flux quanta within a circle halfway through the thickness of the wall of the cylinder, if applied directly along the axis of the cylinder.

ACKNOWLEDGMENTS

The author is indebted to Dr. Donald E. Morris for many stimulating discussions on the subject of normal field effects on superconducting films and for his permission for the use of data from his Ph.D. thesis. Thanks are also due Professor W. A. Little of Stanford for discussions concerning the periodic variation of T_c with magnetic flux. Finally, the hospitality of the General Electric Research Laboratory during part of the preparation of this paper is gratefully acknowledged.

PHYSICAL REVIEW VOLUME 129, NUMBER 6 15 MARCH 1963

Threshold for Electron Radiation Damage in ZnSe*

B. A. Kulp and R. M. Detweiler

Aeronautical Research Laboratories, Wright-Patterson Air Force Base, Ohio

(Received 7 November 1962)

A threshold for the displacement of an atom from the ZnSe lattice by electron bombardment has been observed at 240 keV. An electron of 240 keV transfers a maximum energy of 8.2 eV to the selenium atom and 10 eV to the zinc atom. The displacement is observed by the production at 85°K of a broad fluorescence band which is resolvable into two overlapping bands with peaks at 5460 and 5850 Å. The radiation damage anneals completely at a temperature of 160°K.

INTRODUCTION

Like CdS and ZnS, ZnSe is a II–VI compound semiconductor often grown by vapor-phase deposition at high temperature under various conditions of atmospheric control.[1–3] This method of growth results in crystals of questionable stoichiometry and quality. Many of the fluorescence properties of these compounds are believed to be a result of crystal defects in conjunction with or independent of chemical impurities.

Electron bombardment has proven to be a useful tool to produce defects in silicon which involve vacancy-impurity[4,5] as well as multiple-vacancy complexes.[6] Earlier studies in this laboratory have shown that it is possible to isolate defects of different atoms in compound semiconductors by measuring the threshold energies for the production of various fluorescence bands in these materials.[7,8] This latter technique has been applied to single-crystal ZnSe and the results of bombardment experiments with electrons in the energy range 225 to 500 keV are described here.

* Submitted in part to the faculty of the U. S. Air Force Institute of Technology as partial fulfillment for the requirements of the degree MSc in Nuclear Engineering by RMD.

[1] R. Frerichs, Phys. Rev. 72, 594 (1947).
[2] D. C. Reynolds and S. J. Czyzak, Phys. Rev. 79, 543 (1950).
[3] F. A. Kroger, H. J. Vink, and J. Van den Boomgaard, Z. Physik. Chem. (Leipzig) 203, 1 (1954).
[4] G. D. Watkins and J. W. Corbett, Phys. Rev. 121, 1001 (1961).
[5] J. W. Corbett, G. D. Watkins, R. M. Chrenko, and R. S. McDonald, Phys. Rev. 121, 1015 (1961).
[6] J. W. Corbett and G. D. Watkins, Phys. Rev. Letters 7, 314 (1961).
[7] B. A. Kulp and R. H. Kelley, J. Appl. Phys. 31, 1957 (1960).
[8] B. A. Kulp, Phys. Rev. 125, 1865 (1962).

EXPERIMENTAL

The crystals used in these experiments were grown by vapor phase deposition by L. C. Greene of this laboratory. The electron bombardments were carried out in vacuum with a Van de Graaf accelerator at a dc level of irradiation of 4 to 20 $\mu A/cm^2$, at a temperature near liquid nitrogen temperature. The fluorescence was measured with a Perkin-Elmer glass prism spectrometer with a type 6199 photomultiplier detector. The infrared fluorescence was measured with a lead sulfide detector. The spectrum following 500 keV bombardment was taken with a Cenco 1-m grating spectrometer with 103A-F film. During bombardment the crystals were mounted on a cold finger beneath a liquid nitrogen Dewar in the beam of the accelerator. The fluorescence was observed through a quartz window. The fluorescence was excited by electrons with an energy of 275 keV at an intensity of 4 $\mu A/cm^2$. The energy was so chosen that the intensity did not change appreciably in the five minutes required to scan the wavelength region of interest.

DATA AND RESULTS

A. Electron Bombardment

Figure 1 shows the fluorescence spectrum of a single crystal of ZnSe before and after bombardment by 10^{16} electrons/cm^2 at an energy of 500 keV at 85°K. The fluorescence following bombardment has been resolved into two bands with a symmetrical intensity distribution and peaks at 5460 and 5850 Å. The wavelengths are arrived at in the following manner: the fluorescence of several crystals in which the band at 5460 Å appeared alone was examined, the intensity of the 5460 Å band from one of these crystals was then normalized to a best fit to curve B of Fig. 1. The other band was arrived at by subtraction. We note that the two fluorescence bands produced by electron bombardment are found in selected "as grown" crystals, a condition similar to the four fluorescence bands produced by electron bombardment in CdS.[7,8]

The fluorescence spectrum of these crystals was investigated in the infrared region up to 2.5 μ. Bands at 1.0, 1.65, 2.0, and 2.2 μ were observed both at 300 and 85°K. All decreased in intensity as the radiation produced band increased in intensity at 85°K.

