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Confirmation of the temperature-dependent photovoltaic effect on Fermi-level measurements by photoemission spectroscopy

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Soft x-ray photoemission spectroscopy measurements of Fermi-level positions within the band gap of clean, GaAs(100) surfaces demonstrate that photovoltaic charging produces a major shift in the apparent band bending at low (50–100 K) temperatures. These measurements confirm recent predictions of Hecht [M. H. Hecht, Phys. Rev. B **41**, 7918 (1990)], based on restoring currents limited by carrier transport through the depletion region, highlight the effects of photovoltaic charging for clean (versus metallized) semiconductor surfaces, and justify Hecht's claims for a reassessment of many previous low-temperature photoemission studies of Fermi-level movement.

I. INTRODUCTION

Over the past several years, there have been numerous photoemission spectroscopy studies of semiconductor band bending which have been performed at low (50–100 K) temperatures. A major objective of these studies has been to ascertain the role of metallization in the charge exchange of metal atoms with semiconductor surfaces, free of morphological complications such as adsorbate clustering.[1–5] The detailed Fermi-level movements observed for coverages below the metallization regime have spurred considerable analysis and speculation. Within the past year, Aldao *et al.*[3] have demonstrated that many of the reported low-temperature effects were dependent on the semiconductor doping and could, in fact, account for apparent differences in Fermi-level stabilization between adsorbates on *n*-type versus *p*-type semiconductors. Likewise, Vitomirov *et al.*[4] demonstrated the temperature-dependent nature of these adsorbate-induced Fermi-level changes. However, the physical origin of all these Fermi-level effects have remained unclear until now.

Recently, Hecht[6] has calculated the effect of the photoemission process itself on the band bending due to photovoltaic charging and concluded that such effects can be considerable in the low-temperature regime. Here the incident photons induce not only photoelectric emission from near-surface atoms of the semiconductor but also produce electron-hole pairs within the semiconductor surface space-charge region which separate in the electric field of the depletion region, resulting in a reduction of the band bending (see Fig. 1, upper diagram). For *n*-type band bending, electrons move away from the surface while minority holes move in the opposite direction. Acting to reduce this internal electric field and maintain steady-state charge balance are currents between the surface and bulk coupled with surface recombination (see Fig. 1, lower diagram). Hecht derived these restoring currents in terms of thermionic emission over the surface barrier plus field emission through the barrier and demonstrated their strong temperature dependence for the conditions used in many of the recent low-temperature experiments.[6] Previously Margaritondo, Brillson, and Stoffel,[7] Demuth *et al.*,[8] and most recently, Yablonovitch *et al.*[9] noted the importance of photovoltaic effects at room temperature on semiconductor band-bending measurements via photoemission spectroscopy. Even earlier, Gatos and Lagowski[10] and others employed such photovoltaic effects to study the properties of surface states on semiconductor surfaces.

Here, we report soft x-ray photoemission spectroscopy (SXPS) measurements of Fermi-level position and band bending for the clean GaAs(100) surface at low and elevated temperatures. These studies demonstrate a large photovoltaic shift of the Fermi level from its equilibrium position, in good agreement with the Hecht calculations for GaAs over the same temperature range. The results also confirm the photovoltage proposed to analyze recent observations of Alonso *et al.*[11] In order to perform these measurements, we have used clean GaAs surfaces with surface Fermi levels near midgap but with densities of surface states sufficiently low to avoid strong extrinsic "pinning" (e.g., less than 10^{14} cm^{-2}).[12] SXPS valence-band measurements of the valence-band maximum relative to the Fermi level of the semiconductor provide a gauge of the band bending. We compare this clean surface Fermi-level position for different specimen tempera-

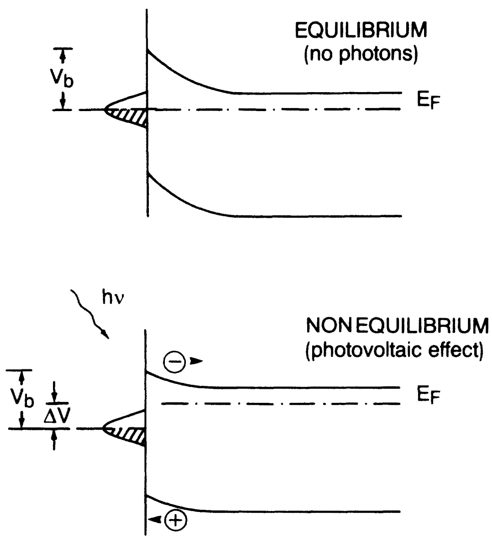

FIG. 1. Schematic energy-band diagram of a semiconductor surface space-charge region with an arbitrary charge distribution localized near the semiconductor-vacuum interface without (upper) and with (lower) photon illumination. The indicated movement of photoexcited charge acts to reduce the equilibrium band bending V_B by a photovoltage ΔV. The magnitude of ΔV depends on a bulk-to-surface recombination current, as controlled by thermionic emission over and tunneling through the surface barrier.

