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THE INFLUENCE OF THE AMORPHOUS PHASE ON BORON ATOM DISTRIBUTIONS
IN ION IMPLANTED SILICON

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ABSTRACT

The nuclear reaction, $^{10}\text{B}(n, ^4\text{He})^7\text{Li}$, has been used to investigate the B depth distribution obtained by ion implantation into crystalline Si in a "random" direction and into amorphous Si produced by Si ion bombardment. The presence of the amorphous phase before B ion implantation has a pronounced effect on the B depth distribution (i.e. implantation into misaligned crystalline Si is not equivalent to implantation into amorphous Si). The presence of an amorphous phase has a marked effect on the amount of diffusional broadening of the B distribution during annealing at 900°C.

INTRODUCTION

A knowledge of the atom distributions resulting from ion implantation doping of semiconductors is important both from the point of view of testing theories of the mechanisms of energy loss of ions in solids and from the practical importance of ion implantation in semiconductor device technology. Many of the early determinations of the depth distribution of B ion

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implanted Si relied upon inference of the B atom profile from a determination of the free carrier profile. [1-7] In such experiments, the sample must be annealed at elevated temperatures in order to remove compensating defects generated by the radiation damage accompanying the ion implantation process. The B atom depth distributions are modified by diffusion processes occurring during annealing. Recently, experiments which determine the B atom depth distribution have been conducted. Cairns et al. used characteristic x-rays generated from B atoms by heavy ion bombardment in conjunction with layer removal techniques in order to profile B ion implanted layers. [8] These authors were forced to use very high B concentrations (greater than 10^{16} cm^{-2}) because of the lack of sensitivity of their technique. A sensitive technique capable of profiling B atom distributions over a wide concentration range is the ion microprobe, as demonstrated for B ion implantations by Lecrosnier and Pelous. [8] Several other groups have utilized the ion microprobe to obtain B atom distributions in ion implanted Si. [9-11] A technique for profiling B atom distributions in ion implanted Si which does not require layer removal and which has reasonable sensitivity is the use of the nuclear reaction $^{10}\text{B}(n, ^4\text{He})^7\text{Li}$. [12] In this investigation, we employed this nuclear reaction to compare the distributions obtained by ion implantation of B into amorphous Si and into crystalline Si in a "random" direction. We also studied the changes in such distributions caused by annealing at 600 and 900°C.

EXPERIMENTAL PROCEDURE

The analytical technique employed to obtain B distributions has been discussed in detail by Ziegler et al. [13] The basis for this technique is that ^{10}B atoms are converted into monoenergetic ^4He particles (1471 KeV) by the reaction with thermal neutrons. The number of ^4He particles emitted is proportional to the number of ^{10}B atoms in the sample and the energy of the ^4He after it emerges from the sample is a measure of the depth at which the ^{10}B atom was located. A semiconductor particle detector is used to measure the number and energy of the emitted ^4He particles. A calibration standard, prepared by a surface implantation of ^{16}O $^{10}\text{BF}_2$ cm^{-2} at 30 keV into Si, served to indicate both the number of counts per B atom and to calibrate the energy of the ^4He coming from ^{10}B at the wafer surface (1471 keV). A second energy calibration was obtained from ^{241}Am particles (5485 keV) emitted by a very thin source of ^{241}Am .

The experiments were conducted at the High-Flux Beam Reactor at the Brookhaven National Laboratory. The thermal neutron beam was calculated to have flux of $\sim 10^8$ neutrons $\text{cm}^{-2} \text{ sec}^{-1}$. The experimental apparatus is shown in Figure 1. The collimated

Fig. 1. A diagram of the scattering chamber. The thermal neutron beam traveled a short distance in air from the beam collimation system to the entrance.

beam entered the vacuum chamber holding the targets through .05 cm thick Al windows. The targets were placed at a 45° angle to the beam. Particles emitted normal to the semiconductor target face were detected by a solid state surface barrier detector subtending a solid angle of .019 sr. Typical counting rates were 300-700 counts min⁻¹ for a sample containing 10^{16} B atoms cm⁻².

The samples were prepared by ion implanting ^{10}B into <100> Si wafers (1 ohm-cm, n-type) offset by 7° to minimize channeling effects. The ion beam was raster scanned to provide uniform implantations. Dose rates during implantation were between .25 and 1 $\mu\text{a cm}^{-2}$. The annealing of samples was conducted in a tube furnace under a flowing N_2 atmosphere.

