Radiation Damage Experiments and the Nature of Thermal Spikes in III-V Compounds*

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Specimens of gallium antimonide were irradiated at liquid nitrogen temperature with 12-Mev deuterons. The results of resistivity measurements during irradiation and of x-ray observations after the irradiation suggest very strongly that thermal spikes are introduced under these conditions. In particular from the shape and the intensity of the x-ray reflections the conclusion is drawn, that in these spike regions the material is present in a liquid-like lattice configuration, markedly different from the matrix configuration. The observations on annealing support the suggested model.

I. INTRODUCTION

IN the last fifteen years, experimental and theoretical investigations in the field of radiation damage have contributed to our knowledge of the solid state at an increasing rate. Initially most attention was given to the production of Frenkel defects (displaced pairs). Moreover, irradiation with monoenergetic electrons proved to provide a successful tool for determining the threshold energy E_d required to produce displacements. This energy was found to be 25 ev in the case of copper by Eggen and Laubenstein[1] and about 30 ev in germanium by Klontz and Lark-Horovitz.[2] Dessauer[3] had emphasized as early as 1923 that the large amount of energy a moving charged particle transfers to the electronic system of a material through which it passes (electron spikes) could induce atomic rearrangements if it were converted into vibrational energy sufficiently rapidly. Such conversion is of major importance in organic materials and in certain salts; however, there is little evidence to date to indicate that it is rapid enough to produce significant effects in metals and valence crystals. Although it was recognized that collisions between the incident particle and nuclei either above or below the threshold value E_d could heat the lattice locally (thermal spikes), it was not felt in early work that this incidental thermal effect was important in metals and semiconductors, at least near room temperature. Seitz[4] discussed thermal spikes and pointed out that typical spikes produced by incident charged particles would cool to the ambient temperature in a time of the order of 10^{-11} sec, that is, over a time of the order of 100 atomic oscillations. Thus the heated regions are cooled to ambient temperature rapidly.

Brinkman[5] extended the model of the thermal spike to the case in which the transferred energy is substantially larger than the threshold energy E_d and in which the incident or primary particle causing the damage displaces a number of atoms in succession. He termed such highly chaotic regions displacement spikes. In such cases he decided that the thermal effects would be adequate to anneal some of the displacements produced initially and could generate others as a result of fluctuations (see Fig. 1). On the whole the material in the spike could be regarded to have undergone melting and resolidification. He believed that the resolidified material would be highly imperfect if the ambient temperature were sufficiently low and that most of the residual damage could be ascribed to this imperfection, of which the part associated with the residuum of atoms displaced initially would be relatively small. In the case of copper irradiated with 12-Mev neutrons he estimated that the region of the displacement spike would contain about 2×10^4 atoms and possess linear dimensions of the order of 50–75 A.

It appears that the interpretation of experimental results in terms of the foregoing models is not always beyond doubt. The nature and relative importance of the spikes is still in question. Moreover, all the stages observed during the annealing are not well understood. For example, the damage resulting in metals after neutron and deuteron bombardment at liquid helium temperature[6,7] is interpreted in different ways.

In order to clarify this situation it is necessary to investigate widely different materials under controlled conditions and with different tools. It was Seitz's suggestion to combine two of the major additions to solid state physics in the last few years: radiation damage and the highly interesting III-V compounds. It is well known that the properties of these compounds are greatly influenced by impurities and lattice defects.[8] They crystallize in the zinc blende structure. X-ray reflections can occur as main lines and as superlattice

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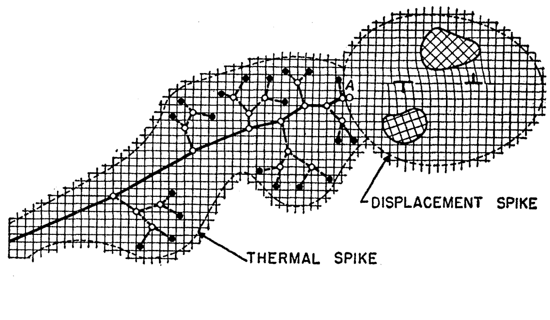

FIG. 1. Schematic representation of a displacement spike in a two-dimensional lattice (after Brinkman[5]).

lines. It was thought that an investigation of the damage of the III-V compounds with x-ray techniques could give valuable information. In this experiment GaSb was irradiated with approximately 2×10^{17} 12-Mev deuterons/cm^2 with the University of Illinois cyclotron. During irradiation the specimens were kept as close as possible to liquid nitrogen temperature. After the irradiation, the x-ray reflections of the irradiated part were compared with the reflections of the nonirradiated part of the same specimen. Also the behavior during annealing was studied.[9]

We shall present evidence here which implies that thermal spikes, that is, regions in which a substantial amount of energy has been transferred directly to the lattice, can indeed produce significant changes in the lattice under appropriate circumstances. The effect presumably is independent of the production of Frenkel pairs. Naturally the most energetic thermal spikes occur under circumstances in which Frenkel pairs are generated; it is clear that such pairs are present under the conditions discussed below. Nevertheless, it appears that the thermal effects are of overwhelming importance in determining the changes to be described.

