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Synchrotron-radiation-induced surface photovoltage on GaAs studied by contact-potential-difference measurements

D. Mao and A. Kahn
Department of Electrical Engineering, Princeton University, Princeton, New Jersey 08544-5263

M. Marsi and G. Margaritondo
Department of Physics and Synchrotron Radiation Center, University of Wisconsin–Madison, Madison, Wisconsin 53706

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We used the Kelvin method to study the synchrotron-radiation-induced surface photovoltage (SPV) on GaAs(110) and its impact on the photoemission study of metal-semiconductor interfaces formed at low temperature. We find that varying the temperature alone does not induce significant change in band bending in the semiconductor, but that the combination of low temperature and synchrotron-light illumination on lightly doped n-type GaAs induces a large and quasipermanent SPV. It is also found that low-intensity stray light can induce measurable SPV on these samples. Highly doped low-temperature p-type GaAs does not exhibit significant SPV under synchrotron-radiation illumination.

It was recently shown that surface photovoltage (SPV) which occurs during photoemission-spectroscopy (PES) measurements of the formation of metal-semiconductor interfaces could substantially modify the semiconductor band bending.[1–3] In addition to the photoemission process, the absorption of photons creates a cascade of inelastically excited electron-hole pairs. The carriers thermalize to the band edges and are separated by the built-in field of the depletion region. They induce a field which is in opposite direction to the built-in field and which reduces the band bending.[4–6] In a lightly doped semiconductor at low temperature (LT), the rate at which carriers from the bulk arrive at the surface and recombine with trapped holes or electrons is negligible. The resulting SPV can be large and can invalidate the measurements of semiconductor band bending. In particular, on both n- and p-type semiconductors, E_F appears to be closer to the band edges than it is under equilibrium. For metal-semiconductor interface studies, SPV is believed to have had an important contribution to the band-bending asymmetry versus coverage on n- and p-type LT GaAs samples reported by several groups (Fig. 1).[7,8] Low- to medium-doping n-type samples and highly doped p-type samples were generally used in these experiments, leading to substantial SPV or band flattening at low coverage on n-type samples and negligible effects on p-type samples.

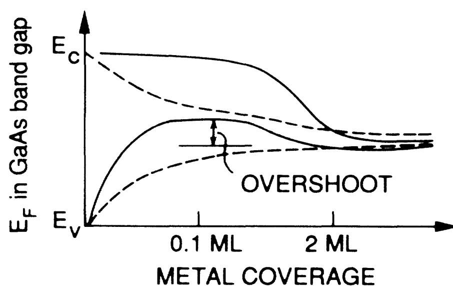

FIG. 1. Typical RT (dashed curves) and LT (full curves) Fermi-level movements at the (110) surface of weakly doped n-type and highly doped p-type GaAs measured with synchrotron-radiation photoemission spectroscopy (Ref. 7).

A considerable effort has recently been put in the photoemission study of this PES-induced SPV coupled with studies of temperature and doping dependence of band bending. Yet, because of the inherent perturbation brought about by the photons used to investigate the surface, the results remain somewhat ambiguous. Specifically, it is impossible to distinguish between temperature and illumination effects on band bending. In the present work, we remove this ambiguity by taking contact-potential-difference (CPD) measurements with a Kelvin probe, a technique which does not involve photons and which, in principle, is totally noninvasive. The probe is used in conjunction with synchrotron radiation to study the magnitude and hysteresis of the PES-induced SPV. In order to evaluate the role of SPV in our previous PES LT results,[7] we perform the CPD measurements on GaAs samples with doping concentrations identical to those used previously, i.e., n-type doped at 10^{17} cm^{-3} and p-type doped at 10^{18} cm^{-3}. We confirm that (1) upon temperature variation, the band bending does not change significantly in the dark; this addresses directly the issue raised by the dynamic-coupling model of Vitomirov *et al.*;[9] (2) the low-coverage LT PES results on lightly doped n-type GaAs are indeed dominated by SPV; and (3) highly doped p-type GaAs exhibits negligible SPV when illuminated with synchrotron radiation.