Figure 2 shows the intensity of the band shown in Fig. 1 in the wavelength region 5400 to 5500 Å as a function of the number of electrons/cm^2 striking the crystal at various electron energies. The zero slope of the 225 keV electrons indicates a threshold for the production of the band between 225 and 250 keV. The linearity of the intensity as a function of the number of electrons is quite evident and somewhat amazing in view of the many possibilities for recombination in this initially quite impure material.

Figure 3 shows the rate of production of the fluorescence band as a function of electron energy. The sharp change as the threshold is approached is clearly evident as is the tail very near the threshold. The experimental data are qualitatively in agreement with the analysis by Loferski and Rappaport[9] and the experimental data for germanium of Brown and Augustyniak[10] which more nearly approach the real physical situation for displacement of an atom from a lattice site than the treatment of Seitz and Koehler.[11] It is to be noted here that no damage is detectable in this type of crystal under bombardment at 300°K for the same period of time required to produce the maximum intensity shown in

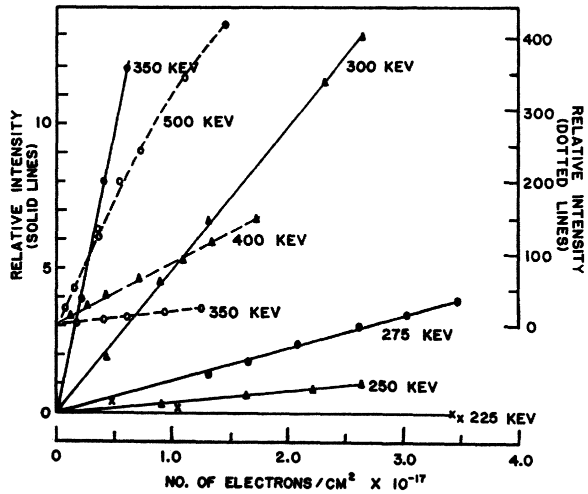

FIG. 2. Intensity of the fluorescence in wavelength region 5400–5500 Å as a function of bombardment and electron energy.

Fig. 2. Furthermore, the bands reported here are not produced in all crystals by electron bombardment. The crystals used in these experiments were selected on the basis of the production of the bands by bombardment and are not all from the same crystal growing runs, nor did all crystals from any given crystal growing run show the effect. The data presented here were taken with the same crystal but the effect was observed and quantitatively the same in several different crystals.

B. Isochronal Annealing of the Fluorescence Bands Produced by Electron Bombardment

The annealing of radiation damage in semiconductors has been the subject of a number of investigations.[12–15]

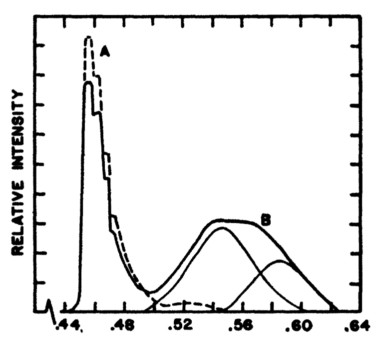

FIG. 1. Fluorescence spectra of ZnSe (A) before and (B) after bombardment at 85°K with 500-keV electrons. Spectra taken at 80° excited with 275-keV electrons 5 μA/cm^2.

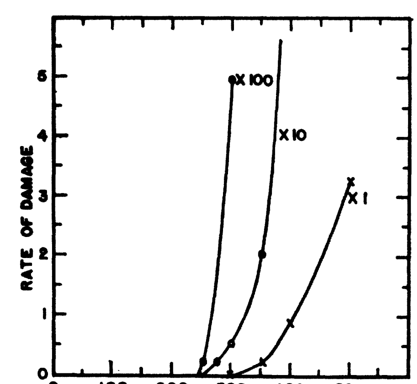

FIG. 3. Rate of increase of fluorescence as a function of electron energy. Note expansion of intensity by factors of 10 and 100.

[9] J. J. Loferski and P. Rappaport, J. Appl. Phys. **30**, 1296 (1959).

[10] W. L. Brown and W. M. Augustyniak, J. Appl. Phys. **30**, 1300 (1959).

[11] 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.

[12] R. C. Fletcher and W. L. Brown, Phys. Rev. **95**, 585 (1953).

