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Role of photocurrent in low-temperature photoemission studies of Schottky-barrier formation

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Photoelectron spectroscopy is frequently used to study band bending in semiconductors due to charge stored in surface or interface states. This paper examines how such experimental results are modified by photovoltages generated within the band-bending region not only by ambient light sources, but by the incident x rays themselves. Recent experiments which have suggested dopant-dependent and reversible temperature-dependent band bending in the initial stages of formation of the metal-GaAs(110) interface are used as an example. It is shown here that the reported dependence derives from a photovoltaic effect.

Photoelectron spectroscopy (PES) is frequently used to study band bending in semiconductors induced by charge stored in surface or interface states. The band bending is due to depletion of carriers in a region near the surface which may be from several hundred Å to several μm thick. A built-in electric field exists in the depletion region, and electron-hole pairs created by photon absorption are separated by the field, producing an opposing, or "open circuit" voltage. This well-known phenomenon is conventionally applied to light sensing and energy generation, but is also relevant to PES. In particular, the core-level and valence-band energies as measured by PES can be affected not only by ambient light sources, but by the incident x rays themselves. Although this effect is small at room temperature, it can be as large as the built-in band bending at low temperature. The photovoltaic effect is to be contrasted to the surface charging effect due to excitation of electrons into the vacuum, which is commonly observed in PES of insulating layers. While the latter always results in a positively charged surface, the photovoltaic effect acts in opposition to band bending of either sign and, since most of the photons are absorbed well below the surface, is far more important.

PES measurements of band bending are often applied to the study of Schottky-barrier formation. In such a study a thin, usually nonconducting, metal film is deposited on a semiconductor substrate at a controlled temperature. The semiconductor core-level or valence-band shifts are used to determine the band bending, and thereby the barrier height is inferred. Typically it is difficult to characterize the energy reference of the metal-derived spectral features, as the line shapes evolve as a function of metal thickness.

The importance of the photovoltage in the Schottky-barrier experiment is shown schematically in Fig. 1(a). In the dark, the semiconductor surface is pinned by the adsorbate film. The potential difference between semiconductor Fermi level and conduction band V_d corresponds to the Schottky-barrier height V_b. During the PES experiment, however, the sample is illuminated by soft x-ray photons which excite electron-hole pairs in the depletion region. The pairs are separated by the built-in field and produce a bias voltage V across the interface. This reduces the observed V_d without necessarily changing V_b, and implies that the measured metal Fermi-level and core-level position will shift in binding energy. At low temperature the effect is enhanced as the ability of the diode to discharge the surface is reduced. Typically, $V_d = V_b - V$ is measured by the PES experiment, and V_b is inferred by assuming $V=0$. Direct measurement of V_b requires consideration of both metal and semiconductor reference energies, which is problematical. In a conventional interpretation [Fig. 1(b)] it is assumed that only V_b changes with temperature, the bias V across the diode is zero, and hence that the metal Fermi level is constant.

In a characteristic PES experiment using synchrotron radiation, 10^9 photons/sec might be delivered in a 2×4 mm^2 spot. The photons have energies in the range 50–150 eV, and if it is assumed that resulting decay processes produce 25 electron-hole pairs per photon, a maximum photocurrent density $J_{pc0} = 10^{-7}$ A/cm^2 would result, where the actual current is $J_{pc} = J_{pc0}(1-e^{-\alpha W})$. Photons in this energy range have characteristic absorption coefficients (α) of 10^4 to 2×10^5 cm^{-1} in common semiconductors, as compared to characteristic depletion

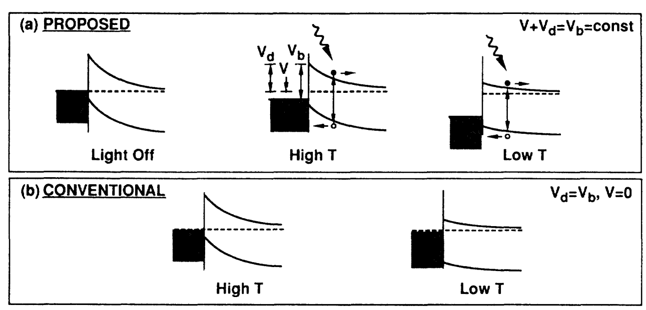

FIG. 1. (a) In the proposed model, turning on the light excites electron-hole pairs in the semiconductor. The carriers are separated by the built-in field and produce a bias voltage V across the interface. The effect is enhanced at low temperature due to increased diode resistance. The barrier height V_b is assumed constant such that $V_b = V - V_d$, where V_d is the measured conduction-band position with respect to the bulk Fermi level. (b) In a conventional interpretation, $V=0$ and V_b changes with temperature.

widths (W) of 10^{-6} to 10^{-4} cm. Hence the reduction of photocurrent due to the finite depletion width is small. By comparison with the incident x-ray flux, room light passing through a viewport might cause currents as large as 10^{-5} A/cm^2, and a glowing filament might cause 10^{-3} A/cm^2.