All experiments were done in ultrahigh vacuum (UHV) with a base pressure of less than 1×10^{-10} Torr. The Kelvin probe consisted of a vibrating gold probe with a spherical tip (~1.5 mm diam) coupled through bellows to a speaker outside the vacuum chamber. The vibration frequency was 290 Hz and the vibration amplitude was a few tens of micrometers. During operation, the probe is brought to a mean distance to the sample surface of about 0.1 mm. Because of the CPD between the two surfaces,

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the periodic change in probe-sample capacitance induces an alternating current. The current is nulled when the CPD is balanced by an external potential of equal magnitude and opposite sign applied to the probe. The alternating current is amplified with a current-sensitive preamplifier and detected with a lock-in amplifier. The measurement of the current-nulling voltage is carried out automatically, using a negative-feedback integrator circuit to adjust the bias potential of the preamplifier. The response time of the whole circuit is less than 1 sec. In order to investigate the photovoltage induced by the synchrotron light, the probe was placed so as not to block the soft x ray from the probed surface. The sample was positioned with the synchrotron light illuminating the surface at a near-grazing angle. Since the vibration amplitude of the probe was much smaller than the probe-sample distance, the photoemission from the probe tip and from the sample contributed only a direct current and did not affect the measurement.

The experiments were carried out on the Mark II Grasshopper beam line at the Synchrotron Radiation Center (Stoughton, WI) of the University of Wisconsin–Madison. For most of the experiments, we used 65-eV photons and 50 μm for the monochromator exit slit, a setting typical of our previous PES studies of GaAs.[7] We also took measurements with different photon energies and slit settings. Very little difference was observed. At 65 eV, the photon flux was 10^9 photons/sec for a typical machine current of 60–100 mA. The size of the beam was 1 mm×3 mm. The overall photon intensity was 10^{10} photons/sec cm^2. The GaAs samples were Si doped ($n = 7.8\times10^{16}$ to 1.3×10^{17} cm^{-3}) and Zn doped ($p = 10^{18}$ cm^{-3}). All samples had Ohmic contacts at the back and were grounded throughout the experiment. The samples were cleaved *in situ*. Near-flat-band conditions were ascertained by a work-function difference between *n*- and *p*-type samples of at least 1.2 eV. The sample holder was thermally connected to the cold finger of a He refrigerator through a copper braid and the lowest temperature at the sample surface was ~60 K. In this set of experiments, we evaporated Ag on GaAs from a resistively heated tungsten basket. The flux of Ag was monitored with a quartz-crystal microbalance. On GaAs(110), 1 monolayer (ML) of Ag has a nominal thickness of 1.3 Å.

CPD measurements give the difference between the work function of the sample and that of the probe. The latter is assumed to be constant. The change in the sample work function, $\Delta\phi$, is a sum of $\Delta q V_B$ (change in band bending) and $\Delta\chi$ (change in surface dipole and semiconductor electron affinity). Each experiment was designed so as to minimize the change in surface dipole by always varying the temperature from room temperature (RT) to LT after a RT deposition. No change in overlayer morphology is expected in these conditions. We also made the usual assumption that any change in CPD upon exposure to the radiation was due to a change in band bending rather than in surface electron affinity.

To test the reversibility of band bending with temperature,[9] we first deposited 0.12 Å of Ag on the RT, cleaved GaAs(110) surface. A 0.45–0.50-eV increase in work function was observed (Fig. 2). Given the clustered mor-

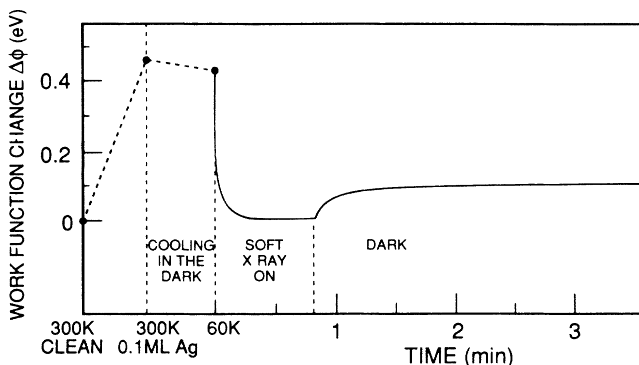

FIG. 2. Evolution of the work function of *n*-type GaAs with 0.12-Å Ag deposition, with temperature variation and with exposure to synchrotron light. The Ag deposition is done at RT.

