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Surface photovoltage effects in photoemission from metal/GaP(110) interfaces: Temperature-dependent Fermi level movement

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In recent experiments of metal deposition onto cleaved GaP(110) surfaces we have shown that light sources used in photoelectron spectroscopy may induce a surface photovoltage (SPV), which causes a substantial deviation from the ground state potential distribution, and may induce errors in the determination of band bending by photoemission. Here we analyze the temperaturedependent movement of the surface Fermi level in *n*- and *p*-type GaP(110) surfaces as a function of indium and silver deposition, taking into account the presence of the SPV. It is found that changes in the substrate temperature not only modify the adlayer morphology and metallicity, but also the surface electron-hole recombination rate. We observe that the temperaturedependent shift of the semiconductor core levels is always accompanied by a similar shift of the metal core level and Fermi edge, suggesting that the reversible temperaturedependent protect for metal/III-V semiconductor interfaces is related to the SPV, and does not represent a ground state property of the interfacial electronic structure. Implications of these results on current models concerning Schottky barrier formation are discussed.

I. INTRODUCTION

The investigation of the basic mechanisms controlling the Schottky barrier (SB) height in metal/semiconductor contacts is of great current interest. While most authors seem to agree that the final Schottky barrier height is determined through a filling of near-surface gap states by the metal electrons, the processes causing the adjustment of the surface Fermi level as a function of metal overlayer thickness, from submonolayer coverages onwards, are still at the center of intense debate.¹⁻³ The investigation of the interfaces formed at low temperature (LT), and their comparison with those grown at room temperature (RT) has been of crucial importance for testing the adequacy of the different Schottky-barrier models, since interfaces grown at low temperatures are believed to possess a higher degree of ideality. Recently, a series of experiments conducted under conditions of different doping and substrate temperature has led to the conclusion that, beyond the well-known defect and midgap state models, additional mechanisms are necessary in order to explain the astonishing variety of coverage- and temperaturedependent Fermi level movement behavior.4,5 One of these has been the so-called dynamic coupling model (DMC), which was put forward for an explanation of results which showed that-for lightly doped (LD) GaAs(110) interfaces-the amount of surface band bending can be changed gradually, from flat bands to the final pinning position, as a function of the substrate temperature. This apparently well established correlation between changes in substrate temperature and surface band bending has been questioned more recently, on the grounds that most of the photoelectron spectroscopy (PES) studies have apparently overlooked the possibility that the photoionization light could cause a nonequilibrium charge distribution which affect the results. We have in fact recently demonstrated that such nonequilibrium situation does occur for instance in PES measurements of different metals on GaP(110) substrates, and that the surface photovoltage (SPV) induced seriously affects the evaluation of the corresponding surface band bending.^{6,7} The effect was so significant for the analysis of Fermi level pinning that we concluded Ref. 6 recommending a careful revision of the previous photoemission work where the condition of Fermi-level equilibrium was implicitly assumed but not experimentally confirmed. A similar conclusion was independently arrived at by Hecht from calculations of SPV in metal/GaAs contacts for different substrate temperatures and doping levels.⁸ These calculations indicated that the recently reported dopant-dependent and temperature-dependent band bending behavior^{4,5} could be reinterpreted in light of the SPV effect. Given the large number of interface studies possibly affected by the surface photovoltage phenomenon, an experimental evaluation of different aspects of SPV in photoemission is of particular importance. Here we focus on the temperature dependence of the surface photovoltage, for Ag/GaP(110) and In/GaP(110). Our results for these interfaces present the experimental evidence illustrating the photovoltaic origin of the observed photoemission line shifts.

II. EXPERIMENTAL

The experiments were performed at the TGM5 and TGM6 toroidal grating monochromators on the wiggler/

