JOURNAL OF MATERIALS SCIENCE 15 (1980) 1684–1690

Defect distribution near abraded surface of III-V compound semiconductors

MASAHIRO KITADA
Central Research Laboratory, Hitachi Ltd, Kokubunji, Tokyo 185, Japan

Microstructures of damaged layers near the abraded surface of GaP, $GaAs_{0.6}P_{0.4}$, and GaAs single crystals have been observed with a transmission electron microscope. The damage due to 0.3 μm Al_2O_3 abrasion consists of dislocations. Dislocation densities in the "abrasion band" and other regions are larger than 5×10^{11} cm^{-2} and about 10^{11} cm^{-2}, respectively. Dislocation density decreases with increasing distance (depth) from the abraded surface. The depths of the damage layers for GaP, $GaAs_{0.6}P_{0.4}$, and GaAs are about 0.4, 0.55, and 0.8 μm, respectively. The Burgers vector of dislocations is $a/2[1\ 1\ 0]$, and A and B dislocations are observed. During annealing, the dislocations are rearranged and eliminated by the reaction of the dislocations with different Burgers vectors and climbing motion. The rearrangement temperatures for dislocations in GaP and GaAs are about 500 and 450° C, respectively. Electrical resistance changes in the damaged layer of GaP are recognized by electrical resistance measurements.

1. Introduction

Semiconductors of III-V compounds must be mechanically treated to permit their use in various semiconductor devices. These mechanical treatments include slicing, dicing, scribing, lapping and abrasion.

Abrasion damage near the surface of semiconducting crystals has been investigated by measuring the variations in etching rate [1, 2], the metallographic structure changes after etching [3, 4], X-ray diffraction [5], and measuring optical constants [6]. A transmission electron microscope (TEM) has been used to study the nature of abrasion damage in Si and the existence of dislocations in the abraded Si layer was reported [7]. In addition, the effect of damage on the external EL efficiency of GaP has been confirmed [8]. However, in the case of III-V compound semiconductors, the detailed microstructures of the damaged layer for crystals other than Si have not yet been determined.

In this work microstructures of abrasion damage in GaP, $GaAs_{0.6}P_{0.4}$, and GaAs single crystals have been studied in detail by means of TEM. The relationship between the damage and electrical properties of the crystals has also been measured.

2. Experimental details

The GaP, $GaAs_{0.6}P_{0.4}$, and GaAs crystals used in this study were grown by vapour-phase epitaxy for the (1 0 0) orientation, and liquid-phase epitaxy for the (1 1 1) orientation on a pulled substrate. The Te-dopant concentration of n-type specimens was 5×10^{16} to 3×10^{17} cm^{-3}, and resistivity was 2 to 3×10^{-1} Ωcm. Dislocation density in the epitaxial layer was about 5×10^4 cm^{-2}. Epitaxial layer thickness was 100 μm for VPE and 50 μm for LPE.

The surface of the specimens was abraded on a rotating micro-polishing cloth using Al_2O_3 particles with an average diameter of 0.3 μm and distilled water as a lubricant. The abrasion load was 250 g cm^{-2} and abrasion time was about 30 min. Some of the specimens were subsequently annealed at 300 to 900° C for 1 h in Ar. The abraded specimens were rinsed in distilled water and then ethanol. They were then dried in an N_2 gas stream.

For the TEM examination, the pulled substrates and unabraded portion of the grown crystals were removed by etching with a 2:1 mixture of HNO_3 : HCl. The etching was continued until the abrasion damage was observed. Surface damage of the abraded layer was removed progressively

0022–2461/80/071684–07$02.70/0 © *1980 Chapman and Hall Ltd.*

using the above etchant to examine the depth distribution of dislocations. The removed thicknesses were measured by interferometric microscopy.