It should be emphasized at the start that these experiments do not prove that Brinkman's point of view is generally valid. The III-V compounds possess the remarkable property that the density of the liquid phase is higher than that of the solid. This feature appears to influence the stability of the disorder produced by thermal spikes in a way that probably does not occur in more normal materials.

II. EXPERIMENTAL

Single crystalline specimens of GaSb (1.0×1.5 cm) were cut electrochemically and ground to a final thickness of 0.4–0.5 mm, which is nearly equal to the range of 12-Mev deuterons in this material. The samples were glued (GE 7031 varnish) on the aluminum block, which was tightly connected to the liquid nitrogen container by means of a copper block (see Figs. 2 and 3). The crystals were oriented in such a way that the deuteron beam was normal to the (100)-plane. At the top and bottom of the specimens thermocouples were soldered (Fig. 4); the leads of these couples were also used to measure the resistance of the specimens during irradiation. An aluminum screen, which made it possible to irradiate only a well-defined part of the specimen, was mounted in front of the specimens. Thin aluminum foils (20–200μ) on the front side of the screen prevented decomposed pump oil from the cyclotron chamber from hitting the specimens and served to shorten the effective range of the deuterons. The shadowed part in Fig. 4 was bombarded whereas the other parts were not irradiated. The latter served as a reference. Before making the x-ray measurements, the screen was rotated so that the whole specimen could be seen by the x-rays. Cu K_α radiation was used. It was monochromatized by a curved quartz crystal. Thin windows of Mylar were built in the sump to keep the loss of x-ray intensity small. The reflected beam was registered on Kodak no-screen x-ray film, which was placed at a distance of 60–100 cm from the specimens. It was possible to scan the specimen from one side to the other with the x-ray beam by moving the whole sump parallel to the (100) plane of the specimen. Near the top and the bottom the line-shaped x-ray beam hit those parts of the specimen which were not irradiated; the center part of the x-ray beam was reflected from the part of the specimen which was irradiated.

GaSb crystallizes in the zinc blende structure, which is similar to the diamond structure, having alternative Ga and Sb atoms. Thus the (100) planes are occupied by either Ga or Sb atoms, giving rise to the existence

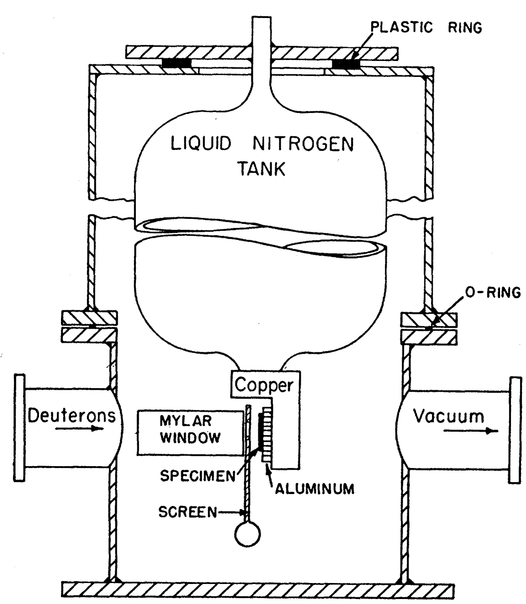

FIG. 2. Cross section of the equipment used in the present experiments.

[9] A preliminary report of this investigation has appeared. U. Gonser and B. Okkerse, Phys. Rev. **105**, 757 (1957).

of superlattice lines. The measurements were made on 3 reflections, namely: the superlattice line (200), $\theta=14°41'$; the main line (400), $\theta=30°28'$; and the superlattice line (600), $\theta=49°30'$.