In equilibrium, the generated photocurrent is countered by a restoring current from the semiconductor (I_{sm}) and current transmitted through the metal film $I_m = V/R_m$. I_m becomes important as the resistivity R_m of the film decreases with increasing thickness, assuming (as is typically the case) that the film is grounded through Ohmic contacts at the sample edges. This explains the ultimate onset with increasing thickness of band-bending characteristic of the "bulk" Schottky barrier. For the purposes of this discussion, it is assumed that $I_m \ll I_{sm}$. Calculations incorporating the effect of finite I_m (to appear elsewhere) demonstrate why p-type diodes, which are typically more heavily doped, converge on the bulk value for the barrier height more rapidly than n-type diodes.

Since current flow across the interface is limited by the transport of carriers through the depleted region, the restoring current can reasonably be treated in the context of a Schottky barrier regardless of the nature of the surface pinning. The fundamental current-voltage relationship is[1]

$$J_{pc} = J_{pc0}(1 - e^{-aW}) = J_{sm} = J_0(T)\exp(-V_d/E_0)(1 - e^{-qV/kT}) , \quad (1)$$

where the definition of E_0 depends on the dominant current flow mechanisms. Eliminating the final term allows the simple solution

$$V_d = E_0 \ln(J_0/J_{sm}), \quad V \geq kT/q , \quad (2)$$

where the range of applicability reflects the fact that at $V = kT/q$, the error introduced in V_d is typically less than 20 mV.

In the temperature and doping range of interest ($N_d \geq 10^{17}$ and $T \leq 300$ K), J_{sm} consists of contributions both from thermionic emission over the barrier and field emission (tunneling) through the barrier.[1] The latter results in additional current at low temperatures and high doping. Since only approximately 1% of the photons are absorbed within an electron escape depth of the surface, the contribution of photoelectrons emitted into the vacuum can be ignored. Additional contributions such as recombination, hole injection, quantum-mechanical reflection, and the discrete distribution of dopants are beyond the scope of this analysis. In particular, the recombination-generation current may be competitive with thermionic field emission at low temperature. Since the observed band banding varies logarithmically with restoring current, however, such effects will not substantively change the reported results.

The thermionic field emission solution for J_0 and E_0 (ignoring image charge lowering and nonideality) is[2]

$$J_0/J_{sm} = (1/J_{pc0})A^{**}T^2\exp(V_n/E_0 - qV_n/kT)(q/akT) \times (\pi E_{00} q N_d/2\epsilon_s)^{1/2}[\cosh(qE_{00}/kT)]^{-1} , \quad (3)$$

where $E_0 = E_{00}\coth(qE_{00}/kT)$, $E_{00} = 18.5\times 10^{-15}(N_d/m_r\epsilon_r)^{1/2}$, A^{**} is the modified Richardson constant, N_d is the substrate doping, $m^* = m_r m_e$ is the effective mass, $\epsilon_s = \epsilon_r\epsilon_0$ is the permittivity of the semiconductor, and V_n is the potential difference between the Fermi level and the bottom of the conduction band in the bulk of the semiconductor. For n-type GaAs, $A^{**} = 8.16$ A K^{-2}cm^{-2}, $\epsilon_r = 13.1$, and $m_r = 0.067$ are used. E_0 is typically less than 30 meV, and hence the photovoltage varies slowly with changes in incident photon flux.

The characteristic decay time of a typical diode can be calculated from the differential capacitance[1] and the resistivity, and is on the order of several seconds in the case that $N_d = 10^{17}$ cm^{-3} and $V_d - V_n = 0.4$ eV.