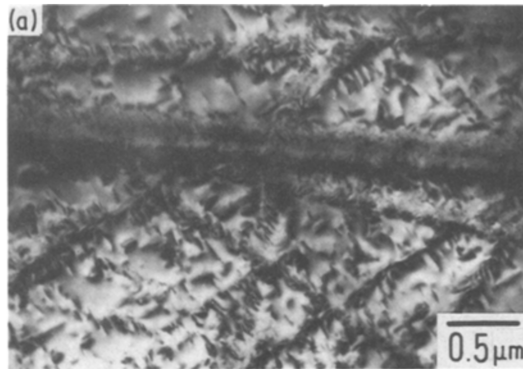
Electrical resistance of the damaged layers was measured using the conventional four-point probe method. A p-type specimen was made for this experiment by diffusing Zn at 600° C [9] and its surface impurity concentration was about 5×10^{17} cm^{-3}. The p-n junction depth was about 2 μm.

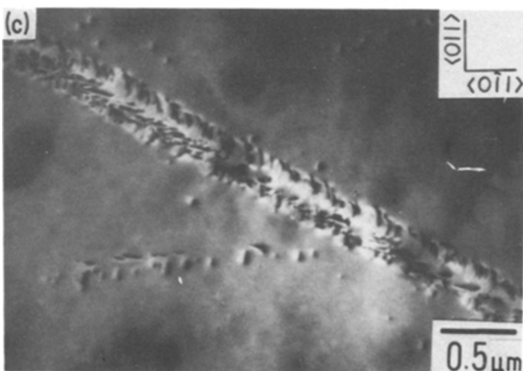
3. Results

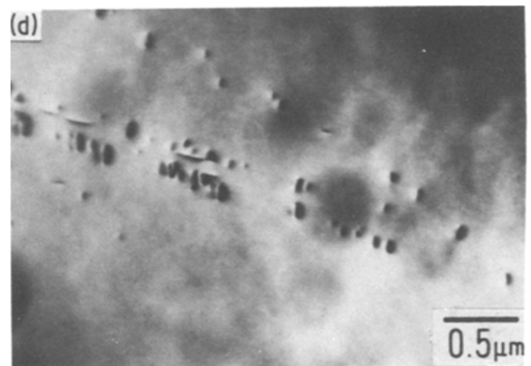
3.1. Damaged layer microstructures

The microstructures near the surface of the abraded (1 0 0) GaP specimen are shown in Fig. 1a. Here, "abrasion bands", which have a high dislocation density, and a comparatively "less damaged" region are observed. The width of the abrasion bands were 0.05 to 0.3 μm and the dislocation density was larger than about 5×10^{11} cm^{-2}. However, when the dislocation density in the abrasion band was larger than 5×10^{11} cm^{-2}, it was difficult to resolve each dislocation line. In the less damaged regions, the dislocation density was about 10^{11} cm^{-2}. From these results, it was found that the dislocations were induced near the GaP surface and the GaP crystal was deformed plastically by abrasion.

Next, about 500 Å was etched from the abraded surface of the GaP specimen and the dislocation distribution is seen in Fig. 1b. Here, the dislocation density has decreased. The dislocation densities of the abrasion bands and the less damaged regions were about 10^{11} and 7×10^{10} cm^{-2}, respectively. When about 1500 Å is removed from the original surface, dislocations in the less damaged regions were almost non-existent, and only dislocations in the abrasion bands remain, as shown in Fig. 1c.







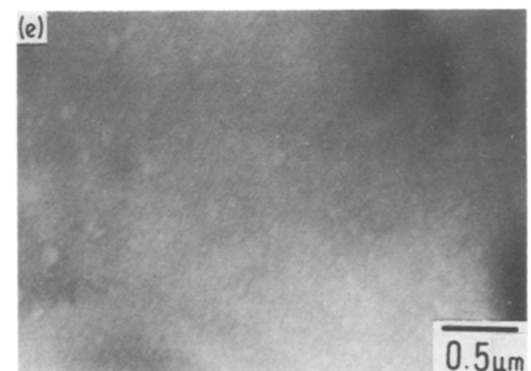


Figure 1 Electron micrographs of abraded (1 0 0) GaP specimen, as-abraded (a), and removed with about 500 Å (b), 1500 Å (c), 3000 Å (d), 4500 Å (e).