tures, including temperatures of 50–100 K where photovoltaic effects are predicted to be large for GaAs, to elevated temperatures of 470–550 K, where thermionic emission currents increase substantially and where such photovoltaic charging should be quite small. Our results demonstrate that photovoltaic effects can be as large as 0.75 eV for GaAs at low temperature. These findings coupled with previous temperature-dependent observations confirm the predictions of Hecht and bring into question much of the interpretation associated with previous low-temperature Schottky-barrier studies.

II. EXPERIMENTAL

Our SXPS measurements used the 3-m toroidal grating monochromator at the University of Wisconsin's Synchrotron Radiation Center in Madison, WI. We used photon energies of 47 eV with a high-energy grating at a spectral resolution of 0.25 eV in order to obtain valence-band spectra of clean, GaAs(100) surfaces under ultrahigh-vacuum (UHV) conditions. Under these conditions, photon flux measured by a gold diode in the synchrotron radiation beam is 3×10^{11} photons/sec. Focused into a 4- by 1-mm image, this beam yields a photon flux of 8×10^{12} photons $cm^{-2}sec^{-1}$ on the specimen surface.

The GaAs specimens consisted of an epitaxial GaAs(100) layer 7500-Å thick and with a doping of 5×10^{16} cm^{-3} grown on a liquid-encapsulated Czochralski-grown semi-insulating substrate of GaAs. Ohmic contacts were made at the edges of the front surface by masked evaporation. The surfaces were intentionally misoriented 4° away from (100) toward the [111]*B* direction (As dangling bonds perpendicular to the step edges) in order to ensure an intermediate density of states deep within the semiconductor band gap (and, as will be shown, Fermi level stabilized near midgap). These specimens were grown in a Varian Gen II molecular-beam epitaxy (MBE) system, capped with a thick As_4 layer by cooling the specimen overnight in an As ambient, then shipped under nitrogen pressure to our experimental station in Wisconsin. We obtained clean surfaces by thermally desorbing the As cap layer in stages under UHV conditions, using the characteristic features of the GaAs valence band and the As 3*d* to Ga 3*d* intensity ratio as figures of merit. In order to provide cooling to 60 K, we mounted these specimens on a copper holder suspended from a copper carousel attached to a CTI Cryogenics cryotip via a heavy Cu braid. Ta clips and backing for the 5- by 10-mm GaAs wafer sections provided annealing capability used for decapping and for high-temperature photoemission experiments. An Optitherm radiometer allowed temperature measurements in the range above 470 K without contact with the specimen surface, while a (7% Fe)-Au/chromel thermocouple provided low-temperature measurements of the specimen holder. In order to perform SXPS measurements at elevated temperatures while continuing to hold the specimen on the cooled specimen mount, we heated the Ta and GaAs resistively to a desired temperature above 470 K, then collected valence-band spectra over short time periods immediately after shutting off the heating current. Under these conditions, it was possible to obtain SXPS valence-band spectra at temperatures between 60 and 570 K during which temperature variations were no more than 25 K. We also obtained wide series of valence-band spectra as the specimen cooled continuously from an elevated starting temperature.

Extrapolation of the valence-band edge to the background for the clean GaAs(100) surface provided a measure of the valence-band edge position. Likewise, the leading edge of the 6*s* step feature of a thick (100 Å) Au film is used to determine the Fermi level of the photoemission spectrometer. In this manner, one can obtain a measure of the energy difference between the GaAs Fermi level and its valence-band maximum.

