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Displacement of the Cadmium Atom in Single Crystal CdS by Electron Bombardment

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A threshold for the production of two fluorescence bands in CdS under electron bombardment at −196°C has been observed at 290 kev. This corresponds to a maximum energy transfer of 7.3 ev to the cadmium atom. The fluorescence bands produced are at about 6050 A and 1.03 μ. An overlay experiment in which cadmium atoms diffused into the CdS lattice in interstitial positions produced the 6050 A band which is therefore believed to be a result of cadmium interstitial atoms. The 1.03 μ band is believed to be a result of cadmium vacancies. This latter band can also be produced by heating undoped CdS crystals to 200°C in air, argon or vacuum.

INTRODUCTION

THE growth of CdS crystals by the vapor deposition method[1,2] at high temperatures results in crystals of questionable stoichiometry. Methods for analysis for stoichiometry are difficult, tedious, and insensitive. The various defects—sulfur and cadmium vacancies and interstituals—are probably the centers for several of the self-activated fluorescence bands in this material. It is therefore of great interest to determine which fluorescence bands in CdS are a result of sulphur and cadmium interstitials and vacancies, respectively.

Displacement of an atom from its lattice point by electron bombardment offers a unique and controllable means of producing vacancy-interstitial pairs of the host atoms of a crystal. For a compound such as CdS, where the atomic weights of the constituents are greatly different, it should be possible to observe two distinct thresholds for displacements, one at a lower energy representing displacement of the lighter element and another at a higher energy representing displacement of the heavier element. Kulp and Kelley[3] have observed a threshold for displacement in CdS at 115 kev. Bombardment by electrons above this energy produces two fluorescence bands at liquid nitrogen temperature. One band at about 7200 A is attributed by these authors and others[4] to the presence of sulfur vacancies, the other, green edge emission, to the presence of sulfur interstitials.

The electron energy necessary to displace the cadmium atom should be about three and one half times that to displace the sulphur atom if the displacement energies are the same.[5]

EXPERIMENTAL

The crystals used in these experiments were "pure" crystals. Spectrographic analysis showed maximum impurities to be 5 ppm of Si and 1 ppm of Mg in some samples. No other impurities were detectable. The crystals were cleaved from large single crystals and were "thick," that is, the thickness of the crystals were greater than the maximum range of the electrons. The electron bombardments were carried out in air or in vacuum with a Van de Graaff type accelerator at a dc level of irradiation of 2 to 5 μa/cm^2. The C axis of the crystal was perpendicular to the electron beam.

The fluorescence measurements were made either with a Bausch and Lomb grating monochrometer or a glass prism monochrometer with a PbS detector. For exciting fluorescence with band gap light a Sylvania 100-watt concentrated arc lamp was used with a Corning type 9782 filter to isolate the spectral region near the CdS absorption edge.

Two separate experiments were performed using the electron beam to excite the fluorescence of the CdS crystals. The first was with the crystal at liquid nitrogen temperature, the second with the crystal at room temperature. For the low temperature bombardment the crystals were cemented to a copper cold-finger below a liquid nitrogen Dewar with a conducting cement (General Cement Silver Print) and bombarded inside the vacuum chamber of the accelerator. For the room temperature experiments, the crystals were bombarded in air.

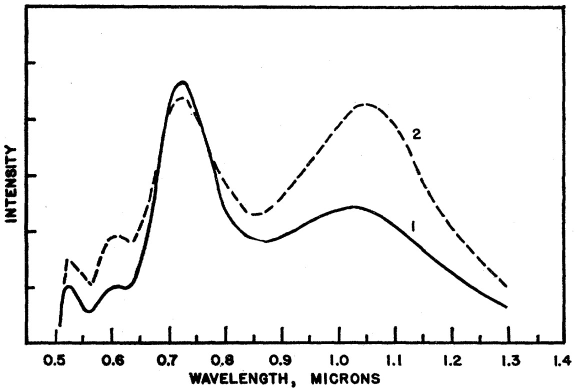

FIG. 1. Fluorescence spectrum of CdS at −196°C under electron bombardment 250 kev 5 μa/cm^2, (1) initially, (2) after 2×10^{16} electrons/cm^2.

