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Surface Properties of II–VI Compounds

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Single crystals of ZnO, ZnS, ZnSe, ZnTe, CdS, CdSe, and CdTe have been cleaved in ultrahigh vacuum ($p \leq 2\times10^{-11}$ Torr) and measurements have been made of photoemission, contact potential, and surface photovoltage. In some cases, metal contacts were deposited onto the clean surfaces and the Schottky barrier heights determined. Photoelectric thresholds were similar for compounds having the same chalcogen, being higher for chalcogens with higher electronegativity. For a given chalcogen, the electron affinity of the crystal was about 0.8 eV smaller for the zinc compound than for the cadmium compound. Band bending observed was consistent with a band of surface acceptors near the conduction-band edge and a band of surface donors near the valence-band edge. Schottky barrier heights were close to the value given by the difference between the semiconductor electron affinity and the metal work function, provided the work function used was that for the specific metal-substrate system in question.

INTRODUCTION

COMPARED to the wealth of information now available on the bulk properties of the II–VI semiconductors,[1] there is only a small amount of information relative to their surface properties. These properties, aside from their own intrinsic interest, have a bearing on the behavior of interfaces. The present paper is a result of a research program devoted to gaining a better understanding of surfaces and interfaces of these materials.

Clean surfaces were prepared by cleaving single crystals in a vacuum of about 10^{-11} Torr. Measurements were made of the spectral dependence of the photoelectric yield, contact potential, and surface photovoltage. In some cases, diodes were fabricated by evaporating metal dots onto the clean surface. The work function of the metal was determined *in situ* and the barrier height was determined from capacitance measurements. These last measurements also made possible the determination of the position of the bulk Fermi level.

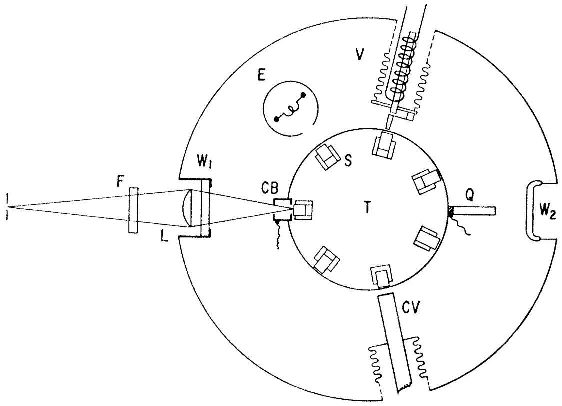

FIG. 1. Experimental arrangement. Samples S on turret T may be rotated about an axis perpendicular to the plane of the figure. Cleaving is done at CV, photoemission measurements made at CB, contact potential measurements at V, and surface photovoltage measurements at Q. See text for details.

EXPERIMENTAL PROCEDURE

The experimental arrangement is shown in Fig. 1. A number of samples S are mounted on the turret T, which can be rotated about an axis perpendicular to the plane of the figure, so that each sample may be brought in turn in front of a number of stations for processing and measurement. Cleaving is done by a blade and anvil at CV.

For the photoelectric measurements, radiation from a vacuum monochromator[2] passes through filter F, lithium fluoride lens L, lithium fluoride window W, and is brought to a focus on the cleaved face of the sample. Photoelectrons flow to the collector bucket CB and through a vibrating reed electrometer to ground. The necessary collecting field is provided by biasing the sample turret 5.5 V negative with respect to ground. A baffle plate (not shown) prevents scattered light from reaching surfaces which could produce false photocurrents. A repeller electrode (not shown) prevents electrons from escaping from the collector bucket through the light entrance aperture, and also prevents any stray photoelectrons from the baffle plate from reaching the collector bucket. All these elements are coated with aqua dag to minimize photoelectron emission. As the wavelength of the ultraviolet is scanned, the filter is changed at frequent intervals in order to eliminate short-wave stray radiation from the beam. At each stop the lens is also adjusted to keep the image in focus. In order to monitor the ultraviolet beam, one sample position is occupied by a crystal of $CaWO_4$, which serves as a fluorescent converter. Its quantum efficiency as a function of exciting wavelength has been calibrated by comparison with sodium salycilate. The $CaWO_4$ is unaffected by the vacuum bake-out. The blue fluorescence of the $CaWO_4$ is detected by a photomultiplier outside window W_2. For each photoelectric scan, the same regime is exactly duplicated with the $CaWO_4$ crystal in place of the sample.

