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$$D=\left[\left(\frac{\Delta\sigma}{\sigma\Omega}\right)_{\perp}-\left(\frac{\Delta\sigma}{\sigma\Omega}\right)\mathrm{Bkg}_{\perp}\right]\Big/\left[\left(\frac{\Delta\sigma}{\sigma\Omega}\right)_{\parallel}-\left(\frac{\Delta\sigma}{\sigma\Omega}\right)\mathrm{Bkg}_{\parallel}\right].$$

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PHYSICAL REVIEW B VOLUME 5, NUMBER 4 15 FEBRUARY 1972

Fluorescence of Graded-Band-Gap $CdS_x Se_{1-x}$ Crystals Produced by Diffusion

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The fluorescence of CdS_xSe_{1-x} mixed crystals with band-gap gradients as large as 1200 eV/cm has been investigated at 77 °K. The graded samples were produced by heating CdSe or CdS_xSe_{1-x} platelets in a sulfur-selenium atmosphere. Some of the diffused crystals were post-treated in a cadmium atmosphere. Removal of surface material shifted the fluorescence spectra of the diffused crystals to longer wavelengths. The spectral position of fluorescence peaks was determined as a function of the thickness of the removed surface layer. Composition profiles were deduced from these data by correlating fluorescence wavelength with crystal composition. Error-function curves gave a good fit to experimentally determined profiles. Diffusion constants of 7.0×10^{-13} and 1.6×10^{-12} cm^2/sec were determined for diffusion temperatures of 600 and 650 °C, respectively.

I. INTRODUCTION

The optical band gap is strongly dependent on composition in most II-VI compound mixed-crystal systems. Optical methods have been used to study composition variations in graded-band-gap mixed crystals of these compounds grown from the vapor phase. Measurements of the spatial dependence of absorption in $CdS_x Se_{1-x}$, $Zn_x Cd_{1-x} S$, and $Zn_x Cd_{1-x} S_y Se_{1-y}$ graded mixed crystals have been made by Reimers,[1] and in $Zn_x Cd_{1-x} S$ by Indradev *et al.*[2] A positional variation in the band-edge fluorescence peak wavelength of $Zn_x Cd_{1-x} S$ crystals has been observed by Van Ruyven and Dev.[3] Bille *et al.*[4] have measured the dependence of stimulated emission wavelength on position in $CdS_x Se_{1-x}$ graded crystals.

Band-gap gradients of 2 eV/cm or less were reported for crystals grown from the vapor phase. Gradients of up to 100 eV/cm have recently been obtained by Biter and Williams[5] by epitaxial growth of CdS onto ZnS substrates and interdiffusion. Photoluminescence observed in the graded region of these crystals was attributed to electron-hole recombination at deep-lying acceptor states.

Graded $CdS_x Se_{1-x}$ crystals have been produced by diffusion from Se vapor into CdS host crystals by Handelman and Kaiser.[6] No measured profiles of band gap vs position were reported, but a diffusion rate was estimated by visual observation of the depth of change of crystal color as a function of diffusion time. In related work, radioactive-tracer techniques have been used by Woodbury and Hall[7] to study impurity diffusion of Se into CdS and CdTe, and by Kato *et al.*[8] to study diffusion of Se into CdTe.

Fluorescence studies on $CdS_x Se_{1-x}$ single crystals with band-gap gradients as high as 1200 eV/cm are reported in this paper. The crystals were prepared by a diffusion process which consists of heating platelets in an atmosphere of sulfur and selenium. Some of the diffused crystals were post treated in a cadmium atmosphere. Photoluminesence spectra of these samples were measured at 77 °K, and subsequent spectra were measured following removal of surface material by etching. Profiles for the diffusion of sulfur into CdSe were determined by correlating the positions of fluorescence peaks with the surface composition of the crystals. Diffusion coefficients were determined for different temperatures and diffusant pressures.

