Surface Sink Effects on Void Formation in GaSb and InSb under Ion Irradiation

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Cellular defect structure forms on GaSb, InSb and Ge surfaces irradiated with energetic ions. These structures are generated after void formation via the movement of point defects induced by ion irradiation. In this transmission electron microscopic study, void formation by thin foil irradiation (irradiation after polishing for transmission electron microscopy (TEM)) was compared with void formation by bulk irradiation (cross-sectioning after ion irradiation), in order to investigate the effect of surface sinks for the point defects. The voids formed in GaSb and InSb by thin foil irradiation with 60 keV Sn⁺ at a temperature of 100–150 K were smaller than those formed by bulk irradiation. The diameters and densities of the voids increased rapidly as the ion dose increased from 1×10^{14} to 2×10^{14} ions/cm² under both types of irradiation. Amorphous halos were observed in the selected area diffraction patterns (SAED) of the thin foil irradiation specimens in addition to the main spots of the zincblende structure at a dose of 1×10^{14} ions/cm². This finding contrasts with the polycrystalline ring patterns observed in the SAED of the bulk specimen under the same dose. It was concluded that the easy escape of interstitials to the surface assists both void formation and amorphization in thin foil irradiation. [doi:10.2320/matertrans.MBW200729]

(Received October 16, 2007; Accepted April 21, 2008; Published June 11, 2008)

Keywords: thin foil irradiation, bulk irradiation, gallium antimonide, indium antimonide, germanium, tin ion, III-V compound semiconductor, void, point defects, vacancy, interstitial, transmission electron microscopy, amorphous

1. Introduction

The authors have found that a fine cellular structure consisting of many cells develops on the Sn⁺ ion irradiated GaSb surface at a low temperature (130–150 K),^{1–3} and verified experimentally that this behavior is due to the self-organizational movement of the point defects induced by the irradiation of energetic ions.^{4,5} The voids are formed by 60 keV Sn⁺ irradiation of a dose less than 4×10^{14} ions/cm². By increasing the irradiation dose, the growth of voids leads to the formation of cells at the specimen surface. The cell diameter and the wall thickness partitioning the cells were about 50 and 10 nm, respectively, and the cell depth was 250 nm when irradiated with 60 keV Sn⁺ to a dose of 8×10^{14} ions/cm² at 150 K.^{2,3} The same or similar behaviors were observed in InSb⁶ and Ge.^{7–10} The authors' study on those materials has been performed mainly by cross-sectional transmission electron microscopy (cross-sectional TEM) in which the bulk samples are thinned after the ion irradiation, therefore, the defect formation and structural change in the bulk materials caused by ion irradiation has been investigated in the study.^{1–4}

Freely migrating defects are annihilated at permanent sinks, therefore, the defect structural evolution will be greatly affected by the presence of sinks. Kiritani *et al.* compared the differences in the damage structures in metals using both thin foil irradiation and bulk irradiation.^{11–14} In their thin foil irradiation experiments, specimens were irradiated after polishing for TEM observation, from which they obtained information about defect clusters formed directly by a single

cascade event. The results of bulk irradiation, in which specimens are polished after irradiation for TEM observation, indicated the effect of freely migrating defects. Thus, comparisons of the damage structures between the thin film irradiation and bulk irradiation will bring some useful knowledge on the defect formation mechanism, however, there are few studies utilizing the surface sinks on semiconductors. Appleton *et al.* studied void formation in bulk irradiation by cross-sectional observation in Ge irradiated with 120 keV In ions.^{7–9} Wang and Birtcher observed the formation of voids in thin foils irradiated Ge with 1.5 MeV Kr ions.¹⁰ However we cannot compare these irradiation experiments because their irradiation conditions were different.

In our previous studies,^{1–4} cross-sectional observation was conducted on bulk-irradiated specimens. In this research, thin foil Sn⁺ irradiation was performed and the effect of surface sinks for the initial stage of void formation (1×10^{14} and 2×10^{14} ions/cm²) was compared with the defect structures of the bulk specimens. Therefore the present study is the first report to compare two irradiation runs in semiconductors.

