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Optical and Electrical Properties of $AgGaS_2$ and $AgGaSe_2$

B. Tell
Bell Telephone Laboratories, Holmdel, New Jersey 07733

and

H. M. Kasper
Bell Telephone Laboratories, Murray Hill, New Jersey 07974

(Received 7 July 1971)

From the results of low-temperature luminescence and reflectivity, both $AgGaS_2$ and $AgGaSe_2$ are determined to have a direct energy band gap. The values are 2.727 and 1.830 eV at 2 °K, respectively. The gap shifts to slightly higher energy at 77 °K, which is opposite to that observed in most semiconductors. Both crystals appear to contain shallow impurities or defects. However, the crystals are semi-insulating as-grown, and various annealing and diffusion procedures have failed to produce useful conductivity.

I. INTRODUCTION

Among the group of I-III-VI_2 ternary semiconducting compounds which crystallize in the chalcopyrite structure are $AgGaS_2$ and $AgGaSe_2$. $AgGaS_2$ has been shown to be potentially useful for nonlinear optics,[1,2] but the semiconducting properties of these materials have not been previously studied.[3] In the present paper, we present optical properties sufficient to determine the presence of a direct band gap, and in addition, describe some doping experiments.

As in our previous study of two I-III-VI_2 compounds, $CuGaS_2$ and $CuInS_2$,[4] we have observed low-temperature exciton reflectivity and near-band-gap sharp-line photoluminescence. The highest-energy luminescence coincides in energy with the reflectivity anomaly. From this result, we conclude that both $AgGaS_2$ and $AgGaSe_2$ have direct band gaps whose values are 2.727 and 1.830 eV at 2 °K, respectively. In addition, luminescence studies at 2 °K indicate that both materials have shallow defects or impurities with binding energies of several tens of millivolts. However, both crystals are semi-insulating "as-grown" and it has proven difficult to achieve useful conductivity of either n or p type. The inability to produce rapid and dramatic conductivity changes is in contrast to our previous work on the copper compounds.[4]

II. CRYSTAL GROWTH

$AgGaS_2$ and $AgGaSe_2$ crystallize in the chalcopyrite structure (symmetry $\bar{4}2m = D_{2d}^{12}$)[3] which is an ordered superstructure of the zincblende type. Both are grown from the melt. The starting materials were silver 99.999% pure, gallium 99.9999% pure, sulfur 99.9999% pure, and selenium 99.999% pure, according to spectrographic analysis. Equivalent amounts of sulfur and the metals were reacted in silica boats contained in evacuated silica ampoules. The melts were then cooled from 1050 °C ($AgGaS_2$) or 950 °C ($AgGaSe_2$) at a rate of 2 °C/h to below 950 °C for $AgGaS_2$ and below 750 °C for $AgGaSe_2$ and then cooled at a faster rate to room temperature. In many cases the silica boats were cracking due to the strongly anisotropic thermal contraction. Frequently the ingots contained crystals of several millimeters in dimension. The ingots of $AgGaS_2$ varied in color from light yellow to dark green. It appears that in the cases with both colors present the yellow material crystallized first and the green material crystallized later. There does not appear to be a sharp boundary between these regions. It is presumed that the color change is due to slight variations in stoichiometry, and we believe that the darker crystals are closer to the ideal composition $AgGaS_2$ and that the yellow crystals are slightly gallium rich. The growth of yellow and green crystals is still under investigation and a detailed report will be published at a later date. The measured lattice constants of $AgGaS_2$ are $a = 5.757$ Å and $c = 10.305$ Å. While the lighter crystals are probably more desirable for nonlinear optics because of less over-all absorption, we have found darker crystals to be superior for the optical properties of interest in this study.

For the case of $AgGaSe_2$, such color variations are not distinguished since the crystals are nearly opaque to visible light. Selecting solid crystals with good natural faces, systematic differences in the quality of the luminescence and reflectivity, such as described for $AgGaS_2$, were not observed. On the other hand, the optical quality of the selenide (as evidenced by reflectivity and luminescence) is inferior to the sulfide. The measured lattice constants for $AgGaSe_2$ are $a = 5.99202 \pm 0.00018$ Å and $c = 10.88626 \pm 0.0003$ Å.

