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RADIATION-INDUCED DAMAGE IN GaP BY MeV HELIUM IONS

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The creation of defects in GaP bombarded with MeV ^{4}He ions has been studied under ultra-high-vacuum condition by Rutherford backscattering/channeling (RBS/C) method, and the absolute damage cross section σ_d for GaP has been determined under bombardment of 1.0 MeV ^{4}He ions, with the measured value 8.0×10^{-18} cm^2. Our experimental results suggest that the defect generation rate is strongly related to the surface condition. When the GaP is covered with a thin amorphous layer, a significant ion beam annealing effect will be observed. The present results show that for GaP the damage is produced mainly by nuclear collision.

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I. INTRODUCTION

Backscattering and channeling spectrometry is extensively used to probe compositional and structural properties of materials within submicron depth below the surface[1,2]. But this technique is perturbational because of the creation or the annealing of disorder induced by ^{4}He ion beam incidence. Therefore, the effect of an analysis beam (MeV He or H ions) on the studied materials is becoming much important for correct interpretation of experimental data and the understanding of MeV ion-solid interactions.

During the past three decades, there were a lot of studies[3−10] concerned with the radiation damage of solids by MeV ^{4}He and ^{1}H ion beams. Especially in recent years, the use of compound semiconductors in the electronic industry has been extended considerably, because of the wide variety of electronic and electro-optical properties exhibited by this kind of materials, such as GaAs, InP and GaP etc., therefore, more and more work about the radiation damage in these materials by MeV ^{4}He and ^{1}H ion beams have been reported in the literature[11−13]. For GaAs and InP semiconductors, a large number of radiation defects have been produced by MeV ^{4}He or ^{1}H probe beams. And annealing effect induced by MeV ^{4}He ions bombardment can be observed easily. In this paper, we will study the behavior of radiation damage in GaP caused by MeV ^{4}He ions incidence. To better understand how the sample surface state influences damage generation, we choose three different surface states, namely, (a) surface which is covered with a thin (1 monolayer) native oxide layer and contains carbon and oxygen contaminations, (b) surface which is covered with a thin (1.1 nm) amorphous layer, and (c) surface which is clean and ordered.

II. EXPERIMENT

The experiments were performed on a NEC 9SDH-2 Pelletron tandem at Fudan University, with the terminal voltage ranging from 0.3 to 3.0 MV and the beam energy spread 1.28 keV. The vacuum in the chamber was kept at 1.3×10^{-8} Pa, in which the sample was mounted on a three-axis high precision goniometer, equipped with a low energy electron diffraction (LEED) system and a four-grid auger electron spectroscopy (AES). The beam was collimated through two apertures with 1 mm diameter, and the scattering ions were detected by a surface barrier detector, situated at a scattering angle of 95° (lab.) related to the incident beam, with the energy resolution 15 keV.

Three different surface states were obtained by the following procedures. First, a sequence of polishing steps was executed until the surface showed a mirror-like face. After washed by ether, the sample was introduced into the UHV chamber. At this time, the sample surface would certainly be covered with a very thin native oxide layer that included carbon and oxygen contaminations, therefore, we called this surface as an unclean surface. In order to get clean and ordered surface, a kind of in situ cleaning treatment, which consisted of a series of sputtering (500 eV Ar ions, incident angle 60°) and annealing (at a temperature about 500°C) cycles, were carried out. When carbon and oxygen peaks in AES spectra were below the detection limit of the analyzer and sharp (1×1) LEED patterns observed, we considered this surface as a clean ordered surface. However, it should be noticed that after this kind of in situ cleaning treatment for single crystal GaP $(\overline{111})$, we obtained a kind of "Ga-rich" surface[14]. If a clean and ordered surface was sputtered by 500 eV Ar ions for 30 min, a thin layer (about 1.1 nm) of amorphous GaP would be formed, that is to say, the third surface state was obtained.

The experiments were performed at room temperature, using a beam of MeV ^{4}He ions as the radiation source and analysis probe. To eliminate the effect of radiation during the process of aligning the beam with the crystal axis, the backscattering spectra should be taken according to the following procedure. First the ^{4}He ion beam was directed to impact on the corner of the sample. After aligning a certain axial direction, we moved the sample so that a virgin area of the sample was exposed to the ^{4}He ion beam for analysis.

III. RESULTS AND DISCUSSION

Figure 1 shows the backscattering spectra of unclean GaP for 1.0 MeV ^{4}He ion beam incident along the < 111 > axial direction at two different damage stages: (a) Virgin. The ^{4}He ion dose during the backscattering measurement of the virgin sample is about $8\times10^{14}/\text{cm}^2$ and the damage induced by the probe beam is so small that it can be neglected; (b) After irradiation by a 1.0 MeV $1.6\times10^{16}/\text{cm}^2$ ^{4}He ion beam incident along the < 111 >

axial direction. Two facts are evident from the spectra: (1) An obvious radiation damage has been introduced by the 1.0 MeV ^{4}He probe beam; (2) Both the minimum yield (χ_{min}) and surface peak (SP) intensity in the backscattering spectra are increased after irradiation.