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[1] *Physics and Chemistry of II–VI Compounds*, edited by M. Aven and J. S. Prener (North-Holland Publishing Company, Amsterdam, 1966).

[2] P. D. Johnson, J. Opt. Soc. Am. **42**, 278 (1952).

Contact potential measurements are made using the vibrating electrode assembly V. In order to provide a reference for the work function, one of the sample positions is occupied by a polished stainless steel block which can be coated with a metal film by an evaporator such as the one indicated at E. The work function of the reference film is determined by photoemission.

Measurement of surface photovoltage is accomplished with the aid of a quartz rod Q. The left end of this rod is coated with a semitransparent metal film, to which an electrical connection is made. In operation, the coated end is spaced about 0.5 mm from the clean surface of the crystal, forming a capacitance of about 0.1 pF between the crystal and the metal film. Light from a xenon flashlamp is introduced through window W_2 and is piped down the quartz rod on to the face of the crystal. At the peak of the flash, about 10^{21} photons/cm^2 sec with energies ranging up to 3 eV illuminate the surface of the crystal. By producing a large concentration of electron-hole pairs near the surface, any band bending present initially is reduced to a very small value. The change in surface potential is coupled capacitatively to the conducting film on the quartz rod and transmitted to an amplifier and oscilloscope. The system is calibrated by applying a known pulse to the crystal through the ohmic contact.

The system is housed in a stainless steel tank containing an ion pump and a titanium sublimator. It is baked at 280°C for 72 h through a bakeable valve into a well-trapped oil diffusion pump, maintaining a pressure of $\leq 10^{-5}$ Torr during bake. After the system is valved off cooled, and pumped internally, a vacuum of $1\text{–}2\times10^{-11}$ Torr is achieved. Vacuum measurements were made with a trigger ion gauge, calibrated against a Lafferty hot-cathode magnetron gauge and a Bayard-Alpert gauge. Small pressure rises were experienced when mechanical operations were performed. A larger pressure rise, about ten times the base pressure, occurred when evaporations were made. This rise lasted only during the 2-min evaporation time, returning quickly to the base pressure at the end of this time. A set of measurements on a freshly cleaved crystal typically requires about 2 h. However, the measurement of contact potential, which is the most sensitive indicator of surface condition, is made within 10 min after cleavage, and repeated at later intervals.

The crystals used were nominally pure, with known impurities in the 10 ppm range or less, excepting two of the five ZnSe crystals measured, which were doped with erbium. All the crystals were *n* type, excepting ZnTe, which had an uncompensated acceptor concentration of about $10^{14}/cm^3$. Uncompensated donor concentrations were in the range 10^{14} to 10^{16} for the *n*-type crystals, except ZnO and the erbium-doped ZnSe, which were in the low 10^{17} range. The samples were crystallographically oriented and cut into parallelopipeds 4 mm×4 mm×6 mm with the long axis perpendicular to the cleavage plane. The four zinc-blende types (ZnS, ZnSe, ZnTe, and CdTe) were cleaved along the 110 plane, while the three wurtzite types (ZnO, CdS, and CdSe) were cleaved perpendicular to the *a* axis. Before mounting, the crystals were etched and provided with ohmic contacts: indium, fired at 250°C in H_2 for the *n*-type crystals, chemically deposited Au for ZnTe.

PHOTOELECTRIC YIELD

Figure 2 shows an energy diagram for the surface of an *n*-type semiconductor. It serves to define the terms used in this report, and to illustrate various parts of the discussion. The same parameters will suffice for a *p*-type semiconductor, except that when the bands bend down at the surface, V_D is considered to be negative. It is expected that the photoelectric yield Y, defined as the number of photoelectrons emitted per quantum absorbed will be very small when $h\nu<\Phi$, and will rise rapidly as $h\nu$ exceeds Φ. Because of the short range of the photoelectrons near threshold, the curve in this region will be insensitive to band bending. Hence the onset of photoemission is considered to be a measure of Φ. The exact dependence of Y on $h\nu$ above threshold is not known, although Kane[3] has shown that various relations of the form $Y\propto(h\nu-\Phi)^n$ where $1\leq n\leq\frac{5}{2}$ can be derived on the basis of different assumptions about the absorption and scattering processes involved. Gobeli and Allen[4] have shown that the relation $Y\propto(h\nu-\Phi)^3$ fits the data near threshold for Si, Ge, and several