The integrated intensity of each reflection is proportional to the square of the structure factor F. Thus for the main line $F=(f_{\text{Sb}}+f_{\text{Ga}})$, whereas for the superlattice line $F=(f_{\text{Sb}}-f_{\text{Ga}})S$. Here f_{Sb} and f_{Ga} are the scattering factors for the Sb and the Ga atoms, respectively, and S is the long-range order parameter. $S=1$ for perfect order whereas $S=0$ for complete disorder. The intensity of the main lines is very strong and independent of the order, but the intensity of the superlattice line is weak and depends on the order.

The beam was shut off at regular intervals to measure the resistance of the specimen. A potentiometer was used to measure the potential drop across the specimen and across a standard resistor. In order to eliminate the

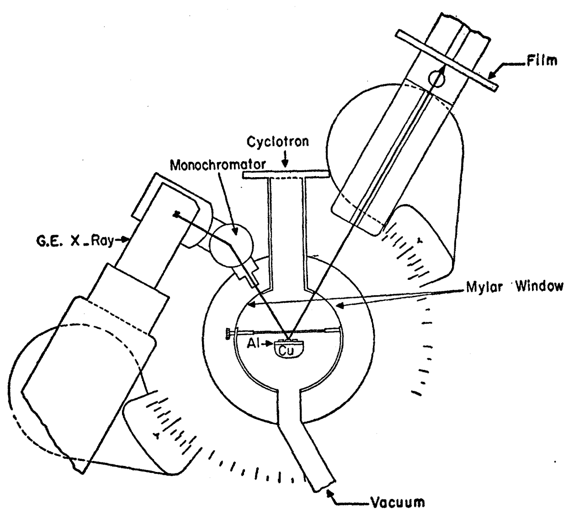

FIG. 3. Top view of the apparatus.

thermal emf, the current was reversed after each measurement; the average of both readings was taken as the proper value. It appeared that the deviation of each reading was equal to either the positive or the negative thermal emf, indicating that the contacts were purely ohmic.

Annealing of the specimens was achieved simply by warming the cryostat to room temperature after evaporating the liquid nitrogen.

III. RESULTS AND DISCUSSIONS

All the x-ray diagrams taken showed the following three effects:

1. Intensity Change

The part of the line representing the damaged part of the specimen remained sharp; however, the intensity in this part is lower than in the part representing the nonirradiated region. The line shapes of the irradiated

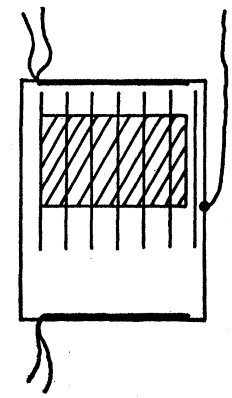

FIG. 4. Specimen with leads for temperature and resistivity measurements. Shadowed part is irradiated. Vertical lines show the locations where x-ray reflections were taken.

and the nonirradiated part as measured with the photomicrometer are given in Fig. 5. One has to assume that some regions in the irradiated part no longer fulfill the Bragg condition for reflection. It appears that the damage is not homogeneous along the deuteron path. The deeper layers are affected more than the surface layers. This conclusion can be drawn from two observations: (a) The ratio of the intensities in the irradiated and nonirradiated parts of the (200) lines, which have a comparatively small Bragg angle, is nearer unity than the ratio of the intensities of the (600) lines, which have a larger Bragg angle. In the latter case the absorption is smaller. (b) Under otherwise similar conditions, the ratio of the intensities is larger when an aluminum foil in which about half of the energy of the deuterons is dissipated is placed in front of the specimen. Reasoning along these lines one would expect that the ratio of the intensities of the (400) lines might be about the average of the ratios of the (200) and of the (600) lines. Actually however, this ratio is of the same order as that for the (200) lines. One can explain this if one assumes that, in addition to the regions

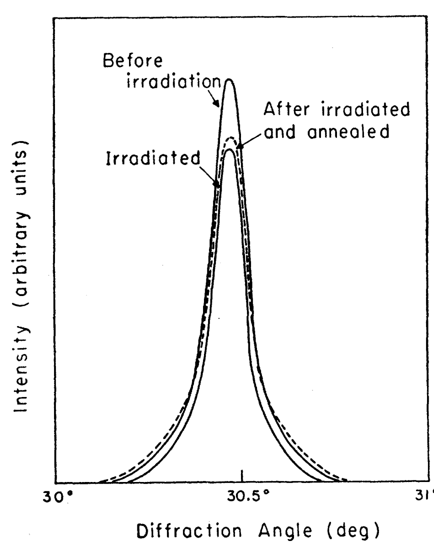

FIG. 5. Line shape of the (400)-reflection after irradiation and after annealing.

