

## Time dependence of photovoltaic shifts in photoelectron spectroscopy of semiconductors

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Photovoltage-induced peaks shifts in photoelectron spectroscopy (PES) were recently shown to be important in studies of semiconductor interface formation [M. H. Hecht, *Phys. Rev. B* **41**, 7918 (1990)]. In that process, the photons used to probe the sample were shown to cause a reduction in surface band bending, hence shifting the spectrum in energy. In this paper it is shown that the time dependence of the charging and discharging process can have an important influence on experimentally observable phenomena. Since the charging process is very fast, the effective photocurrent in a pulsed-synchrotron-radiation experiment may be orders of magnitude higher than previously assumed. Using a simple model of the discharge profile it is shown that the photovoltage persists on a time scale that is macroscopic under typical PES conditions. Finally, a noncontacting method for determining equilibrium surface band bending is proposed.

Photoelectron spectroscopy (PES) is commonly used to follow the movement of semiconductor energy bands during adsorption or interface formation because it uniquely determines both the surface potential and the chemical environment without requiring electrical contact to the front surface. The open-circuit nature of the experiment is clearly an advantage in studying an incompletely formed film, but it was recently demonstrated<sup>1,2</sup> that such surfaces are often not in electronic equilibrium under common experimental conditions. Under illumination (including the low-level illumination of the PES source) minority carriers are swept to the surface of the semiconductor, flattening the bands. In order to remain in equilibrium, an equivalent current of majority carriers must flow to the surface. The supply of restoring current is limited by the depletion-region resistance, which depends exponentially on temperature. As a result, the charging is most pronounced at reduced temperature.

In the earlier work, a simple theoretical model was shown to account for the observed phenomena. The magnitude of the photovoltage was calculated by equating the photocurrent to the restoring current corresponding to a Schottky barrier under bias.<sup>3</sup> The observed disappearance of the photovoltage with increasing overlayer thickness was attributed to a parallel conductance pathway through the surface. In addition to explaining the recently observed temperature and doping dependence of the band bending,<sup>4</sup> this model predicted a small but observable shift with light intensity, an observable shift in the overlayer Fermi level, a distinction between photovoltages on discontinuous and continuous films, and a long time constant for decay at reduced temperature. Each of these phenomena has subsequently been observed. The Fermi-level shift was, in fact, reported by Alonso, Cimino, and Horn<sup>5</sup> simultaneously with the first report of the model. The shift with light intensity,<sup>6</sup> the discontinuous film effect,<sup>7</sup> and the long time constant<sup>8</sup> were reported subsequently. In addition, it was demonstrated that the model holds over a wide temperature range for a clean, stepped surface.<sup>9</sup>

The efficacy of using PES to study Fermi-level pinning

in the initial stages of interface formation is limited in many cases by the influence of the photovoltage. It, therefore, becomes essential to be able to predict the magnitude of the photovoltage as a function of sample characteristics, temperature, and photon source characteristics. While PES is reliable under certain circumstances (low barriers or high temperatures), other tools are required in many cases of interest. The Kelvin probe provides a means to measure work-function differences, but it is intrinsically difficult to separate surface dipole contributions from band bending. It will become clear from the following analysis, however, that measurement of the photovoltage decay profile itself provides an extremely sensitive measure of the equilibrium band bending.

The establishment of the photovoltage at the onset of illumination is a complex problem in carrier dynamics. One such analysis was recently provided by Long *et al.*<sup>10</sup> For the present discussion, it is sufficient to assume that the process occurs on the time scale required for minority carriers to traverse the depletion region at the saturated drift velocity. In the case of GaAs ( $p=10^{18}$ ) with band bending of 0.6 eV at the surface, for example, the depletion region is approximately 300 Å wide and the corresponding transit time is 0.5 psec.<sup>3</sup> As a result, a sample illuminated for a period in excess of 10 psec can be considered to be in steady state.