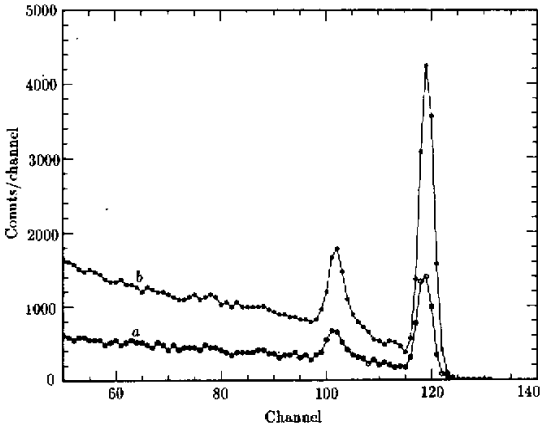

Fig. 1. Experimental backscattering spectra for unclean GaP($\overline{111}$) with the beam of 1.0 MeV ^{4}He ion incident along the < 111 > axial direction. curve *a*: virgin sample; curve *b*: damaged sample.

It is well known that both χ_{min} and SP intensities are two important parameters in a backscattering spectrum[15] which can be used to examine the crystallinity of the substrate. And the SP intensities can be calculated based on the computational method as described in Ref.[16]. Interactions between ions and the crystal were treated as classical binary collisions in the momentum approximation with the Moliere approximation of the Thomas-Fermi potential. It is possible to calculate the increased number of displaced target atoms by comparing the two SP intensities before and after MeV ^{4} He ion beam bombardment. But it is very difficult to measure the SP intensities for P atoms accurately, because of the high dechanneling background in the P region of the backscattering spectrum. For this reason, we only measure the SP intensities for Ga atoms, assuming that the two kinds of atoms, Ga and P, have the same damage behavior.

In order to obtain the radiation damage cross section in GaP, we measured the SP intensities with increasing total dose, ranging from $1.6\times10^{15}/cm^2$ to $1.6\times10^{16}/cm^2$, for 1.0 MeV incident ^{4}He ions. Each backscattering spectrum was obtained by $1.6\times10^{15}/cm^2$ integrated ^{4}He ions, which is the required minimum dose for a good statistical evaluation of radiation damage.

As we know, the amount of the damage produced by MeV ^{4}He ion beam irradiation is the result of the two competitive processes, namely, creation and annihilation of the displaced

atoms in the substrate materials. Therefore, only effective radiation damage cross section σ_{eff} can be determined by the slope of the experimental curve $N_d/N_0 \sim \phi$[5,6],

$$\sigma_{\text{eff}} = \frac{1}{N_0}\frac{\mathrm{d}(N_d - N_0)}{\mathrm{d}\phi} = \frac{\mathrm{d}N_d/N_0}{\mathrm{d}\phi} , \tag{1}$$

where N_0 and N_d are the area densities of Ga atoms which is exposed to the ^{4}He ion beam before and after irradiation respectively, ϕ is the dose of the incident ^{4}He$^+$ ions.

When the damage rate and the annealing rate induced by MeV ^{4}He ion incidence is nearly equal, the defect concentration for the substrate will reach saturation, that is,

$$N_0\sigma_d\phi = (N_d - N_0)\sigma_a\phi \tag{2}$$

or

$$\sigma_d/\sigma_a = N_d/N_a - 1 , \tag{3}$$

where σ_a, σ_d are the annealing cross section for the displaced atoms and the absolute radiation damage cross section for the lattice atoms produced by bombardment of MeV ^{4}He ion beam, respectively.

When the defect concentration for GaP is far from saturation, $(N_d/N_0 - 1) \ll 1$, the effective radiation damage cross section can be written as

$$\sigma_{\text{eff}} = \sigma_d - \frac{(N_d - N_0)}{N_0}\sigma_a . \tag{4}$$

Here the recovery of the displaced atoms induced by thermal migration has not been considered. In fact, the total amount of displaced atoms in GaP produced by MeV ^{4}He ion bombardment is preserved at room temperature; in other words, thermal recovery for displaced atoms in GaP does not occur at room temperature.

Figure 2 displays the dose dependence of N_d/N_0 for GaP which is covered with a very thin amorphous layer, under the condition of 1.0 MeV aligned $< 111 >$ ^{4}He ions with the beam current 0.1–0.2 μA/cm^2. Solid line is obtained by a linear least square fit of the experimental data, and B, S denote the body and the surface region in GaP respectively. The values of effective radiation damage cross sections for other two kinds of surface states are listed in Table 1.

