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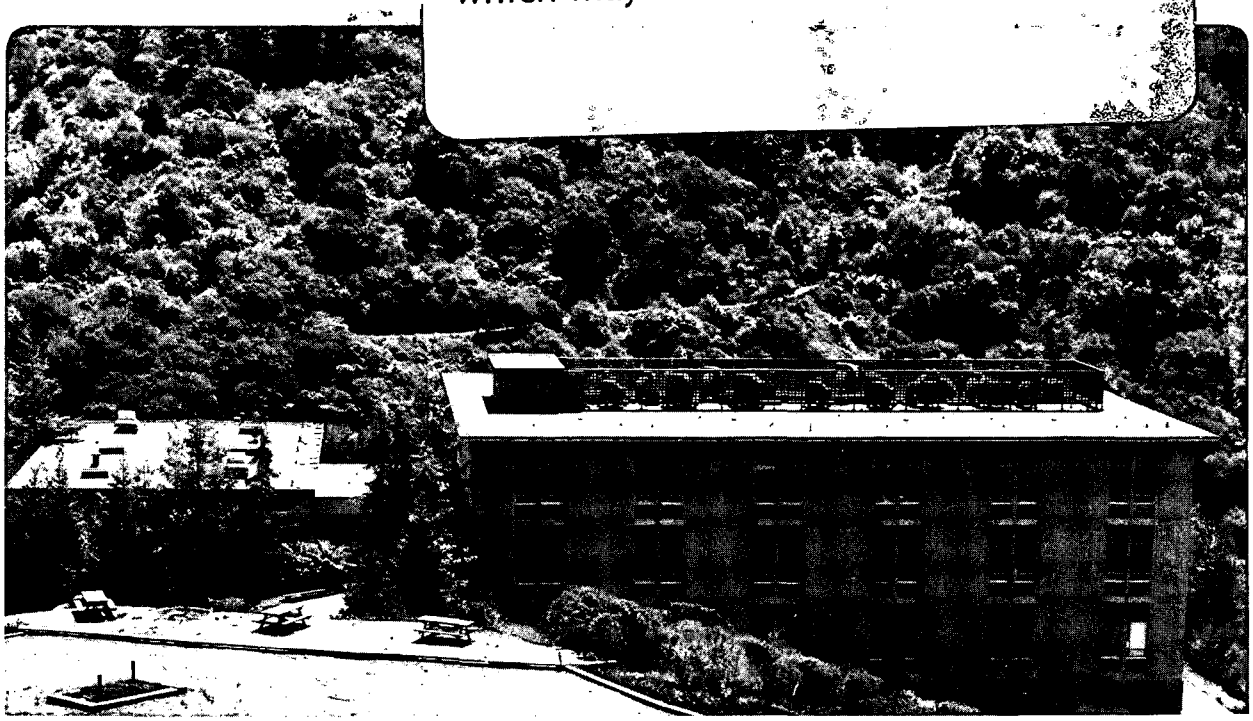

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ABSTRACT

Amorphization of silicon due to implantation of boron ions which is the lightest element used for I.C. fabrication processes, has been systematically studied for various temperatures, voltages and dose rates. A model for formation of amorphous silicon by light ion implantation is proposed. It is suggested that accumulution of point defects and/or clusters is required at the initial stage of amorphization process. Diinterstitial-divacancy pairs are suggested to be the embryos of amorphous zones formed during implantation at room temperature. Out diffusion of highly mobile interstitials during amorphization is though to explain differences in the critical energy for amorphization with low and high energy implantation at liquid nitrogen temperature.

