# Annealing of Radiation Damage in ZnSe

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Electron bombardment of ZnSe at 80°K results in the production of two fluorescence bands at 5460 and 5850 Å. The threshold for damage at 80°K is 240 keV. When the sample is cooled to 4.2°K following bombardment at 80°K the fluorescence spectrum changes, reflecting the temperature dependence of the fluorescence; the peak at 5460 Å disappears, a new one at 6400 Å appears, and the peak at 5850 Å shifts slightly to a shorter wavelength. When the crystals are bombarded at 10°K, fluorescent peaks at 6100 Å and 6400 Å are produced. The threshold for radiation damage at 10°K is 195 keV. The radiation damage at high energies at 10°K anneals in three stages, one at about 60°K, another at 90°K, and the final one at 135°K. The fluorescence spectrum changes following each of the first two annealing stages and disappears completely after the third annealing stage. With equal bombardment times, the fluorescence spectrum at 10 and at 80°K is identical, whether the crystal has been bombarded at 10°K and annealed at 90°K, or bombarded at 80°K without annealing. A Meecham and Brinkman plot has been used to determine the activation energies and the order of reaction of the three annealing stages.

## 1. INTRODUCTION

IN the II-VI compounds, there exists a relationship between the fluorescence and the crystalline defects. When bombarded by electrons at low enough temperatures, simple Frenkel-type defects might be expected to be formed. By selection of electron energies, the defect-fluorescence correlation can be established and a threshold for displacement of the constituent atoms can be measured. In CdS, two displacement thresholds have been measured: one at 115 keV for the displacement of the sulphur atom and one at 290 keV for the displacement of the cadmium atom.[1,2] Electron bombardment of ZnSe at liquid-nitrogen temperature has shown only a single threshold at 240 keV with the production of the two fluorescence bands at 5460 and 5850 Å. This radiation damage anneals completely in a single stage at about 135°K.[3] In fact, not all ZnSe shows radiation damage through fluorescence at 80°K. Those crystals showing damage at 80°K are called type-I ZnSe, while those that do not are called type-II ZnSe. However, when bombarded at liquid-helium temperature, both types of ZnSe show damage. Through the temperature dependence of the fluorescence spectra of the radiation damage and the annealing characteristics, the Frenkel defects and ensuing complexes can be studied.

The various stages of annealing in ZnSe have been studied in detail. The results of this work will be presented here as well as the work showing the existence of a second threshold for radiation damage in this material.

## II. EXPERIMENTAL PROCEDURES

The crystals used in this work were grown by the vapor phase deposition method of Reynolds.[4] The temperature of the hottest zone in the furnace was 1150°C. The crystals were polycrystals of a light greenish-yellow in color and of the order of 1 mm on a side.

The bombardments were carried out with the crystals mounted on a copper cold finger below a liquid-helium bath. The temperature was measured with a Rosemount Engineering Company type-118L platinum resistance thermometer. A Van de Graaff accelerator supplied the electrons for the bombardment and the fluorescence spectra were taken either with a prism spectrometer equipped with a RCA type-7102 photomultiplier tube or a Bausch and Lomb 2-m grating spectrograph with type 103aF film.

## III. RESULTS

### A. Displacement Threshold at Helium Temperature

Bombardment of ZnSe at liquid-helium temperature shows radiation damage below the nitrogen-temperature threshold of 240 keV. Figure 1 shows the rate of increase of fluorescence at 6400 Å as a function of electron energy for bombardment at liquid-helium temperature. The intersection of the curve with the $x$ axis indicates a

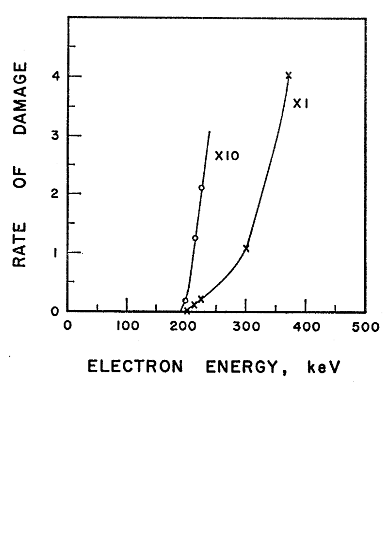


FIG. 1. The rate of radiation damage in ZnSe versus electron bombardment energy.