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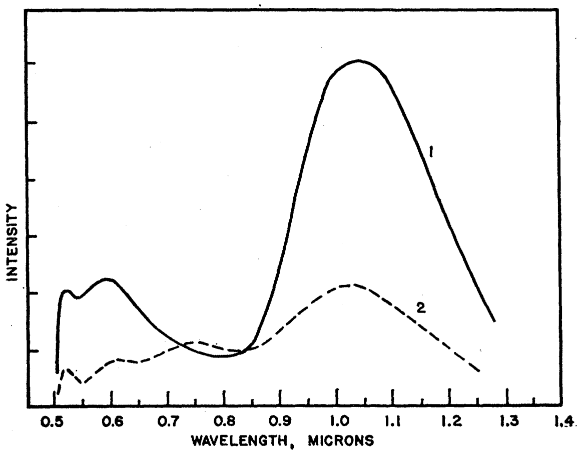

FIG. 2. Fluorescence spectrum after 2×10^{17} electrons/cm^2 at 300 kev. Electron excitation at −196°C. (1) before warming, (2) after warming to 20°C then cooling again to −196°C.

Data and Results

a. Bombardment at Liquid Nitrogen Temperature

Figure 1 shows the fluorescence spectrum at liquid nitrogen temperature under excitation by 250-kev electrons at 5 μa/cm^2. As bombardment is continued for about 2×10^{16} electrons/cm^2 one observes the dotted curve of Fig. 1. Further bombardment at 250 or 275 kev for as long as 5×10^{17} electrons causes no further change in the intensities of the 1.03μ and 6050A fluorescence bands. The 7200 A band continues to decrease in intensity as bombardment continues and the green edge emission band increases in intensity. If the crystal is warmed to 20°C and cooled again to nitrogen temperature, the fluorescence returns to the original curve except the 7200 A band is decreased in intensity depending on the amount of bombardment. If the electron beam energy is raised to 300 kev after this initial bombardment, the band at 1.03 μ and the bands at 6050 A and 5200 A increase in intensity with bombardment. The 7200 A band continues to decrease in intensity. If the electron beam energy is lowered to 275 kev again, the fluorescence intensity of the 1.03 μ and the 6050 A bands remain constant for as long as 10^{18} electrons/cm^2. The 7200 A band continues to decrease in intensity however. Figure 2 shows the fluorescence spectrum after bombardment at 250 kev followed by 2×10^{17} electrons/cm^2 at 300 kev. (Compare to curve 2, Fig. 1.) The effect of warming to room temperature after bombardment at nitrogen temperature and cooling again is shown in Fig. 2, curve 2. Subsequent bombardment at 250 kev restores the fluorescence to about 75% of its intensity before warming. This latter phenomenon appears to be the result of two mechanisms (1) a redistribution of the electrons over the existing levels and (2) an actual annealing of some of the radiation damage. In other experiments the intensities of the 1.03μ band and the 6050 A and the 5200 A bands were increased by bombardment at 350 and 500 kev while only the 5200 A band increased in intensity at 250 and 275 kev (after an initial bombardment of 10^{16} electrons/cm^2). The 7200 A band always decreased in intensity when the fluorescence was excited by the electrons.

b. Bombardment at Room Temperature

The crystals used in part "*a*" of this paper showed no evidence of the 1.03 μ band when observed at room temperature under either band gap light or electron excitation. The fluorescence observed at 20°C was rather intense with a maximum at about 7400 A and a smaller unresolved band at about 6950 A.[6] Under electron excitation these bands steadily decrease in intensity with bombardment. However under band-gap light excitation there was no detectable change in the intensity after bombardment with 10^{18} electrons/cm^2 independent of the electron energy in the range 250 to 500 kev. Another batch of crystals was selected which showed the 6950 A and 7400 A and the 1.03 μ bands under both electron and band-gap light excitation at room temperature.

Figure 3 shows the fluorescence spectrum of these crystals at various bombardment levels at 320 kev with electron excitation. The decrease in all fluorescence is quite apparent, but the 1.03 μ band decreases much more slowly than the shorter wavelength fluorescences. Bombardment at 275 kev subsequently did not change the intensity of fluorescence of the 1.03 μ band even to 2×10^{18} electrons/cm^2.