INTRODUCTION

Boron ion implantation into silicon with high dose ($\geq 5\times10^{15}$ cm^{-2}) at room temperature is well known to produce a high density of residual dislocations or/and dislocation networks after either conventional furnace annealing or rapid thermal annealing [1]. These dislocations can cause serious problems of leakage current or carrier scattering effects in VLSI devices. Control of these defects requires an understanding of their origins, i.e., the radiation damage during implantation and its recovery during annealing. For example, only an amorphous layer created by ion implantation that is continuous all the way to the silicon surface can recrystallize without defect formation [2]. The formation of a continuous amorphous layer is important not only to the microstructural perfection but also to the electrical activity recovery of dopants [3]. Although amorphization of silicon by implantation of various ions has been extensively studied for more than a decade [4], the amorphization by boron ion implantation has not yet been systematically studied, probably due to the difficulty of achieving amorphization by such light ion damage. (Boron ion is the lightest ion implanted in I.C. fabrication processes.) The penetration of a light ion, for which the energy loss is dominated by electronic stopping does not produce high enough concentrations of point defects to form an amorphous zone directly. It requires accumulation of point defects or defect clusters as an incubation stage before amporphization can begin. Small amorphous zones produced by boron ion implantation at room temperature have been discovered and identified in our previous work [5].

Silicon amorphization by boron ion implantation has been systematically investigated at various temperatures, implantation energy and dose rates in this work. The role of silicon self interstitials in amorphization will be discussed to explain the difference in the critical deposition energy for low and high energy implantation at liquid nitrogen temperature. The formation of dislocations and dislocation networks after annealing is suggested to evolve from the stacking faults which were formed by clustering of the point defects created during implantation.

A MODEL FOR THE EMBRYO OF AN AMORPHOUS ZONE

The basic change of microstructure accompanying the transition from crystalline to amorphous silicon is the disappearance of six fold rings with the chair configuration. This was evidenced from X ray diffraction results. The second amorphous peak appears between the 220 and 311 peaks of polycrystalline silicon. The first amorphous peak falls on top of the 111 reflection [6]. This shows that the structure of amorphous silicon still keeps the same first nearest neighbors in nearly tetrahedral bonding as in crystalline silicon, but changes the arrangement of the second and third-nearest neighbors. The longest distance between atoms in the six-fold chair type rings is the third-nearest neighbor distance. These X ray results suggest that most of the six-fold chair type rings are replaced by five, seven and eight fold rings in the amorphous structure. A mixture of five to eight fold rings can be constructed continuously without making any dangling bonds to form a random-network structure, which is about 1.0 percent less dense than the diamond cubic structure [7]. However, pure amorphous silicon was found to have about $10^{20}/cm^3$ dangling bonds by EPR measurements [8]. The amorphous structure can be considered to be made up of a mixture of five to eight fold rings in various proportion and shape with distorted tetrahedral bonds along with additional dangling bonds of a density about $10^{20}/cm^3$ [9]. Then, the density of amorphous silicon is estimated to be 1–2 percent less than that of crystalline silicon. This model is consistent with the 1–2 percent dilatation during polycrystalline-to-amorphous transition in thin film experiments [10].

It has been proposed that amorphous zones can only form at the end of incoming light ion tracks when the pre-accumulated concentration of point defects reaches a critical value [5]. The small changes in density during transition from crystalline to amorphous suggests that point defect clusters of both vacancy and self interstitial types are involved during the accumulation in the first stage. The predominant accumulated point defects, which are relatively in mobile during room temperature implantation, are divacancies and diinterstitials this is confirmed by EPR data for the annealing of radiated silicon [11]. They can recombine through the dissociation of the divacancy or the diinterstitial. However, the dissociation of a divacancy or diinterstitial is improbable at room temperature because the increase in free energy is large compared to KT. The atomic rearrangement associated with the recrystalline to amorphous transition, of a small region containing a divacancy-diinterstitial pair involves little change in volume. It is suggested that such a pair constitutes an embryo of the amorphous phase. The bonding structure surrounding a divacancy on a layer of the (110) plane in silicon can be described as below. The six-fold rings are replaced by 2 five fold and 1 eight fold ring at the center of the divacancy. In a highly defective implanted area, a localized rebonding of this structure can result in 2 five fold rings and 2 seven fold rings. Similarly, the bonding surrounding a split ⟨110⟩ diinterstitial on a layer of (110) plane can be described as in Fig. 1(a). Again, 2 five-fold rings and 2 seven-fold rings are formed after rebonding (Fig. 1(b)).