II. EXPERIMENTAL

The CdSe and CdS_xSe_{1-x} platelets used as host materials for the diffusion were grown in this laboratory by a vapor-transport method[9,10] in a multiple-zone tube furnace filled with argon to about 500 Torr. Powder placed in the center of the hot zone (950 °C) sublimes and condenses to form crystals, some of which are in platelet form, on the walls in a cooler zone.

Platelets with planar surfaces (15–250 μm thick and 5–15 mm^2 in area) were selected for diffusion. A quartz tube containing weighed diffusants and host crystals was connected to a diffusion pump and sealed at a pressure of about 10^{-6} Torr. The diffusion was carried out in a furnace with a temperature gradient of less than 1 °C over the length of the diffusion tube, and fluctuations in the mean temperature of less than 2 °C. Diffusions were carried out for 16 h at temperatures ranging from 600–700 °C. Removal of surface material was accomplished by etching the sample in a 0.05% solution of bromine in methanol.[11] The thickness of the surface layer removed by the etch Δt was determined from the formula $\Delta t = \frac{1}{2}\Delta m/\rho_x A$, where Δm is the mass change, A is the area of the crystal, and ρ_x is the density. The quantity Δt defined here equals half the thickness change of the crystal. The relation

$$\rho_x = x\rho_{\text{CdS}} + (1-x)\rho_{\text{CdSe}}$$

was assumed for the density, using the handbook values $\rho_{\text{CdS}} = 4.82\,\text{g/cm}^3$ and $\rho_{\text{CdSe}} = 5.81\,\text{g/cm}^3$. This formula agrees to within 2% with densities calculated from x-ray data[12,13] on lattice constants in $CdS_x Se_{1-x}$ for values of x between 0 and 1. The value of x was determined from the spectral position of the fluorescence peak, as discussed in Sec. III.

The fluorescence was excited by 3000–5000-Å light from the filtered output of a xenon short-arc lamp. After passing through a mechanical chopper, the exciting beam was focused to a spot on the sample. The beam was incident at an angle of about 45° to the surface of the sample, which was immersed in liquid nitrogen. A lens collected the fluorescence emerging in a normal cone from the surface upon which the exciting light was incident. The light was focused on the slit of a scanning monochromator connected to an S-20 photomultiplier. The photomultiplier output was passed through a lock-in amplifier to a recorder.

III. RESULTS

Fluorescence spectra measured for a number of as-grown CdSe crystals could be divided into two classes, here designated "type-I" and "type-II" spectra. Examples of these spectra are illustrated in Fig. 1. Type-I spectra exhibited a strong maximum at 6830 Å, strongly polarized perpendicular to the c axis, and a weak maximum at about 6750 Å with a component of polarization parallel to the c axis. These peaks evidently correspond to photoconductivity peaks observed in CdSe at 77 °K by Park and Reynolds,[14] at 6830 and 6744 Å, which were attributed by these authors to the excitation of free A and B excitons, respectively. Type-II crystals exhibited a broad-edge emission band with a maximum at about 7120 Å, as well as a strong peak at 6800 Å and a weak one at 6720 Å. The separation and polarization of these latter peaks are similar to the A- and B-exciton peaks in type-I crystals, but the 30-Å shift to shorter wavelengths presently lacks an explanation. Edge emission in CdSe at 77 °K has been studied by Pedrotti,[15] who reported a principle maximum at 7140 Å and phonon replicas at 7235 and 7365 Å.

From investigations on a number of crystals from each of several different growth runs, it was concluded that a growth run produced either all type-I or all type-II crystals.

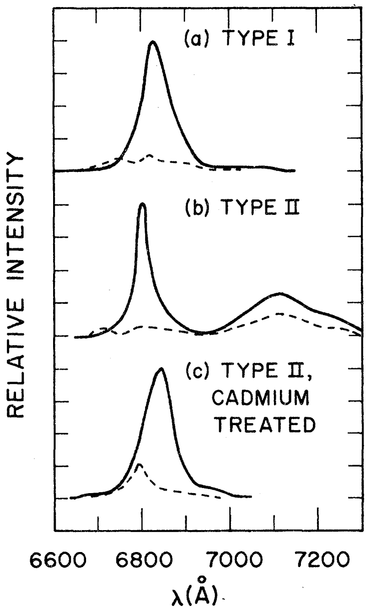

FIG. 1. Polarized fluorescence spectra in CdSe at 77 °K. Solid line represents $E \perp c$; dashed line is for $E \parallel c$.

