

Effect of pressure on the height of the Schottky barrier (ϕ_B) for several semiconductors

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This paper contains the first measurements of the effect of pressure on the Schottky barrier (ϕ_B) at a metal-semiconductor interface. Results are presented for CdS, CdSe, and ZnO together with measurements of the absorption edges for CdSe and ZnO. These results are used in conjunction with previously published flat-band potential measurements on GaAs and InP to relate the change in energy of the top of valence band E_v relative to the Fermi level of the metal to the ionicity of the semiconductor. These measurements are compared to correlations of the change of ϕ_B with work function of the metal which have previously appeared in the literature.

In this paper we report for the first time the effect of pressure on the barrier height ϕ_B of n -type CdS, CdSe, and ZnO Schottky diodes. Although these materials all have the wurtzite crystal structure they cover a wide range of ionicity. It is the bonding character of the semiconductor that controls the formation of ϕ_B . In the past, groups have concentrated on measuring the barrier height of various semiconductor-metal systems.^{1,2} More recently, microscopic techniques for surface analysis have been used to probe the formation of ϕ_B .³ Here, we use high pressure to study the electronic structure of the semiconductor from the measurements of ϕ_B . We show the effect of pressure on the conduction-band minimum at the interface E_c relative to the Fermi level of the metal. This differs from other pressure studies where the movement of E_c is determined relative to the valence-band maximum E_v from the shift in the energy gap E_{gap} . Thus, a pressure study of ϕ_B decouples the measurements of E_c movement from E_v and creates a second frame of reference for interpreting the energy-band movement with pressure.

An accumulation of data on Schottky diodes show a qualitative transition between covalent and ionic semiconductors.^{4,5} The materials in this study range from slightly ionic, CdSe, to more ionic, CdS, to very ionic, ZnO. Data from previous pressure studies on GaAs and InP, which have the zinc-blende structure, are included to extend the discussion to nearly covalent semiconductors. From this wide range of materials we discuss the transition between covalent and ionic semiconductors in terms of their energy-band behavior.

The formation of a Schottky diode occurs at a metal-semiconductor interface when the work function of the metal is greater than the electron affinity of the (n -type) semiconductor. We define the barrier formed ϕ_B to be the potential difference between the Fermi level of the metal and the conduction-band minimum at the interface. The barrier to electrons is characterized by a discontinuous change in potential at the interface and parabolic shape through a region depleted of electrons in the semiconductor conduction band. Various techniques are available for the determination of ϕ_B ; the most generally used are the current-voltage relation, photoe-

mission of electrons, and differential capacitance. The first two methods rely on a bulk flow of electrons where electron image forces act to reduce ϕ_B .⁶ The measured barrier is the effective barrier that the electron sees. The image force lowering of ϕ_B , as defined by Rhoderick,⁶ can be shown to have little pressure dependence. The differential capacitance measurements presented here show this to be true. To check the validity of their use under pressure, each of the three methods was performed on chemically prepared CdS Schottky diodes.

While it is known that CdS, CdSe, and ZnO are piezoelectric materials, this contribution to the change in ϕ_B with hydrostatic pressure can be discounted. The hydrostatic piezoelectric constant for the ideal wurtzite structure is zero. Furthermore, Berlincourt *et al.*⁷ have measured the components of the hydrostatic constant for CdS and CdSe, and have shown this constant to be negligible.

Owing to the nonsymmetric nature of the barrier region, the current dependence on applied voltage is nonlinear. The current-voltage relation is based on H. A. Bethe's thermionic emission theory.⁸

$$J = J_0[\exp(qV/nkT) - 1] \quad (1)$$

where J is the current density, V is the applied voltage, $-q$ is the charge of an electron, and n is an ideality factor ~ 1 . For V greater than $3kT$ the second term in the bracket is negligible. A plot of $\ln J$ vs. V yields J_0 from which ϕ_B can be calculated according to

$$J_0 = (4\pi m^* q K^2 T^2 / h^3) \exp(-q\phi_B/kT) \quad (2)$$

where m^* is the effective mass of an electron in the semiconductor and h is Planck's constant.