[1] B. A. Kulp and R. H. Kelley, J. Appl. Phys. 31, 1057 (1960).
[2] B. A. Kulp, Phys. Rev. 125, 1865 (1962).
[3] B. A. Kulp and R. M. Detweiler, Phys. Rev. 129, 2422 (1963).
[4] D. C. Reynolds and S. J. Czyzak, Phys. Rev. 19, 1957 (1950).

threshold at 195 keV. The damage rate varied between crystals, but both type I and type II showed the same damage when bombarded between the two thresholds.

### B. Annealing Characteristics

The isochronal annealing characteristic of type-I ZnSe crystals following bombardment at 500 keV at liquid-helium temperature is shown in Fig. 2, curve 3.[5] The peak of the fluorescence at 6100 Å at liquid-helium temperature was used as a measure of radiation damage through the 60 and 90°K annealing stages and the 5460-Å band for the third stage at 135°K. The crystal was heat treated for 10-min cycles at the temperature indicated.

The annealing of the damage produced by bombardment in the energy range 195 to 240 keV is shown by curve 1, Fig. 2. This consists of a single stage at about 90°K. As the electron beam energy increases above 240 keV, the annealing stage at 60°K appears. Simultaneously, in type-I ZnSe, the percent unannealed following the 90°K stage increases. The amount of damage remaining following the 90°K anneal varies from crystal to crystal. It is possible, by using the purest crystals available, to find crystals which show complete annealing of radiation damage following the 90°K stage regardless of the electron energy up to 1 meV. These are called type-II crystals. The isochronal anneal of the radiation damage of type-II crystals at electron beam energies greater than 240 keV is shown by curve 2, Fig. 2.

The fluorescence spectrum of radiation damage of a type-II crystal at a bombardment energy of 350 keV is shown in Fig. 3, curve 1. After the annealing stage at 60°K the fluorescence spectrum changes to curve 2.

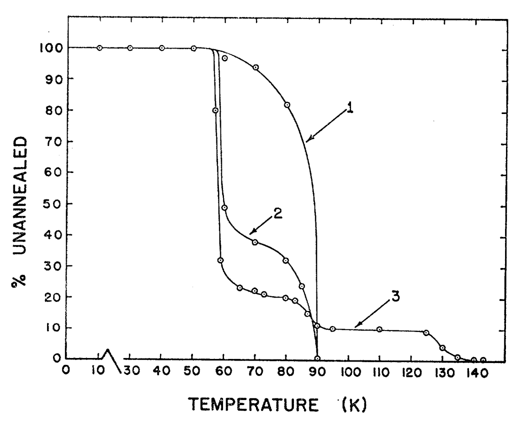


FIG. 2. Isochronal annealing characteristics of ZnSe bombarded at liquid-helium temperature at various energies; (1) Type-I or type-II ZnSe bombarded between 195 and 240 keV, (2) type-II ZnSe bombarded at energies greater than 240 keV, (3) type-I ZnSe bombarded at energies greater than 240 keV.

[5] B. A. Kulp and R. M. Detweiler, *Proceedings of the Seventh International Conference on the Physics of Semiconductors* (Dunod Cie., Paris, 1964).

The difference between curve 2 and curve 1 is shown in curve 3. As the bombardment energy is gradually reduced to 240 keV, the difference between curve 1 and 2 decreases to zero. Curve 3, Fig. 3 therefore represents the fluorescence spectrum resulting from displacement of an atom with a threshold of 240 keV. The peaks in the fluorescence shown here are almost the same as the peaks observed at helium temperature in type-I crystals after the 90°K anneal or after bombardment at nitrogen temperature. However, there are differences in the relative heights of the two bands and in the wavelength of the longest wavelength peak. Thus the temperature dependence of the fluorescence must be taken into consideration in identifying the bands associated with the radiation damage.