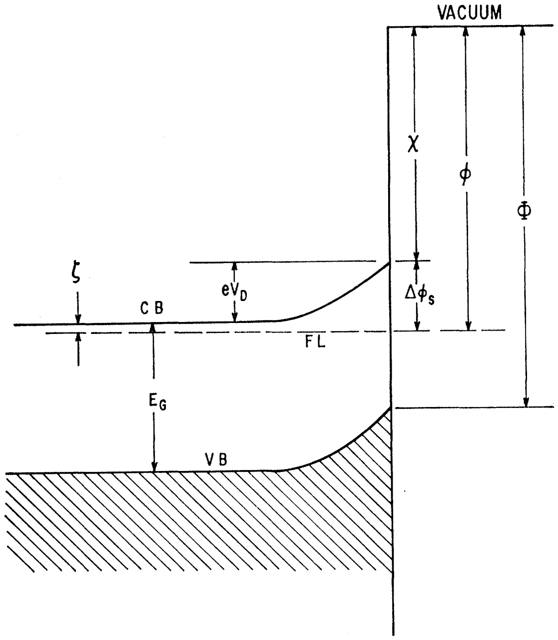

FIG. 2. Energy diagram of the surface of an *n*-type semiconductor. CB indicates the conduction-band edge, VB the valence-band edge, and FL the Fermi level. The remaining symbols represent energy differences defined by the figure.

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[3] E. O. Kane, Phys. Rev. **127**, 131 (1962).

[4] G. W. Gobeli and F. G. Allen, Phys. Rev. **127**, 141 (1962); **127**, 150 (1962); **137**, A245 (1965).

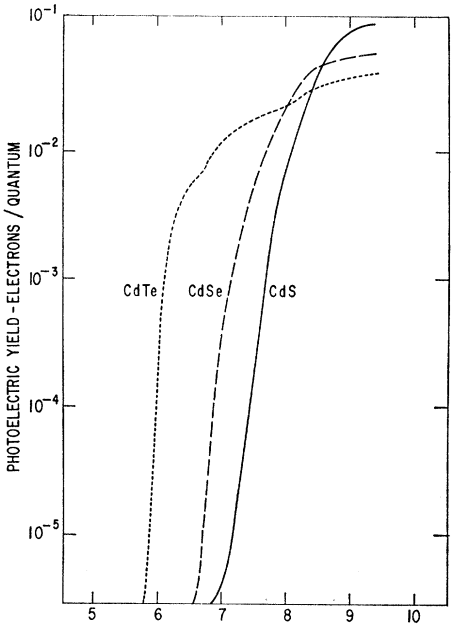

FIG. 3. Photoelectric yield for cleaved faces of three cadmium compounds. CdTe was cleaved in the 110 plane, CdSe and CdS in the $11\bar{2}0$ plane.

III–V compounds. At any rate, it is necessary to make some assumption about Y if Φ is to be determined, since a true threshold cannot be reached experimentally.

Yield curves for three cadmium compounds are shown in Fig. 3 and for four zinc compounds in Fig. 4. No corrections have been applied to these figures for sample reflectivity. Although absolute measurements were not made, an approximate absolute calibration was obtained by matching the yield for CdS at 9.3 eV to the value reported by Kindig and Spicer.[5]

It will be noticed that the curves show "tails" at low yields, the magnitudes of which increase with increasing band gap and threshold. Any power law would approach the vertical asymptotically in a logarithmic plot. Hence there is no single power law which can fit the lower parts of the curves. It is highly probable that more than one emission mechanism is involved at low yields. Figure 5 shows a plot of $Y^{1/3}$ versus $h\nu$ for a few materials. These curves include corrections for sample reflectivity.[6] The narrow band materials, like CdTe, follow the cube law down close to threshold, while the wider band-gap compounds show sizeable tails. There are five possible causes of tails which would be extraneous to the valence-band emission process:

1. High-energy stray radiation in the beam.
2. Photoemission by scattered light from parts of the apparatus.
3. Foreign material or defects such as cracks or cleavage steps on the sample.
4. Emission from bulk defect states above the valence band.
5. Emission from surface states.