The decrease in intensity of the 7400 A band under bombardment observed in these experiments, is apparently in direct opposition to the results published in reference 3 for the effect of bombardment above 115 kev on this fluorescence band at liquid nitrogen temperature. To check this a crystal which did not show the 1.03 μ band but which did show edge emission and

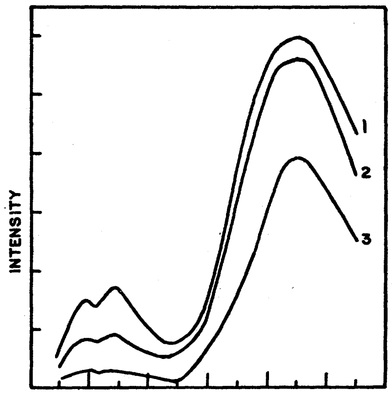

FIG. 3. Fluorescence spectrum of CdS under electron bombardment at 40°C 320 kev, 4 μa/cm^2, (1) initially, (2) after 3×10^{17} electrons/cm^2, and (3) after 2×10^{18} electrons/cm^2.

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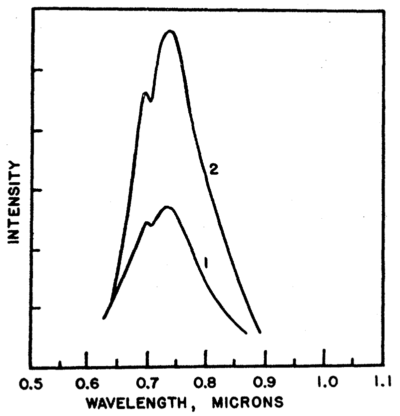

FIG. 4. Fluorescence spectrum of CdS under band-gap light excitation, (1) before and (2) after bombardment at 275 kev with 10^{17} electrons/cm^2.

7200 A fluorescence at −196°C was bombarded at room temperature at 275 kev for 10^{17} electrons/cm^2. Figure 4 shows the fluorescence at room temperature under band gap light excitation before and after this bombardment. The results are in agreement with reference 3. The intensity of the 7400 A band when excited by electrons, however, had decreased during this bombardment. When the 1.03 μ band is present and/or when bombardment is above 300 kev, the intensity of the 7400 A band under band gap light excitation decreases with bombardment. This decrease in intensity of the fluorescences is probably a result of a poisoning center produced by the bombardment.

c. *Annealing of Room Temperature Bombarded Samples*

If the decrease in intensity of the 1.03 μ band as a result of bombardment above 300 kev at 20°C is caused by the production of a poisoning center then heat treatment might be expected to restore the fluorescence. Figure 5 shows the fluorescence of the crystal shown in Fig. 3 following heat treatment at various temperatures. The recovery of the fluorescence of both bands is shown. Above 350°C however the fluorescence decreases again. In a non-bombarded crystal cleaved from the same large crystal, the intensity of the 7400 A band decreased steadily as the heat treating temperature increased while the intensity of the 1.03 μ band first increased up to 250°C then decreased as the temperature of heat treat was increased. The results of the heat treat of the non-bombarded crystal make the interpretation of the heat treating data of Fig. 5 uncertain.

The bombardment experiments can be summarized as follows: (1) At −196°C the 1.03 μ and the 6050 A fluorescence bands are increased in intensity by bombardment at 300 kev and above. (2) At 20°C, a poisoning center is produced by electron bombardment at 300 kev and above which decreases the intensity of the 1.03 μ band. (3) A poisoning center for the 7200–7400 A band under electron excitation is produced by bombardment. (4) The green edge emission is increased in intensity by bombardment in the energy range studied here.

DISCUSSION

The experiments show an intensification of two fluorescence bands in CdS by electron bombardment with a threshold between 275 and 300 kev. The fact that it is necessary to go to −196°C to produce this effect is not surprising in view of the well known complexity of the fluorescences in CdS crystals, especially the dependence of the fluorescence on temperature and quantity and quality of the impurities.[7] Since a threshold has been reported at 115 kev,[3] the threshold observed here is that for the displacement of the cadmium atom from the lattice. A 290-kev electron can transfer a maximum of 7.3 ev energy to a cadmium atom. The calibration of the accelerator was checked by measuring the extrapolated range of 300 kev electrons in aluminum. It was found to be 0.082 g/cm^2. The value 0.08 g/cm^2 is given in Evans.[8] The electron energy therefore is known within ±5%. The value found for the displacement energy for the sulfur atom in CdS was 8.7 ev. Thus it appears that the cadmium atom is bound somewhat less strongly than the sulfur atom. The difference in temperature at which the two displacement thresholds were measured could account for some of this difference. However no such tempera-