RESULTS AND DISCUSSION

In Figure 2, the depth distributions of ^{10}B are presented for samples implanted at 90°K (crosses) and 300°K (open circles) with 5×10^{15} ^{10}B ions cm⁻². The measured number of counts versus energy of ^4He emitted from the sample was normalized to the 10^{16} cm⁻² BF_2 standard and the energy scale was converted to a depth scale with existing literature values for the energy loss of ^4He in Si. [14] The actual B distribution is somewhat sharper than shown in Figure 1 because of the limited energy

Fig. 2. Depth distribution of 5×10^{15} 175 keV ^{10}B ions cm^{-2} implanted into Si in a "random" direction at room temperature (circles) and at 90°K (crosses).

resolution of the solid state particle detector and associated electronics (about 20 keV FWHM). For the 175 keV implants, the discrepancy is about 5%.

The major effect of low temperature implantation is to reduce the amount of B in the tail of the distribution and to enhance the skewness of the distribution. A plausible reason for this temperature effect on the profile is that the more deeply penetrating B has been partially channeled by scattering into oblique channels during room temperature implantations. Most of the 5×10^{15} ions cm^{-2} in the sample implanted at 90°K impinge upon amorphous Si, since a dose of 10^{15} B ions cm^{-2} is sufficient to produce a continuous amorphous layer at that temperature. [15] Such an amorphous layer would curtail further channeling. In experiments such as this in which damage by the implanted species is responsible for the eventual formation of an amorphous phase, channeling can occur during the initial implantation period during which the Si target is crystalline. The skewness observed in the low temperature implantation of ^{10}B into Si indicates that higher moments than the second moment are important in theoretical calculations based on the LSS theory of the ion depth distribution in amorphous solids. [16, 17]

A series of experiments was designed to compare ion

distributions obtained from implantations into crystalline Si in a "random" direction with implantations into amorphous Si and to check the effect of the amorphous phase on subsequent redistribution of the B during typical annealing treatments. The energy of the ^{10}B implantations (50 keV) was chosen to meet the following requirements:

- (1) The more narrow the ion depth distribution, the more pronounced are diffusion effects for a given annealing time; and
- (2) The ion depth distribution must be sufficiently broad to allow for the limited experimental energy resolution available.

Three room temperature implantation conditions were used:

(a) implantation of 50 keV ^{10}B ions into crystalline Si in a "random" direction

(b) implantation of 50 keV ^{10}B ions into crystalline Si in a "random" direction followed by making the surface amorphous to a depth of .5 to .6 μm by implantation of 1×10^{15} 280 keV ^{28}Si ions cm^{-2} (designated as post-damage with Si)

(c) implantation of 50 keV ^{10}B ions into amorphous Si prepared by ion bombardment of crystalline Si (designated as pre-damage with Si) with ^{28}Si ions.

The boron depth distributions obtained for these conditions are shown in Figure 3 with (a) represented by crosses, (b) by

Fig. 3. Depth distribution of 1×10^{15} 50 keV ^{10}B ions cm^{-2} implanted into (a) crystalline Si in a "random" direction (crosses); (b) crystalline Si in a "random" direction followed by post-damage with Si ions to form an amorphous surface layer (filled circles); and (c) amorphous Si produced by pre-damage with Si ions (open circles).

filled circles and (c) by open circles. The implantation of ^{10}B into amorphous Si definitely exhibits more skew in the profile than that obtained by implantation into a "random" direction in crystalline Si. The distribution is not changed by additional damage as indicated by the fact that the distributions for the B implant alone and the B implant followed by post damage with Si are essentially identical, an indication that channeling effects, not radiation enhanced diffusion, [18] are responsible for the "tail" in room temperature implantation of B into crystalline Si.

We also studied the effect on the B profiles of typical annealing cycles used to obtain a high degree of electrical activity of the implanted B; namely, 600°C when an amorphous phase is present [6] and 900°C when B alone is implanted. [2, 4] In Figure 4, the results for case (c); ^{10}B implanted into amorphous

Fig. 4. Depth distribution of 1×10^{15} keV ^{10}B ions cm^{-2} implanted into amorphous Si and with no anneal (solid line); 600°C for 30 minutes (crosses); and 900°C for 30 minutes (circles).