TABLE I. Parameters for initial diffusion in sulfur-selenium atmosphere and for post-treatment in cadmium atmosphere. Time for initial diffusion runs was 16 h.

Crystal type	Composition	T(°C)	m_s/V (mg/cm^3)	m_{Se}/V (mg/cm^3)	p_{S_2} (atm)	p_{Se_2} (atm)
$D1$, $D1^*$(II) $D2$, $D2^*$	CdSe	600	0.043	0.089	0.040	0.023
$D2^{**}$(I)	CdSe	600	0.129	0.192	0.095	0.037
$D3$, $D3^*$(I)	$CdS_{0.09}Se_{0.91}$	650	0.287	0.254	0.22	0.062
$D4^*$(I)	CdSe	700	0.269	1.37	0.26	0.27

crystal	t(h)	T(°C)	m_{Cd}/V (mg/cm^3)
$D1^*$	4.0	600	0.31
$D2^*$	1.0	600	0.70
$D2^{**}$	49.5	600	0.27
$D3^*$	1.0	600	0.31
$D4^*$	15.6	650	0.40

The effect of heat treatment in a cadmium atmosphere on the spectra of CdSe crystals has also been studied. Edge emission in type-II crystals was eliminated by this treatment, a behavior observed in CdS by Handelman and Thomas.[16] Cadmium-treated type-I and type-II crystals exhibited a strong peak active for $E \perp c$ at 6849 Å and a weaker maximum active for $E \parallel c$ at 6800 Å. In some spectra the 6849-Å peak and the A-exciton peak at 6830 Å could be resolved. The 6849-Å peak is tentatively identified as the I_4 line, reported by Reynolds *et al.*[17] at a wavelength 16 Å longer than the A-exciton line in CdSe at 4.2 °K. Hurwitz[18] has shown that this line is very strong in the 4.2 °K fluorescence spectra of cadmium-rich CdSe. This line may be related to the extrinsic line which was observed to replace the A-exciton line in the 77 °K spectra of cadmium-treated CdS by Ibuki and Ohso.[19]

Several diffusion runs in which platelets were heated in an atmosphere of sulfur and selenium have been made. Some of the diffused crystals were post-treated in cadmium vapor. Table I summarizes the conditions for various runs, giving crystal type and composition, temperature T, ratio of diffusant mass to ampoule volume m/V, and diatomic gas partial pressures calculated from these m/V values and polymer equilibrium constants reported by Berkowitz and Marquart[20] for sulfur and deduced from data of Berkowitz and Chupka[21] and of Brooks[22] for selenium. Diatomic gas pressures are important because of evidence[23] that

$$CdSe \longrightarrow Cd + \tfrac{1}{2}Se_2$$

and

$$CdS \longrightarrow Cd + \tfrac{1}{2}S_2$$

are the dominant reactions by which atoms are exchanged between vapor and solid phases in the CdS and CdSe systems.

No fluorescence could be detected in crystals which were diffused in a high pressure of selenium, and the fluorescence efficiency was observed to increase with decreasing selenium pressure. A broad band, having a full width at half-maximum intensity (FWHM) of 300–400 Å, was observed in crystals which did fluoresce. A narrower (60–150 Å FWHM) fluorescence band was found in all crystals, whether or not they fluoresced initially, after post-treatment in cadmium vapor. In the as-diffused crystals which did fluoresce, the peak was shifted 300–400 Å to shorter wavelengths by the cadmium treatment, and the fluorescence efficiency was considerably increased. Figure 2(a) shows the spectrum of one crystal after diffusion in a sulfur-selenium atmosphere, and of a portion of that crystal after post treatment in a cadmium atmosphere. The effect of removing surface material was to shift the spectra of the diffused crystals to longer wavelengths. Figure 2(b) illustrates such a shift in the spectra depicted in Fig. 2(a).