III. RESULTS

Both $AgGaS_2$ and $AgGaSe_2$ exhibit a large distortion from pseudocubic symmetry; the distortion (i.e., a compression along the optic axis) is given by $[2 - c/a]$. Shay and co-workers[5] have shown that, for a crystal-field splitting much greater than the spin-orbit splitting, the crystal-field splitting of the II-IV-V_2 chalcopyrite compounds (e.g., $CdSnP_2$) is approximately given by $\frac{3}{2} b[2 - c/a]$, where b is the deformation potential of the binary analog for [001] compression. Using the deformation potential appropriate to ZnS[6] (i.e., -0.5 eV) and the lattice constants for $AgGaS_2$, the predicted splitting is 160 meV. The crystal-field splitting is presumably comparable for $AgGaSe_2$. Since b is, in general, a negative energy, the crystal-field splitting is negative. That is, the splitting is opposite to that observed in the wurtzite II-VI compounds,[7,8] but the same as that observed in compressed CdTe.[9] In general, the exciton associated with the upper valence band should be active in both modes of polarization, while the second valence band is active only for light polarized normal to the optic axis. However, even for arbitrarily small crystal-field splittings, the lowest-energy exciton is active mainly (80%) for light polarized parallel to z[9] (z refers to the c or optic axis). As the ratio of crystal-field to spin-orbit splitting increases, the lowest-energy exciton becomes nearly completely polarized parallel to z. We are implicitly assuming in the above that the conduction band is s-like and that the valence band is derivable from a threefold degenerate p-like level. In the copper compounds, there is strong evidence for a large admixture of copper d bands into the upper valence bands.[4] However, such d-band mixing should be significantly reduced in silver compounds.

A. Reflectivity

Near normal incidence reflectivity has been observed from as-grown surfaces at 2 and 77 °K using techniques and equipment previously described.[4] The crystals often formed large natural surfaces (~1 cm largest dimension) which were commonly [112] faces. The projection of the z or optic axis was located by the use of x-rays and polarized light, and, except for cleaning, no further surface treatment was performed. Because of the large c/a ratio as described above, the crystal-field splitting of the valence band is sufficiently large so that only one reflectivity anomaly has been observed in each crystal. A splitting of several times the exciton binding energy (i.e., greater than ~100 meV) is probably sufficient to overbroaden (due to auto-ionization) any higher-energy exciton reflectivity. The observed anomalies are due to excitons with the hole associated with the highest valence band, and occur for light polarized parallel to the optic axis. Such anomalies occur only in the vicinity of the lowest direct gap.[8]

The 2 °K reflectivity spectra for $AgGaS_2$ is shown in Fig. 1 for incident light polarized parallel to the optic axis ($E \parallel z$). The main reflectivity peak (the ground state) is observed at 4594 Å, while the weak structure at slightly higher energy is observable only at 2 °K. This structure is seen only for $E \parallel z$

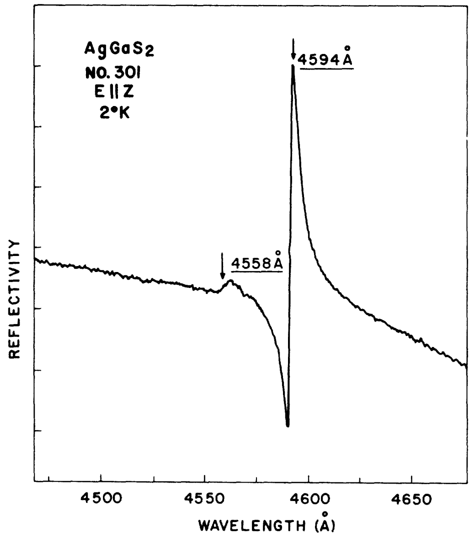

FIG. 1. 2 °K reflectivity spectra on an as-grown [112] face of $AgGaS_2$ for $E \parallel z$ (z is the c optic axis). Actually, only $\frac{2}{3}$ of the intensity is parallel to z for a [112] face. The reflectivity at long wavelength is ~0.25, and the zero reflectivity is the bottom of the scale. Both the ground state and first excited state are indicated by arrows.