Si prepared by pre-damage with Si are shown for no anneal (solid line), 600°C for 30 minutes (crosses), and 900°C for 30 minutes (circles). The recrystallization of the amorphous phase at 600°C has little effect on the B depth distribution (the difference between the sample with no anneal and the crosses is approximately the experimental error associated with the technique). This observation agrees with the ion microprobe results of Hofker et al. [11] Annealing at 900°C produces significant broadening of the B depth distribution. Figure 5 represents the results for annealing

Fig. 5. Depth distribution of 1×10^{15} 50 keV ^{10}B ions cm^{-2} after a 900°C 30 minute anneal for room temperature implantation into crystalline Si (circles) and into crystalline Si followed by post-damage with Si ions to produce an amorphous surface layer (crosses). The depth distribution with no annealing is given by the solid line.

at 900°C for 30 minutes for case (a); ^{10}B implant followed by post-damage with Si (crosses). The solid line is the depth distribution obtained with no annealing. From Figures 4 and 5, it is apparent that the presence of the amorphous phase greatly increases the amount of diffusional broadening of the B profile at 900°C . Since the initial distributions are reasonably gaussian, the amount of broadening of the distribution can be used to obtain an estimate of the apparent diffusion constant, D_{eff} . [4] At 900°C and 30 minutes, the results are:

$$D_{\text{eff}} \approx 5 \times 10^{15} \text{ cm}^2 \text{ sec}^{-1} \text{ (crystalline Si)}$$

$$D_{\text{eff}} \approx 20 \times 10^{15} \text{ cm}^2 \text{ sec}^{-1} \text{ (amorphous Si phase)}$$

Wagner [19] obtained a value of $1.5 \times 10^{15} \text{ cm}^2 \text{ sec}^{-1}$ for the diffusion of B in Si in which the diffusion source was a low energy ion implantation of B. The higher value obtained in this study is consistent with his result because B exhibits a concentration dependent diffusivity at high B concentrations [20, 21]; Wagner's experiments were conducted with a maximum B concentration of the order of mid 10^{18} cm^{-3} , which is an order of magnitude lower than

the concentrations used in this study. The results obtained with an amorphous phase initially present indicate the existence of vacancy sources within such regions. The meaning of D_{eff} in this case is not clear - the apparent diffusivity may be a function of time. Lawrence [22] has demonstrated that plastic deformation caused by an externally applied stress can produce enhanced diffusion, which he interpreted as due to excess vacancies created by the non-conservative motion of dislocations. Tamura et al. [23] have examined amorphous Si layers (produced by P ion implantation) by transmission electron microscopy in isothermal annealing studies at 800°C; they found large numbers of entangled defects such as dislocation loops and stacking faults initially. As the annealing time at 800°C was increased, the defect density decreased and the types of defects present changed. [23] In the final stages, dislocation networks appeared with a few stacking faults present. The enhanced diffusion observed (cf. Figs. 4 and 5) at 900°C for B when an amorphous Si layer was initially present may well be due to excess vacancies generated by the non-conservative motion of structural defects such as dislocations. If this is true, the amount of enhanced diffusion may be time dependent, as observed by Lawrence in his plastic deformation studies. [22]

SUMMARY

The major results of this study are:

- (1) Room temperature implantation of B into crystalline Si oriented in a "random" direction produces a profile with a "tail" probably caused by channeling effects.
- (2) Implantation of B into amorphous Si yields a distribution which is definitely skewed, indicating the importance of higher moments than the second moment in theoretical calculations of the ion profile based on LSS theory.
- (3) Annealing at 600°C with or without an amorphous phase present initially has little effect on the depth distribution for B implantations at room temperature. This observation agrees with the ion microprobe results of Hofker et al. [11], but not with those of Wittmaack et al. [10]
- (4) Annealing at 900°C for implantations into crystalline Si and with no amorphous phase initially present is not inconsistent with "normal" diffusional broadening when the concentration dependence of the B diffusivity is taken into account.
- (5) The presence of an amorphous phase initially produces a significant increase in the amount of diffusional broadening observed for 900°C annealing.

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