Results of calculations using Eq. (3) for a barrier height $V_b = 0.65$ eV, an absorption coefficient $\alpha = 2\times 10^5$ cm^{-1}, and doping $N_d = 10^{17}$ cm^{-3} are shown in Fig. 2. It can be seen that large changes in incident current correspond to relatively small changes in the $V(T)$ trends, particularly at lower temperature. Calculations for p-type semiconductors (not shown) predict a similar trend of increased flattening of bands at lower temperature. It is evident that, at low temperature, it is extremely dangerous to infer barrier height or Fermi-level position from a PES measurement of the substrate valence-band maximum. Even at room temperature, significant band flattening can be observed under bright illumination (such as an ion gauge) for doping levels less than 10^{17} cm^{-3}.

Figure 3 demonstrates the significant effect of doping on the observed band bending. As the dopant density increases above 10^{17} cm^{-3}, the depletion width becomes sufficiently thin that field-emission current can efficiently neutralize the photocurrent. Below 10^{17} cm^{-3}, however,

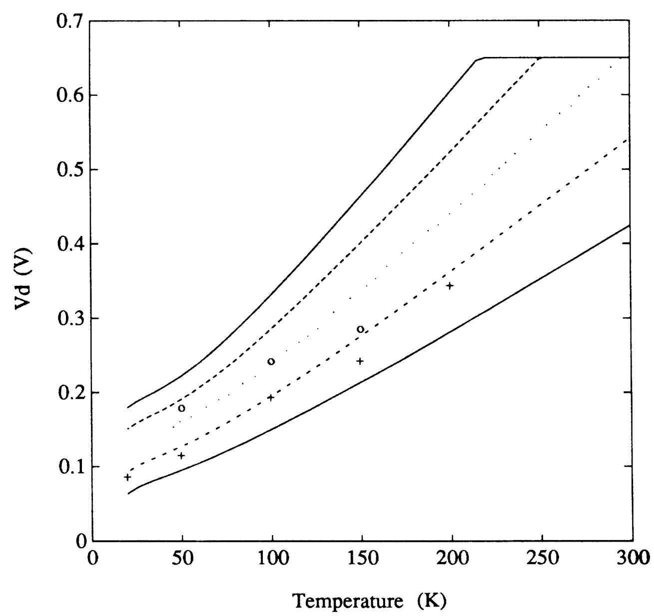

FIG. 2. Calculated $V(T)$ curves for $V_b = 0.65$ V, $N_d = 10^{17}$ cm^{-3}. Individual curves (top to bottom) correspond to $J_{pc0} = 10^{-9}$, 10^{-7}, 10^{-5}, 10^{-3}, and 10^{-1} A/cm^2. Solution diverges for $V_d > 0.625$ V, and is clipped at $V_d = V_b$. Data is for 0.3-ML Ti/GaAs(110) from AVW.

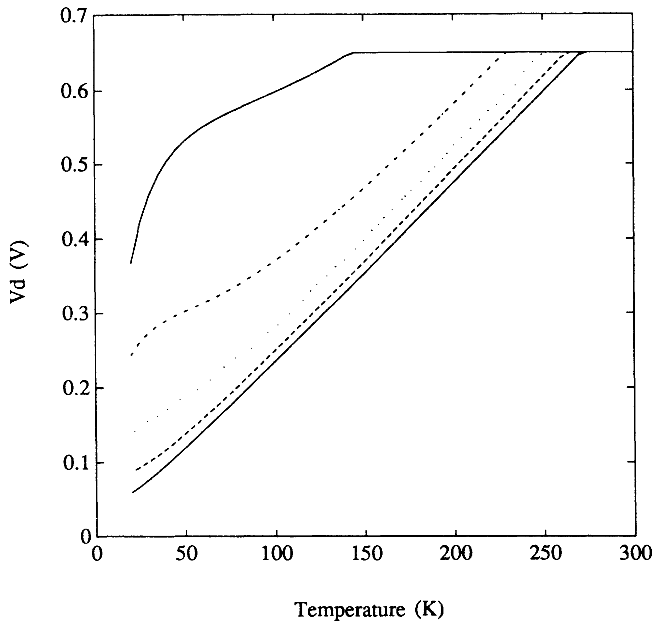

FIG. 3. As in Fig. 2 for $J_{pc0}=10^{-7}$ and $N_d=10^{18}$, 3×10^{17}, 10^{17}, 3×10^{16}, and 10^{16} (top to bottom).

the dependence on doping is weak, as the thermionic component of the current is insensitive to doping. In order to justify neglecting the open circuit voltage, however, a doping level well in excess of 10^{18} cm^{-3} is required for temperatures below 77 K.