The positions of the fluorescence maximum for crystals from two different diffusion runs are plotted as a function of total thickness of the surface layer removed in Figs. 3 and 4. Band-gap gradients averaged over the first 2 μm of thickness are 1200 and 750 eV/cm, respectively, for the two curves.

The broad fluorescence band in as-diffused crystals was weakly polarized ($1.5 < I_{E\perp c}/I_{E\parallel c} < 2.0$) for

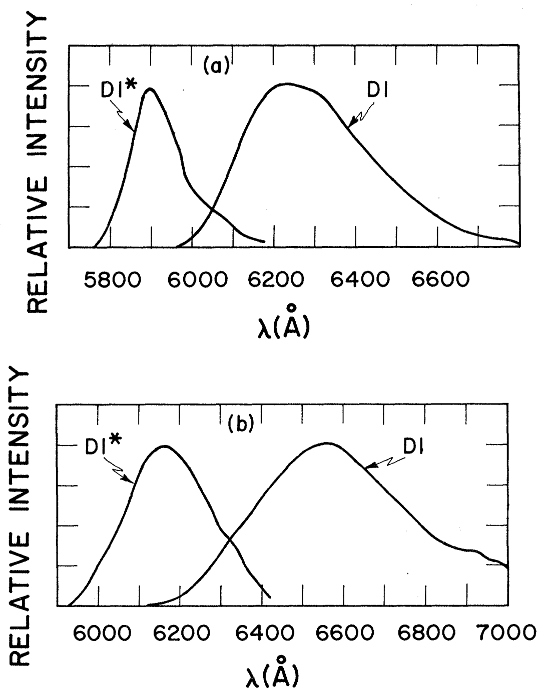

FIG. 2. Fluorescence spectra for diffused crystal $D1$, and for a portion of that crystal $D1^*$ after cadmium vapor treatment (a) before etch and (b) after etch, $\Delta t = 0.97\ \mu$m for both crystals. Pre-etch thickness of $D1$ was 33 μm and of $D1$ was 33 μm and of $D1^*$ was 35 μm.

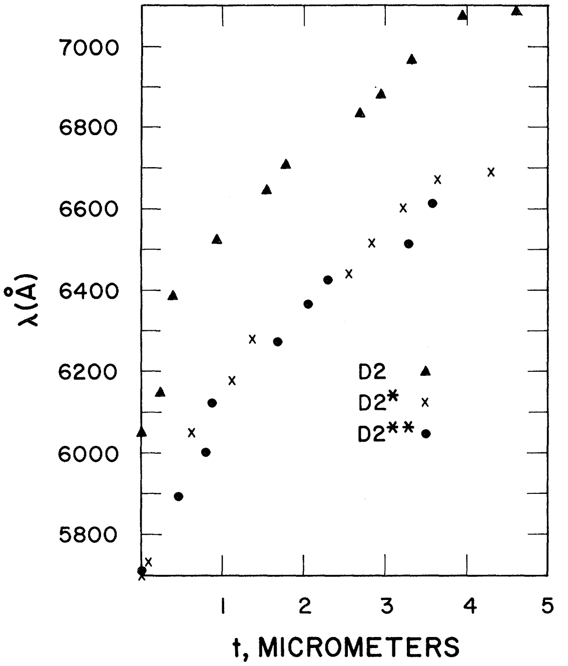

FIG. 3. Dependence of fluorescence peak wavelength on total thickness of surface layer removed for untreated crystal $D2$ and cadmium-treated crystals $D2^*$ and $D2^{**}$. Pre-etch thicknesses were 98, 34, and 33 μm, respectively.

crystals studied. The polarization ratio and half-width did not depend strongly on the amount of material removed from the surface in these crystals. On the other hand, etching did cause significant changes in the polarization ratio and half-width in cadmium-treated crystals with large ($\approx 10^3$ eV/cm) band-gap gradients. This is illustrated by the polarized spectra in Fig. 5. The polarization ratio was observed to increase as increasing amounts of material were removed. Structure was observed in polarized spectra as the wavelength of the peak approached 6800 Å. The half-width of the spectra first increased, then decreased with increasing etching. Spectra of the cadmium-treated crystal with a smaller ($\approx 10^2$ eV/cm) band-gap gradient (crystal $D4^*$) were strongly polarized and exhibited narrow half-widths, both before and after etching, as illustrated in Fig. 6.