The first process has been ruled out by experiments with sharp cutoff filters in the beam. Item number two is less easily evaluated. Singly scattered radiation is prevented from causing false photocurrents, but multiply scattered radiation can make a contribution. Although this contribution is estimated to correspond to $Y \leq 10^{-6}$, because of the uncertainties involved, it cannot be ruled out. It would tend to be worse at high thresholds, as observed, but it could not explain the difference between CdSe and ZnSe, for example. There was no correlation of the tails with perfection of cleavage, and there was no visible evidence of foreign inclusions in the cleavage planes, so item three is considered unlikely. Emission from bulk defect states should be $Y \leq 10^{-6}$ except for the heavily doped samples. Evidence of surface states in these materials will be presented below, but in the absence of any detailed knowledge of the nature of these states it is impossible to predict their contribution to Y. Certainly if there is one state per surface atom, one would expect to see a contribution to Y above 10^{-6}.

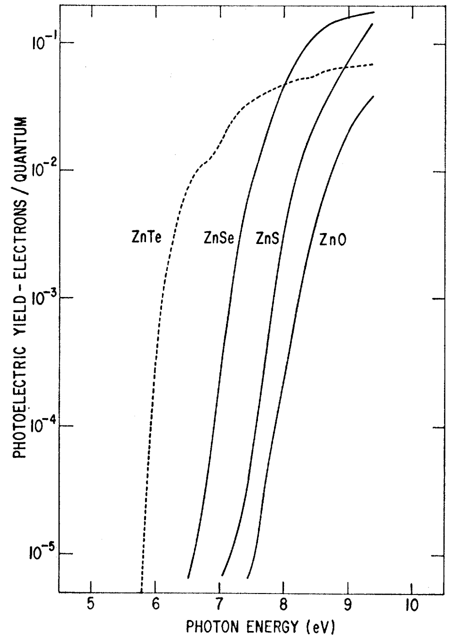

FIG. 4. Photoelectric yield for cleaved faces of four zinc compounds. ZnTe, ZnSe, and ZnS were cleaved in the 110 plane, ZnO in the $11\bar{2}0$ plane.

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[5] N. B. Kindig and W. E. Spicer, Phys. Rev. **138**, A561 (1965).

[6] Corrections were made for the reflectivity of most of the cubic crystals, using data as follows: ZnSe, M. Aven, D. T. F. Marple, and B. Segall, J. Appl. Phys. Suppl. **32**, 2261 (1961); ZnTe, M. Cardona and D. L. Greenaway, Phys. Rev. **131**, 98 (1963); CdTe, D. T. F. Marple (private communication). It was not possible to correct the hexagonal materials, since the degree of polarization of the ultraviolet beam was not known. However, in the worst case, the effect of sample reflectivity on the determination of the threshold is small.

Table I. Values of surface parameters. V_{PV} is the surface photovoltage. Other symbols are defined in Fig. 2.

	Φ (eV)	ϕ (eV)	χ (eV)	$\Delta\phi_S$ (eV)	eV_D (eV)	eV_{PV} (eV)
CdS	7.26	5.01	4.79	0.22	0.07	0.26
CdSe	6.62	5.22	4.95	0.27	0.12	0.10
CdTe	5.78	4.67	4.28	0.39	0.23	0.29
ZnO	7.82	4.68	4.57	0.11	0.01	
ZnS	7.5	(5.4)	3.9	(1.5)	(1.2)	
ZnSe	6.82	4.84	4.09	0.73	0.58	
ZnTe	5.76	5.43	3.53	1.90	−0.18	

Since the mechanisms discussed are extraneous to valence-band emission, any procedure for locating Φ should be such that the tails are ignored, even though their presence will affect the accuracy to some extent. Accordingly, the values of Φ reported here were obtained by the cube-root extrapolation procedure as indicated in Fig. 5. These values are given in Table I. For the tellurides and CdSe, the yield follows the cube law to within 0.1 eV of threshold and hence the uncertainty is believed to be within 0.1 eV, increasing with band gap for the other materials. In the case of ZnS, the uncertainty may be as large as 0.3 eV. Values of χ given in Table I are obtained by subtracting the respective room-temperature band gaps from the values of Φ in the first column. It is evident that the photoelectric threshold is determined primarily by the chalcogen. There is no such simple dependence of the electron affinity on the metal, but the value of χ for a zinc compound is typically about 0.8 eV smaller than the corresponding cadmium compound. The systematics of the photoelectric threshold are further illustrated in Fig. 6, where Φ is plotted against the electronegativity of the "anion" for the materials reported here as well as several III–V compounds reported by Gobeli and Allen[4] and by Fischer,[7] and for several alkali halides reported by Taft and Phillip.[8] This figure shows the dominating influence of anion electronegativity on the photoelectric threshold, but the results should be interpreted only qualitatively. It is well known that crystal structure and orientation play a strong role in surface-dependent properties such as Φ. Hence the simple empirical relationship indicated by the data including three different crystal structures is somewhat fortuitous. One of the II–VI crystals, ZnO, falls well off the line (off the figure), although it is at least in the proper sequence with the other II–VI compounds. One might expect atypical results for the first-row elements.