The structure of amorphous silicon is composed of five to eight fold rings. Therefore, when the two centers, a divacancy and diinterstitial with the rebonded structures get close enough, the region has a structure that is indistinguishable from a small region of amorphous silicon. The energy required for breaking silicon covalent bonds to initiate the rebonding is of the order of one electron volt. The strain energy of point defect clusters or the thermal vibration energy of the silicon lattice are far below the energy needed for rebonding. Only the nuclear stopping energy brought by an incoming ion can break silicon bonds and reform five or seven fold rings in the region near the ion track. Therefore amorphous zones should be formed near the end of light ion tracks when the light ion enters a region with a critical concentration of the accumulated divacancies and diinterstials at room temperature. Four vacancy clusters and two diinterstitials could also

play a similar role, however, the most probable case would be divacancy diinterstitials pairs, which constitute the majority of the accumulated point deflect clusters.

TEMPERATURE EFFECT ON AMORPHIZATION MECHANISM

Owing to the effects of diffusion and the clustering of point defects, the amorphization mechanism for boron ion damage should be somewhat different at different temperatures. At liquid nitrogen temperature, vacancies are almost immobile. Although some of the interstitials are known to migrate by athermal diffusion at 4°K, diinterstitials should be also be nearly immobile at 77°K [12]. Therefore, little segregation of point defects or recombination through diffusion can be expected during ion implantation at liquid nitrogen temperature. With uniform scanning of an ion beam during implantation, the accumulation of point defects should be relatively uniform at liquid nitrogen temperature. In this case mechanism (A) proposed in the previous paper [5] describes the amorphization process, i.e., the amorphous zones are formed independently during the second stage of amorphization. For ion implantation close to absolute zero temperature (less than 4°K) at which both vacancies and interstitials are immobile, the amorphization process can be described adequately by Gibbons' simple overlap model [4].

The diffusion and clustering of point defects during ion implantation at room temperature are expected to be much more pronounced than is the case at liquid nitrogen temperature (estimated as $D_I = 3.16\times10^{-4}cm^2/s$, $D_V = 4.15\times10^{-9}$ cm^2/s at 300°K [14]). Divacancies, diinterstitials and 4-vacancy clusters are known to be formed during ion implantation [11]. In addition, extrinsic stacking fault loops with diameters of 50–100Å were found in the specimens of $3\times10^{16}/cm^3$ boron implantation at room temperature. This shows that relatively long range diffusion of silicon interstitials is occurring at room temperature and that there is enough mobility of vacancies to at least form small vacancy complextes containing two or more vacancies. The distribution of small point defect clusters during ion implantation at room temperature should no longer be as uniform as it would be at liquid nitrogen temperature, mechanism B, proposed in the previous work [5] is expected to describe the amorphization process at room temperature. When point defects are mobile there is a less clear separation between stage 1 and stage 2 because of non-uniform distribution of defect clusters throughout the volume. The critical density of point defect clusters needed for formation of an amorphous zone may exist in only a fraction of the irradiated volume. If additional defect clusters are formed preferentially in the strain field of already existing amorphous volumes then most of the new amorphous material would form adjacent to an already existing amorphous region, resulting growth rather than random coalescence. Schematic figures of the two mechanisms A and B are shown in Fig. 2.

Near the areas in which stacking faults are formed, no amorphous zones can be formed because the stacking faults provide sinks for almost all the interstitial atoms necessary for the first stage accumulation. For 50°C implantation, amorphous zones are rarely observed after boron ion implantation with doses up to $1\times10^{16}/cm^3$, and a higher density of stacking fault loops are observed than at room temperature. Intrinsic stacking fault loops of 50 Å in diameter were also observed [9], due to higher mobility for vacancies at this temperature, and presumably loss of interstitial atoms in this region to some other nearby sink.