The temperature dependence of the nitrogen-temperature damage shows a marked change at about 40°K.

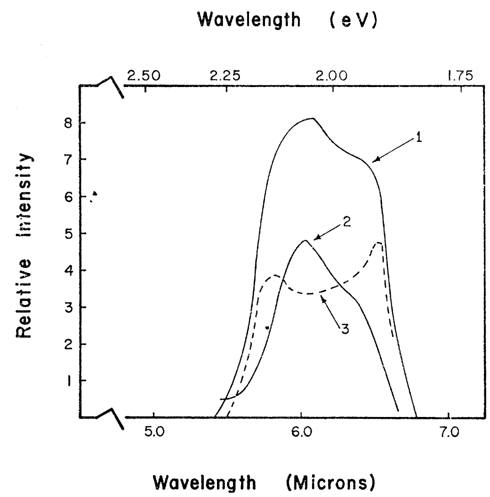


FIG. 3. The fluorescence spectrum of type-II ZnSe bombarded at 350 keV at 10°K, (2) The fluorescence of this crystal at 10°K after the 60°K anneal. (3) The difference between curves 1 and 2.

The exact point varies from crystal to crystal. As the temperature decreases through about 40°K, the fluorescence at 5450 Å decreases and the 6400-Å band appears. This behavior can be explained by the following model. The complex, which is formed at nitrogen temperature, appears to involve a vacancy and a chemical impurity, perhaps with a trapped electron. As the temperature decreases, there is a change in the ionization state of the complex resulting in its dissolution. The vacancy then becomes a fluorescent center. There is a slight difference in wavelength between the 6400-Å peak of the nitrogen damage at 10°K and the 6440-Å peak of the difference curve (3) of Fig. 3. The difference may be due to the perturbation of the vacancy by the chemical impurity in the 80°K damage case.

### C. Activation Energies and Order of Reactions

Meechan and Brinkman[6] have developed a method whereby utilizing the isochronal annealing characteristics and a single isothermal annealing characteristic, the activation energy and the order of the reaction of the various annealing stages are determined. Figure 4 shows a Meechan-Brinkman plot for determining the activation energies of the three annealing stages. The points for each stage lie quite well on straight lines, the slopes of which give the activation energies for annealing.

Figure 5 shows the plot to determine the order of the reaction according to the theory of Meechan and Brinkman. The points are plotted to give the best fit to a straight line the slopes of which are given in the figure. The first points of the curves for $T$ equal to 60 and 80°K are somewhat off, but correcting these causes the other points to deviate more seriously from a straight line. The slopes of the first two curves are rather exactly unity, indicating second-order reactions, while the slope of the third line is about 2.5 indicating a reaction of the order of 3 or 4.

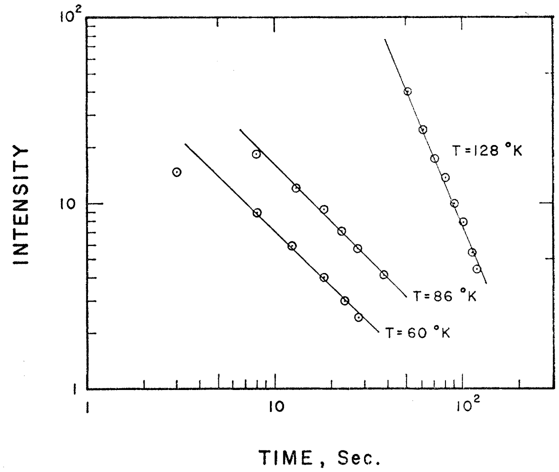


FIG. 5. Plot to determine the order of the reactions for annealing.