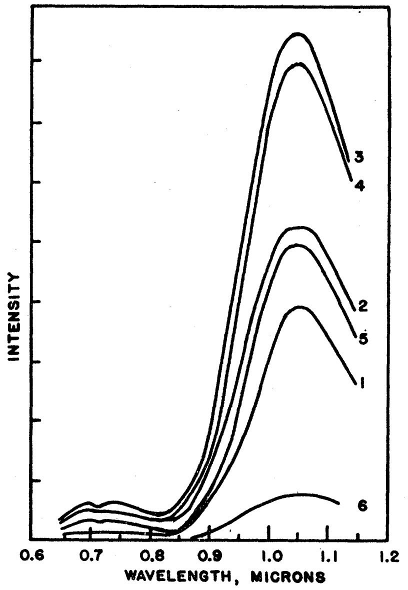

FIG. 5. Fluorescence spectra of bombarded crystals of Fig. 3 under electron excitation following heat treatment for ½ hour in argon. (1) Original and 200°C, (2) 250°C, (3) 300°C, (4) 350°C, (5) 400°C, and (6) 450°C.

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[7] See for example, (a) M. Avinor, thesis, University of Amsterdam, 1959 (unpublished) and (b) W. Van Gool, thesis, University of Amsterdam, 1961 (unpublished).

[8] R. D. Evans, *The Atomic Nucleus* (McGraw-Hill Book Company, Inc., New York, 1955), p. 624.

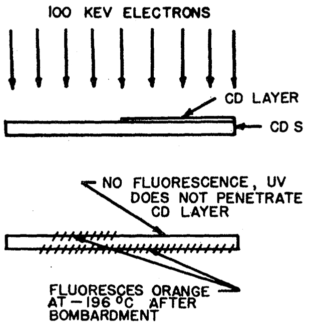

FIG. 6. Cadmium overlay experiment.

ture dependence of the displacement threshold is observed in germanium where Lofferski and Rappaport[9] found a threshold energy of 360 kev at 16°C and Brown and Augustyniak[10] found 355 kev±5 kev at 79°K.

Defects Responsible for the 6050A and 1.03-µ Bands

The production of defects stable at liquid nitrogen temperature indicates that the centers are probably simple ones, that is interstitials or vacancies not in association with other impurities. The possibility of interstitial diffusion under electron bombardment has been discussed by Kulp and Kelley in the case of sulfur in CdS. An experiment of the type shown schematically in Fig. 6 using sulfur instead of cadmium resulted in the production of green edge emission at liquid nitrogen temperature. For the Cd overlay experiment a few micrograms per cm^2 of cadmium metal was evaporated onto a crystal 0.010-in. thick. The sample was bombarded with 100 kev electrons at 0°C. After 5 μa-hrs/cm^2 a broad orange fluorescence under and next to the evaporated cadmium layer was observed at liquid nitrogen temperature under uv stimulation. The maximum intensity of the fluorescence is located at 6050 A ±50 A. The 6050 A fluorescence is thus attributed to the cadmium interstitial. This band, though rare, has been observed in as-grown crystals and in the residue of the furnace charges of some crystal growing runs.

The 1.03μ band is rather broad and the experimental error in the peak wavelength is estimated to be $\pm 0.02\ \mu$ based on reproducibility, the asymmetry of the band and the fact that slit widths of 0.5 and 1.0 mm were necessary to get sufficient intensity in the bands. This band is observed in many as-grown crystals, "pure" and copper and silver doped. It is often observed under electron excitation but not under uv or bandgap light excitation at 20°C and −196°C. It can be produced in many crystals which do not have it by heating to 200°C in vacuum or in air. The results of the experiments described here indicate that it is a result of cadmium vacancies.

Whether or not this is the same band observed by Grillot and Guintini and others[9–11] in copper doped CdS is not known. It may be that just as there are three blue fluorescences in ZnS, one for silver doped, one for copper doped and a self activated one,[12] there are three distinct bands in the vicinity of 1 μ in CdS. An example of multiple bands is seen in copper and silver doped CdS at low temperature in the vicinity of 6400 A. In this case Warschauer and Reynolds[13] have shown that the fluorescence is polarized parallel to the C axis in copper doped and perpendicular to the C axis in silver doped samples. This clearly indicates two distinct centers. The 1.03 μ band observed here does not seem to be polarized in the crystals used in these experiments.

Browne[14] has proposed that the 8200 A and the 1.02 μ bands observed by Grillot and Guintini[11] and Garlick *et al.*[12] are actually from the same defects, namely cadmium vacancies. In a separate communication[15] this author has shown that an 8500 A band believed to be the same as the 8200 A band above, is decreased in intensity by electron bombardment. In addition the 1.03 μ band is produced by heat treatment while the 8500 A band is not, therefore unless there are separate bands near 1 μ for undoped, silver doped, and copper doped CdS the data here indicates that there are separate centers for the 8500 A and 1.03 μ bands.