Because of dynamic annealing at about 200°C [14], at some temperature between 25°C and 200°C no amorphous zones can ever be formed during boton ion implantation even with very high fluence. Due to the high mobility of both vacancies and interstitials at such temperature, the produced Frenkel pairs either recombine or segregate into larger clusters such as dislocation loops. Therefore the critical concentration of diinterstitial-divacancy pairs for

amorphization can never be reached even within localized areas. The amorphization mechanism for boron ion implantation is expected to gradually change with implantation temperature; the evolution of the amorphization mechanism from very low temperature to the critical temperature at which no amorphous region can be formed, is suggested to follow the sequence: (1) simple overlap model at temperature near 0°K, (2) mechanism A at 77°K, (3) mechanism B at room temperature (300°K), (4) no amorphous material formed at all (400°K).

OUT DIFFUSION OF SILICON INTERSTITIALS DURING AMORPHIZATION

A deeply buried amorphous layer extending from 4.9 μm to 5.3 um depth away from surface was found in a specimen of $1\times10^{15}/cm^2$ boron ion implanted silicon with 4 MeV at liquid nitrogen temperatures (Fig. 3(a)). The deposition energy density profile (also known as damage profile) calculated from Brice's theory is shown in Fig. 3(b). The critical energy for amorphization corresponds the energy density at the crystalline-amorphous interface. It was estimated as 3×10^{20} KeV/cm^3 for this boron 4 MeV implantation. For boron 100 KeV implantation, a similar calculation gives around 2.2×10^{21} KeV/cm^3. This is the product of $5\times10^{15}/cm^2$ by 4.5 eV/Å, which is the energy density at the 1100 Å depth amorphous-crystalline interface for 100 KeV boron implantation at liquid nitrogen temperature. The difference in the critical energy for low and high voltage implantation was almost one order of magnitude. This can be explained by out-diffusion of silicon interstitials during ion implantation.

Both silicon interstitials and vacancies are necessary for amorphization by ion implantation. However, at liquid nitrogen temperature, vacancies hardly move and interstitials which have higher mobility diffuse to favored sinks such as free surface. In this condition, the build up of interstitial concentration under steady irradiation with point defect pair production rate P is approximately by [15]:

$$dC_I/dt = P(1 - C_v)(1 - Z_{IV}C_v) - Z_{IV}M_IC_IC_v - Z_{II}M_IC_I^2$$

$$-Z_{IL}M_I(C_IC_{IL})^{1/2}\ C_I - M_IC_SC_I$$

where M_I is the interstitial mobility and Z's are the site numbers of spontaneous reaction of each process. The first term in the equation represents the effective production rate of free interstitials. The fraction of atomic sites at which primary damage can take place is $(1-C_v)$ where C_v is the concentration of vacancies, and knocked-on atoms remain as interstitials only when they do not jump into regions of spontaneous recombination Z_{IV} around a vacancy. The second term expresses the recombination of interstitial atoms and vacancies. The third term represents the formation rate of diinterstials. The fourth term formulates the absorption of silicon interstitial atoms into interstitial loops, where C_{IL} is the concentration of interstitials which have already been absorbed to loops of concentration C_L. The last term describes the escape of interstitials to permanent sinks C_s in concentration. The most obvious permanent sink is the surface for a thin foil. The value C_s can be approximated from random walk theory as $C_s \simeq (a/h)_{1/2}$ where a and h are lattice constant and thin specimen thickness respectively. For regular ion implantation, the ions penetrate into the target and stop at a shallow depth under the implanted surface. So, most of the out-diffused interstitials only escape to the nearest surface, not two surfaces as in a thin specimen. The distance from the amorphous-crystalline interface to the nearest surface can be treated as h/2 for C_s. The distance to the surface for the nearest crystalline-amorphous interface for 4 MeV and 100 KeV implantation are at 4.9 μm and 1100 Å respectively. The ratio of C_s for 100 KeV to that 4 MeV implantation is about 6.7. This is very close to the critical energy proportion for these two different implantation voltages 7.3 (≃2.2×

