HgSe, a highly electronegative stable metallic contact for semiconductor devices*

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Schottky barriers formed by the highly electronegative substance HgSe on n-ZnS and on n-ZnSe have been characterized by capacitance-voltage and photoresponse measurements. The barriers are about 0.5 eV greater than Au barriers on these n-type substrates. HgSe contacts are stable under ambient conditions and are easily fabricated, making them attractive for device use.

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Metallic contacts used in the fabrication of semiconductor devices ordinarily range from electropositive metals like Al to the most electronegative elemental metal, namely Au. The considerable advantages to be gained from metallic contacts more electronegative than Au have been described recently[1-4] and one such contact material, a high polymer of sulfur and nitrogen, characterized.[5] The latter substance is relatively unstable, however, and not well suited to conventional semiconductor device processing. We describe here an alternative, highly electronegative contact material, HgSe, which is stable and amenable to ordinary device processing. Since this semimetallic material is itself a II-VI compound, it is structurally compatible with the common tetrahedral semiconductors of nonzero band gap.

That the Hg chalcogenides should be highly electronegative is suggested by trends recently noted[6] for Schottky barriers on the Zn and Cd chalcogenides. These trends show that, at an interface with Au, the valence-band maximum E_v of these compounds lies below the Au Fermi level by an amount characteristic of the anion of the compound. Changing the cation from Zn to Cd does not move E_v, but does reduce the band gap. Further changing the cation from Cd to Hg produces zero band gap[7] and hence semimetallic characteristics. Depending on how well anion control of E_v is maintained as these materials become semimetals, the Fermi level of these materials could lie substantially below that of Au.

In this letter we report on experiments performed to evaluate the Schottky barrier energies of HgSe on substrates of single-crystal Al-doped ZnS and ZnSe.

ZnS and ZnSe crystals were heat treated in liquid zinc to yield n-type carrier concentrations of about 5×10^{16} cm^{-3} for the ZnS and 5×10^{17} cm^{-3} for the ZnSe, as measured by the capacitance-voltage method. Ohmic contacts were made to the substrates by wetting the surface with an amalgam of Hg-In-Cd and heating to 450 °C for 1 min.[8]

The samples were cleaved in air, and HgSe dots were grown on the freshly cleaved surface in the apparatus of Fig. 1. A drop of triple-distilled Hg was placed inside the chamber on a quartz receptacle to provide Hg vapor for the growth. Hg pressure inside the chamber is determined by the Hg temperature (25 °C), the relative areas of the hole in the base of the chamber and the Hg surface, and the cleanness of the Hg surface. This establishes a Hg pressure of somewhat less than the room-temperature vapor pressure of 1.4×10^{-3} Torr,[9] so that Hg will not condense on either the specimen or the chamber walls. Se was evaporated from a shielded evaporator through a hole in the bottom of the HgSe growth chamber. The substrate was placed directly over the hole on a fine screen evaporation mask to define small (approx. 3×10^{-4} cm^2 area) dots of Se. Reaction between the evaporating Se and Hg vapor present in the chamber takes place at room temperature to form approximately stoichiometric HgSe as the Se

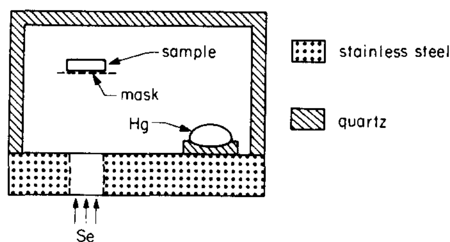

FIG. 1. Schematic diagram of the HgSe growth chamber. The chamber is placed inside an ion-pumped vacuum system. Se is evaporated into the chamber from below, and, upon condensing onto the sample, reacts with Hg vapor present in the growth chamber to form HgSe.

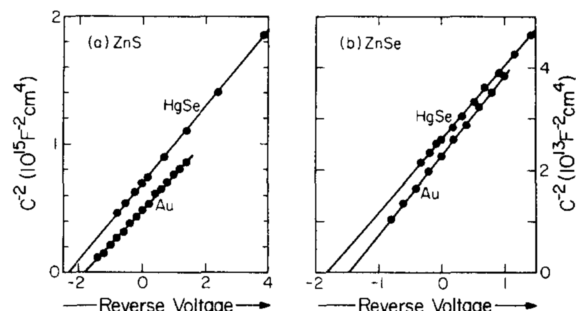

FIG. 2. Capacitance-voltage plots of HgSe and Au (from Refs. 5 and 12) Schottky barrier data. The voltage intercept plus a small correction gives the barrier energy.