undulator beamline at the BESSY (Berliner Speicherring-Gesellschaft für Synchrotronstrahlung) storage ring in Berlin. These beamlines give access to a high flux of photons from about 30 to 300 eV, with resolution $E/\Delta E \sim 1000$ under normal operating conditions. Data were recorded with a commercial angle-resolving photoelectron spectrometer (ARIES by VSW Ltd.) equipped with a moveable hemispherical electron energy analyzer. Overall resolution (electron plus photons) was about 60 meV at a photon energy of 55 eV, with photon flux about $(1-7) \times 10^{13}$ cm⁻² s⁻¹ as evaluated from the yield of a gold photodiode. If not otherwise specified, spectra were recorded under 40°C to 50°C angle of incidence of the light and normal emission (analyzer acceptance angle about 2°). The photon energy was determined to within 0.05 eV from core level emission excited by second-order light from the diffraction grating. The reference level for the spectra was measured from the Fermi edge of a gold foil in contact with the samples which was cleaned in situ. N-(sulphur)-doped $(2 \times 10^{17} \text{ to } 2 \times 10^{18} \text{ cm}^{-3})$ and p-(zinc)-doped (1.7 to 5.8×10^{17} cm⁻³) prenotched bars of GaP were cleaved in situ, at an operating pressure of 5×10^{-11} mbar. The crystals were mounted in ohmic contact with the specimen holder, which allowed cooling to about 100 K using liquid nitrogen. Since crystal temperatures were measured at the back of the crystal bars, the actual surface temperature is subject to a fairly large error. Usually, the experiments were performed simultaneously on n-type and p-type crystals, which were mounted close to each other, thus ensuring similar amounts of metal deposition, and the exclusion of extraneous shifts due to differences in photon energy, etc. Indium and silver were evaporated from baskets made of tungsten mesh and heated by tungsten wires; this arrangement gave reproducible evaporation rates, at operating pressures of 1×10^{-10} mbar. The evaporation rates were controlled in situ by a quartz microbalance and the nominal metal layer thicknesses are given in angstroms (Å).

III. RESULTS AND DISCUSSION

A. Evidence for surface photovoltage (SPV)

Typically, the formation of the SB is investigated by analyzing the movement of the surface Fermi level into the semiconductor gap as a function of the metal dose. The conventional method to determine the surface band bending by photoemission consists in measuring the position of the valence-band maximum of the clean semiconductor surface with respect to the Fermi level of a metal film in contact with the semiconductor, and in deriving the band bending from the energy shifts of the bulk component of a sharp and intense semiconductor core level. This method implicitly assumes that the condition of Fermi level equilibrium is met [Fig. 1(a)]. The situation of an illuminated thin metal film on top of a semiconductor surface is analogous to that of an open-circuit photodiode, however, and thus transport processes which may lead to a nonequilibrium situation are possible, if this interface is illuminated such as in a photoemission experiment.

There are indeed several examples in the literature illus-



FIG. 1. Schematic picture of the arrangement of electronic states in equilibrium (left), and under illumination from a light source which causes electron-hole pairs to be generated at the interface, giving rise to a surface photovoltage (SPV), which shifts the valence and core levels of the semiconductor substrate. Also shown is the energy difference Δ_n between the reference Fermi level (gold reference) and that of the metal overlayer on the semiconductor surface, which is used to measure the magnitude of SPV.

trating that illumination of such interfaces can cause a nonequilibrium situation,^{9,10} and that even the low light flux used in a photoemission experiment may be sufficient for such processes.^{11,12} The photoionization light can induce a surface photovoltage (SPV) leading to a nonequilibrium situation if the surface recombination of the electron-holes pairs created by the light and/or secondary processes can be neglected [Fig. 1(b)]. In this case, the electric field in the depletion region produces an accumulation of minority carriers at the surface, which will compensate the space charge, a situation best described by a quasi-Fermi level [dashed line in Fig. 1(b)]. This in turn causes a rigid shift of all semiconductor and metal levels. This shift will be of different sign for n-doped and for p-doped substrates; it must be taken into account for a correct determination of the surface band bending, or else the PES measurements will lead to erroneous conclusions.6 The presence of a SPV in our measurements on metals/GaP(110) can be easily inferred from the spectra of Fig. 2. They correspond to 5 Å of Ag deposited on a n-type and a p-type GaP(110) surface, for room temperature deposition (top) and for deposition at 100 K (bottom). A nonequilibrium situation for both substrate temperatures is clearly present: on p-type substrates the emission from the Fermi edge of Ag (shown on the right) is observed at higher kinetic energies than that from the gold reference (shown in the top spectrum), while on *n*-type substrates it occurs at lower kinetic energies. The opposite sign of the shifts for n and *p*-type materials rules out charging of the samples and/or of the metal clusters¹³ as a source for the shifts. From the schematic diagram in Fig. 1, and the direction of the shifts we conclude instead that they have a photovoltaic origin.