10^{21} KeV/cm^3 divided by 3×10^{21} KeV/cm^3). Although more quantitative data are needed to make a conclusion, it seems reasonable to suggest that the out-diffusion of interstitials could be one of the important factors for amorphization due to low voltage implantation.

SUMMARY OF SILICON AMORPHIZATION BY BORON ION IMPLANTATION

It was known that a continuous amorphous layer cannot be formed at room temperature even with a very high dose 3×10^{16}/cm^3, when regular low beam currents (1–2 μA)d were used [5]. Seen from the above equation, if the production rate of Frenkel pairs created by ion damage is greatly increased with other parameters being kept almost constant, the steady state concentration of interstitials and vacancies will be increased. The amorphization by ion damage can be enhanced by high beam current implantation. However, the increase of dose rate usually also raises the wafer temperature and thereby increases the mobility of interstitials and vacancies M_I and M_V. This results in an increase of the values of the second, third, fourth and fifth terms in the equation, resulting in a decrease of the interstitial concentration. Amorphization with high beam currents involves a competition between point defect production rate and the increase of their mobility due to beam heating. With a high beam current (2 mA) and an efficient cooling system which keeps wafers below 35°C it is possible to produce an amorphous layer 1200 Å which is continuous to the surface with 35 KeV implanation [9]. However, the increase of wafer temperature by high beam current also enhances segregation into point defect clusters. A wide transition region (750 Å) in which there is partial amorphization and many stacking fault loops or point defect clusters was found for the specimen boron implanted with a 2 mA beam current. This wide transition region is the origin of profuse secondary defects, which may be detrimental to electrical properties of post-annealed specimens.

As discussed above, once extrinsic stacking fault loops are formed, the surrounding region will have insufficient interstitials for amorphization and thus will remain crystalline. The amorphous-crystalline transition region was observed to contain such small extrinsic stacking fault loops in the still crystalline areas in the as implanted conditions. The stacking fault loops were mainly extrinsic bounded by 1/3⟨111⟩ Frenkel partials,. After annealing at 550°C or above, the amorphous layer was recrystallized and two layers of dislocation loops were left at the region which had been the transition region [2]. With further annealing the 1/3 ⟨111⟩ loops converted to perfect loops when a Shockley partial 1/6⟨112⟩ is nucleated.

$$1/3[111] + 1/6[11\bar{2}] \rightarrow 1/2[110]$$

Nucleation of Shockley partial discolations is possibly aided by internal stresses during annealing for recrystallization [16].

CONCLUSION

Amorphization by implantation of boron ion has been systematically studied for various temperatures, voltages and dose rates. Based on theoretical considerations and experimental results, a new amorphization model for light ion damage is proposed consisting of two-stages. The role of interstitial type point defects or clusters in amorphization is emphasized. Due to the higher mobility of interstitials out-diffusion to the surface particularly during amorphization with low energy can be significant. The proposed model represents an improved understanding of the mechanism of silicon amorphization during light ion damage at various temperatures. The stacking fault loops found in specimens implanted with boron at room temperatures are considered to be the origin of secondary defects formed during annealling.