III. RESULTS

Figure 2 illustrates the valence-band spectrum for the thermally cleaned GaAs (100) 4°→[111]*B* surface described in Sec. II. The well-defined features within the upper 12 eV are characteristic of clean GaAs. Extrapolation of the leading edge of this 60-K spectrum indicates a Fermi-level position 1.33 eV above the valence-band maximum (VBM). Since the GaAs band gap is 1.51 eV at 60 K, this corresponds to an *n*-type barrier height (conduction band to Fermi level) of 0.18 eV. Also shown in Fig. 2 are the valence-band edges for the same surface at 60 K and the surface raised to 500 and 550 K. Here the extrapolated VBM shifts from 1.33 to 0.63 to 0.58 eV below the Fermi level, respectively. Thus the difference in temperature between SXPS measurements on the same GaAs sur-

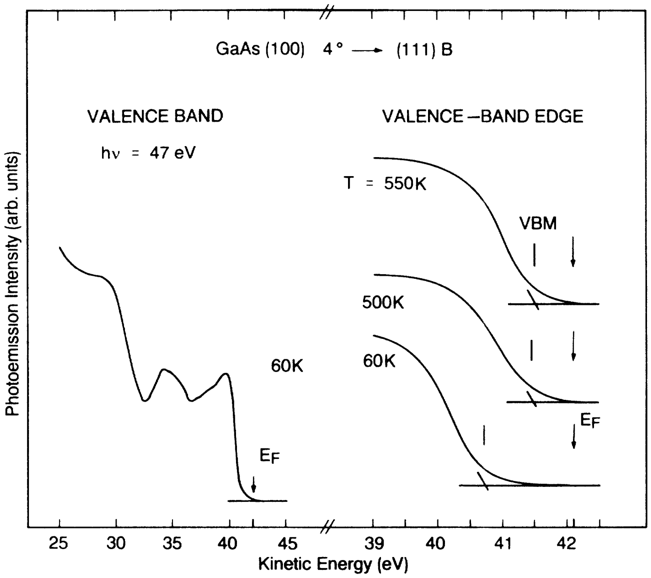

FIG. 2. SXPS valence-band spectra of a clean, misoriented GaAs (100) 4° → [111]B surface at the indicated temperatures, exhibiting characteristic clean-surface features. The extrapolated valence-band edge moves closer to the Fermi level (arrow) with increasing temperature.

face produces a ~0.75-eV shift in relative Fermi-level position.

The thermal dependence of the valence-band edge was reversible. Following each high-temperature measurement, we allowed the specimen to return to its base temperature of 60 K. In every case, the valence-band edge returned to its original value. Here the absence of any overlayer helped prevent any irreversible effects since, unlike in the case of metal-semiconductor interfaces, the surface chemistry and morphology of the clean surface are unlikely to change.

At different temperatures, the valence-band edge displayed very different responses to changes in illumination. At 60 K, order-of-magnitude changes in soft x-ray illumination via changes in filters and monochromator throughput slits result in less than a 50-meV change in measured Fermi-level position. Likewise, at 60 K, a projection lamp focused on the specimen during the SXPS measurement with an estimated visible photon flux of 10^{16}-10^{17} $cm^{-2}sec^{-1}$ produces less than a 50-meV Fermi-level shift. When the GaAs temperature is raised to 500 K, the same projection-lamp illumination shifts $E_F - E_{VBM}$ from 0.63 to 0.73 eV. Thus, the high-intensity illumination at elevated temperature shifts the semiconductor levels 0.1 eV toward the flat-band condition showing a definitely more pronounced effect than at 60 K.

We have also carried out a series of SXPS measurements of the extrapolated valence-band edge during a continuous decrease in temperature from 550 to 60 K at the rate of ~2 $K sec^{-1}$. These valence-band spectra exhibited continuous shifts in the extrapolated edge which spanned an energy range of 0.75 eV. Preliminary measurements suggest that the valence-band shift between room temperature and 550 K is less than 0.25 eV.

IV. DISCUSSION

The valence-band shifts with temperature shown in Fig. 2 confirm the recent predictions of Hecht of large photovoltaic effects on the Fermi-level position as measured by photoemission spectroscopy. Using clean GaAs surfaces to avoid any artifacts due to adsorbate-substrate interactions, we find Fermi-level shifts as large as 0.75 eV between 60 and 550 K. The reversibility of these shifts in cycling between low and elevated temperatures is further evidence that such effects are not due to chemical interactions. Photovoltage effects will also be present for coverages of metal which do not short out the induced photovoltage. However, analysis of such photovoltaic phenomena requires a detailed characterization of the overlayer morphology and is not the subject of this paper.