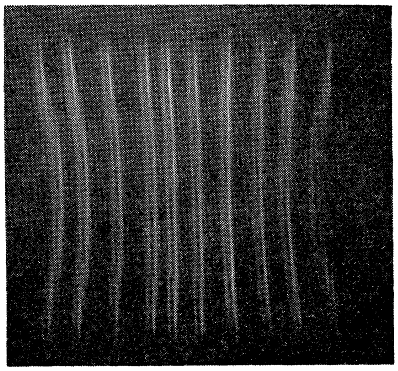

FIG. 6. Set of (400) reflections obtained by moving the specimen parallel to the (100) plane.

which do not fulfill the Bragg condition, there are other disordered regions which act as transition regions to the single crystalline matrix.

2. Curvature of the Lines

Several parts of the specimen could be investigated by moving parallel to the (100) plane. Figure 6 shows the lines obtained. It appears that there is a tendency for the lines to be convex towards the center of the specimen. This curvature is especially pronounced at the boundary of the irradiated and nonirradiated part. This effect was found for all lines and for all specimens irradiated. The only possible explanation seems to be that a bending of the lattice planes occurs. One can account for this behavior if one assumes that the material contracts on irradiation. This contraction can be associated with the abnormal behavior of the III-V compounds on melting, the specific density of the liquid being higher than in the solid state.[10] Buschert[11] showed in the case of InSb that the number of nearest neighbors is close to 6 at 13°C above the melting point, whereas it is only 4 in the solid state. Hendus[12] demonstrated that the number of nearest neighbors increases from 4 to 8 in the case of germanium.

We conclude that parts of the specimen corresponding to thermal spikes are transformed into a more dense configuration having a liquid-like coordination. These transformed regions become centers of negative pressure in the matrix. Because the nonirradiated part of the specimen can be considered as a solid frame, the irradiated part can relax only near the surface. This produces bending of the planes.

3. Change in Lattice Parameter

A change in lattice parameter was observed in several x-ray diagrams. It seems that this effect is dependent mainly on the geometry and boundary conditions of the specimen. In the case of a thin specimen a lattice parameter increase (about 0.1%) was found, whereas in thicker specimens, about 4 times as thick, the lattice parameter change was very small. One has to bear in mind that we scan only the matrix material with the x-ray beam and the conclusions concerning spikes are more or less indirect. It may well be that along with the appearance of displacement spikes, as described in Brinkman's model, Frenkel pairs are introduced in the matrix material, resulting in an expansion of the lattice, but the crystal as a whole, including the high density spikes, decreases in volume.

The effects observed are given schematically in Fig. 7. Thus the x-rays observations seem to suggest that the irradiation results in a region with a structure different from the matrix. We like to think that the material is transformed locally to the liquid configuration. These parts do not contribute to the reflected intensity, and produce a decrease in intensity in those parts of the lines representing the irradiated region. The irradiated part of the specimen contracts as a result of the transformation from solid to liquid configuration and produces curved reflections. There will be disordered regions between the spike regions and the original lattice. These give rise to the observed intensity ratios of the main and superlattice lines.

Two other observations are in agreement with this model.

1. Resistivity Measurements

The changes in resistivity induced by bombardment with deuterons, alpha-particles, electrons, and neutrons has been studied extensively in Ge,[13] in InSb,[14] and in GaSb.[15] Most of the results were interpreted with use of the model proposed by James and Lark-Horovitz,[16]

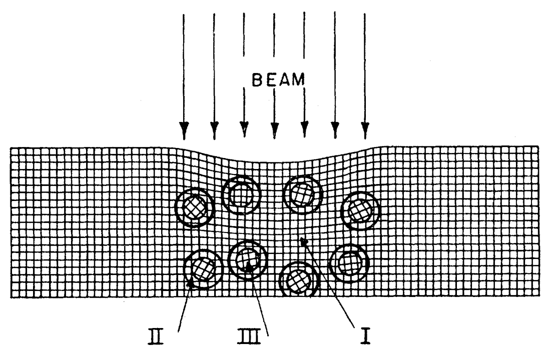

FIG. 7. Cross section of the specimen and suggested model of the damage. Region I represents the matrix material, region II the gradually disordered region, and region III the liquid lattice configuration region.

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which considers the energy levels associated with Frenkel defects. This model could be employed very successfully when the specimens were irradiated at room temperature. The model does not work very well, however, in cases in which the irradiation is carried out at low temperature. An explanation for this fact can be found in the frozen-in temperature spikes.