Most of the diffused crystals exhibited only one fluorescence peak. However, some spectra showed a narrow, strongly polarized peak and a broad, weakly polarized band at longer wavelengths, just as in type-II CdSe crystals. The short-wavelength peak was much the weaker of the two peaks in crystals which had not been cadmium treated. The relative positions of these peaks are plotted in Fig. 7 for the crystals in which two peaks were observed. This plot is interpreted as giving the approximate separation between the edge emission peak and the

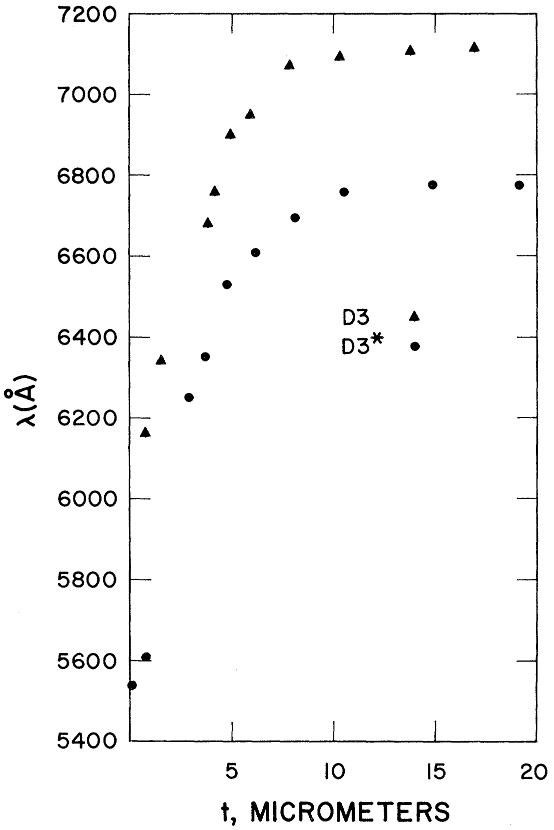

FIG. 4. Dependence of fluorescence peak wavelength on total thickness of surface layer removed for untreated crystal $D3$ and cadmium-treated crystal $D3^*$. Pre-etch thicknesses were 181 and 250 μm for $D3$ and $D3^*$, respectively.

A-exciton wavelength.

Composition profiles were determined by correlating fluorescence wavelength with crystal composition. Park and Reynolds[14] have experimentally determined the correlation between the A-exciton energy and composition in the CdS_xSe_{1-x} system. The spectral position of the fluorescence peak in cadmium-treated crystals was assumed to corre-

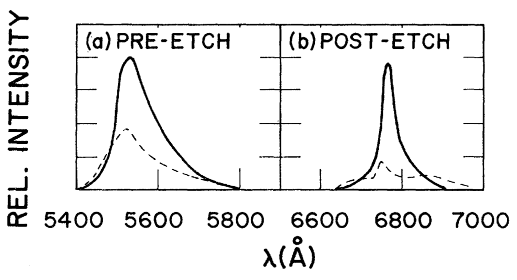

FIG. 5. Polarized spectra of cadmium-treated crystal $D3^*$ (a) before etch and (b) after etch, $\Delta t = 10.2$ μm. Solid line represents $E \perp c$; dashed line represents $E \parallel c$.