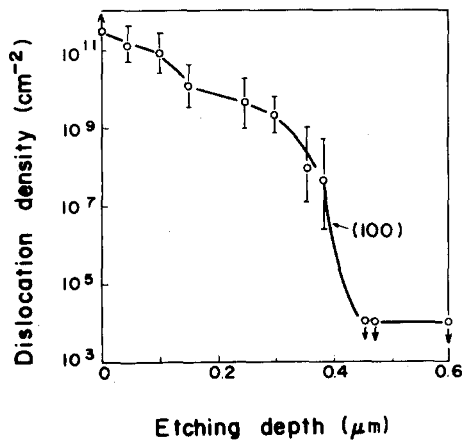


Figure 2 Dislocation distribution of abraded (1 0 0) GaP specimen.

The average dislocation density in this specimen was 10^{10} cm^{-2}. In the specimen with about 3000 Å removed, the average dislocation density was 10^9 cm^{-2} as shown in Fig. 1d.

An electron micrograph of the specimen after removing about 4500 Å is shown in Fig. 1e. Here, no dislocation induced by abrasion were observable. The measured densities of dislocations in GaP induced by abrasion are shown in Fig. 2.

The depth of damage in GaP specimens is about 4000 Å, and the observed defects induced by abrasion consist only of dislocation lines. The existence of vacancies induced by the intersection of dislocations was also considered. However, it is difficult to confirm the existence of vacancies when using TEM.

The dislocations in GaP induced by abrasion tend to lie perpendicular to each other and appear to be oriented in the $[\bar{1}\,1\,0]$ or $[1\,\bar{1}\,0]$ directions apparently. Some of the dislocations are arrayed like a dislocation pair mentioned later. The Burgers vectors of these dislocations were determined experimentally using the $\mathbf{g}\cdot\boldsymbol{b} = 0$ method proposed by Hirsch *et al.* [10] Here, the Burgers vector of GaP induced by abrasion is $a/2$ [1 1 0].

The measured dislocation density in the damaged layer on the (1 1 1) B plane in GaP specimen is shown in Fig. 3. The dislocation density and damaged depth for the specimen was slightly smaller than that of the (1 0 0) specimen. Likewise, the dislocation distributions of GaAs and $GaAs_{0.6}P_{0.4}$ with the (1 0 0) surface abraded were measured. The dislocation densities, normal to the abraded surface, are shown in Fig. 4 for these crystals.

3.2. Effect of annealing

The abraded GaP specimens were annealed at 300 to 900° C in Ar in order to examine the rearrangement and extinction of induced dislocations. After annealing at 300 to 400° C, the dislocation distribution in abraded GaP did not change when observed by TEM. However, when the annealing temperature was above 500° C, the originally straight dislocation lines in abraded specimens curved and aggregated as shown in Fig. 5a. In addition, the dislocation density decreased with increasing annealing temperatures.

After annealing at 650° C, most of the dislocations in the less damaged regions disappeared. The dislocation density in the abrasion bands also decreased by annealing at 650° C for 1 h. The average dislocation density was about 5×10^9 cm^{-2}. The dislocations in the abrasion bands tangled complicatedly and some of the dislocations formed dislocation networks as shown in Fig. 5b.

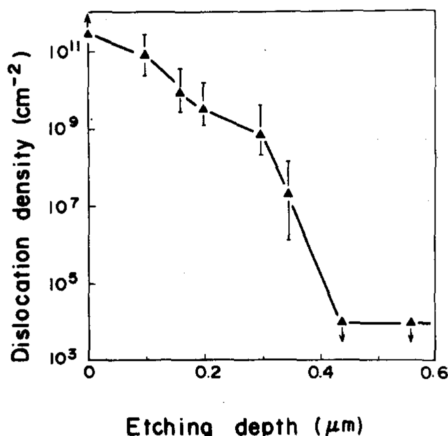


Figure 3 Dislocation distribution of abraded (1 1 1) B GaP specimen.