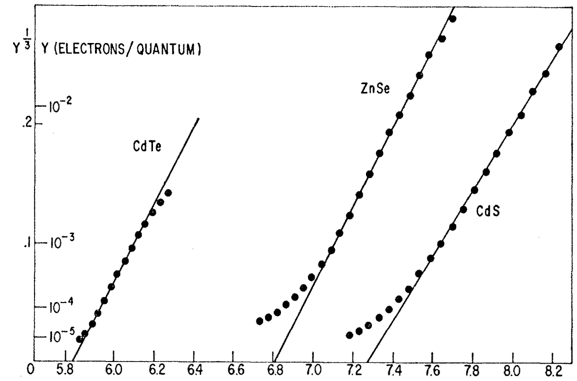

Fig. 5. Cube-root plot of the photoelectric yield for three crystals.

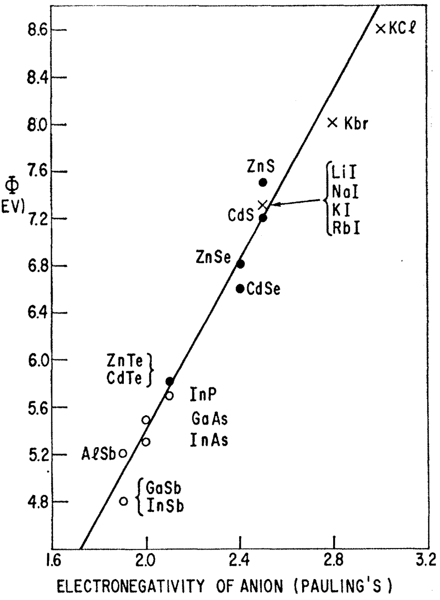

Fig. 6. Plot of photoelectric threshold against electronegativity of the nonmetal constituent. For comparison, some results by Gobeli and Allen and by Fischer for III–V compounds, and by Taft and Phillip for alkali halides are given (see Refs. 4, 6, and 7).

CONTACT POTENTIAL AND SURFACE STATES

The values of ϕ determined from the contact potential measurements are given in Table I. From ϕ and χ, $\Delta\phi_s$ is readily obtained, and with a knowledge of ζ one can obtain the band bending eV_D. This quantity has about the same absolute accuracy as Φ, so the relative accuracy is much poorer. In the case of ZnS, the value of ϕ is also uncertain. After cleaving, the contact potential drifted for about an hour. Even the high contact resistance ($\sim 10^7\,\Omega$) could not explain such a slow drift. The large band bending in this case is also very surprising.

The sign of the band bending for the six n-type samples indicates a negative surface charge resulting from acceptor states below the Fermi level at the surface. The reproducibility of the contact potential from sample to sample suggests a fairly high concentration of acceptors near the Fermi level, which is near the conduction-band edge in most cases. It is significant

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[7] T. E. Fischer, Phys. Rev. **139**, A1228 (1965); **142**, 519 (1966).
[8] E. A. Taft and H. R. Phillip, J. Phys. Chem. Solids **3**, 1 (1957).

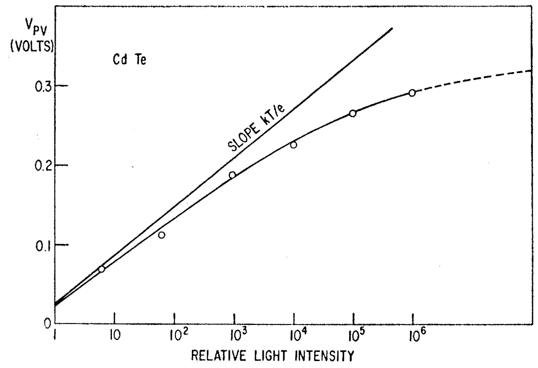

FIG. 7. Surface photovoltage versus light intensity for CdTe. The straight line represents $V_{PV}=(kT/e)\ln I+\text{const}$, an expression expected to hold at low light intensities. These results illustrate the saturation observed at high light levels, indicating nearly complete flattening of the bands.

that for zinc telluride the band bending is negative and the Fermi level lies near the valence band at the surface, as would be caused by a group of donors not far from the valence-band edge.

