Electric-Field Dependence of the Surface Dipole of Semiconductors*

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Modulation of photoemission from n-type GaSb by additional light leads to the conclusion that the surface dipole (i.e., the electron affinity and the ionization energy) of semiconductors is influenced by the electric field of the space charge. Comparison of calculated with observed modulation yields an escape depth of 100 Å for photoelectrons from clean surfaces.

It is well known that the work function of clean semiconductor surfaces can be modified by various means, e.g., by application of external electric fields,[1] by illumination,[2,3] by changing the temperature,[3] or by varying the doping of the bulk material.[4] Such modifications of the work function are always associated with shifts of the Fermi level in the band gap at the surface, i.e., with changes in band bending. In general, the surface dipole, which is expressed in terms of electron affinity or ionization energy of the semiconductor, is assumed to remain unchanged.

Recently, Smith[5] has shown that the surface dipole of metals can be modified by the application of large external electric fields. It is quite logical to extend this concept to semiconductors and to investigate whether the surface dipole can also be changed by internal fields such as those resulting from space charges. Semiconductors are attractive because the space-charge field can be modulated by absorption of light[2,3,6] and because the band bending, the ionization energy, and their modulation can be measured by photoemission.[7] Thus, the field dependence of the surface dipole can be observed directly.

The experimental evidence presented here was obtained from the cleaved (110) surface of an n-type ($N_D = 3.9\times10^{17}$ cm^{-3}) GaSb crystal. This surface presents an inversion layer.[8] An interaction between this field and the surface dipole would tend to decrease the latter. A decrease in band bending (surface photovoltage) will thus lower the surface field and increase the surface dipole and, hence, the ionization energy and the photoelectric threshold.

Figure 1 shows the observed modulation of photoemission by additional illumination. The abscissa shows the photon energy of the uv light causing photoemission. The ordinate displays the fractional change in yield caused by additional infrared and visible light from an incandescent lamp (a flashlight). It was verified that this additional light did not produce photoemission by itself. In addition to the change in total yield, we also measured energy distributions that showed a decrease in band bending (i.e., a surface photovoltage) of 0.2 eV.

The crucial feature of the data (Fig. 1) is the change in sign of dY/Y. At higher photon energies (of uv), the modulating light causes an increase in emission; as the photon energy approaches the photothreshold ($h\nu = 4.72$ eV),[8,9] the additional light causes a large decrease in emission. It has been recognized earlier[3,10] that a decrease in band bending should enhance the photoemission of n-type semiconductors. It does so by increasing the number of electrons excited at a depth below the surface that are capable of overcoming the surface barrier. A decrease in emission that is inversely proportional to the photon energy above threshold is a strong indication for an increase in photothreshold[11] and there-

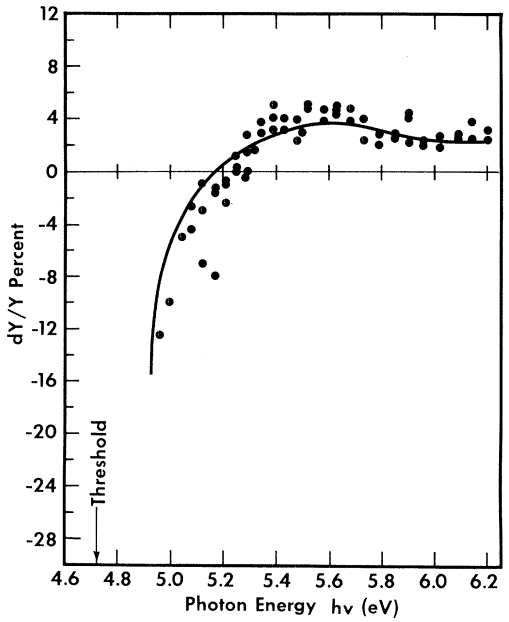

FIG. 1. Photomodulation of photoelectric emission from n-type GaSb at 77°K. The abscissa gives the photon energy of the light causing electron emission. The solid curve is the calculated modulation (see text).

fore in ionization energy. The total modulation can be estimated with the following approximate model.

In the presence of band bending, the uv light produces an internal energy distribution N of excited electrons that is fixed with respect to the band edges. It is convenient to express this distribution $N(\eta)$ as a function of the difference $\eta = H(x) - E$ between the energy E of a given electron and the highest energy $H(x)$ obtainable at depth x with a given $h\nu$. We approximate the band bending by a constant field F, and denote by H the value of $H(x)$ at the surface ($x = 0$), so that $H(x) = H - Fx$. We choose the potential *in vacuo* as the origin of energy and thus obtain

$$H = h\nu - E_0, \tag{1}$$

where E_0 is the photoelectric threshold. We assume that the transmission of the surface is proportional to the kinetic energy of electrons *in vacuo* and that electrons excited at a depth x reach the surface with probability $e^{-x/\lambda}$. The photoelectric yield Y can then be expressed as

$$Y = \text{const} \int_{\eta=0}^{H} \int_{x=0}^{(H-F)/\eta} N(\eta)(H - Fx - \eta) e^{-x/\lambda} dx d\eta. \tag{2}$$