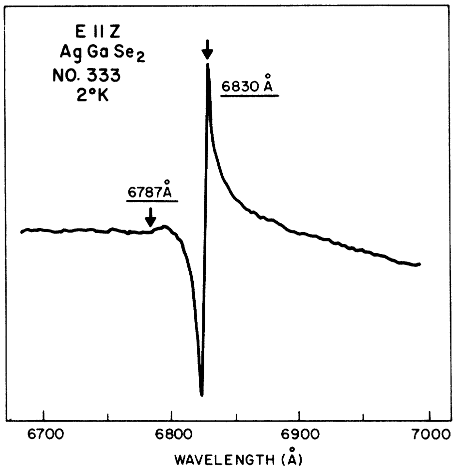

FIG. 2. 2 °K reflectivity spectra for a [112] face of $AgGaSe_2$ for $E \parallel z$ (z is the c or optic axis). The ground state and what is probably the first excited state are indicated by arrows. The zero reflectivity level is not shown.

and is ascribed to the first excited state ($n = 2$). For $E \perp z$, the ground-state anomaly is nearly reduced to the background level, and no higher-energy anomalies are seen within at least 100 meV. (The absolute reflectivity value is ~ 0.25, as estimated from room-temperature refractive-index measurements.[2,10]) From the position of the excited state (~ 21 meV higher in energy) and the simple Bohr relationship (the binding energy equal to $\frac{4}{3}$ of the energy of the first excited state), the binding energy G of the exciton is 28 meV. At 2 °K, the lowest-energy direct gap is $E_x + G = 2.699 + 0.028 = 2.727$ eV. At 77 °K, only the ground-state reflectivity is seen at 4585 Å. The energy of the reflectivity maximum is therefore shifted ~ 9 Å (5 meV) to higher energy and, consequently, the band gap is slightly shifted to higher energy. Such a temperature shift is opposite to that observed in the II-VI compounds,[7,8] and may be partly due to anisotropic thermal contraction.

A single reflectivity anomaly is also observed in $AgGaSe_2$ at both 2 and 77 °K. This anomaly is observed predominantly for incident light polarized parallel to the optic axis. At 2 °K, the reflectivity maximum occurs at 6830 Å (1.815 eV) as seen in Fig. 2. We believe that the weak structure at 6787 Å (~ 11 meV higher in energy and observed only at 2 °K) is the $n = 2$ state of the exciton. The exciton binding energy, therefore, is ~ 15 meV, so that the energy gap at 2 °K is 1.830 eV. At 77 °K, the reflectivity maximum occurs at 6820 Å, so that the band gap again shifts to higher energy.

The exciton binding energies determined for both materials are essentially identical to those determined in the II-VI compounds of closest energy gap [CdS (28 meV) and CdSe (16 meV), respectively].[8] This means that the exciton effective mass, and, consequently, the electron and hole masses, should be comparable to those determined for the II-VI compounds. Actually, taking into account the larger dielectric constant for $AgGaS_2$,[11] the exciton reduced mass is twice that for CdS.

B. Photoluminescence

Photoluminescence was observed from both compounds in an immersion Dewar at 2° and 77 °K employing He-Cd laser excitation (~ 50-mW maximum power at 4416 Å). The 2 °K spectra (Figs. 3 and 4) are dominated by extrinsic effects which are probably excitons bound to impurities or defects. Both crystals also exhibit structureless longer-wavelength emission which is relatively stronger in $AgGaSe_2$ than in $AgGaS_2$. The position of the exciton reflectivity maximum is indicated by arrows in both Figs. 3 and 4. There is a slight discrepancy (~ 3 Å) between the reflectivity maximum and the peak of the highest-energy luminescence in $AgGaS_2$. Nevertheless, the occurrence of luminescence at the position of the free exciton (as observed in reflectivity) is strong evidence that the crystals are direct gap. The luminescence at 77 °K has an entirely different appearance, and is presum-