The decay of the photovoltage upon cessation of illumination was recently derived by Hamers and Cahill<sup>11</sup> in the interpretation of surface photovoltage measurements using a scanning tunneling microscope (STM). A more general derivation is presented here for application to PES spectroscopy. The change in photovoltage with time can be written in terms of the capacitance per unit area  $C=dQ/dV$  and the restoring current  $J=dQ/dt$  as

$$t - t_0 = \int_{V_0}^V \frac{C}{J} dV. \quad (1)$$

Within the depletion approximation,<sup>3</sup> the capacitance is

$$C = \epsilon_s/W = (q\epsilon_s N_d/2V_d)^{1/2}, \quad (2)$$

where  $V_d = V_b - V - V_n$  and  $V_b$  is the Schottky-barrier

height or, in the case of a free surface, the relevant band edge measured with respect to the Fermi level.  $\epsilon_s$  is the permittivity of the semiconductor,  $N_d$  is the bulk doping,  $q$  is the electronic charge, and  $V_n$  is the bulk Fermi-level position with respect to that same band edge. All quantities are defined so as to be positive in the general case.

The current  $J$  is defined according to conventional Schottky-barrier theory<sup>3</sup> as

$$J = J_s e^{V/E_0} (1 - e^{-qV/kT}), \quad (3)$$

where  $E_0 = kT/q$  in the thermionic emission limit. For the present calculation, the saturation current  $J_s$  is defined for thermionic field emission as

$$J_s = A^* T^2 e^{-(V_b - V_n)/E_0} \times e^{-qV_n/kT} (q/kT) (\pi E_{00} V_d)^{1/2} [\cosh(qE_{00}/kT)]^{-1}, \quad (4)$$

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, and  $m_r = m^*/m_e$  is the effective mass.

The importance of the rapid onset of the photovoltage lies in the predominance of pulsed synchrotron radiation as a photon source for PES studies. While the time structure of such sources is variable, typical pulse lengths are in the range 100–1000 psec, with pulse frequency in the range 1–100 MHz.<sup>12</sup> The typical duty cycle is on the order of 1%. Following the above discussion, the photovoltage can be treated in steady state during the light pulses, and the peak photocurrent should therefore be used to calculate the photovoltage rather than the average photocurrent which is commonly used.

The implications of using the peak rather than the average photocurrent are exemplified in Fig. 1. Using the method of Ref. 1, the photovoltage corresponding to an

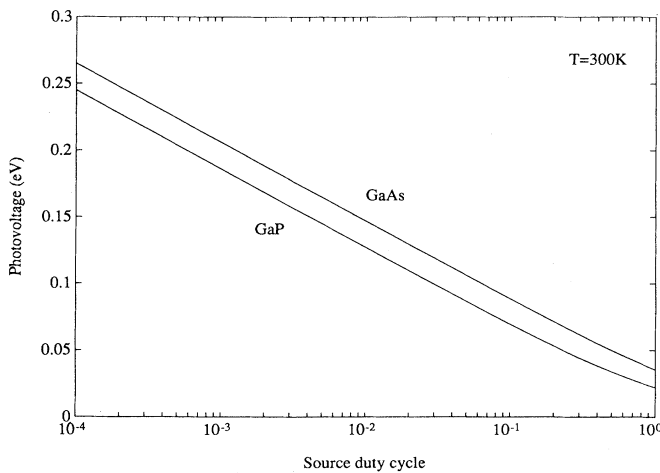


FIG. 1. The photovoltage induced by synchrotron radiation at an average power level of  $10^{-6}$  A/cm<sup>2</sup> for GaAs ( $n=10^{17}$  cm<sup>-3</sup>) and GaP ( $p=3 \times 10^{17}$  cm<sup>-3</sup>), both at room temperature. The photovoltage, which is measured only during the light pulses, is plotted as a function of the source duty cycle, and is calculated by solving the steady-state photovoltage equations for the peak photocurrent.

average photocurrent of  $10^{-6}$  A/cm<sup>2</sup> is plotted as a function of the duty cycle of the source. For both cases shown in the figure the photovoltage is insignificant under constant illumination, but becomes very significant under pulsed conditions. The two cases have been selected to be representative of a large body of room-temperature studies of semiconductor surfaces. The upper curve has been calculated for GaAs ( $n=10^{17}$ ) with midgap Fermi-level pinning at the surface. The second case, GaP ( $p=3 \times 10^{17}$ ) with a surface barrier of 0.75 eV (Fermi level to valence-band edge), represents the system studied by Alonso, Cimino, and Horn.<sup>5</sup> In that work the photovoltage was directly observed as an apparent Fermi-level shift, and the reported result clearly corresponds to the calculation for the pulsed source.