2. Experimental

60 keV Sn⁺ ion irradiation was performed for (100) GaSb, and (100) or (111) InSb, when the substrate temperature is about 100–150 K and the ion dose was 1×10^{14} and 2×10^{14} ions/cm². In the case of thin foil irradiation experiments, GaSb and InSb with (100) orientation were punched out into disks with a 3 mm diameter and dimpled on one side. Then the disks were thinned by chemical polishing in a HCl:HNO₃ (1:1) solution. After that, the disks were ion irradiated and observed by TEM. Annealing experiments were performed on some of the irradiated specimens at 373, 473 and 573 K. The annealing time and atmosphere were 30 min and Ar + 3% H₂ at all temperatures. In the case of

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Fig. 1 Comparison of defect structures in GaSb formed under thin foil irradiation ((a) and (c), top view) and bulk irradiation ((b) and (d), cross-sectional view) with 60 keV Sn^+ at a temperature of 100–150 K.

bulk irradiation for TEM observation, the implanted (100) GaSb and (111) InSb wafers were bonded face-to-face with epoxy resin and 0.5-mm-thick silicon wafers were bonded on both sides. The wafers were then punched out into 2-mm-diameter disks and inserted into brass cylinders. Each was then sliced and polished mechanically to a thickness of 200 μm and dimpled to a thickness of 100 μm . Finally, they were thinned by ion milling with argon. The observation of damaged structures was made with an electron microscope (JEOL JEM-2010 or 2010F) operating at 200 kV.

3. Results and Discussion

Figure 1 shows the defect structures formed in GaSb irradiated by 60 keV Sn^+ at a temperature of 100–150 K. Photographs (a) and (c) are the plan views of the foil irradiated specimens from the ion irradiation direction, and (b) and (d) are the cross-sectional views of the bulk irradiated specimens from the perpendicular direction to the ion irradiation direction. The ion dose was 1×10^{14} ions/ cm^2 for (a), (b) and 2×10^{14} ions/ cm^2 for (c), (d). Only a few voids with diameters of about 15 nm were formed in the thin foil irradiated to a dose of 1×10^{14} ions/ cm^2 , and the density of the voids was impossible to estimate. A high density of voids (8.0×10^{10} voids/ cm^2) having diameters of about 25 nm were formed in the thin foil specimen irradiated to a dose of 2×10^{14} ions/ cm^2 . Some voids observed at a higher dose under thin foil irradiation were not round, and seemed to be

formed by the coalescence of several voids. Only amorphous halos were observed in addition to the main (100) spots of the zincblende structure for both thin foil irradiation specimens, forms which the amorphization in irradiated thin foil GaSb seems to occur without polycrystallizing process.

In the cross-sectional bulk specimens, irradiated to a dose of 1×10^{14} and 2×10^{14} ions/ cm^2 , the diameters of the voids were about 20 nm and 50 nm, and the void densities were 1.9×10^{10} and 2.3×10^{10} voids/ cm^2 , respectively. The diameters and densities of the voids increased rapidly between 1×10^{14} and 2×10^{14} ions/ cm^2 which was just the same as thin foil irradiation. Polycrystalline ring patterns were observed in the cross-section of the bulk specimen with main (110) spots for both doses.

The high density of the voids and the formation of an amorphous phase observed in thin foil irradiation will be due to the easy escape of the induced interstitials to the surface. Two mechanisms are proposed for the amorphous formation. One is that the absence of the interstitials in the irradiated region increases the vacancy concentration leading to the formation of the high density of the voids and the amorphization of the irradiated matrix. The other is that the escaped interstitials from the irradiated region form an amorphous layer on the surface. Anyway, it was concluded that the behavior of interstitials is important to the amorphization. On the other hand, in bulk irradiation, the interstitials stored near the ion range form a strain region in which polycrystallites are formed.

Fig. 2 Annealing behavior of voids at 373, 473 and 573 K for 30 min in GaSb thin foil irradiated at a temperature of about 103 K.

Fig. 3 Comparison of defect structures in InSb formed under thin foil irradiation ((a), top view) and bulk irradiation ((b), cross-sectional view) with 60 keV Sn^+ at a temperature of 100–140 K.

