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VALENCE-BAND BENDING TO THE FERMI LEVEL AND RADIATIVE RECOMBINATION IN ZnS WITH LIQUID ELECTRODES*

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In groups IV and III-V semiconductors the band bending at interfaces is controlled by surface states, whereas in II-VI semiconductors such as ZnS the band bending is controlled by the electrodes.[1] The work function of the anode must equal or exceed the sum of the electron affinity and band gap of the II-VI semiconductor in order for the band bending to be sufficient to bring the valence-band edge into coincidence with the Fermi level at the surface, thereby facilitating hole injection. From the photoelectric threshold[2] of CdS and related measurements[3] on ZnS, we estimate that the threshold anode work function for hole injection into ZnS is 7 eV. This high value explains the previous failures to achieve positive hole injection into ZnS except by "formed" patches or by tunneling through insulating barriers.[4] The work function of oleum (fuming sulfuric acid) is believed on the basis of its strong oxidizing power to be approximately this value. This is supported by the observation of hole injection into anthracene which is concurrently dissolved by the oleum.[5]

We have observed blue electroluminescence at room temperature originating in copper-activated zinc sulfide crystals at the interface with an oleum (H_2SO_4 plus 30% excess SO_3) anode. The experimental setup consisted of a U tube containing the oleum with an opening near the bottom approximately 1 mm in diameter to which the crystal was cemented. The other electrode was a mercury-indium amalgam. There is negligible chemical reaction of the oleum with the ZnS crystal. With oleum as the anode, evolution of gas was observed and found to correspond to the order of magnitude of one molecule per charge carrier. This can be explained by the conductivity of the oleum being due to hydrogen ions which are neutralized on injection of positive holes into the crystal and then form H_2 molecules. Strong rectification was observed. Figure 1 gives the energy band diagram of the ZnS-oleum junction in thermal equilibrium, showing the p-type inversion layer at the ZnS-oleum interface. The injection of positive holes with forward bias and radiative recombination of electrons with trapped holes are also shown in Fig. 1. Measurements of the voltage drop in the anode region yield 3.4 V for the diffusion voltage. Figure 2 gives the electroluminescent brightness versus current. The superlinear range can be explained by saturation of nonradiative recombination states. The light originates at the anode with the shape of the opening in the U tube. The position of the metallic electrode had no effect on the brightness-current relation, although the voltage changed due to different series resistance of the crystal. From measurements compared to a standard lamp the efficiency is approximately 10^{-4} photons per electron with 12 V

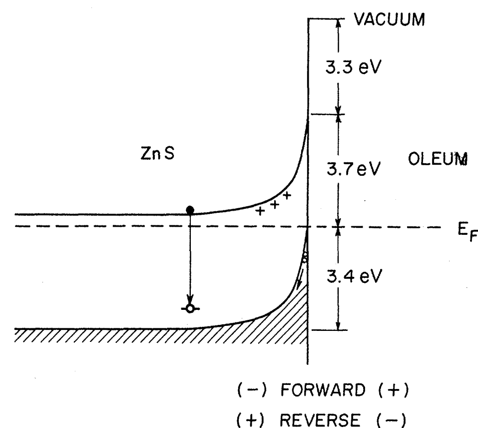

FIG. 1. The energy band diagram of ZnS near the anode in thermal equilibrium.

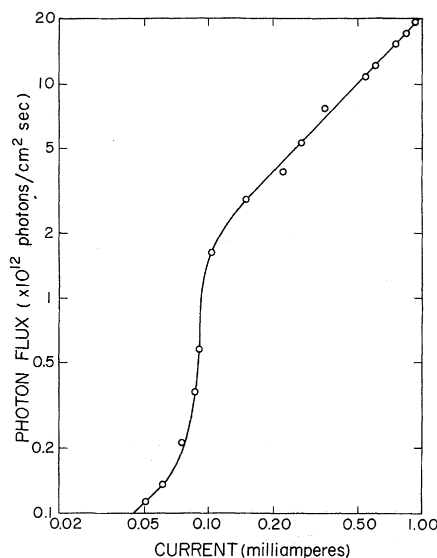

FIG. 2. Emitted photon flux versus current at room temperature.

applied between anode and cathode, corresponding to a current of 0.27 mA.

If the polarity is reversed the current is reduced by a factor of 10^4 at 12 V. The voltage across the ZnS-oleum junction in the reverse direction is essentially equal to the total applied voltage. We observed emission of white light at high reverse bias of 190 V, with a simultaneous steep increase in current. This can be explained as avalanche radiation, which is consistent with the presence of an inversion layer. With ordinary concentrated sulfuric acid (98% H_2SO_4) no anode electroluminescence is observed. This indicates that oxidizing power or work function is the primary requirement for hole injection, not hydrogen ion concentration.

These measurements show that bending of the valence band to very near the Fermi level and positive hole injection can be achieved in ZnS with high work function anodes. Our studies on ZnS support the interpretation that the injection of positive holes into anthracene occurs by band bending with inversion,[5] and that the dissolving of anthracene by oleum is not an essential part of the mechanism of the light generation.

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METHOD FOR DETERMINING SILICON DIFFUSION COEFFICIENTS IN SILICON AND IN SOME SILICON COMPOUNDS

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Self-diffusion data in silicon are of considerable interest for a fuller understanding of diffusion mechanism operating in group-IV semiconductors. But due to the unavailability of any suitable experimental technique no direct measurement has been possible so far. Different authors[1-4] have predicted different parameters for self-diffusivity in silicon. Some of these are compiled in Table I.

Since self-diffusion in silicon is expected to be vacancy controlled (in line with other diffusion data available in group-IV semiconductors), direct diffusivity measurements could also substantiate the model of solute diffusion in diamond lattice proposed by Swalin[5] and the values of the energies of formation and motion of silicon lattice vacancies.[6] Moreover, the concept of partial-acceptor nature of silicon lattice vacancies[5] could be substantiated by direct diffusivity measurements in p- and n-type material as in germanium[7] and silicon carbide.[8]