Substantial information about the surface potential can be obtained by observing the decay of the photovoltage following cessation of illumination. Such a measurement was recently reported by Mao *et al.*<sup>8</sup> In that work, the work function of Ag/GaAs was followed as a function of temperature and time using a Kelvin probe. At 60 K the authors reported a work-function shift of 400–450 meV with illumination. Following the method of Ref. 1 it can be shown that the power levels used in this experiment are not sufficient to completely flatten the bands. It can be estimated, however, that the measured shift is consistent with a barrier height of  $V_b \approx 650$  meV.

A photovoltage decay curve calculated for the conditions reported by Mao *et al.* is shown in Fig. 2. The importance of the decay curve becomes immediately obvious by comparison of the three curves in Fig. 2, which correspond to barrier heights differing by 10 meV. It can be seen that, on the time scale of this measurement, the photovoltage also differs by 10-meV steps. An alternative way to state this result is that the postillumination band-bending profile  $V_d(t)$  is insensitive to the actual barrier height  $V_b$ , while the preillumination value is sensitive only to  $V_b$ . The postillumination profile therefore establishes

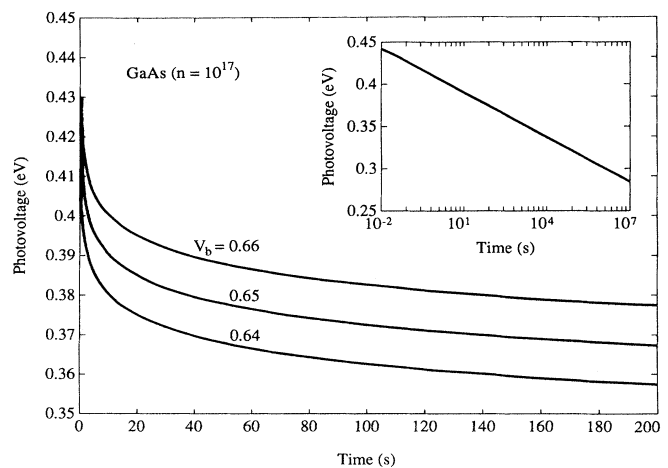


FIG. 2. Time-dependent photovoltage calculations for GaAs ( $n=10^{17}$  cm<sup>-3</sup>) at 60 K, on the time scale of Ref. 8. It can be seen that the decay rate is extremely sensitive to the Schottky-barrier height. Inset: Same result plotted for a logarithmic times scale.

the absolute band-bending scale.

This result suggests an extremely accurate method to determine the equilibrium (unilluminated) barrier height. Referring to Fig. 2, the zero on the photovoltage axis is established precisely by the preillumination Kelvin probe measurement. Having experimentally established the origin, the measured decay curve following a pulse of light can be compared to the calculated family of curves to establish the barrier height. As a result of the exponential nature of the decay, the degree of band flattening produced during the light pulse does not substantially influence the measurement as long as it is sufficiently large. Since this method does not require complete flattening of the bands, it is far more reliable and generally applicable than earlier methods.

Comparison to the preillumination level converts a relative measurement of  $V_b$  to an accurate absolute measurement. The proposed approach has the advantage that it requires only a relative measurement of the surface potential, which both the Kelvin probe and the STM do quite well. A few cautions exist with respect to the proposed measurement. Since the photovoltage scales approximately as  $e^{-qV_b/kT}$ , the accuracy of the result is limited by the accuracy to which the sample temperature has been determined. In addition, since the decay must be measured with respect to the equilibrium (dark) value, it can only be applied to a technique which measures potential without illumination, such as the Kelvin probe or the STM. As discussed below, the dark condition may not be obtainable under some circumstances because photovoltages due to previous light exposure may persist indefinitely. In addition, corrections to the theory used to model the decay may be required to account for alternative conduction mechanisms and the details of the carrier diffusion process.