Another method for determining ϕ_B is the photoemission of electrons from the metal over the barrier. For the case where incident photon energy on the metal is greater than $q\phi_B$ by $3kT$, electron emission is described by the Fowler relation.⁹

$$R \sim (h\nu - q\phi_B)^2 \quad (3)$$

where R is the photocurrent per incident photon. The threshold $q\phi_B$ is found by plotting $R^{1/2}$ vs $h\nu$ and extrapolating $R^{1/2}$ to zero.

The differential capacitance method for determining ϕ_B does not require a bulk flow of electrons across the interface. The barrier height is found by monitoring the response of the depletion region in the semiconductor to a small change in the reverse applied voltage. The equation that governs the differential capacitance versus reverse applied voltage can be expressed in terms of ϕ_B .⁶

$$1/C^2 = (2/qN_d\epsilon_s)(\phi_B - \xi + V_r - kT/q), \quad (4)$$

where C is the measured capacitance per unit area, N_d is the donor density, ϵ_s is the dielectric constant of the semiconductor, ξ is the potential difference between E_c and the Fermi level in the semiconductor bulk, and V_r is the reverse applied voltage. A plot of $1/C^2$ vs V_r yields ϕ_B at $1/C^2 = 0$.

Although Eqs. (1)–(4) have been developed for ideal metal-semiconductor contacts, they are widely used in characterizing real devices. A criterion for applicability of Eqs. (1)–(4) is that the ideality factor n of Eq. (1) be between 1.0 and 1.1. This test was applied and satisfied for all diodes used for current-voltage or capacitance experiments. In addition, the plots of $1/C^2$ vs V_r [Eq. (4)] were linear over a 2-V range of V_r and were parallel for all pressures, as were the plots of $\ln J$ vs V from Eq. (1). Finally, the values of ϕ_B at atmospheric pressure obtained by the various methods correspond to those reported elsewhere.

All experiments are carried out from low pressure to high pressure at 300 K. The optical data are taken by scanning from low to high photon energies. Pressure release data showed that the effects are reversible.

APPARATUS AND PROCEDURE

The Schottky diode configuration used in the pressure experiments is shown in Fig. 1. It consists of a wire lead soldered to a screw that is threaded into a brass pellet. The pellet serves as a base for the ohmic contact to the back of the

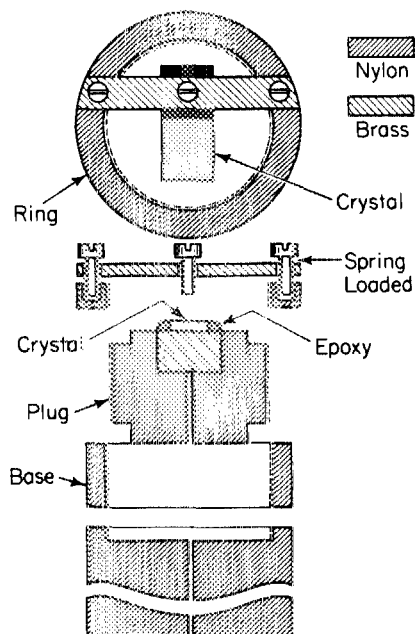


FIG. 1. Schematic drawing of sample holder for Schottky barrier measurements.

semiconductor. Electrical contact to the front is made either by a spring-loaded, polished, 0/80 screw tip or by a fine silver wire probe. A wire lead soldered to the support bar completes the device. The device is threaded onto a nylon holder and fitted into the nylon sleeve of the pressure cell electrical plug. The high-pressure equipment used in the experiments has been described elsewhere.¹⁰

The current-voltage measurements were made using a locally built function generator and potentiostat in conjunction with a Houston Instruments model 2000 X-Y recorder. The differential capacitance measurements were made with a Boonton 72B capacitance meter. Both the current-voltage and capacitance data were obtained with the diode completely sealed from light.

The photoelectric measurements were made using an Oriel model 6333, 100-W tungsten-halogen lamp. The light was dispersed through a Kratos GM-252 monochromator with a 1000-nm blazed grating and was focused onto the diode face through a sapphire window plug. The photoresponse was recorded as either the difference of light and dark dc currents on a Keithley 616 electrometer or by a lock-in technique. The photoresponse was corrected for incident photon flux variations using a Dexter 2M, 48 junction thermopile detector.