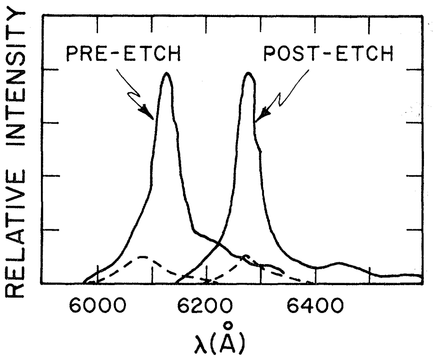

FIG. 6. Polarized spectra of cadmium-treated crystal $D4^*$ (a) before etch and (b) after etch, $\Delta t = 4.0$ μm. Crystal was 18.9 μm thick prior to etching. Solid line represents $E \perp c$, dashed line represents $E \parallel c$.

spond to the A-exciton wavelength. In crystals which had not been cadmium treated and which exhibited only a single broad fluorescence band, the A-exciton wavelength was deduced from the wavelength of the fluorescence peak using the curve in Fig. 7. The composition corresponding to the experimentally determined A-exciton wavelength was then deduced from the data of Park and Reynolds. Figures 8 and 9 plot composition as a function of position as determined from the data of Figs. 3 and 4, respectively. A good fit to the data was given by an error function curve: $x = (x_1 - x_0)[1 - \mathrm{erf}(t/2(D\tau)^{1/2})] + x_0$, where D is the diffusion constant, τ is the diffusion time, x_1 is the sulfur mole fraction at the surface, and x_0 is the sulfur mole fraction in the undiffused crystal. This profile is expected[24] for diffusion into a semi-infinite slab with surface composition held constant.

Experimental composition profiles were used to estimate the number of moles of sulfur and selenium exchanged between the vapor and solid phases in each run. It was concluded that the pressures of S_2 and Se_2 did not change by more than 5% during the course of any of the diffusion runs.

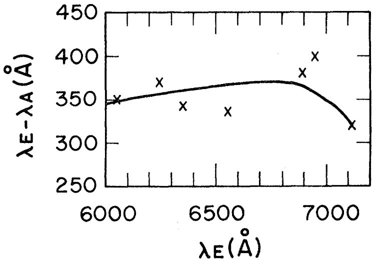

FIG. 7. Dependence of position of edge-emission peak on position of A-exciton peak, determined from data on crystals in which both peaks were present.

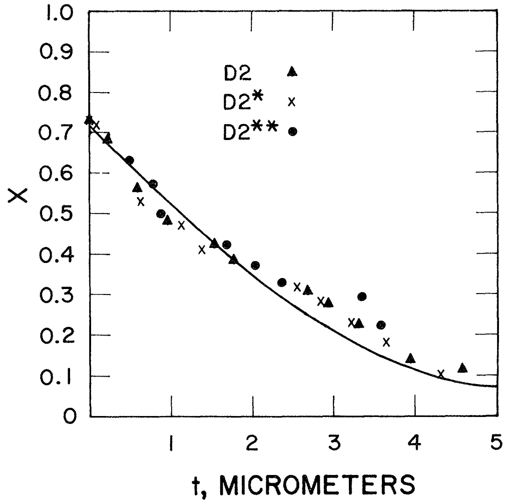

FIG. 8. Composition profile deduced from data of Fig. 3 by correlating the spectral position of fluorescence peaks with crystal composition (see text). The solid curve is the error-function curve corresponding to the values $x_1 = 0.71$, $x_0 = 0$, $D = 7.0 \times 10^{-13}$ cm²/sec.

IV. DISCUSSION

The fluorescence properties of steeply graded, mixed CdS_xSe_{1-x} crystals are similar in some respects to the properties of pure CdSe crystals. The fluorescence of diffused crystals which have not been cadmium treated exhibits a broad half-width and weak polarization characteristic of edge emission of type-II CdSe platelets. The edge emission appears after diffusion even in type-I crystals, in which it was not present prior to diffusion. This is consistent with the association of edge emission with defect centers arising from a deficiency of cadmium,[16] which in the present experiments results from heating the crystals in a chalcogen atmosphere.