There are several ways in which the amount of light-induced, i.e., nonequilibrium, band bending may be measured. One of these is the Kelvin probe for the measurement of work function change.¹⁴ However, Kelvin probe measurements cannot differentiate between band bending changes and those caused by a change in the dipole contribution to the work function; at very low depositions, much below one monolayer, it may be reasonably safe to assume that no dipole layer change occurs, but this assumption breaks down



Kinetic energy with respect to Gold reference ${\rm E}_{\rm F}$ (eV)

FIG. 2. Influence of the SPV on the semiconductor core level and metal Fermi level of a 5 Å silver layer on GaP(110) at low (100 K) and room temperatures. Note different energy scales for core and valence level spectra. Also shown is the reference Fermi level determined from a gold plate in good electrical contact with the samples.

at higher coverages. In photoemission, the distance Δ_n (Δ_p) between the Fermi edge from the metal deposited onto a *n*-type (*p*-type) sample and that from the gold reference can be used as a measurement of the SPV effect; however, this method only gives accurate results once a Fermi edge evolves. One could therefore say that the two methods are complementary.

The magnitude of SPV will vary, in general, as a function of the incident light conditions, metal coverage and morphology, substrate temperature and doping concentration.¹⁵ We can see in Fig. 2, for instance, that for the same doping, light conditions and metal coverage, Δ_n is much bigger at 100 K (1 eV) than at 300 K (0.4 eV). Since SPV induces a shift on all levels of semiconductor substrate and metal overlayer, the Ga 3*d* peaks (shown on the left side) are also affected by the SPV. However, whereas the gold reference Fermi edge is a clear reference for evaluating the shift due to SPV on the metal valence-band emission, such a reference for the Ga(3*d*) peak does not exist. Still, the SPV effect can be easily detected on the Ga(3d) peaks from Fig. 2; at both RT and LT, the distance between the Ga(3d) core levels from a p-type and a n-type substrate is equal to within about 100 meV to the sum of Δ_n and Δ_p from the corresponding metal Fermi edges. Thus, the apparent difference in the energy positions of the core levels from the *n*- and *p*-doped substrate does not reflect any intrinsic property of the SB formation process, but for the major part is an artifact of the measurement technique. This need not necessarily be so, of course: what it means is that the surface Fermi levels in nand p-type GaP(110) for such a silver layer are already very close, and, presumably, close to the final position for a thick metal film. Since some difference in Fermi level evolution may occur at low coverages (although from the recent results concerning the SPV influence it seems that this might be much smaller than hitherto believed), the energy difference between the core levels and those of the Fermi edges obviously does not have to be equal.

B. Measurement of surface photovoltage by photoelectron spectroscopy

In order to investigate whether the differences reported in the band bending behavior of metal/III-V contacts as a function of the substrate temperature³⁻⁵ are real, or simply caused by SPV from the incident light, we need a precise knowledge of the limitations and capabilities of photoemission for measuring SPV. We notice from Fig. 2 that we can determine Δ_n and Δ_n , and measure the magnitude of the SPV. Thus, the corresponding substrate core level energies can be corrected for any SPV shifts to obtain the actual values for the Fermi level in the semiconductor gap.⁶ We have therefore a means of distinguishing between band bending and SPV effects. This possibility is very important considering the additional knowledge of the SB formation problem accessible by photoemission; in contrast to other techniques which can also be employed to measure SPV, PES has the advantage of providing important information on the evolution of the chemical, morphological, and metallic properties of the interface.^{3-7,13,16} Other authors¹⁷ have attempted to evaluate the magnitude of the SPV effect (using also PES) by studying the changes in the core level position of the semiconductor as a function of the incident photon flux; from the small (< 100 meV) changes observed in this way they concluded that only a small part of the changes in E_F as a function of temperature was due to SPV effects.¹⁷ Such method of measurement carries several inherent and obvious difficulties. This method may visualize the existence of SPV, but it does not provide an absolute measurement of the SPV effect. It is not clear that the absolute dark value (SPV = 0) can be achieved by reducing the initial photon flux by 3 or 4 orders of magnitude. In fact, the calculations of Hecht for 0.3 ML-Ti on GaAs(110)-LD at 100 K with an initial SPV of 240 meV predict that a reduction in photon flux by 4 orders of magnitude will only result in a decrease of SPV by less than 100 meV.8 The discharging time of the open circuit photodiode should also be considered in these experiments, in order to assure that the SPV effect induced by the first irradiation has completely disappeared before starting a new measurement with new photon flux conditions. Measurements of the time dependence of SPV carried out by Mao et al.¹⁴ on GaAs(110) substrates indicate that on lightly doped samples at low temperature, the discharging time is very large, up to several hours.