The energy-gap shift of CdSe and ZnO was determined from a wafer polished on both sides to a thickness of about 1 mil. The wafer was mounted perpendicular to the incident beam in the pressure bomb. Photon transmission was detected with an EMI 9558-QA photomultiplier tube and an Ortec photon counting system. Linear dispersion from the monochromator for both ZnO and CdSe measurements was 1 nm. During the energy-gap measurements, a 300- and 450-nm blazed grating was used for the ZnO and CdSe, respectively.

Single-crystal CdS (obtained from Dr. George Samara of Sandia National Laboratories) was cut into wafers $\sim 2 \times 2 \times 0.5$ mm. The ohmic contact was made with In-Ga eutectic between the crystal and brass header. The wafer was epoxied to the header with Torr Seal (Varian Associates). The front surface was mechanically polished with No. 600 grit followed by 1.0-, 0.3-, and 0.05- μ m alumina. The crystal was then chemically polished to a glassy finish on a home-built polisher¹¹ using 6M HCl. The preparation of ZnO (3M) was identical to the preparation of CdS.

Single-crystal CdSe (Cleveland Crystals) was prepared similar to CdS and ZnO. Prior to evaporating 1000 Å of In for the ohmic contact, the wafers were etched in a mixture of 30 : 20 : 10 : 0.1 of HNO_3 : H_2SO_4 : CH_3COOH : HCl and rinsed with concentrated H_2SO_4 and deionized water. The indium was alloyed to the CdSe under hydrogen. After mechanical polishing, the front surface of CdSe was chemically polished with a 1 : 1 : 1 mixture of HCl : H_3PO_4 : H_2O .

Metals were deposited in a vacuum evaporator (Denton Vacuum, DV-502) at about 10^{-6} Torr. The thickness of the deposition was monitored by an oscillating quartz detector (R. D. Mathis Company, TM-100). To construct the diodes for the photoelectric measurements, two evaporations were made: (1) a semitransparent 30-Å film over the entire surface and (2) a 500-Å contact to half the crystal surface. For the other measurements, a single patch ~ 0.01 cm², 500 Å thick

was deposited. Rates of deposition varied between 2 and 5 Å/s. Experiments were run within a day or two of diode fabrication.

RESULTS

CdS

The effect of pressure to 10 kbar at 300 K on $q\phi_B$ of chemically prepared CdS/Au diodes is presented in Figs. 2–4. Within experimental accuracy, each method used to determine $q\phi_B$ yields the same increase with pressure: 10.4 meV/kbar from the current-voltage method, 9.8 meV/kbar from photoemission method, and 10.5 meV/kbar from the differential capacitance method. Also plotted in the figures is the shift of the energy gap ΔE_{gap} which is 5.1 meV/kbar.¹⁰ For the current-voltage and differential capacitance pressure runs, the ideality factor n was in the range of 1.04–1.09 for individual diodes and remained constant throughout the experiment.

At 1 atm, the measured value of $q\phi_B$ from all three methods ranged from 0.67 to 0.82 eV which is in good agreement with reported values for CdS/Au diodes.^{1,2} During two photoemission pressure runs, oriented CdS (0001) produced the same ϕ_B pressure shift as randomly oriented CdS. Although the initial value of ϕ_B varied somewhat from device to device, the pressure coefficient of ϕ_B is always the same.

The change of $q\phi_B$ with pressure measures the change of E_c (the conduction-band minimum) with pressure relative to the Fermi level of the metal, whereas the shift in the energy gap with pressure measures the movement of E_c relative to E_v (the valence-band maximum). The difference between the pressure shifts of $q\phi_B$ and E_{gap} yields the movement of E_v relative to the Fermi level. Thus, for CdS, E_c moves ~ 10 meV/kbar and $E_v \sim 5$ meV/kbar relative to the metal Fermi level.

A comparison can be made between the measurement of ϕ_B and the measurement of the flat-band potential in an