The emission in the diffused, cadmium-treated platelets with smaller band-gap gradients shows the narrow half-width and strong polarization dependence characteristic of the principal line in pure CdSe. The emission in crystals with larger ($\approx 10^3$ eV/cm) gradients is less strongly polarized ($I_{E\perp c}/I_{E\parallel c} \approx 2$) and broader (FWHM = 150 Å in $D1^*$ and $D2^*$ and 110 Å in $D3^*$) than the principal peak in pure crystals ($I_{E\perp c}/I_{E\parallel c} > 10$, FWHM = 50–70 Å). A possible explanation for the weaker polarization dependence is that extrinsic emission lines active for $E \parallel c$, such as the one seen in cadmium-treated CdSe platelets, are participating strongly in the fluorescence. The relatively greater contribution for $E \parallel c$ might imply that the energy difference between A and B valence bands is less in steeply graded crystals than in crystals of uniform composition. A possible cause of the broadening in unetched crystals is that a significant change in band gap

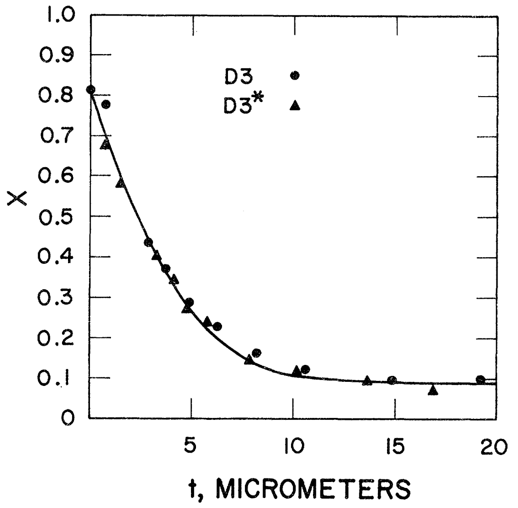

FIG. 9. Composition profile deduced from data of Fig. 4 by correlating the spectral position of fluorescence peaks with crystal composition. The solid curve is the error-function curve corresponding to the values $x_1 = 0.81$, $x_0 = 0.09$, $D = 1.6 \times 10^{-12}$ cm^2/sec.

occurs in the finite thickness of the crystal from which light is emitted. Factors to be considered in calculating line broadening due to this effect include the depth of penetration of pump radiation into the crystal, exciton and/or electron-hole ambipolar diffusion lengths, and reabsorption of light in the crystal. The absorption coefficient for band-gap photons, such as were used to excite fluorescence in the present experiment, is measured to be greater than 10^5 cm^{-1} in pure CdSe[25] and is probably not much different in $\mathrm{CdS}_x\mathrm{Se}_{1-x}$. The depth of penetration of pump radiation is evidently too small to introduce significant broadening. Results of Bleil and Broser[26] suggest an upper limit of 12 μm for exciton or electron-hole diffusion lengths in CdS at 77 °K. A diffusion length of 0.4 μm is estimated from the broadening observed in the present experiment, neglecting reabsorption. The additional spectral broadening observed in etched crystals could result from variations in the surface composition of the crystal due to nonuniform etching. The presence of surface irregularities in etched crystals was confirmed by microscopic examination.

Composition profiles (Figs. 8 and 9) deduced from data on as-diffused crystals were in good agreement with profiles based on data from cadmium-treated crystals. This indicates that heating the diffused crystals in a cadmium atmosphere did not greatly change the distribution of sulfur and selenium atoms. Even in the case of prolonged cadmium treatment (crystal $D2^{**}$), no noticeable difference in composition profiles was evident. Woodbury and Hall[7] have determined experimentally that the coefficient for chalcogen self-diffusion in II-VI compounds is proportional to p_{Cd}^{-1} and that the coefficient for diffusion of selenium into CdS is proportional to $p_{\mathrm{S}_2}^{1/2}$. Diffusion constants have been calculated for the conditions used in the cadmium treatments in the present experiment, assuming a p_{Cd}^{-1} dependence. The cadmium pressure in the initial diffusion runs was calculated from equilibrium constants reported by Goldfinger and Jeunehomme.[23] Diffusion constants were calculated to be five orders of magnitude smaller during the cadmium treatment than during the initial diffusions.