In recent Schottky-barrier studies, it has generally been concluded that at low temperatures, thicker metal films are required to establish the bulk barrier height.[3-6] The conclusions of several of these studies, however, must be modified when the effect of the photovoltage is considered. As an example, consider the recent results of Aldao, Anderson, Capasso, Vitomirov, Waddill, and Weaver[3] (AVW). AVW were the first to report that the temperature dependence of the band bending for thin metal films on GaAs is reversible, and that a distinct dependence on doping level is found which is similar for both *n*- and *p*-type substrates. The temperature dependence was shown by AVW to correspond to an equation of the general form $J=F(T,N_d)/A^*T^2\exp(-V_d/E_0)$ [compare Eq. (1)].

AVW explain their observations in the context of a dynamic coupling model, which treats J as an empirically determined parameter associated with quantum-mechanical coupling between the metal adatoms and the semiconductor substrate beyond the depletion region. This interpretation suggests a fundamentally electronic character of Schottky-barrier formation. It is argued here that the AVW results can be explained more readily by the photovoltaic effect. This interpretation differs from the interpretation of AVW in that (1) the barrier height V_b is assumed to be constant, while the observed conduction-band shifts result from an offset V of the quasi-Fermi level across the interface, and (2) an external current source determines the equilibrium bias. This interpretation is consistent with the observed temperature dependence of V_d as well as the observed, reversible shift of the metal core-level position which suggests surface charging.

In Fig. 2, the Ti/GaAs(110) measurements of AVW are shown in comparison to the photovoltage calculations. All of the calculated curves are qualitatively similar to the AVW data, although the best fit corresponds to 10^{-3} A/cm^2. The data differs from the 10^{-5} A/cm^2 curve [consistent with the experimental conditions of AVW (Ref. 7)] by only ~0.1 eV. This difference could reflect an overestimate of the restoring current, or simply a small referencing error. The expected variation with doping shown in Fig. 3 is also consistent with the observations of AVW.

In conclusion, it has been shown that low-temperature PES measurements of metal-semiconductor systems are strongly affected by photovoltaic charging of the metal film. This charging explains the band-bending behavior observed by AVW and others, as well as the observed shift of the metal core lines with temperature. The charging is not normally observed on the freshly cleaved semiconductor since the bands are already flat, and there is no electric field in the semiconductor. It is, however, expected (and has been observed by AVW) on defected semiconductor surfaces. In the limit of a thick metal film the photovoltage may be shunted to the substrate. Measurements of the equilibrium band bending, such as those in Ref. 6, are therefore not necessarily in error.

Although the most obvious measure of photovoltaic charging is the dependence of band bending on photon flux, it must be emphasized that this dependence is extremely weak under typical conditions. An order-of-magnitude change in flux at low temperatures might cause less than a 10% change in photovoltage.[7] Other definitive measurements would be observation of the time dependence of the charging, or the temperature and doping dependence of the offset between the metal and the semiconductor core levels.[8] In addition, the charging should be observable in thicker metal films if care is taken to form a high-resistance diode.

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[2]The equation has been linearized by incorporating V into the term $aW/(1-e^{-aW})$, which goes to one for small aW. In practice, aW is always less than two, and is typically less than one in the region of interest.

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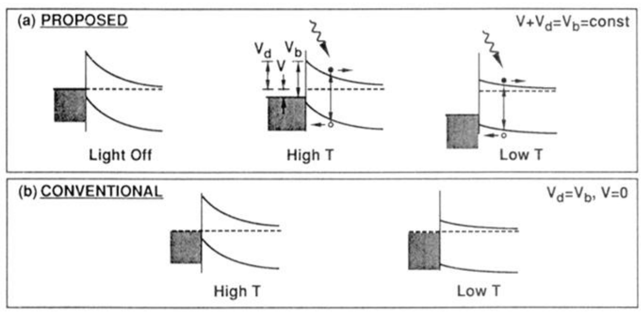
[7]Experimental conditions are reported in C. M. Aldao, G. D. Waddill, P. J. Benning, C. Capasso, and J. H. Weaver, Phys. Rev. B **41**, 6092 (1990), and a weak photon flux dependence is reported, consistent with these calculations.

[8]M. Alonso, R. Cimino, Ch. Maierhofer, and K. Horn (unpublished) have recently observed a Fermi-level shift in the limit of thick metal films on GaP.



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