ELECTRICAL TRANSPORT AND CONTACT PROPERTIES OF LOW RESISTIVITY n TYPE ZINC SULFIDE CRYSTALS

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so that there is reasonable assurance that the basic excitation mechanism is understood. The theory should be applicable to most short-pulse gas lasers where heavy-particle diffusion effects are not important.

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ELECTRICAL TRANSPORT AND CONTACT PROPERTIES OF LOW RESISTIVITY n-TYPE ZINC SULFIDE CRYSTALS[1]

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This Letter describes some electrical contact and transport properties of ZnS single crystals having room-temperature resistivities in the range of 1 to 10 ohm-cm. Previous electrical transport measurements on ZnS have been done mainly at high temperatures[2] or under photoexcitation.[3] Electrical contacts to ZnS which display ohmic characteristics at room temperature have been described by Alfrey and Cooke.[4] A serious limitation to a more extensive investigation of the electrical properties of ZnS has been the difficulty in providing ZnS crystals with contacts which would stay ohmic at low temperatures. It has also been difficult to dope ZnS n-type without simultaneously introducing large concentrations of native acceptor defects.

The investigation of the nature of electrical contacts to ZnS was carried out by cleaving the crystals in a vacuum and immediately evaporating a layer of the desired metal on the cleaved surface. Barrier heights were measured using the voltage variation of the capacitance, the volt-ampere characteristic, and the barrier photoresponse. The detailed procedure has been described previously.[5] In all cases the measurements agreed within approximately 0.1 eV. The barrier heights for a number of metals are shown in Fig. 1 plotted against the electronegativity of the metal. The previously reported results on CdS (ref. 5) are also shown in Fig. 1 for comparison. It can be seen that, with the exception of Al,

the points all fall within approximately 0.1 eV of the straight line of unity slope and intercept of 0.3 eV. This result suggests that a meaningful formulation would be $\varphi_B = x_m - \chi$ where φ_B is the barrier height, x_m is the electronegativity of the metal, and χ is a type of "electron affinity" of the semiconductor, as given by the intercept in a plot such as Fig. 1. (The zero of this quantity is arbitrary and does not corre-
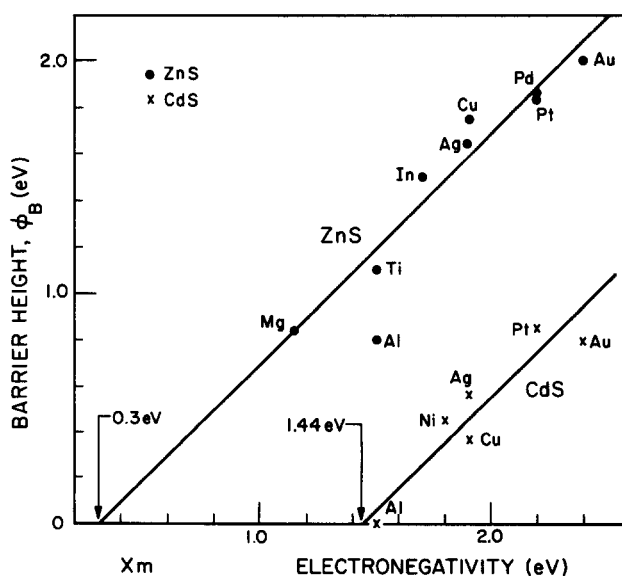

Fig. 1. Barrier heights of various metals on ZnS and CdS as a function of the electronegativity of the metal.

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spond to the vacuum level.) As noted previously,[5] the usual formulation using the metal work function results in a much larger scatter, and hence its usefulness is questionable in the present case. It is possible to argue that this will be the case for any semiconductor where the barrier heights are strongly dependent on the metal. In these materials, the binding is largely of an ionic type, the wave functions are localized,[6] and the conduction and valence bands are best identified with the positive and negative ions.[7] Under these conditions the electron transfer across an interface is an atomic process and hence the interface energetics should be more dependent upon atomic properties like the electronegativity than upon gross average properties like the work function.

The present results demonstrate graphically why it is difficult to make ohmic metal contacts to ZnS. In contrast to many of the Group IV and III-V materials where the barriers are fixed by a large density of surface states, the problem in electroding ZnS stems mainly from its very low electron affinity which, according to Fig. 1, is 1.14 eV below that of CdS. The best electrical contacts to n-type ZnS would, therefore, be provided by a metal with a low electron affinity. A satisfactory contact must also meet other specifications, e.g., it should be mechanically compatible with the crystal and should not introduce any undesirable dopants.

Contacts with the best overall performance were obtained by etching the ZnS crystals in hot (250°C) pyrophosphoric acid and immediately scribing on the contacts, with an In wire dipped in Hg. After adding more In to each contact,[8] they were fired in 350°C in H_2 atmosphere.

Hall-effect measurements between about 100° and 400°K revealed the presence of two types of levels near the conduction band of ZnS, as shown in Fig. 2a. Hexagonal or cubic crystals doped with Al by firing at 1050°C in liquid ZnAl alloy showed a level 0.014 eV below the conduction band edge. I-doped cubic crystals exhibited the same level when fired at 950°C in liquid Zn. In view of the high donor concentration in these crystals ($>10^{18}$ cm^{-3}) the 0.014-eV level probably represents a hydrogenic donor level whose ionization energy has been lowered by impurity banding. In I-doped cubic crystals and less strongly Al-doped crystals fired in liquid Zn above 1050°C the Fermi level has varied between 0.10 and 0.29 eV. In I-doped crystals there appears to be a relatively stable level at 0.10 eV. Freeze-out on a 0.18-eV level in an Al-doped crystal is shown in Fig. 2a. Such behavior is quite similar

to that seen in n-type CdS and ZnSe which have also been reported to display shallow[9,11] as well as deep[10,11] levels near the conduction band edge, with some variability in the ionization energies of the deep levels. In samples where the ionized donor concentration was measured using the voltage variation of the capacitance of a surface barrier, the results agreed well with the Hall measurements.