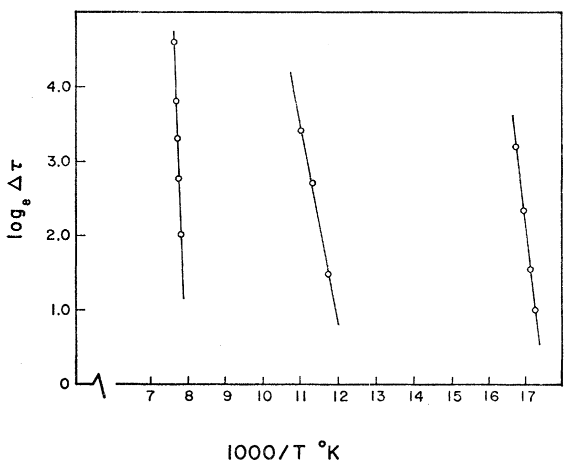


FIG. 4. Meechan-and-Brinkman plot to determine activation energies.

## IV. DISCUSSION

### A. Identity of the Thresholds for Damage

Previous experiments on CdS have shown the existence of two thresholds for production of electron radiation damage, one at 115 keV[1] and one at 290 keV.[2] The lower threshold is interpreted as that for the displacement of the sulfur atom from the lattice with an energy transfer of 8.7 eV. The higher threshold is that for displacement of the cadmium atom with an energy transfer of 7.3 eV. Other compound semiconductors in the III-V series have also shown two thresholds for radiation damage.[7,8] Therefore, it is reasonable to devise a model for the two displacement thresholds observed in ZnSe as displacements for the zinc atom and the selenium atom. On the basis of the hard-sphere collision model of Seitz and Keohler[9] with relativistic correction, the energy transferred to the zinc atom is 7.8 eV for a 195-keV electron and 10 eV for a 240-keV electron. Similarly the energies transferred to a selenium atom are 6.2 and 8.2 eV, respectively. If the lower energy is chosen for the displacement of the selenium atom, the displacement energy for the two constituent atoms differs by 3.8 eV, which is much larger than for any other II-VI or III-V compounds. Furthermore, in Bauerlein's[8] review paper reference is made to the other compound semiconductors where the metallic atom is always displaced with the lower energy. Thus, we associate the threshold energy of 195 keV with the zinc atom (displacement) with a displacement energy of 7.8 eV, and the threshold at 240 keV with displacement of the selenium atom with an energy transferred of 8.2 eV. It should be noted here, that Bauerlein on the basis of the change in slope of the cross-section curve, Fig. 3 of Ref. 1 identified the threshold at 240 keV with the displacement of the zinc atom and predicted a threshold for the displacement of the selenium atom at 320 keV. However, on the basis of the data and experiments presented in Ref. 2 and here, it is shown that the fluorescence resulting from the displacement of the zinc atom appears with a threshold of 195 keV.

Some crystals do not show radiation damage in fluorescence. Furthermore, there is generally a difference in growth rates of the fluorescence bands for various crystals under identical bombardment conditions. However, depending on the Fermi level, the presence of a

[6] C. J. Meechan and J. A. Brinkman, Phys. Rev. **103**, 1193 (1956).

[7] F. E. Eisen and P. W. Bickel, Phys. Rev. **115**, 345 (1959).

[8] R. Bauerlein, Z. Physik **176**, 498 (1963).

[9] F. Seitz and J. S. Koehler, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1956), p. 331.

dominant recombination center, or of a fluorescence poison (e.g., Fe or Ni), a particular fluorescence transition can be of low efficiency. Degrees of this condition can certainly be expected, so that the growth rate of a particular band could vary greatly from crystal to crystal depending on other chemical or structural impurities. The growth rate of a particular fluorescence band can still be linear with number of electrons over a wide range of energies.