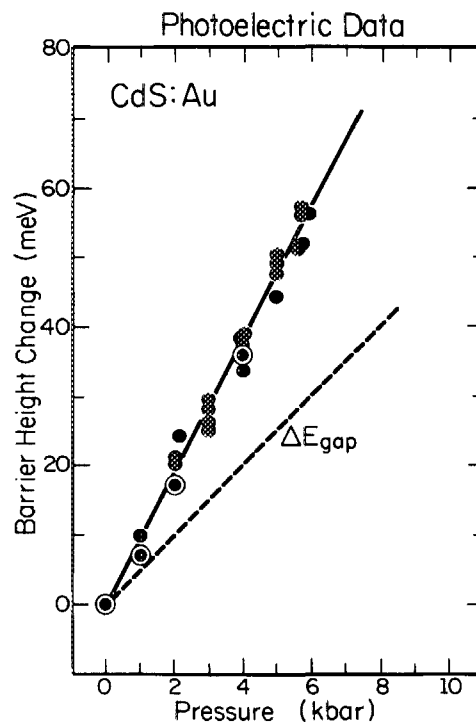


FIG. 3. Change in barrier height ($q\phi_B$) with pressure from photoelectric measurements for CdS:Au.

electrochemical cell involving semiconductor electrodes.^{10,12} In particular, Gulino¹⁰ has reported the pressure-induced shift of the flat-band potential qV_{fb} in n -type CdS as 9.5–11.4 meV/kbar. In his data, the degree of band bending is determined by the movement of the semiconductor energy bands, E_c and E_v , relative to the Fermi level of the counter electrode, which was Pt. Thus, the measurement of V_{fb} is analogous to the measurement of ϕ_B .

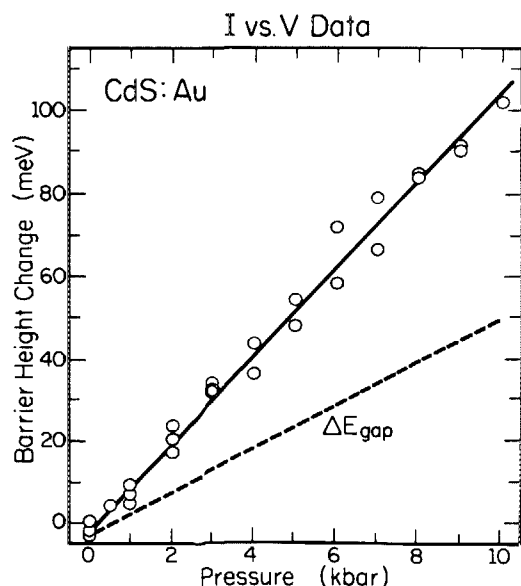


FIG. 2. Change in barrier height ($q\phi_B$) with pressure from I - V measurements for CdS:Au.

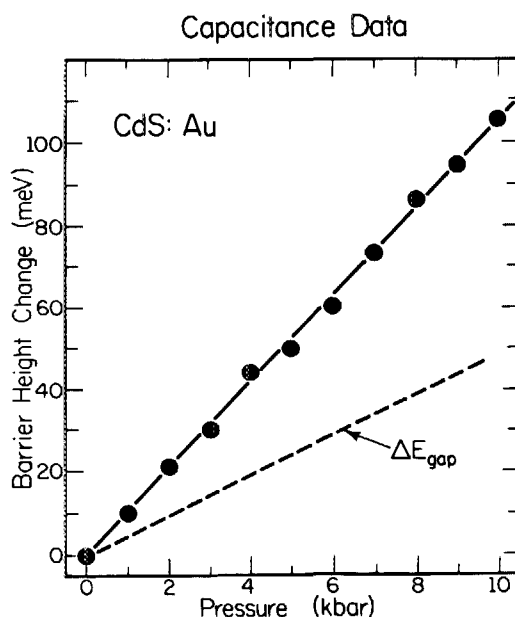


FIG. 4. Change in barrier height ($q\phi_B$) with pressure from differential capacitance measurements for CdS:Au.

CdSe

Figure 5 presents the absorption measurements of CdSe from 1 atm to 10 kbar. The pressure shift from the two experimental runs shows the direct gap of CdSe increasing at 5.0 meV/kbar.

Figure 6 indicates $q\phi_B$ increases at 7.0 meV/kbar as determined by photoemission experiments. 1-atm measurements of $q\phi_B$ range between 0.59 and 0.70 eV, in agreement with Consigny and Madigan's values for chemically prepared CdSe/Au Schottky diodes.¹³ Gulino's¹⁰ reported shift of V_{fb} for CdSe is different from the present findings. We attribute the difference in energy-band movement (particularly in the lower pressure range) to chemistry at the CdSe surface in the electrochemical cell. Our findings indicate E_c moves ~ 7 meV/kbar and E_v moves ~ 2 meV/kbar relative to the Fermi level in the metal.