Our temperature-dependent results compare favorably with Hecht's calculations of the absolute magnitude of barrier reductions based on photovoltaic band flattening and its partial cancellation by restoring surface-to-bulk currents. Figure 3 illustrates similar calculations of band bending for GaAs at different illumination levels over a wide range of temperatures. As shown, the photo-flattening effect is greatest for low temperatures, especially at the low doping levels used in this experiment (5×10^{16} cm^{-3}). Furthermore, large changes in illumination intensity have a relatively small effect on the photoflattening at the near-saturation illumination intensities common to photoemission experiments. In our experiments, the synchrotron radiation flux of 8×10^{12} photons sec^{-1} in a focal spot of 4 mm by 1 mm with an assumed electron-hole pair

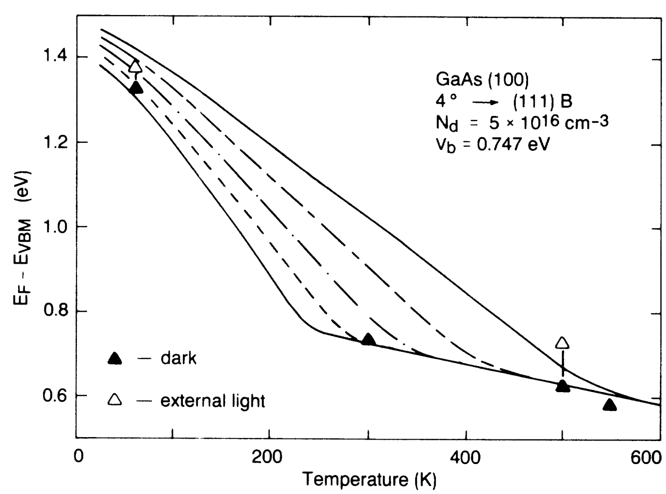

FIG. 3. Fermi-level positions with respect to the valence-band edge as measured in Fig. 2 and as calculated by taking into account the photovoltaic voltage. From top to bottom, the curves are for photogenerated current densities of 10^{-1}, 10^{-3}, 10^{-5}, 10^{-7}, and 10^{-9} $A cm^{-2}sec^{-1}$, respectively. In our experiment, this density is calculated to be 1.3×10^{-5} $A cm^{-2}sec^{-1}$ for synchrotron light-generated current (filled triangles) and ~10^{-2} $A cm^{-2}sec^{-1}$ for projection-lamp-generated current (open triangles). The excellent agreement between theory and experiment supports the role of significant photovoltaic charging in the low-temperature SXPS measurements.

production rate of 10 for each 47-eV photon yields a photogenerated current density of 1.3×10^{-5} A cm^{-2} (filled triangles). At a temperature of 60 K, Fig. 3 shows that this flux density produces a photovoltaic shift of 0.7–0.75 eV for GaAs (with a doping density of 5×10^{16} cm^{-3}). Our results here display a photovoltaic shift which is in excellent quantitative agreement between the measured $E_F - E_{\rm VBM}$ positions measured at the different temperatures and those calculated from the thermionic-emission recombination current. Points of agreement include the absolute starting position of the Fermi level at 60 K, the room-temperature position, as well as the slight Fermi-level movement at elevated temperatures. The slope in the line of zero photovoltage (nearly horizontal) as a function of temperature reflects the decrease in band gap with increasing temperature. Figure 3 also shows that only a slight (<50 meV) decrease in $E_F - E_{\rm VBM}$ is expected between 550 and 500 K, and $\sim$100 meV between 500 and 300 K. In addition, Fig. 3 illustrates the illumination dependence of the Fermi-level with a visible light source (open triangles). Here the 3–4 orders of magnitude increase in photon flux translates into roughly 2–3 orders of magnitude increase in photocurrent. Such illumination produces a 100 meV Fermi-level shift toward the flat-band condition at 550 K. At 60 K the corresponding shift is only 50 meV. A more detailed comparison of our results with calculations is now in progress.

V. CONCLUSIONS

We have performed SXPS measurements of the Fermi-level position within the band gap of clean GaAs(100) to confirm the temperature-dependent photovoltaic effect on Fermi-level measurements by photoemission spectroscopy. These measurements support the recent calculations of Hecht in detail and show that such photovoltaic phenomena are large and reversible. Furthermore, we demonstrate that photoemission flux densities are sufficiently large to produce nearly saturated photoflattening of the bands within the depletion region of the semiconductor. The existence of this major correction to Fermi-level positions for low temperatures has serious implications for numerous low-temperature studies published over the past few years.

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