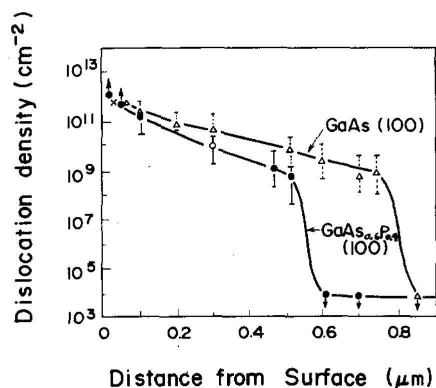
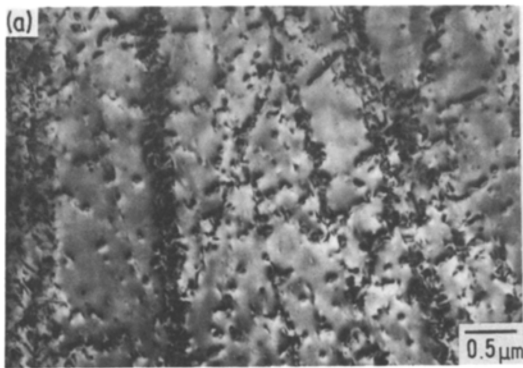
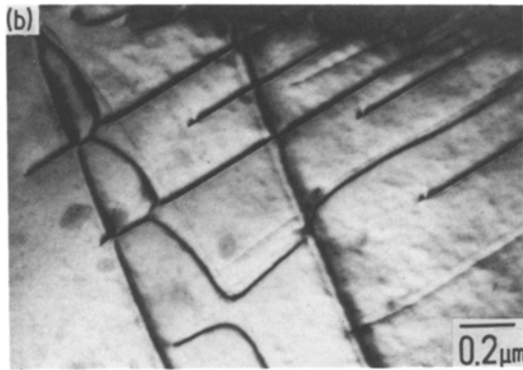


Figure 4 Dislocation densities of abraded (1 0 0) GaAs and $GaAs_{0.6}P_{0.4}$ specimens.





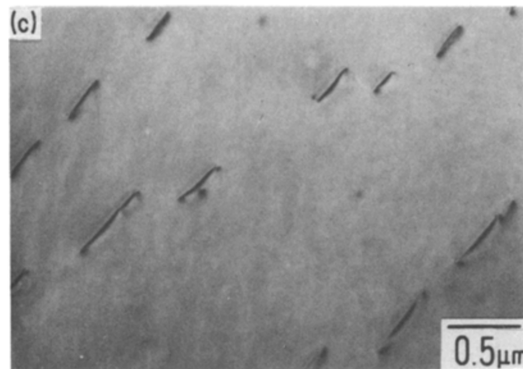


Figure 5 Electron micrographs of (1 0 0) GaP specimen annealed at 500° C (a), 650° C dislocation network (b), and 900° C (c).

When the annealing temperature was raised to 750° C, almost all of the dislocations were eliminated and the abrasion bands could not be observed. Here, the dislocation density decreased to about 3×10^8 cm^{-2}. In this specimen, the dislocations tend to lie along the [1 $\bar{1}$ 0] and [$\bar{1}$ 1 0] directions and the dislocation lines became longer than they were before annealing. Annealing at 900° C further decreased the dislocation density to about 10^7 cm^{-2} as shown in Fig. 5c. Here, the dislocation lines tend to lie along the [1 1 0]

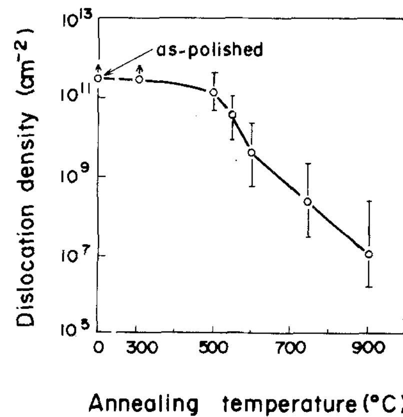


Figure 6 Dislocation density of annealed (1 0 0) GaP specimen.

direction of GaP. It is considered that these were dislocations which remain from the abrasion bands. However, the abrasion band grooves were not observed.

The effect of annealing temperature on the dislocation density near the abraded surface of GaP is depicted in Fig. 6. Likewise, the dislocation densities after annealing for abraded GaAs and $GaAs_{0.6}As_{0.4}$ are shown in Fig. 7.