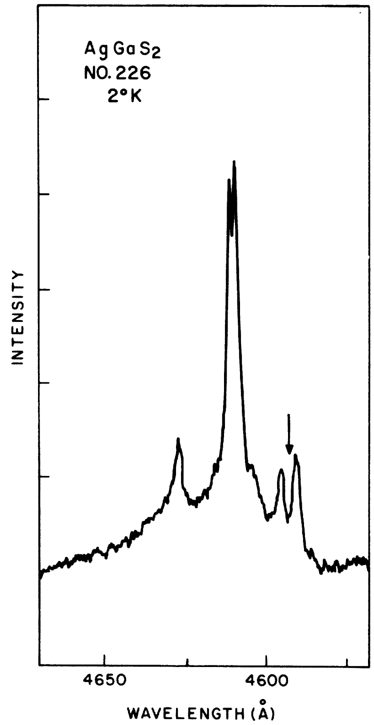

FIG. 3. 2 °K luminescence spectra for $AgGaS_2$. The position of the free exciton as determined from reflectivity is indicated by the arrow. Spectra obtained with minimum excitation intensity.

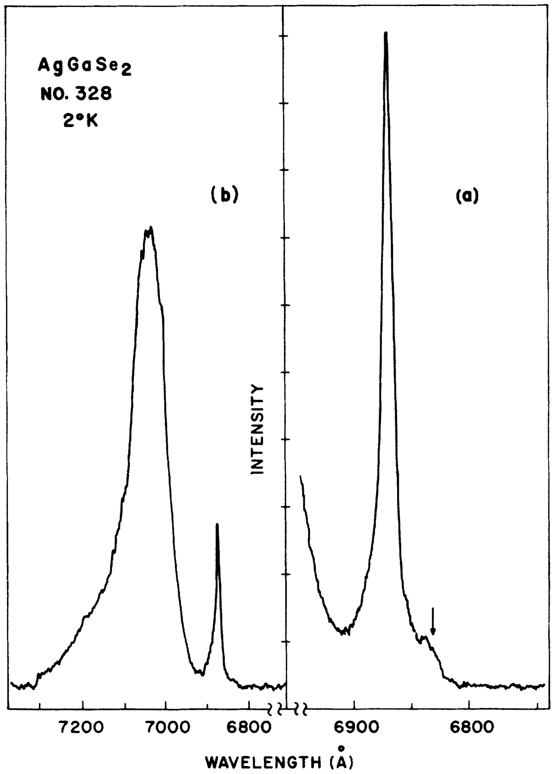

FIG. 4 (a) 2 °K luminescence spectra for AgGaSe$_2$ showing the near-band-gap emission and the position of the free exciton determined from reflectivity. (b) Compressed version of the same spectra also showing the broader longer-wavelength emission. Both (a) and (b) were obtained with minimum excitation intensity.

ably dominated by intrinsic effects. The observed emission is assumed to be due to the radiative decay of the free exciton, and is shown in Fig. 5 for AgGaS$_2$. The position of the reflectivity maximum at 77 °K is indicated by the arrow.

We have attempted to characterize the 2 °K extrinsic luminescence in AgGaS$_2$ using the generalization of Haynes's[12] rule as recognized by Halsted and Aven[13] for the II-VI compounds. Since the free exciton parameters for AgGaS$_2$ are similar to CdS, it might be expected that impurity excitons would also be similar. The dissociation energy (the energy difference between the free exciton and an impurity exciton) in CdS of an exciton bound to a neutral donor is ~7 meV and for a neutral acceptor is ~18 meV.[14] The binding energies are five times the dissociation energy for donors, and roughly ten times the dissociation energy for acceptors.[13]

The doublet observed in AgGaS$_2$ at ~4610 Å has a dissociation energy between the donor and acceptor value. If we assume that the doublet is due to neutral acceptors, then acceptor binding energies would be around 110 meV. Higher-energy lines (~4600 Å), which are not too prominent in this particular crystal, would then be associated with neutral donors whose binding energies would then be in the range 15–25 meV. On the other hand, if the doublet is associated with excitons bound to neutral donors, donor binding energies would be roughly 50 meV. Annealing studies, which could possibly distinguish the donor or acceptor nature of some of the observed lines, have not been informative. In any case, the luminescence in AgGaS$_2$ indicates the presence of relatively shallow donors, and with considerably less certainty, the presence of shallow acceptors.