It can be seen from the inset in Fig. 2 that, even if the bands were entirely flattened, decay to 0.45 eV would occur in the first millisecond following illumination. The inset also indicates that a significant photovoltage persists well beyond the conceivable life of the experiment. In practice, mechanisms such as surface conduction, ion adsorption, or bombardment by low-energy electron sources in the vacuum chamber will eventually discharge the surface. The calculation does, however, support the speculation of Mao *et al.*<sup>8</sup> that prior exposure of the sample to light (e.g., during surface preparation) could prejudice even an experiment performed under low light conditions.

The actual time scale over which the photovoltage decay may be measured is a strong function of barrier height and temperature. Hamers and Cahill,<sup>11</sup> for example, measured the decay of photovoltage on a Si surface ( $n=10^{17}$  cm<sup>-3</sup>) with a barrier of  $V_b=0.6$  eV. Even for this relatively common system, the photovoltage decay can be measured on a microsecond time scale at room temperature. At slightly reduced temperatures (e.g., 200 K), the same measurement could be performed on a time scale of seconds. In Fig. 3 a calculation is shown for the Ag/*n*-GaP interface, which is reported by Alonso, Cimino, and Horn<sup>5</sup> to have a barrier as high as 1.5 eV. It can be

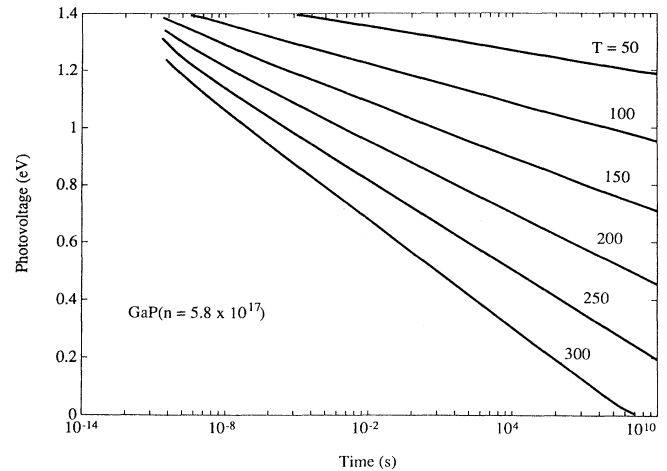


FIG. 3. Photovoltage decay for the GaP ( $n=5.8 \times 10^{17}$  cm<sup>-3</sup>) interface with Schottky-barrier height  $V_b=1.5$  eV. Photovoltage is easily produced at room temperature during PES measurement (see Ref. 5) and will not decay to zero even at room temperature.

seen that, even at room temperature, a photovoltage greater than 200 meV will persist for hours. At 100 K, no appreciable decay of the photovoltage will be observed at all. The dynamic barrier height measurement must be performed above room temperature.

In conclusion, it has been shown that room-temperature PES measurements of the surface potential of common semiconductor systems may be affected by photovoltages due to the pulsed nature of the synchrotron-radiation sources. A simple method is presented for calculating the time-dependent decay of a photovoltage at semiconductor surfaces and at semiconductor/metal interfaces which produces good agreement with experimental measurements using PES and related techniques. It is proposed that precise measurements of Fermi-level pinning may be performed by comparing the preillumination potential of a surface to the decay rate, using an instrument such as a Kelvin probe or an STM which is capable of accurate relative measurements of surface potential. It is shown that the photovoltage decay can be measured even at room temperature for semiconductors with barriers in excess of  $\sim 0.5$  eV. At reduced temperatures (or at room temperature if the barrier is sufficiently high) it is shown that the photovoltage may persist indefinitely.

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