3.3. Interaction of dislocations

Among the dislocations induced by abrasion, dislocations, which apparently formed pairs, were observed. The specimen shown in Fig. 8 was slightly abraded in order to study the interaction of dislocations. In general, dislocation pairs have been observed in ordered alloys. However, GaP is not an ordered alloy. The vectors of these side-by-side dislocations are assumed to be A and B dislocations [11] of III-V compounds by the contrasts.

An example of the interaction of paired dislocations is shown in Fig. 9. Electron-beam heating

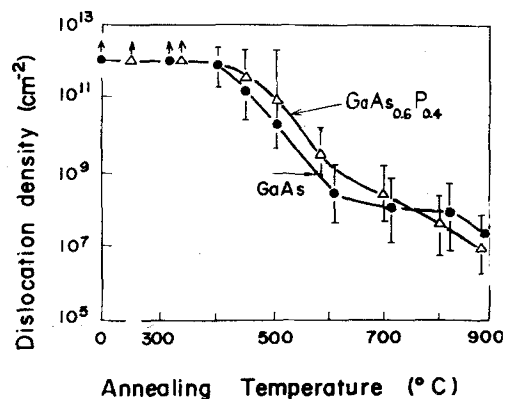


Figure 7 Dislocation densities of annealed (1 0 0) GaAs and $GaAs_{0.6}P_{0.4}$ specimens.

Figure 8 Electron micrographs of slightly abraded (1 0 0) GaP specimen.

caused the dislocations (for example A and B in the figure), which are on the same crystal plane, to approach each other and react. As a result, the dislocations formed a dislocation loop as shown in fig. 9. The reaction of a pair of dislocation lines was carried out both at the ends and in the middle of the dislocation lines marked E and M as shown in the figure, where, points E and M indicate an end and a middle reaction point, respectively. At points E and M, it is considered that the reaction $a/2[\bar{1}\ 1\ 0] + a/2[1\ \bar{1}\ 0] = 0$ may occur. The reacted dislocation lines marked G began to shrink due to electron-beam heating.

Thus two dislocation lines having opposite vectors form a dislocation loop, and then the loop shrinks until completely eliminated. However, clear photographs of the detailed behaviour were not obtained with electron microscope observation because the reactions occurred extremely rapidly.

3.4. Electrical resistance measurements

The electrical resistance changes of n- and p-GaP caused by abrasion were measured using the four-point probe method. The surface resistance ratios $\rho d/\rho o$ are shown in Fig. 10, where ρd and ρo are the sheet resistances of damaged and non-damaged specimens, respectively. The surface resistances of n- and p-GaP increased and decreased, respectively, as the result of abrasion. The resistance changes returned to the normal values after removing the damaged layers.

4. Discussion

The GaP abrasion mechanism is considered to consist of grooving, chipping, and cleaving by the abrasive particles. In the abrasion bands, the sharp corners of the abrasive particles push the GaP surface and an extremely large stress is applied. Thus, in stress-concentrated area, the GaP crystal is plastically deformed by the surface-induced dislocations. When the induced dislocation density becomes larger than 10^{11} to 10^{12} cm^{-2}, these dislocations probably pile up successively and the stress concentration increases. At the point where this stress is concentrated, the dislocations are immobile. Consequently, cracks are introduced.

These cracks then propagate and the cracked GaP chips are successively torn from the GaP surface. In less damaged regions, it is assumed that the abrasion mechanism is the same as that in the abrasion bands. However, the dislocation density is smaller than that of strong plastically deformed regions.

The removal of atoms owing to friction between the crystal and abrasive particles is also considered. However, in order to recognize these phenomena, another more appropriate experimental techniques will be necessary.