It is very tempting to interpret these results in terms of the simple model proposed by Levine and Mark,[9] in which intrinsic surface states in these materials can be described essentially as a narrowing of the band gap for the first atomic layer. In such a case, the Fermi level would be pinned near a surface band edge if it lay within the bulk forbidden gap but outside the surface forbidden gap. If the bulk Fermi level lies within the surface forbidden gap, the bands will be flat. However, only a very small number of extrinsic states would be required to bend the bands if the doping is low. As little as 10^{-6} monolayer of adsorbed impurities having acceptor character could bend the bands by several tenths eV. It may be that this is the situation for ZnS. where only one sample, of rather high resistivity, has been measured.

SURFACE PHOTOVOLTAGE

Measurement of surface photovoltage gives the possibility of measuring the band bending directly and therefore gives a check on the other measurements described above. However, certain problems present themselves here, and as a result the application of this method has been limited to three materials thus far. These problems are related to the wide band gaps, the difficulty of obtaining satisfactory ohmic contacts, and in some cases simply the unavailability of suitable samples.

The results for the three cadmium crystals are given in the last column of Table I. Figure 7 shows the surface photovoltage for CdTe as a function of light intensity. At low light levels the photovoltage should be proportional to $(kT/e)\ln I$, and a line corresponding to this relation is shown for comparison. The leveling off of the curve toward saturation is clearly seen, indicating that the flattening of the bands is rather complete. The residual band bending would appear to be about 0.03 eV. Since this is about equal in magnitude and opposite in sign to the correction for the Dember voltage[10] both these corrections have been omitted in the results given.

The agreement in the band bending by the two methods (last two columns in Table I) is very good for CdSe and CdTe. Part of the discrepancy for CdS can be explained by the fact that the crystal which was used in the photovoltage measurement had a somewhat exceptional contact potential. Thus while the value of eV_D given in the table is an average for five crystals measured by the photoelectric contact potential method, only one of these was measured for surface photovoltage. Its value of eV_D was 0.16 eV. Hence, the discrepancy for this crystal is only 0.10 eV. One possibility for a divergent result in the case of a photovoltage measurement is band bending in the bulk, caused by nonuniform trap distributions. No special filtering was used to eliminate bulk absorption in these experiments.

METAL-SEMICONDUCTOR CONTACTS

It has been shown[11] that the barrier heights of metal contacts to CdS follow the relation

$$\Delta\phi_{ms}=\phi_m-\chi, \tag{1}$$

where ϕ_m is the metal work function. However, the value of χ determined from this equation was about 3.9 eV, in considerable disagreement with the value determined here and from earlier photoemission studies.[5,12] In the present work, diodes were made between gold and each of the three materials CdS, CdTe, and ZnO. Capacitance measurements were made inside the vacuum system by contacting the film with a gold probe. Some surprising results were obtained. First, the work function of gold was found to be much higher than any available literature values. This discrepancy has now been resolved by recent publications giving new results compatible with ours.[13] Secondly, the work function of gold shows remarkable substrate effects, apparently caused by quasi-epitaxy. On a polished stainless steel substrate, twenty samples averaged 5.40±0.05 eV. On the clean 110 plane of CdTe, a value of 5.08±0.02 eV was obtained for three samples. For the $11\bar{2}0$ plane of CdS or ZnO the average value of 5.59±0.03 eV was obtained for five samples. The results of the diode measurements are given in

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[9] J. D. Levine and P. Mark, Phys. Rev. **144**, 751 (1966).

[10] See *Semiconductor Surfaces*, edited by A. Many, Y. Goldstein, and N. B. Grover (North-Holland Publishing Company, Amsterdam, 1965), p. 276.

[11] W. G. Spitzer and C. A. Mead, J. Appl. Phys. **34**, 3061 (1963); A. M. Goodman, *ibid.* **35**, 573 (1964); A. M. Cowley and S. M. Sze, *ibid.* **36**, 3212 (1965); D. V. Geppert, A. M. Cowley, and B. V. Dore, *ibid.* **37**, 2458 (1966).