The temperature dependence of the Hall mobility of an n-type ZnS crystal is shown in Fig. 2b. The figure also shows the mobility calculated for the case of scattering by polar optical modes (this has been found to be the dominant scattering mechanism in all pure II-VI compounds in this temperature
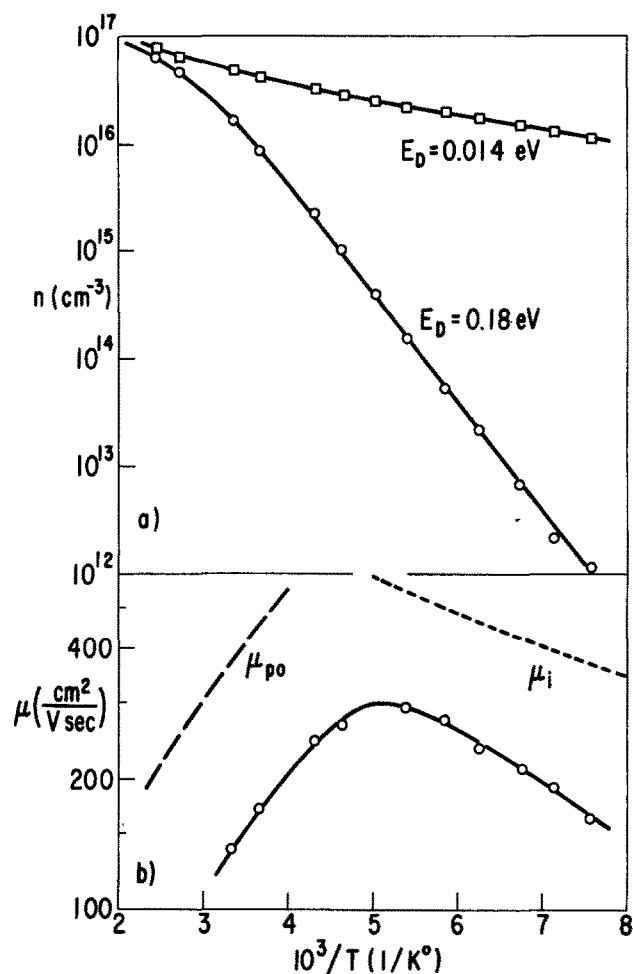

Fig. 2. (a) Temperature dependence of the electron concentration in ZnS. Circles: Al-doped hexagonal ZnS fired at 1050°C; squares: I-doped cubic ZnS fired at 950°C. (b) Temperature dependence of the Hall mobility of an Al-doped hexagonal ZnS crystal fired at 1050°C. The dashed curve represents the calculated mobility of ZnS assuming scattering by the polar optical modes to be the predominant mobility limiting mechanism. The dotted curve is the mobility calculated for scattering by charged impurities.

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range), and for the case of scattering by charged impurities. The concentrations of ionized donors and acceptors used in the calculations were obtained from the Hall data on the same crystal. It can be seen in Fig. 2b that the behavior of the experimental mobility can be understood in terms of these two scattering mechanisms.

The presented data show that ZnS, like its close homologues CdS and ZnSe, can be made in low-resistivity n-type form, and that it displays an energy-level structure and mobility behavior similar to these compounds. The observed difference of 1.14 eV in the electron affinities of CdS and ZnS is close to the difference in the band-gap energies of these materials (2.4 eV and 3.6 eV, respectively, at room temperature, from electrical measurements[12,13]), indicating a vacuum level which is in both cases approximately the same energy above the valence band edge, a fact not surprising since the valence band can be identified with a sulfur ion in each case.

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PREPARATION OF FERRITE FILMS BY EVAPORATION

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(electron beam melting; E)

Several methods of preparing thin ferrite films have been developed in recent years, e.g. pyrolytic spraying of organic complexes with proper metallic ion contents,[1] evaporation of the metal constituents and subsequent oxidation at elevated temperatures,[2] spraying suspensions of hydroxides against hot substrates,[3] and cathodic sputtering.[4,5] However, in addition to being time-consuming some of the above methods are hazardous. For example: 1) metal-organic complexes are very reactive especially in moist air and most of them are extremely toxic; 2) long annealing times are necessary to convert the evaporated metals into ferrites; 3) it is extremely difficult to prepare mixed ferrite films using the hydroxide spraying method; 4) very pure poly-crystalline magnetite and hematite had to be cut and ground into discs to successfully sputter these materials; in addition, it took approximately 30 min to obtain a 1000-Å film (33 Å/min); 5) the same objections as in number 2 exist, e.g. long annealing times are necessary to convert the metal films into ferrites. In this Letter results are presented on the direct evaporation of ferrite powders in an oxygen atmosphere.

Pressed ferrite powders were placed into a water-cooled copper trough. The vacuum system was pumped until it reached the 10^{-6}-torr range (approximately 20 min). Then by bleeding in oxygen, the pressure was adjusted to 5 μ. The evaporation was carried out using a Denton DEG-801 Electron Beam Gun.[7] While in general electron guns have to operate at a maximum pressure of 10^{-4} torr, the unique design of this gun makes it possible to operate at pressures as high as 10 μ. The materials were deposited onto single-crystal rock-salt and glass substrates held at room temperature. The evaporation rate was 1000 Å/min.

The films deposited onto rock-salt substrates