Gatos [12] reported that the damaged depth of the (1 0 0) GaAs by abrasion was larger than that of the (1 1 1) B. In this experiment, the damaged depth of the (1 0 0) GaP was slightly larger than that of the (1 1 1) B. It is believed that dislocations

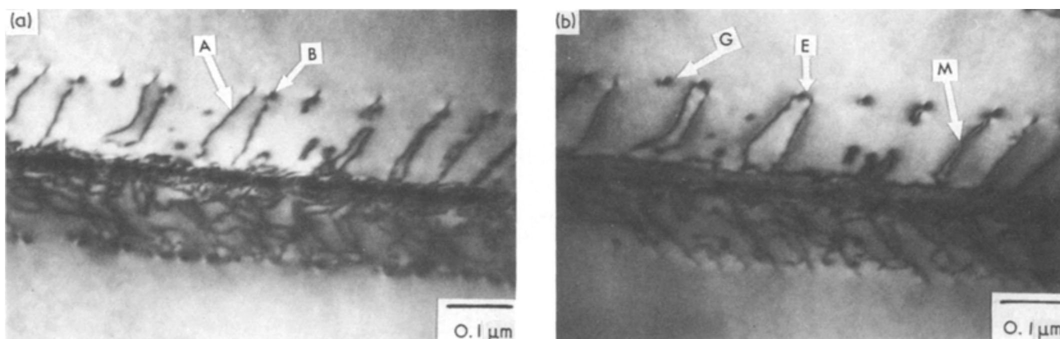


Figure 9 Continuous observation of interaction of dislocations in abraded (1 0 0) GaP specimen. A and B indicate A and B dislocations, respectively. E and M indicate end and middle reaction points of dislocations.

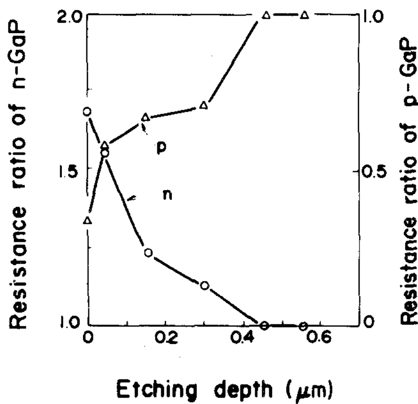


Figure 10 Surface resistance ratios versus etching depth of abraded p- and n-GaP specimens.

are induced from the free surface of the GaP crystal. Induced dislocations are arrayed like dislocation pairs or dipoles as shown in Fig. 8. The two dislocations form a dislocation loop as the result of electron-beam heating, as shown in Fig. 9.

The Burgers vectors of the dislocation lines are opposite to each other and exist on the same crystal plane. Therefore, it is possible that the two dislocation lines react and disappear according to the reaction $a/2[\bar{1}\ 1\ 0] + a/2[1\ \bar{1}\ 0] = 0$. However, since the mechanism for inducing dislocations is very complex, the detailed mechanism could not be determined from these experimental results.

The annealing-out mechanism for dislocations induced by abrasion is considered to consist both of a sink to the free surface of the crystal by climbing motion, and the reaction between dislocations. In the climbing motion, the mobilities of Ga and P vacancies depend on the diffusion constants in GaP. Moreover, they depend on the partial pressure of phosphorus vapour. In the present work, annealing was carried out in an Ar atmosphere. Consequently, it is considered that the phosphorus atoms in GaP sublimate easily into the atmosphere from the GaP surface. Therefore the climbing motion of B-dislocations occurs preferentially near the GaP surface. As another mechanism for dislocation elimination other than climbing motion, annihilation by the reaction $a/2[\bar{1}\ 1\ 0] + a/2[1\ \bar{1}\ 0] = 0$ is considered. Dislocations form a dislocation node due to a reaction such as $a/2[1\ \bar{1}\ 0] + a/2[0\ 1\ \bar{1}] + a/2[\bar{1}\ 0\ 1] = 0$ [13], these dislocations are stable and form a dislocation network as shown in Fig. 5b.

On the other hand, the dislocation densities near the surface of abraded GaP are at least more than $10^{11}\ cm^{-2}$. Consequently, recrystallization in GaP abraded regions by annealing must be considered. However, even if recrystallization occurs, perhaps, the recrystallized grains would not have been observed to grow epitaxially on a non-damaged GaP matrix. In the present work, recrystallized grains or sub-boundaries were not observed.