The annealing behavior of voids in thin foil irradiated GaSb at 373, 473 and 573 K for 30 min are shown in Fig. 2. The void size decreased slightly upon annealing. The amorphous structure persisted during annealing at 373 K, but polycrystalline structures appeared upon annealing at 473 K. Crystallites were preferentially formed on the void surfaces, which leads us to conclude that the void surface is a nucleation site for crystallites. In addition, another conclusion is that the density of the amorphous phase is higher than that of the crystalline phase, because the experimental results revealed that the voids shrunk when the surrounding amorphous region was crystallized.

A comparison of the defect structures formed in InSb under thin foil irradiation ((a), top view) and bulk irradiation ((b), cross-sectional view) is shown in Fig. 3. The voids were formed under both types of irradiation. The diameter of the voids was about 50 nm in thin foil irradiation. The diameter and depth of the voids were about 40 nm and 65 nm,

respectively, and the thickness of the partitioning void walls was about 10 nm in the cross-section of the bulk specimen. Though not strictly comparable owing to the difference in irradiation direction, the void size in InSb is larger than that in GaSb, and the shape of voids in InSb is more spherical than that in GaSb under the same irradiation conditions.

Figure 4 shows the dose dependence of void growth for thin foil irradiation and bulk irradiation. It is revealed that the growth rate of the void diameter in bulk irradiation is larger than that in thin foil irradiation, in addition to the fact that the voids in the thin foil specimen are much smaller than those in the bulk specimen. This supports the authors' idea in the previous papers²⁻⁴⁾ that some parts of the interstitials induced by ion irradiation contribute to the development of the cells (hollows) by being absorbed in the partitioning walls.

Figure 5 shows the size distribution of voids in thin foil irradiation. The diameter of voids ranged from 7 to 30 nm,

Fig. 4 Dose dependence of void growth for thin foil irradiation and bulk irradiation in GaSb and InSb with 60 keV Sn^+ at a temperature of 100–150 K.

Fig. 5 The size distribution of voids in GaSb thin foil irradiated at a temperature of 100–120 K.

and the peak diameter is about 16 nm in GaSb irradiated to a dose of 1×10^{14} ions/cm². The diameter of voids ranged from 8 to 50 nm, and the peak diameter was about 27 nm in GaSb irradiated to a dose of 2×10^{14} ions/cm². The presence of small voids at a dose of 2×10^{14} ions/cm² suggested continual nucleation. When InSb was irradiated to a dose of 2×10^{14} ions/cm², the void diameter ranged from 40 to 60 nm and its peak was about 54 nm. The void diameter in InSb is considerably larger and its distribution is smaller compared with GaSb.

In the case of Ge, thin foil irradiation and bulk irradiation were performed by Wang *et al.* and Appleton *et al.*, respectively.^{7–10} In these studies, no polycrystalline structure was observed even in the bulk irradiated specimen, unlike GaSb and InSb. The present authors also observed the same results with Ge. This may be caused by the

difference in defect structure evolution between a single-component system and binary system, which is a challenge to be clarified hereafter.

4. Conclusion

The void formation in thin foil GaSb and InSb by 60 keV Sn^+ irradiation at about 100–150 K was compared with the void formation in bulk samples. The defect formation behavior was much different between thin foil irradiation and bulk irradiation. The irradiated region in the thin foil was amorphized and the smaller voids were formed more densely in the thin samples compared with the bulk samples under the same irradiation condition. It is believed that such behavior in thin foil irradiation comes from the easy escape of the irradiation induced interstitials to the surface sink. In addition, it was clarified, from the annealing experiment of the irradiated specimen, that the atomic density in the amorphous phase is higher than that in the crystalline. The differences in defect structural evolution between thin foil irradiation and bulk irradiation will provide useful information for understanding the self-organizational formation of the cellular structure in semiconductors. Further studies are being conducted.

Acknowledgments

This work was supported by Nippon Sheet Glass Foundation for Materials Science and Engineering, Grant-in-Aid for Young Scientists (Start-up) and the Murata Science Foundation.

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