[13] G. Bemski and W. M. Augustyniak, Phys. Rev. **108**, 645 (1957).

[14] L. W. Aukerman and R. D. Graft, Phys. Rev. **127**, 1576 (1962).

[15] W. L. Brown, W. M. Augustyniak, and T. R. Waite, J. Appl. Phys. **30**, 1258 (1959).

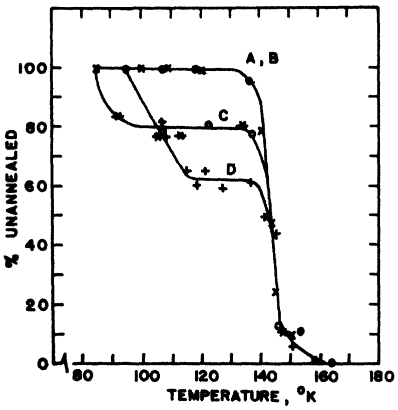

FIG. 4. Percent of damage remaining after heat treatment 15 min at each temperature.

While the process is not well understood even in silicon and germanium which have received the most intensive study, it provides valuable information as to the type of defect likely to be present following electron bombardment.

Figure 4 shows the percent damage left after each heat treatment under the assumption that the intensity of the fluorescence band is directly proportional to the number of centers produced. This appears to be a good assumption especially at lower irradiation levels since the curves in Fig. 2 are quite linear. The damage was produced by 500-keV electrons at 85°K. The intensity was measured at 85°K under electron excitation with 275 keV electrons, 4 μA/cm^2. Curves A and B are for different crystals. Curves B, C, and D are for the same crystal but with different irradiation levels; B the least, C more, and D about 3 times the irradiation dosage as for curve B. Crystal A did not show the intensity effect noted in the other crystal. The various points in C are for two different annealing runs. The principal annealing takes place in a temperature range between 140 and 160°K, in a single step process in many crystals. In some crystals, however, the single step process occurs only for a low concentration of defects. The annealing is complete, and following annealing bombardment above the threshold of 240 keV is necessary to restore the fluorescence bands discussed here. There is no change in the other fluorescence bands other than a slight increase in intensity during the annealing process.

DISCUSSION

In CdS, where the two types of atoms have a large difference in mass, two thresholds for electron radiation damage are observed. In ZnSe the mass difference is much less, 65 and 79, but nonetheless if the displacement energy is the same or less for the lighter element than for the heavier, there should be two distinct thresholds for the production of electron radiation damage. In CdS the displacement for the cadmium atom was 7.3 eV, somewhat less than the 8.7 eV measured for this sulfur atom. If the same situation holds for ZnSe then the two thresholds will be displaced sufficiently for clear and easy resolution. We have not observed a threshold for the production of a different fluorescence band than reported here. Therefore, we cannot assign the threshold reported here at 240$\pm$10 keV for the displacement of a particular atom. At 240 keV an electron can transfer a maximum of 8.2 eV to a selenium atom and 10 eV to a zinc atom. These displacement energies are quite consistent with the displacement energies observed in CdS.

The appearance of two fluorescence bands which anneal out together at a very low temperature suggests that the defects observed here are the simple vacancy and the simple interstitial. However, lower temperature bombardments are necessary before this can be stated with certainty. Bombardments near liquid helium temperature are planned for the near future.

There is no direct evidence in these crystals that other fluorescence centers active in the range in 2.5 μ are produced by the bombardment. However a rather interesting difference is observed in the sensitivity of the infrared fluorescence bands. At the start of the bombardment series the infrared bands were observable only at electron beam currents of about 4 μA/cm^2. Toward the end, however, the light from the Van de Graaff filament was sufficient to saturate the intensity of these bands. This change in sensitivity is taken as an indication of further damage to the crystal which does not anneal out below room temperature.

APPENDIX. NUMBER OF CENTERS OBSERVABLE BY FLORESCENCE TECHNIQUES

Using the range-energy data for electrons of Nelms,[16] electrons of 500 keV initial energy will penetrate approximately 0.32 mm before their energy is below the 240 keV threshold for displacement of the selenium atom. Using the cross-section calculation of Seitz and Koehler[11] and considering the energy degradation inside the crystal an estimated 2×10^{15} atoms/cm^2 were displaced by 1.5×10^{17} electrons/cm^2 at 500 keV. The crystal was 2 mm$\times$3 mm in size so that 1.2×10^{14} atoms were displaced in this crystal.

The signal observed was actually about 500 times the minimum detectable with the equipment used in these experiments, so that the minimum number of radiation damage centers observable *in these crystals* is about 2×10^{11}.

[16] A. T. Nelms, National Bureau of Standards Circular No. 577 (U. S. Government Printing Office, Washington, D. C., 1956).