Kroger[16] *et al.* have proposed on the basis of conductivity measurements, that the cation vacancy with one hole trapped is located about 1.5 ev from the valence band. Bube[17] believes that this is too high in the forbidden gap for this defect level and would seem to prefer it to be nearer 1.0 ev above the filled band. The energy of the center observed here is just about midway between the two values presented above. However, there is nothing in the experimental data presented here to indicate the position of the trap relative to the allowed energy bands in the crystals or to determine the nature of the center itself.

CONCLUSION

The appearance and disappearance of the fluorescence bands as the temperature is cycled and as electron bombardment progresses makes interpretation of the results of these experiments difficult. However it seems obvious that each of the centers produced by the bombardment experiments must exist in more than

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one ionization state.[14] The particular state of ionization of each defect is determined by the position of the Fermi level. This is sensitive to the total number and type of impurities in the crystal and hence varies greatly from crystal to crystal. The time required for the establishment of steady state conditions is often rather long, for example the slow rise in photoconductivity in CdS observed by Bube.[17] Quasi steady-state conditions might be expected to exist during and following the periods of heavy ionization caused by electron bombardment which can cause a change in the distribution of the electrons over the existing defects. Temperature cycling or long decay times or both may be required before a return to equilibrium is accomplished. This is evidenced by the decrease in intensity of the 7200 A band under bombardment at low temperature followed by the partial recovery of this fluorescence by warming to 20°C then cooling again. The initial increase in intensity of the 1.03 μ band during bombardment at 275 kev, below the threshold, and its decrease following warming and cooling is an example of a similar phenomenon with opposite effect. Much work remains to be done before any real understanding about the character of the defect levels in CdS can be accomplished. Electron bombardment near the thresholds for displacement of the cadmium and sulfur atoms offers a new approach to the problem; however, the results obtained are complicated.

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Valence Bands of Germanium and Silicon in an External Magnetic Field*

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The problem of the valence band structure of germanium and silicon in the presence of an external magnetic field is considered from a quantum-mechanical point of view. The analysis is carried out using first- and second-order perturbation theory. The approach is an extension of methods of Shockley and Kane to include the effects of the magnetic field. The usual approximation of the decoupling of the V_1 and V_2 bands from the V_3 band is not made, thus making the analysis applicable to Si as well as Ge. Spherical energy bands are not assumed in this calculation and the case of $k_H \neq 0$ is considered. Detailed analysis is carried out for the magnetic field H in the [001] direction. The analytical results obtained are more general than those of Luttinger but reduce to the latter if certain approximations are introduced.

Numerical calculations of the Landau energy levels are carried out for certain special cases. The results predict an increase of the hole effective mass with the magnetic field. They also indicate mixing of the Landau levels even at $k_H = 0$, which leads to a prediction of new transitions some of which are of "negative mass" type. The mixing is more pronounced in Si than in Ge. Calculations for $k_H \neq 0$ show that the ϵ_1^- levels possess negative curvatures near $k_H = 0$. Gradual "crossing" or reordering of the heavy hole levels is found at relatively high k_H.

I. INTRODUCTION

THE quantum-mechanical effective mass formalism for treating problems of magnetic energy levels (Landau levels) in semiconductors has been developed by Luttinger and Kohn.[1] The method has been extended by Luttinger[2] who used it to analyze the valence band of germanium. Since in the valence band of Ge the spin-orbit splitting is rather large, Luttinger has been able to consider the V_1 and V_2 bands separately from the V_3 band. He has written down a 4×4 matrix, a diagonalization of which should yield the energy levels for electrons in a Ge crystal which is subjected to a magnetic field in the [111] direction. In deriving this, Luttinger assumed that the momentum of the electrons in the direction of the magnetic field (k_H) is zero. He has then simplified the problem further by assuming the energy bands to be isotropic. This reduced the problem to the solution of two 2×2 determinants which Luttinger has carried out. He also formulated a perturbation approach to the anisotropic problem. The numerical results for Ge have been given by Goodman.[3] One of the most interesting results obtained by Luttinger and Goodman is the unevenness in the spacing of the Landau levels at low quantum numbers, an effect which has been experimentally observed.[4–6]

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