ZnO

The optical absorption data in Fig. 7 show the energy gap of ZnO increasing at 2.7 meV/kbar. In Fig. 8 the barrier heights of ZnO/Au and ZnO/Pd diodes increase with pressure at 11.6 meV/kbar. With the exception of one low-pressure run by capacitance measurements, ϕ_B was determined using the current-voltage method. These data indicate, relative to the Fermi level, motions of $E_c \sim 11.6$ meV/kbar and thus $E_v \sim 9$ meV/kbar.

At 1 atm, values of ZnO/Au and ZnO/Pd Schottky barriers range from 0.67 to 0.68 eV and from 0.58 to 0.62, respectively. These values agree with those reported by Neville and Mead.¹⁴

DISCUSSION

The results as presented above are significant and new, however, further interpretation is possible by examining the trend from the materials studied. It is obvious from the results that the more ionic the semiconductors, the larger the movement of E_v relative to the metal Fermi level. Hence, E_v moves least in CdSe and most in ZnO. In correlating

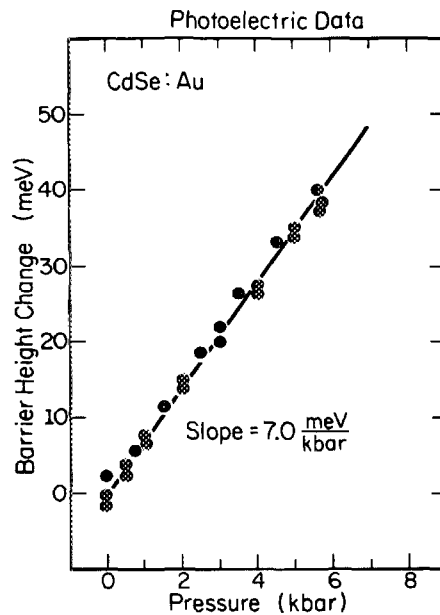


FIG. 6. Change in barrier height ($q\phi_B$) with pressure from photoelectric measurements for CdSe.

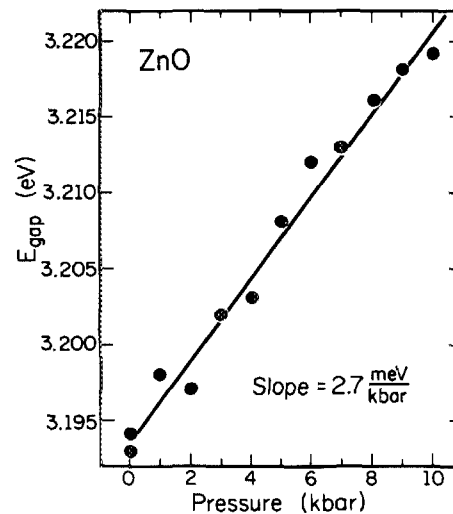


FIG. 7. Change in absorption edge (E_g) with pressure for ZnO.

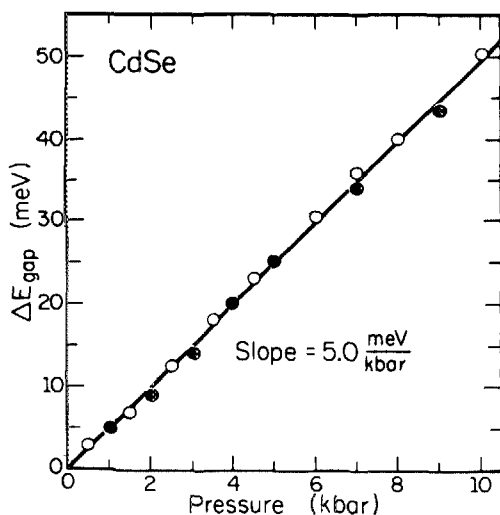


FIG. 5. Change in absorption edge (E_g) with pressure for CdSe.

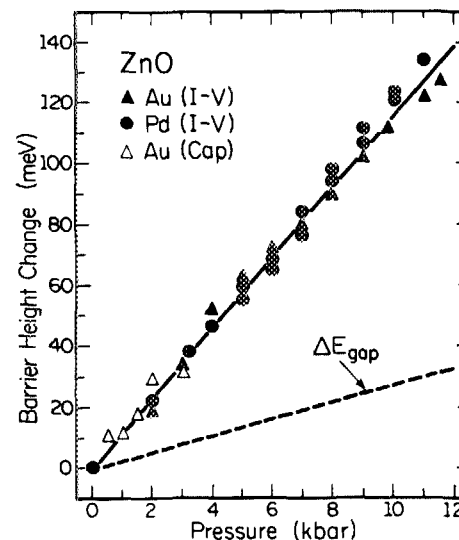


FIG. 8. Change in barrier height ($q\phi_B$) with pressure for ZnO.