The experimental energy distributions[8] and the yield near threshold[8,9] $Y \propto (h\nu - E_0)^3$ can be approximated with

$$N(\eta) = \text{const} \times \eta.$$

Integration of (2) yields

$$\text{const} \times Y = \tfrac{1}{6}H^3 - \tfrac{1}{2}\lambda F H^2 + \lambda^2 F^2 H - \lambda^3 F^3 + \lambda^3 F^3 e^{-H/\lambda F} \tag{3a}$$

which can also be written as

$$\text{const} \times Y = \lambda^3 F^3 \sum_{n=4}^{\infty} (-1)^n \frac{H^n}{n!(\lambda F)^n}. \tag{3b}$$

The total change in photoelectric threshold is then simply

$$\frac{\Delta Y}{Y} = \frac{1}{Y}\frac{dY}{dF}\Delta\lambda F + \frac{1}{Y}\frac{dY}{dH}\Delta H. \tag{4}$$

It is easily seen from (3a) and (3b) that near threshold

$$\frac{1}{Y}\frac{dY}{dH}\bigg|_{H\to 0} \propto \frac{4}{H} = \frac{4}{h\nu - E_0} \quad \text{and} \quad \frac{dY}{dF}\frac{1}{Y}\bigg|_{H\to 0} \propto -\frac{1}{\lambda F}; \tag{5}$$

for large values of $H/\lambda F$, both derivatives tend towards $1/H$.

Most quantities in (3) and (4) can be determined from measurement. An investigation[8] of surface properties of GaSb showed that for this particular sample, $F = 2.3 \times 10^5$ V/cm. From the displacement in energy distributions caused by the modulating light, we obtain $\Delta F = -3 \times 10^4$ V/cm. ΔH can be determined by plotting $[Y(h\nu) - \Delta Y(h\nu)]^{1/3}$ near threshold: $\Delta H = 15 \pm 5$ meV. The only adjustable parameter is the escape depth λ. The best fit to the data (Fig. 1) was obtained with $\Delta H = 12$ meV and $\lambda = 100$ Å. In fact, it was found that the modulation spectrum (4) was quite sensitive to the choice of λ, so that we consider the data of Fig. 1 as a quite reliable determination of the escape depth for electrons. Such a determination can certainly be improved by allowing for the variation of the field $F(x)$ and by refining the measurements.[11]

The modification of the surface dipole by a space-charge field is not limited to GaSb. In the case of GaAs, we have measured an ionization energy $\xi = 5.40$ eV for p-type materials, where the bands are flat, and $\xi = 5.30$ eV for n-type material with a space-charge field.

For silicon, Rowe[11] has reported photomodulation measurements similar to those in Fig. 1. He observed a decrease of dY/Y at lower $h\nu$ but no negative values. We believe that his data can be explained more realistically by our model than by the lifetime broadening he proposes. It is also possible that the decrease in threshold observed by Allen and Gobeli[4] for n-type silicon is due to an interaction between the space charge and the surface dipole.

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Carrier Transport and Potential Distributions for a Semiconductor *p-n* Junction in the Relaxation Regime

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Experimental current-voltage characteristics and potential distributions are presented for a *p-n* junction in high-resistivity GaAs, whose dielectric relaxation time τ_D exceeds carrier lifetime τ_0. The condition $\tau_D > \tau_0$ defines the new "relaxation regime" for which theory predicts behavior entirely different from that of the familiar ideal rectifier of conventional semiconductor physics with $\tau_D \ll \tau_0$. The predicted field distributions and the linear and sublinear current-voltage relationships are observed. These results confirm the theory in detail.

A new semiconductor regime is realized when the dielectric relaxation time $\tau_D = \rho\epsilon$ exceeds the carrier diffusion-length lifetime τ_0.[1-3] This "relaxation-case" regime can be obtained in crystalline or amorphous semiconductors doped with deep traps, which raise the resistivity ρ and shorten the lifetime τ_0. We call the conventional semiconductor behavior the "lifetime case," since $\tau_0 \gg \tau_D$ is always assumed.[4]

Departures from local neutrality are predicted for the relaxation case,[1-3,5] and a small-signal injected neutral pulse drifts in the majority-carrier direction.[1,5] In addition, the net local recombination rate is approximately zero after an initial rapid recombination.[1-3] The injected minority carriers can both reduce the majority-carrier concentration and fill ionized traps.[2,3] Injected minority carriers thus *increase* resistivity because of this recombinative depletion. "Lifetime-case" injection, of course, *reduces* resistivity.[4]

This paper describes current-voltage and potential-distribution measurements for GaAs *p-n* junctions which illustrate and confirm the theory of the relaxation regime. The current-voltage dependence of a relaxation-case junction is found to be completely different from the well-known "ideal-rectifier" junction with its exponentially increasing forward current and saturated reverse current.[6]

Oxygen-doped and compensated single crystals of *n*-type GaAs with $n_0 = 3\times10^7$ electrons/cm^3 and mobility $\mu_n = 4.5\times10^3$ cm^2/V sec were used. Zinc diffusion created a 3×10^{-4}-cm deep *p* layer with $p_s > 10^{20}$ holes/cm^3 at the surface. Ohmic In-Au contacts were evaporated and alloyed. The volume resistivity after these treatments was found by potential probing (in region "1*f*" of Fig. 1) to be $\rho = 1.5\times10^8\ \Omega$ cm at 22°C. With $\epsilon(\mathrm{GaAs}) \approx 10^{-12}$ F/cm, we get $\tau_D = \rho\epsilon \approx 10^{-4}$ sec $\gg \tau_0 \lesssim 10^{-8}$ sec.