Table 1. Values of effective radiation damage cross sections σ_{eff} for GaP induced by 1.0 MeV aligned $< 111 >$ ^{4}He ion beam incident upon three different surfaces.

	Surface state		
Region	Oxide	Clean	Amorphous
Surface	6.0×10^{-18} cm^2	6.7×10^{-18} cm^2	-0.3×10^{-18} cm^2
Body	7.1×10^{-18} cm^2	5.4×10^{-18} cm^2	5.5×10^{-18} cm^2

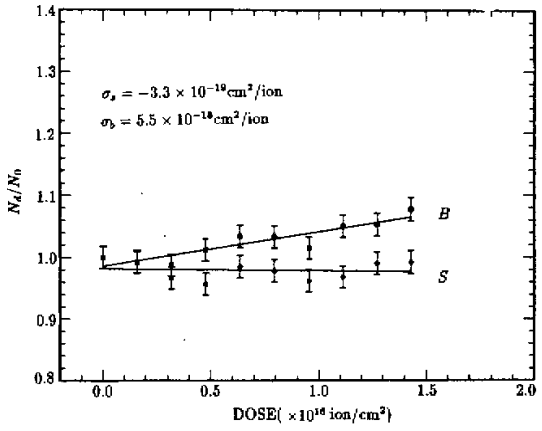

Fig. 2. Dose dependence of N_d/N_0 for 1.0 MeV aligned $< 111 >$ ^{4}He ion bombardment on GaP($\overline{111}$) which is covered with a very thin amorphous layer. B, S represent the body and the surface region in GaP respectively; σ_s and σ_b are obtained by a least square fit to the experimental data.

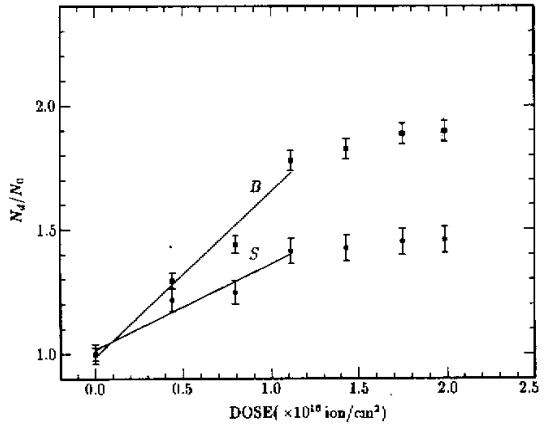

Fig. 3. Dose dependence of N_d/N_0 for 1.0 MeV ^{4}He ions impact on GaP which is covered with a very thin native oxide layer. B, S represent the body and the surface region in GaP respectively. Solid lines show the large slopes compared with those in Fig.2.

Figure 3 shows the relation between N_d/N_0 and ϕ for GaP which is covered with a thin native oxide layer, with the 1.0 MeV ^{4}He ion beam incident along a random direction. It can be easily found from the spectrum that the damage generation rate produced by a random incident beam is about 10 times larger than that produced by an aligned beam. Meanwhile, both in the body and in the surface region of the sample, the defect concentration tends to

saturation at a dose about $1.2 \times 10^{16}/\mathrm{cm}^2$ for ^{4}He ions. From Fig.3, Eq.(3) becomes

$$\sigma_a = k\sigma_d \,, \tag{5}$$

where

$$k = \frac{N_d}{N_0} - 1 = \begin{cases} 0.95 & \text{body} \\ 0.4 & \text{surface} \end{cases} \tag{6}$$

The absolute radiation damage cross section for GaP was determined to be $8.0\times10^{-18}\,\mathrm{cm}^2$ from Eqs.(4), (5) and (6) together with the measured value σ_{eff} of GaP which is covered with a thin native oxide layer. Here it should be mentioned that the magnitude of σ_d can be derived from the k values either in the body region or in the surface region of the sample, which suggests that our experimental results are well self-consistent. In order to give a clear understanding of the ion beam annealing phenomenon for GaP, the magnitudes of annealing cross sections for three different surface states induced by MeV ^{4}He ion bombardment have been estimated quantitatively. Because the values of the $(N_d/N_0 - 1)$ are very small under the aligned beam condition in our experiments, we can use Eq.(4) to calculate the ion beam annealing cross sections for the three different surface states, the calculated values are listed in Table 2.

Table 2. Values of the annealing cross sections σ_a for GaP induced by 1.0 MeV aligned $< 111 >^4$He ion beam incident upon three different kinds of surfaces.

