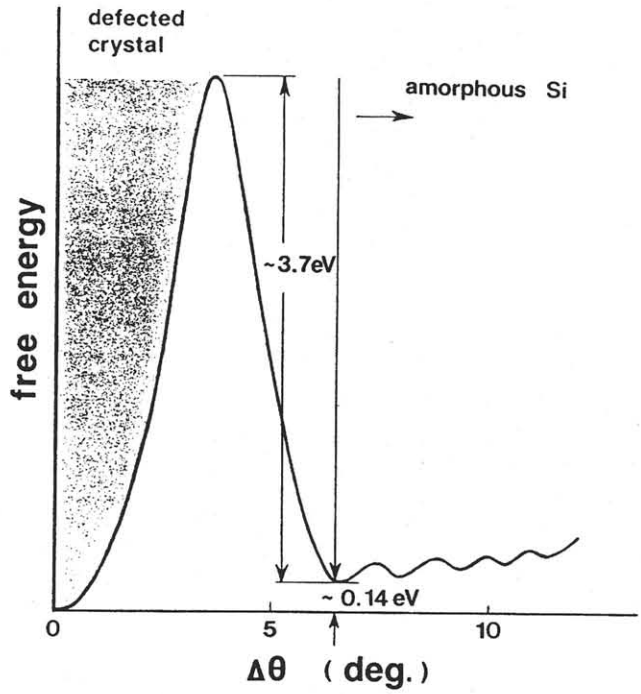

Fig. 4 Schematic diagram of the free energy as a function of Δθ.

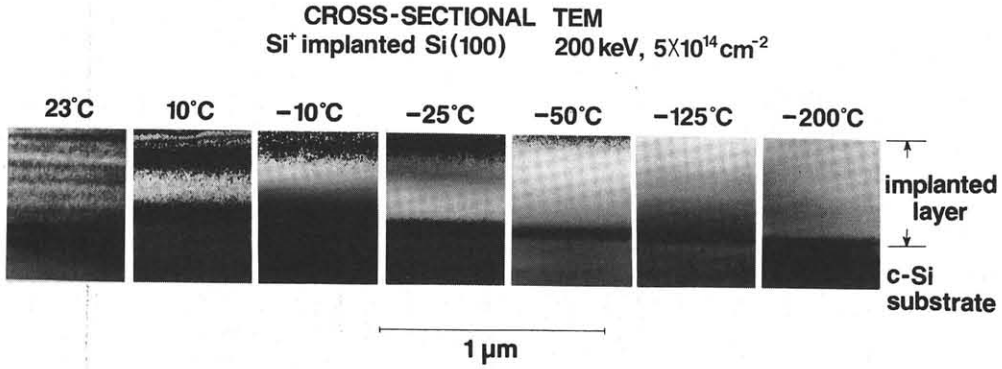

Fig.3 Cross-sectional TEM micrographs for the samples shown in Figure 1.