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TABLE I. The range of measured barrier energies (in eV) on various samples of HgSe on ZnS and ZnSe.

	ZnS	ZnSe
C-V	2.3—2.7	1.9—2.0
Photoresponse	2.5—2.7	2.0—2.1

evaporates. Pressure measured at the vacuum system ion pump was less than 10^{-6} Torr during the Se evaporation.

One typical one-week-old HgSe on ZnS sample was examined by Auger electron spectroscopy to obtain a qualitative measure of the composition of the HgSe layer. No oxygen or carbon was detected in the HgSe layer and it was determined, to within the 10% accuracy of the method, that the layer is stoichiometric. The growth technique thus produced relatively pure HgSe that is stable in air. Some oxygen was found at the HgSe-ZnS interface.

Measurements of the resultant Schottky barriers were made using capacitance-voltage (*C-V*) and photoresponse techniques.[10] All measurements show a barrier significantly larger than the Au barrier on the same substrate.

Typical *C-V* data for HgSe on both ZnS and ZnSe are shown in Fig. 2. The barrier is determined by adding a correction for the diffusion potential to the voltage intercept of the data for the junction.[11] The range of values determined from data taken on several samples is given in Table I. These are to be compared with established Au Schottky barrier heights of 1.9—2.0 eV on ZnS and 1.35 eV on ZnSe.[10,12] Barriers determined by the *C-V* method on different ZnS samples were spread over a fairly wide range, indicating the effects of an interfacial layer. On ZnSe, *C-V* data were more consistent, and therefore taken to be more reliable.

In Fig. 3, we present photoresponse curves for HgSe on ZnS and ZnSe. Using these data, which are summarized for all samples in Table I, we are able to better define the HgSe on ZnS barrier to be roughly 2.4 eV, 0.4—0.5 eV higher than for Au. The data for ZnSe show two distinct slopes. Extrapolating the high-energy part of the data to zero response, we obtain a barrier energy of 2.0 eV for HgSe on ZnSe. Extrapolation of the low-energy part of the data for ZnSe yields values of the barrier energy which were still larger than those obtained for Au on ZnSe but were inconsistent with the values obtained from the *C-V* data.

C-V and photoresponse data for HgSe on both *n*-ZnS and *n*-ZnSe show the Schottky barrier energies for these interfaces to be about 0.5 eV larger than Au-semiconductor barriers on the same substrates. We can, therefore, assign an effective electronegativity for HgSe of about 2.9 on the Pauling scale,[13] 0.5 larger than for Au.

C-V measurements were made on one sample both immediately after fabrication and after exposure to air for one month. The barrier changed less than 50 meV

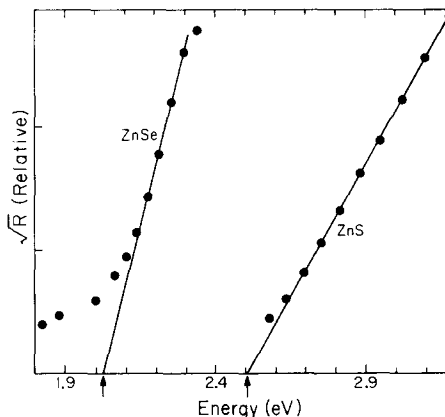

FIG. 3. Photoresponse determination of HgSe barrier energy. An extrapolation of the square root of short-circuit photocurrent vs photon energy is used to obtain the barrier energies shown by the arrows.

over that period. This measurement and the Auger data demonstrate the stability of the HgSe contact under ambient conditions.

In summary, capacitance-voltage and photoresponse measurements show that HgSe has an effective electronegativity greater than Au, by perhaps 0.5 on the Pauling scale. This semimetallic contact material was found to be stable under ordinary ambient conditions, to be easily fabricated, and is, of course, structurally compatible with other tetrahedral semiconductors. It should be useful for Ohmic contact to *p*-semiconductors and to produce higher barriers on *n*-semiconductors. Further work is being carried out to further characterize HgSe and other Hg-rich chalcogenide compounds and alloys.

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