For AgGaSe$_2$, the exciton line and the proximity of the broad emission are indicative of shallow impurities. This broad emission saturates at high pump levels, and shifts slightly to shorter wavelength as the pump power is increased. This behavior is consistent with a donor-acceptor pair band model.[15]

C. Electrical Properties

The crystals as-grown were highly insulating (>10^8 Ω cm). We have previously found that several of the I-III-VI$_2$ compounds behave similar to the II-VI compounds in that rapid and dramatic conductivity changes are achieved by annealing in maximum or minimum chalcogen pressures.[14] However, annealing AgGaS$_2$ and AgGaSe$_2$ under maximum and minimum sulfur and selenium pressures, respectively, and quenching to room temperature leaves the crystals still highly insulating.

We have also tried several doping experiments both by diffusion and during growth. Most of the diffusion experiments were performed on AgGaSe$_2$ since it was felt that the doping prospects for a narrower gap material should be more favorable. The diffusions were performed at 700–750 °C for at least 72 h. The following dopants were tried:

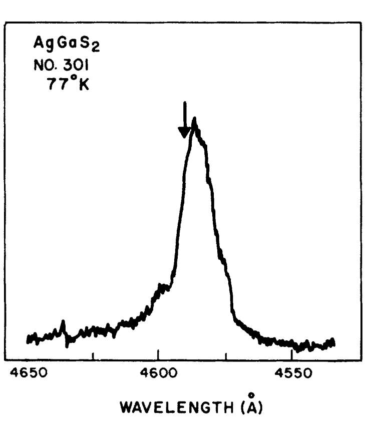

FIG. 5. 77 °K luminescence spectra for AgGaS$_2$ with the position of the free exciton, as determined by reflectivity, indicated by the arrow.

Cl, Br, I, Sn, Zn, and P. In no case was there conclusive evidence of bulk conductivity. It is possible that the diffusion rates are significantly slower than those observed in II-VI compounds (e.g., CdS),[16] but we have been equally unsuccessful in doping with Ge, P, and Zn during growth.

As discussed in connection with luminescence, both crystals show evidence of containing relatively shallow impurities. These impurities might be contained in some form of neutral complex and therefore unable to contribute carriers, or the crystals might be self-compensating for both *n*-and *p*-type conductivity.

ACKNOWLEDGMENTS

We wish to thank R. L. Barns for obtaining the lattice constants quoted in Sec. II, and R. A. Laudise and A. G. Chynoweth for their interest in this work. In addition, we thank J. L. Shay and G. D. Boyd for several useful discussions, J. J. Wiegand for x-ray work, and Mrs. A. A. Pritchard and A. L. Albert for sample preparation.

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Temperature-Induced Wavelength Shift of Electron-Beam-Pumped Lasers from CdSe, CdS, and ZnO

J. M. Hvam
Physics Laboratory III, Technical University of Denmark, Lyngby, Denmark
(Received 3 May 1971)

Experimental results on the temperature dependence of the laser frequency and threshold pump power are presented in the range from liquid helium to room temperature for electron-beam-pumped CdSe, CdS, and ZnO lasers. A linear shift of the laser frequency at high temperatures and a relatively slow linear increase of threshold with increasing temperature are found. A model is proposed that takes into account the reabsorption in the crystal below the lowest exciton energy. The results of this model are in quantitative agreement with the experimental data. The absorption coefficient at the laser frequency is determined in the three materials.

INTRODUCTION

Laser emission from II-VI semiconductors has been reported by several authors,[1,2] even at elevated temperatures.[3,4] In ZnO, CdS, and CdSe, Packard, Campbell, and Tait[5] reported laser emission due to the phonon-assisted annihilation of free excitons (Ex-LO). Later, Benoit a la Guillaume and co-workers reported that at least three different processes could lead to laser action in CdS,[6] the first being the Ex-LO process mentioned above; the second, the exciton-exciton collision process; and the third, the exciton-electron collision process. However, these processes alone fail to explain the temperature behavior of the laser action observed at elevated temperatures.[7,8]

Leheny *et al.*[8] proposed that the temperature behavior of the laser action in CdS was strongly influenced by reabsorption in the crystal at higher temperatures. In this paper, we investigate the application of a similar model to electron-beam-pumped CdSe, CdS, and ZnO lasers. The model