phology of Ag on RT GaAs (Refs. 7 and 10) and the similarity in the Ag, Ga, and As electronegativities, the surface dipole induced by 0.1 ML Ag is expected to be negligible. Thus, $\Delta\phi = 0.45–0.50$ eV represents the increase in band bending, which is consistent with the RT band bending measured with photoemission spectroscopy.[7] We confirmed at this point with the Kelvin probe that the RT low-coverage surface photovoltage induced by the soft x ray was small (< 30 meV). The probe was then moved away from the surface and the sample was cooled in complete darkness. The CPD was measured again at 60 K and a change of less than 0.1 eV was found (Fig. 2). As mentioned above, the change in overlayer-induced dipole can be neglected. Furthermore, the GaAs electron affinity decreases by about 50–70 meV between RT and 60 K.[11,12] Thus the small change in CPD can be attributed to $\Delta\chi$ and indicates that the band bending is almost the same at RT and LT at submonolayer coverage. As soon as the LT sample was exposed to synchrotron light, however, a $\Delta\phi$ equal to -0.4 to -0.5 eV was observed, indicating almost complete band flattening (Fig. 2). Saturation of the work function decrease occurred in about 10–20 sec. In another experiment, the sample was also illuminated with an external halogen lamp. Similar results were obtained, with an SPV larger by 0.1–0.15 eV than that induced by the synchrotron light. It is important to note that stray light due, for example, to improperly-covered windows, can also induce significant $\Delta\phi$.

The results given above clearly link the observed $\Delta\phi$ to the exposure to light, i.e., surface photovoltage. The magnitude of this photovoltage is almost equal to the original band bending induced by the Ag overlayer. It explains the substantial difference depicted in Fig. 1 between the low-coverage band bending behaviors on weakly doped *n*-type GaAs at LT and RT,[7,8] and brings the first unambiguous experimental evidence that the reversible band bending observed by Vitomirov *et al.*[9] was in fact due to surface photovoltage.

Another parameter of interest, which is not accessible with PES measurements, is rate of decay of the photovoltage. It was found to be very slow at low coverage, as indicated in Fig. 2. After turning off the soft x ray, the

work function increased to a stable value 0.1 eV higher than under illumination in about 1 min. The slow rate of increase of the work function can be understood in terms of the various discharge mechanisms. When the soft x ray is turned off, the bands are nearly flat, the barrier for electrons is small. The bulk-to-surface currents (tunneling and thermionic emission currents) lead to a rapid initial discharge. As soon as the photovoltage is reduced by 0.1 eV, the thermionic emission drops and tunneling decreases, leading to a considerable slow down of the band bending recovery. With nearly flat bands, the surface charge density responsible for the photovoltage is approximately the charge density in the depletion layer in the dark. For $n = 10^{17}$ cm^{-3} and $qV_B = 0.5$ eV, it is about 10^{12} electrons/cm^2, or 10^{-7} C/cm^2. After the initial small discharging, the barrier height for electrons is of the order of 0.2–0.3 eV. This would yield a tunneling current of the order of 10^{-12} A/cm^2 and a lower bound for the discharge time of 10^5 sec, i.e., a quasipermanent effect (Fig. 2). We also measured the rate of recovery as a function of metal coverage and found a dramatic increase in the rate of SPV discharge near 1 ML. These experiments, which confirm the thesis of surface charge leakage as a primary vehicle for SPV discharge when the overlayer approaches metallicity, will be reported elsewhere.[13]

The quasipermanent SPV on LT lightly doped GaAs surfaces has obvious implications for the study of the LT formation of Schottky barriers, regardless of the investigation technique. It is indeed almost unavoidable to expose the sample to some light during experiments on interface formation, e.g., the bright metal source used for evaporation. Our results show that once a photovoltage has been generated, a deleterious effect will persist unless the sample is warmed up or the surface is discharged by other means. Furthermore, since the LT tunneling current, and therefore the supply of carriers, is extremely small once a 0.2–0.3-eV barrier is formed on a lightly doped semiconductor, the occupation of any significant density of surface states will not reach equilibrium unless carriers are excited by an external source, i.e., photons.

The highly doped p-type GaAs samples were investigated with the same sequence of experiments as described above. The initial RT deposition of 0.12 Å produced a 0.42-eV downward band bending, in agreement with previous RT PES data.[10] The subsequent cooling in complete darkness induced a $\Delta\phi$ of less than 0.1 eV, implying again a negligible change in band bending. Unlike with lightly doped n-type GaAs, however, exposure to synchrotron light or room light at LT had no effect on the measured work function, indicating a negligible SPV. We conclude, therefore, that the PES data on E_F position as a function of LT metal deposition (Fig. 1) were not substantially influenced by SPV. This allows us to confirm, in particular, that the overshoot of E_F at submonolayer coverage beyond its pinning value is an intrinsic property of the interface[7,8] and not an artifact of the measurement.

In conclusion, the CPD measurements combined with synchrotron-radiation illumination of the interface under study provide unambiguous experimental evidence that the reversible variation in GaAs band bending as a function of temperature corresponds to a photovoltaic effect induced by the photoemission radiation. On low-temperature, lightly doped samples, the effect is large, even with weak light intensity on the sample, and is quasipermanent. No significant photovoltaic effect was found on highly doped p-type GaAs.

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