In Fig. 8 the resistivity of a p-type specimen of GaSb is plotted as a function of the integrated flux. The general behavior of the curve can be explained if one assumes that the initial increase can be attributed to semiconductor effects which are very sensitive to changes in trapping levels. The more gradual decrease in resistivity is associated with the transformation from solid to liquid configuration which can also be described

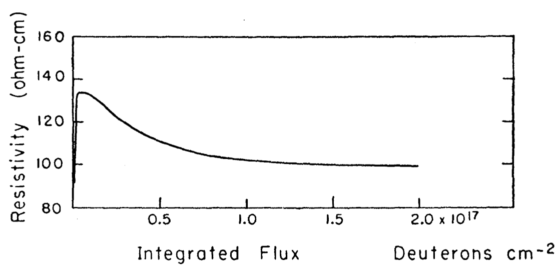

FIG. 8. Resistivity of a specimen as a function of the integrated flux.

as a transformation from a semiconductor to a metallic behavior. An increasing number of spikes is introduced as irradiation proceeds. These regions represent volumes having lower resistivity than the surrounding matrix and decrease the resistance of the specimen.

2. Behavior on Annealing

The curvature of the x-ray lines disappeared on warming, at about −110°C. In fact a slight bending into the opposite direction was observed in those parts of the lines which correspond to the deuteron irradiated section. The intensity in this part of the lines increased and line broadening occurred at the same time. The line shape after annealing is compared with the original shape in Fig. 5. These observations can be explained by postulating that the high temperature phase in the spike region is able to transform to the stable configuration during annealing. As a result, the density in these regions has to decrease. However, many imperfections in the matrix will either persist or be formed and produce high strains locally. In fact, some of the specimens broke during the annealing because of these strains, thus indicating the tremendous magnitudes of the residual stresses. One specimen broke only halfway initially. The (400) lines obtained at low temperatures are superimposed on this specimen in Fig. 9. It is interesting to observe that the direction of the changes in curvature are in agreement with the model suggested.

Still further, it was found that the resistivity in-

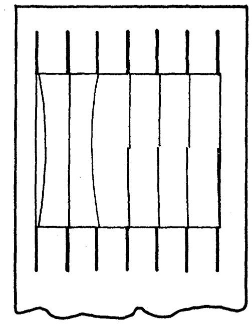

FIG. 9. Schematic reproduction of reflections superimposed on the part of the specimen from which each line was reflected after a specimen initially broke only halfway.

creased on annealing. This is to be expected if the region having liquid-like configuration and a metallic behavior transform to the normal configuration but leave a high concentration of physical imperfections.

Cleveland and Crawford[15] found no indication of the existence of spikes having metallic behavior in GaSb. Unfortunately the neutron irradiation was carried out at −125°C at which temperature irradiation annealing probably takes place. Thus the spike regions in their specimens do not correspond to the frozen-in high-temperature phase, but more nearly to the regions implied in Brinkman's displacement spike model.

IV. CONCLUSION

One can explain the results of the experiments if one assumes that spikes are introduced in this material during irradiation with 12-Mev deuterons at liquid nitrogen temperature. These spikes have some of the general properties of the displacement spikes suggested by Brinkman. There are, however, important modifications. Brinkman regarded the regions as more or less supercooled molten zones having nearly the same number of nearest neighbors as the surrounding matrix. In the present model, however, a phase transformation actually takes place. In the III-V compounds it is preferred to describe the spikes not only as regions containing displaced atoms, but as regions possessing a well-defined lattice configuration which is different from that of the matrix.

In a forthcoming paper the question of radiation-induced phase changes will be discussed more generally. Particular attention is given to materials having a high-temperature phase with a higher density and to materials having abnormal behavior at the melting point, the density of the liquid state being higher than that of the solid.

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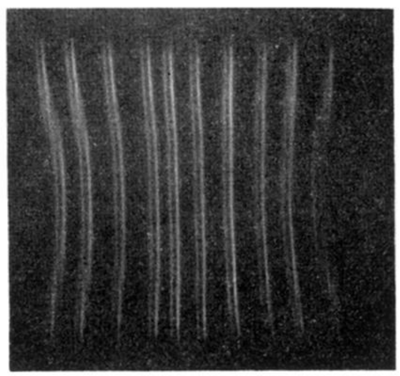

FIG. 6. Set of (400) reflections obtained by moving the specimen parallel to the (100) plane.