### B. Annealing Characteristics

It has been pointed out that irradiation with the electrons just above the threshold would be expected to produce simple damage consisting of isolated Frenkel pairs (vacancies and interstitials).[10] The lowest temperature for annealing of radiation damage in metals is reported to be about 15°K [11] and that for germanium is 20°K.[12] Watkins[13] has reported interstitial aluminum in bombarded silicon at 10°K and suggests defect migration might make this possible, but he does not support this with any other evidence. He also shows that the vacancies become mobile at about 60°K. Divacancies formed by electrons of 1.0 to 1.5 meV are evident, however, at 20°K. Thus it appears that there is a probability that complexes such as divacancies are formed by high-energy electrons either in a secondary collision process or by short-range thermal-spike diffusion at the bombarding temperature. However, if we assume that simple defects are indeed formed when bombarding at just above the displacement energies, the annealing characteristics of the first two stages are determined by the diffusion characteristics of these defects. In metals it is generally accepted that interstitials diffuse with a lower activation energy than the vacancies.[14] In semiconductors however, especially the anion in partially ionic crystals where the defects are charged, it is probable that the vacancies are mobile before the interstitials.[15] Under this assumption, then, and considering annealing characteristics of the damage produced by electrons of energy between 195 and 240 keV, the annealing stage at 60°K represents the diffusion of the selenium vacancy with an activation energy of 0.35 eV. In type-I crystals some of the vacancies recombine with selenium interstitials, others combine with a foreign impurity and form complexes which are responsible for the radiation damage remaining above 90°K or observed when the crystal is bombarded at nitrogen temperature. In type-II crystals the foreign impurities are not present and all of the selenium vacancies recombine with selenium interstitials. The final annealing stage at 135°K appears to be the decomposition of the center itself with an activation energy of 0.4 eV. It should be noted here that the 5460- and 5850-Å fluorescence bands observed following bombardment at 80°K have been observed separately in as-grown crystals. Thus under different conditions these centers can be made stable at least to 300°K.

The annealing stage at 90°K is associated with the diffusion of the zinc defect, probably the vacancy with an activation energy of 0.15 eV, and recombination with the zinc interstitials formed during the bombardment. The diffusion energy at the 60°K annealing point is almost a factor of 2 larger than the diffusion energy of the 90°K anneal, which is consistent with the activation energies for diffusion of the anion and cation in other compound semiconductors.[8] In addition, further evidence that the first two annealing stages involve similar situations is obtained from Fig. 4. The order of the reactions for these stages is two. This might be expected for a random bimolecular process such as vacancy-interstitial annihilation. The order of the final stage of annealing would be expected to be of a higher order if a more complex situation is involved.

When the crystals are bombarded on a cold finger at liquid-nitrogen temperature, the zinc damage is not observed. While the ZnSe crystals are somewhat insulating in character, the temperature rise of the crystals at the beam current used in these experiments is not more than about 8°K (calculated and measured). Even lowering the current to a few tenths of a microampere does not enable the zinc displacement to be observed at liquid-nitrogen temperature. Thus it appears that the actual or effective temperature inside the crystal is greater than 90°K even though the calculated temperature in the crystal is about 85°K.

## CONCLUSIONS

It has been shown that valuable information concerning vacancies and interstitials, their properties and their contribution to fluorescence in II-VI compounds can be obtained from electron bombardment experiments at low temperatures. Still to be determined is the exact model for the fluorescence, that is whether the various bands are caused by recombination of a free electron with a trapped hole, or vice versa. This might be determined by photoconductivity measurements together with a determination of the sign of the carrier. It should also be noted that several other fluorescent bands have been produced by bombardment above the selenium threshold and annealed at various temperatures up to 225°K. The bands have peaks at 6100 and 7500 Å. The details of these centers is of current interest.

[10] G. Dienes and G. H. Vineyard, *Radiation Effects in Solids* (Interscience Publishers, Inc., New York, 1957), p. 161.

[11] J. W. Corbett, J. M. Denney, M. D. Fisher, and R. M. Walker, Phys. Rev. **108**, 954 (1957).

[12] J. W. MacKay, E. E. Klontz, and G. W. Gobeli, Phys. Rev. Letters **2**, 146 (1959).

[13] G. D. Watkins, *Proceedings of the Seventh International Conference on the Physics of Semiconductors* (Dunod Cie., Paris, 1964), p. 97.

[14] H. B. Huntington and F. Seitz, Phys. Rev. **61**, 315 (1942); H. B. Huntington, *ibid.* **61**, 325 (1942); **91**, 1092 (1953).

[15] G. J. Dienes and G. H. Vineyard, *Radiation Effects in Solids* (Interscience Publishers, Inc., New York, 1957), p. 136.