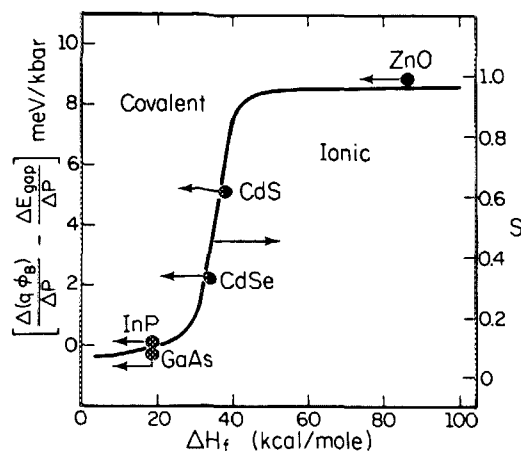


FIG. 9. The difference in pressure coefficients for $q\phi_B$ and E_{gap} plotted vs heat of compound formation for various semiconductors. The line drawn for comparison corresponds to a plot of S ($S = d\phi_B/d\phi_m$ for a semiconductor) vs the heat of formation. ϕ_m is the metal work function.

Schottky barrier height data to the ionicity of the semiconductor, Kurtin *et al.*⁴ were first to show a distinction between covalent and ionic materials. They plotted S (the slope of a plot of ϕ_B versus the metal work function), which is an index of interfacial behavior measuring the degree of Fermi level pinning, against the electronegativity difference of the compound semiconductor. The result is a sharp transition between covalent materials such as GaAs and InP, and ionic materials such as ZnO and SiO.² Brillson later noted the same correlation exists when S is plotted against the heat of formation ΔH_f of the semiconductor.⁵ The rapid change in S occurs near a difference of electronegativity of 0.6–0.8 or a heat of formation of 30–40 kcal/mol. The line in Fig. 9 represents the line used both Kurtin and Brillson. Data on GaAs and InP are taken from Zurawsky *et al.*¹² Their flat-band potential measurements show that the increase in barrier height is due solely to the movement of E_c away from E_v (i.e., no movement of E_v relative to E_F).

Motions of energy bands thus far have been described relative to E_F . It can be shown from the free-electron model and the compressibility of gold that the metal Fermi level of that material increases at an upper limit of about 2 meV/kbar. While this may increase the reported motions of E_v and E_c in an absolute sense, it does not affect the interpretation of energy-band movement. In Fig. 9 we have plotted the difference in pressure coefficients of $q\phi_B$ and E_{gap} vs ΔH_f . The abscissa can be expanded as follows:

$$\frac{\Delta(q\phi_B)}{\Delta\pi} - \frac{\Delta E_{gap}}{\Delta P} = \frac{(\Delta E_c - \Delta E_F)}{\Delta P} - \frac{(\Delta E_c - \Delta E_v)}{\Delta P} = \frac{(\Delta E_v - \Delta E_F)}{\Delta P} \quad (5)$$

Hence, whether or not E_F is pressure dependent, the abscissa still relates motion of E_v with pressure to ΔH_f for various semiconductors.

The significance of this correlation is understood in terms of the anionic nature of the valence band. For covalent materials such as GaAs and InP, the pressure coefficient of $q\phi_B$ is simply the same as for E_{gap} with n -type diodes. If the semiconductor exhibits small amounts of ionic bonding such as in CdSe and CdS, the pressure coefficient of $q\phi_B$ is greater than that of E_{gap} . CdSe and CdS are in transition between the Bardeen ($S = 0$) limit and Mott ($S = 1$) limit.⁴ ZnO typifies the Mott limit. The anionic nature of the valence band of ZnO results in the lack of Fermi level pinning and to the pressure-induced motion of E_c and E_v . Figure 9 presents direct physical evidence for the transition between covalent and ionic materials in terms of the behavior of the band energy with pressure.

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