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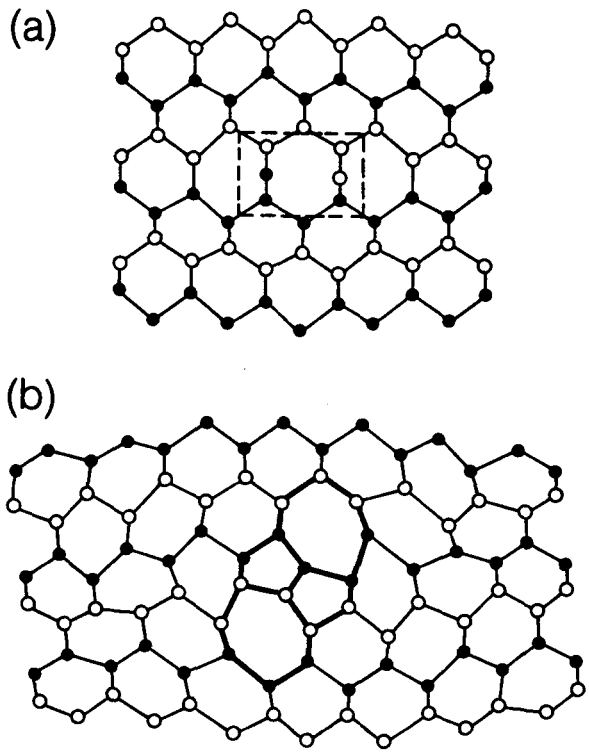

Fig. 1. (a) The bonding surrounding a split-⟨110⟩ diinterstitial. (b) Rebonding of the structure in (a).

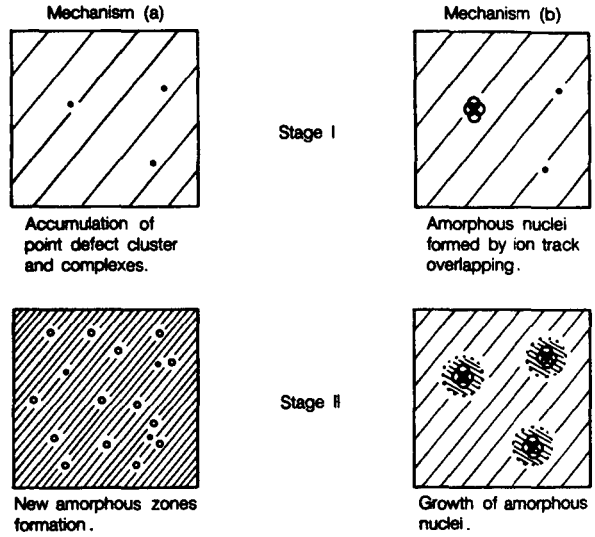

Fig. 2. Schematic figure of two suggested amorphization mechanisms.

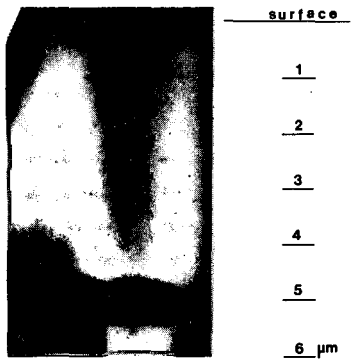

Fig. 3a. Cross-section view of 4 MeV boron ion implanted silicon at liquid nitrogen with $1\times10^{15}/cm^2$ fluence (in Dark Field image), showing a buried amorphous layer at 5 μm depth.

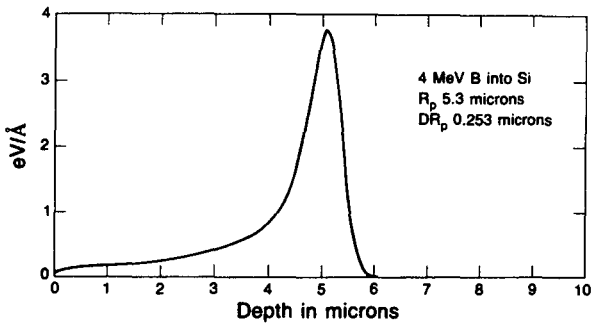

Fig. 3b. The damage energy deposition profile for 4 MeV boron ion implanted silicon (calculated from D.K. Brice's formula).

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