Region	Surface state		
	Oxide	Clean	Amorphous
Surface	$2.0\times10^{-17}\,\mathrm{cm}^2$	$1.3\times10^{-17}\,\mathrm{cm}^2$	$8.4\times10^{-17}\,\mathrm{cm}^2$
Body	$1.0\times10^{-17}\,\mathrm{cm}^2$	$2.6\times10^{-17}\,\mathrm{cm}^2$	$2.5\times10^{-17}\,\mathrm{cm}^2$

From Table 1, the effective radiation damage cross section in the surface region of GaP is negative for the sample which is covered with a very thin amorphous layer. This suggests a significant annealing effect in that region of the sample induced by ^{4}He ion bombardment. From Table 2, we can find that σ_a for the sample with an amorphous layer is more than four times larger than that for other two samples, which is in agreement with the negative value of σ_{eff}. In fact, during the RBS/C experiments, no matter how strong is the interaction between incident ions and target atoms, it will not increase the degree of order macroscopically in a completely amorphous sample because there are no predominant crystal lattice sites present. Although some fine crystal particles, crystallized by MeV ^{4}He ion bombardment, will distribute among the sample, these find crystal particles will have no effect on a backscattering spectrum because of their disorderly orientations. Only those located at the interface area can be epitaxial grown in the same orientation as the GaP substrate[17]. As a result, the true amount of the displaced atoms, which can be in recovery, induced by MeV

^{4}He ion bombardment is about 3 times less than those of original amorphous region. Hence, the actual annealing cross section is much larger than that in Table 2.

It is worthy to mention that the values of the effective radiation damage cross section in the surface and the body regions are approximately equal except for GaP which is covered with a very thin amorphous layer. This is far different from that of Si crystal because of a few nanometers in thickness of the native oxide layer on Si surface or C and O contaminations during experiments[6,7]. But under our UHV condition, C and O contaminations are negligible during experiment, and the thickness of the native oxide layer for GaP is only about 1 monolayer. Meanwhile, the amount of damage produced by irradiation with an aligned beam is much smaller than that with a beam of random incident ions. This is in accord with the observation that the close encounter probability between the incident ^{4}He ion and the target nuclei for an aligned beam is about one order of magnitude smaller than that for a random beam, which suggests that the radiation damage is produced predominantly by elastic collisions among nuclei. This mechanism is similar to that for other materials, such as Si and Ge[8]. We considered that the type of chemical bonding between target atoms determines the mechanism in producing the radiation defects, as many authors believed. Note that our experimental results is contrary to that of Dearnaley et al.[18] Maybe the beam spread angle for a wide beam in their experiments is too large to obtain the true backscattering/channeling spectrum. However, the newest experimental results also support ours[19].

In order to compare the measured absolute radiation damage cross section with the prediction of the modified Kinchin-Pease model[17], we have calculated the radiation damage cross section ($\sigma_{k-p} = 4.5 \times 10^{-18}\,\mathrm{cm}^2$) for 1.0 MeV ^{4}He ion incidence with displacement energy of 10 eV[20] for Ga and P atoms, based on the method described in Ref.[21]. The predicted value is less than the measured value σ_d. Here it should be mentioned that the ionization-induced displacement within the material is not considered in the modified Kinchin-Pease theory. In fact, the electronic ionization indeed contributes to the damage production for valence crystal. When vacancy is generated by MeV ^{4}He ion bombardment, the loss of valence electrons would reduce the binding energy, and thus decrease the threshold energy for atomic displacement. As a result, an increased number of point defects, generated by electronic ionization, will enlarge the Kinchin-Pease prediction. On the other hand, radiation damage cross section σ_t can be calculated by TRIM91 code, but we cannot compare σ_t with the value of σ_d, because σ_t is highly influenced by the value of the threshold energy E_d for atomic displacement; moreover, there is no accurate E_d available. If we choose E_d as 6 eV and 10 eV for Ga and P atoms respectively, σ_t will be $6.8\times10^{-18}\,\mathrm{cm}^2$; similarly, σ_t will be $8.2\times10^{-18}\,\mathrm{cm}^2$ for E_d equal to 6 eV and 9 eV for Ga and P atoms respectively.

IV. CONCLUSIONS

The radiation damage for GaP crystal in different surface states has been studied at room temperature in an UHV chamber. Our experimental results suggest that the defect generation rate is strongly related to the surface state. Because of a very thin native oxide layer, the unclean GaP crystal shows similar behaviors to the clean and ordered sample. Meanwhile a significant ion beam annealing effect has been observed in the sample which is covered with a very thin amorphous layer. The absolute radiation damage cross section σ_d for 1.0 MeV ^{4}He ion bombardment has been measured as $8.0 \times 10^{-18}\,\mathrm{cm}^2$. Finally, the results suggest that for GaP the damage is produced mainly by nuclear collision.

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