Diffusion coefficients of 7.0×10^{-13} and 1.6×10^{-12} cm^2/sec have been determined for the 600 and 650 °C diffusion runs by fitting error function curves to experimental profiles. The good fit of error-function curves to experimental profiles implies that the diffusion coefficient is not strongly dependent on the sulfur mole fraction x. This contrasts with the results of Biter and Williams[5] on diffusion in $\mathrm{Cd}_x\mathrm{Zn}_{1-x}\mathrm{S}$, which showed a rather strong dependence of diffusion coefficient on composition. Woodbury and Hall[7] found that a "fast" and "slow" diffusion process were required to explain their results on diffusion of Se in CdS, and that exponential curves fit most of their data better than error functions. The data in the present experiment were fit better by error functions than by exponentials, and no evidence for two processes was found. However, diffusion constants obtained by Woodbury and Hall[7] for the slow process under conditions of saturated sulfur pressure, 1.2×10^{-12} cm^2/sec at 650 °C and 4.3×10^{-13} cm^2/sec at 600 °C, were close to the values seen in the present experiment.

V. CONCLUSIONS

Steeply graded mixed $\mathrm{CdS}_x\mathrm{Se}_{1-x}$ crystals with good fluorescence properties can be produced by solid-state diffusion. Composition profiles in these crystals can be determined from photoluminescence measurements. Fluorescence spectra can also provide information on exciton or electron-hole diffusion processes in steeply graded crystals.

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Interlayer Bonding and the Lattice Vibrations of β-GaSe

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The lattice vibrations of the layer compound β-GaSe have been investigated by means of infrared and Raman experiments. Reflectivity measurements for $\vec{E} \perp c$ over the range 175–4100 cm^{-1} have shown one infrared-active mode at 213.9 cm^{-1}. Six Raman lines have been observed at 19.1, 60.1, 134.6, 213.1, 249, and 307.8 cm^{-1}. A group-theoretical analysis of the lattice vibrations, which shows the origin of the conjugate modes in layer compounds, is presented. Electrostatic as well as van der Waals coupling between the layers is indicated by the large localized effective charge obtained from the infrared measurements.

I. INTRODUCTION

Layer compounds are characterized by highly anisotropic bonding forces and structurally identical layers. The forces between the layers are known to be weak by comparison with the forces within the layers. One therefore expects that the interlayer coupling will have a small effect upon the vibrational frequencies of the lattice. A special case of some importance arises when the primitive unit cell contains two layers and there is an inversion center between the layers. Then the normal modes occur in pairs that are either symmetric or antisymmetric with respect to inversion. These so-called conjugate modes can be easily studied, provided that they are optically active, by means of a combination of infrared and Raman experiments.

Such experiments[1–3] have recently been carried out for the layer compounds MoS_2, As_2S_3, and As_2Se_3, and the conjugate optical modes have been observed to be nearly degenerate in energy. The hexagonal layer compound MoS_2 has only one pair of conjugate modes that are optically active: the E_{1u} infrared-active and the E^1_{2g} Raman-active pair. A frequency difference of ≈ 1 cm^{-1} was previously reported by the authors for these two vibrations. For As_2S_3 and As_2Se_3, however, several pairs of conjugate modes are optically active; Zallen *et al.*[3] have observed frequency splittings as large as 6 cm^{-1} between conjugate pairs.

In this paper we present infrared and Raman data on another semiconducting layer compound of wide interest, GaSe. In the previously mentioned investigations it was assumed that the interlayer forces were primarily of the van der Waals type. This is a common assumption for layer compounds and one which clearly needs justification. Indeed, we shall propose that the interlayer interaction in GaSe contains an ionic or Coulomb contribution. The principal evidence for this is the large localized effective charge which has been determined