Similar results were experimentally obtained for GaAs and $GaAs_{0.6}P_{0.4}$ annealing. The relationship between the damaged depth and the energy gap of these tested compounds is shown in Fig.11. It is well known that this type of relation exists [12]. In the present work, this relationship becomes more obvious than that of previous results since direct information has been obtained. In addition, the relationship between damaged depth and Knoop hardness of the tested compounds is shown in Fig. 12. It is assumed that these relationships indicate a dependence on Pierls force for dislocation movement. However, details to support this have not yet been obtained.

The electrical resistance of n-GaP was increased

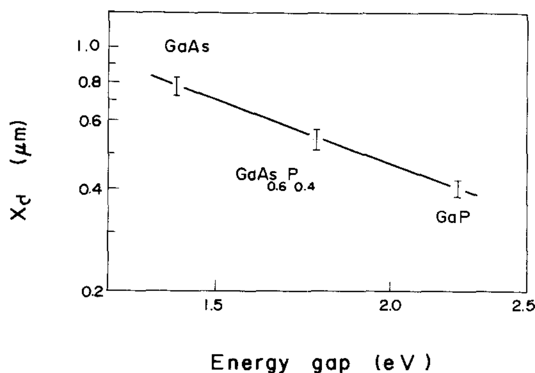


Figure 11 Relationship between damaged depth, Xd, and energy gap of compounds.

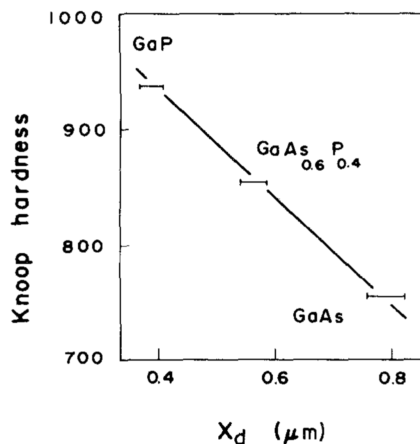


Figure 12 Knoop hardness versus damaged depth, Xd, of compounds.

due to abrasion. This means that electrons are trapped by abrasion damage or compensated by holes generated by abrasion. On the other hand, the resistance of p-GaP decreased with abrasion. This means that the number of holes apparently increased. In other words, it is considered that the apparent increase in hole number is due to damage which generates holes in p-GaP caused by abrasion. If the effects of other defects can be ignored, for example, impurities, vacancies, it is assumed that induced dislocations play a major role as a hole generation source. Lack of electrons in A dislocations results in a hole generation. Therefore, if A and B dislocations contribute equally to the resistance change, it is considered that the A dislocation density is larger than that of B dislocation.

References

1. P. R. CAMP, *J. Electrochem. Soc.* **102** (1955) 586.
2. J. W. FAUST, Electrochemical Society Meeting, Buffalo, New York (1958), ASTM Symposium on Electro-Device Components and Materials, Special Technical Publication no. 246 (1958).
3. E. W. PUGH and L. E. SAMUELS, *J. Electrochem. Soc.* **108** (1961) 1043.
4. *Idem, ibid.* **109** (1962) 409.
5. E. S. MEIERAN, *Trans. Met. Soc. AIME* **242** (1968) 413.
6. C. E. JONES and A. R. HILTON, *J. Electrochem. Soc.* **112** (1965) 908.
7. R. STICKLER and G. R. BOOKER, *Phil. Mag.* **8** (1962) 859.
8. N. E. SCHUMAKER and G. A. ROZGONYI, *J. Electrochem. Soc.* **119** (1972) 1233.
9. MASAHIRO KITADA, *J. Appl. Phys.* **48** (1977) 279.
10. P. B. HIRSCH, A. HOWIE and M. J. WHELAN, *Phil. Trans. A.* **252** (1960) 499.
11. P. DELAVIGNETTE, H. B. KIRKPATRICK and S. AMELINCKX, *J. Appl. Phys.* **32** (1961) 1098.
12. H. C. GATOS, M. C. LAVINE and E. P. WAREKOIS, *J. Electrochem. Soc.* **108** (1961) 645.
13. MASAHIRO KITADA, *J. Mater. Sci.* **12** (1977) 207.

Received 23 August and accepted 27 November 1979.