[12] J. J. Scheer and J. van Laar, Philips Res. Rept. **16**, 323 (1961).

[13] E. E. Huber, Jr., Appl. Phys. Letters **8**, 169 (1966); J. C. Riviere, *ibid.* **8**, 172 (1966).

TABLE II. Parameters for gold contacts on three semiconductors. Values of χ are from Table I. Values of ϕ_{Au} were determined *in situ* by measurements of contact potential, while $\Delta\phi_{ms}$ results were derived from capacitance measurements.

Material	χ (eV)	ϕ_{Au} (eV)	$\chi-\phi_{\mathrm{Au}}$ (eV)	$\Delta\phi_{ms}$ (eV)
CdS	4.79	5.59	0.80	0.79
CdTe	4.28	5.08	0.80	0.63
ZnO	4.57	5.59	1.02	0.90

Table II. Fair agreement with Eq. (1) is obtained, provided the appropriate metal work function is used. One does not expect exact agreement with Eq. (1) since it does not take into account modifications in the surface double layers when the two materials are placed in intimate contact.

ACKNOWLEDGMENTS

The author wishes to acknowledge important contributions to this work by a number of his colleagues. M. Aven provided samples of ZnSe and ZnTe, made a number of special firings for purification of these and other crystals, and provided valuable consultation in many aspects of the work. R. E. Halsted and H. D. Coghill supplied crystals of CdTe. P. D. Johnson made his vacuum spectrometer available for the photoelectric measurements. D. T. F. Marple provided unpublished measurements of reflectivity of CdTe. The applicability of surface photovoltage measurements to this work arose out of conversations with D. A. Cusano. Technical assistance throughout this program has been provided by J. Z. Devine.

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Many-Body Effects in the Optical Properties of Semiconductors*

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The high-frequency optical absorption of semiconductors of the diamond structure type has been investigated theoretically for the almost-free-electron energy-band model isotropically extended to three dimensions. Model-independent arguments show that ignoring interactions between particles so that all excitations are infinitely long-lived leads to calculated values of the absorptive part of the dielectric constant, $\epsilon_2(q\rightarrow 0,\omega)$, well below the experimental results for Ge and Si. Within our model, we have investigated self-energy and vertex corrections to $\epsilon_2(\omega)$ due to many-body effects resulting from the Coulomb interactions between particles. Both these corrections significantly raise the theoretical value of $\epsilon_2(\omega)$, bringing them substantially closer to experimental ones.

I. INTRODUCTION

THE subject of the optical properties of both metals and semiconductors[1] is usually investigated experimentally through the determination of the reflectance and characteristic energy-loss functions, which are directly interpretable in terms of the complex dielectric constant

$$\epsilon(\mathbf{q},\omega)=\epsilon_1(\mathbf{q},\omega)+i\epsilon_2(\mathbf{q},\omega) \tag{1.1}$$

in the optical $(\mathbf{q}\rightarrow 0)$ limit.

Ehrenreich and Philipp have considered theoretical analyses of their experimental results for the metals Ag and Cu,[2] and semiconductors of the diamond structure type, such as Si and Ge.[3] In this paper we are interested in the latter set of experiments. Specifically, we concern ourselves with the absorptive part of the dielectric constant.

One of the main difficulties with a theoretical development for $\epsilon_2(\omega)$ in the semiconductor case is that some model for the electronic band structure must be considered, since an external photon of energy $\hbar cq$ cannot create an electron-hole pair in a free electron gas in the $q\rightarrow 0$ limit without violating energy-momentum conservation. Therefore, $\epsilon_2(\omega)$ would vanish in the absence of a lattice, as it does in the usual random-phase approximation (RPA)[4] treatment of the free-electron gas. Once crystal structure is introduced, however, momentum need be conserved only up to a reciprocal lattice vector, so that interband transitions give rise to a finite value for $\epsilon_2(\omega)$, for ω's larger than the minimum inter-

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[1] J. Tauc, in *Progress in Semiconductors*, edited by A. F. Gibson and R. E. Burgess (Temple Press Books, Ltd., London, 1965), Vol. IX.

[2] H. Ehrenreich and H. R. Philipp, Phys. Rev. **128**, 1622 (1962).

[3] H. R. Philipp and H. Ehrenreich, Phys. Rev. **129**, 1550 (1963).

[4] David Pines, *Elementary Excitations in Solids* (W. A. Benjamin and Company, Inc., New York, 1964), Chap. 3.