We have hence, preferred to use the most direct method for measuring the SPV induced by the synchrotron light, i.e., to determine the shifts Δ_n and Δ_p on metal valence-band emission. Figure 3, which illustrates the evolution of the PES features for indium deposited onto GaP(110) at 100 K, serves to discuss the coverage range where this method can be reasonably used. The main problem is its limitation for low metal coverages. The condition that a clear Fermi edge from the deposited metal is required can be somewhat relaxed, such that we can still correct for SPV at lower coverages. Even before a sharp metallic Fermi edge appears, some broad emission from the states near the top of the valence band, which eventually evolve into the Fermi edge, can be used for this purpose, although with a larger error margin. This is evident from the data in Fig. 3. The bottom curves on the right show the VBM part of the spectrum of n- and p-type GaP(110). The Fermi level for the clean surfaces is fairly close to the band edges. For a dose of 1 Å, some extra emission is evident, and for 3.4 Å a fairly sharp edge due to the valence-band emission of In within the semiconductor band gap is clearly detectable, and is unambiguously shifted to lower (higher) kinetic energies for the *n*-type (*p*-type) substrate. Higher coverages yield the effects demonstrated for



FIG. 3. Evolution of the metal states near E_F as a function of metal deposition, for indium on GaP(110), indicating the magnitude of SPV. Also shown are the Ga 3d and In 4d core levels.

J. Vac. Sci. Technol. A, Vol. 9, No. 3, May/Jun 1991

Ag deposition in Fig. 2. The corresponding core level spectra, shown on the left-hand side, also exhibit the shifts in energy seen on the Fermi edge; for a discussion of overlayer growth and interface chemistry, see.¹⁵ As in the case of silver overlayers, even very thick overlayers (60 Å, top spectra) still exhibit a sizeable SPV. In this context it is interesting to note that for Ag and In overlayers on GaAs(110) the surface Fermi levels for *n*-and *p*-type material were found to coincide only at very high coverages, beyond 30 Å.¹⁸ In the light of the present results one might speculate that the difference in the Fermi levels observed in metal/GaAs(110) overlayers at high coverage were also affected by SPV.

C. Fermi level movement for interfaces formed at low temperature: SPV effects

The evaluation of the true Fermi level position in the semiconductor band gap, i.e., after correction for SPV as explained above, is shown in Fig. 4 as a function of In coverage. The open symbols give the values without considering the SPV effect, whereas the solid symbols show the positions after correcting by the SPV (where applicable). Note the high similarity between our diagram without SPV correction (Fig. 4, open symbols) and the E_F diagram for metals on low-doped GaAs(110) at LT by Aldao et al. (see, for example Fig. 3 of Ref. 5): nearly flatbands for n- and p-type substrates at low metal coverages, and nearly symmetric behavior for n and p materials, with no apparent overshoot in the *p*-type curve. Note also, at higher coverages, the drop from flat bands towards midgap observed on the uncorrected *n*-type curve; it exhibits a close resemblance to the shape of the curve typically found for Schottky barriers formed at low temperatures on (low-doped) n-type III-V semiconductors.^{1,3-5,18} Hence, it seems that most of the conclusions from our data for metal/GaP(110) can be reasonably generalized to other metal/III-V (110) interfaces formed at low temperature, and in particular, to those grown on LD-GaAs(110).

Keeping in mind such considerations, let us examine the values from Fig. 4 after the SPV correction (solid symbols). The situation is quite different; the E_F positions from *n*- and



FIG. 4. Position of surface Fermi level in the semiconductor band gap, as a function of (nominal) metal coverage. Open symbols give the uncorrected values, obtained by the method commonly used in the literature up to now, whereas full symbols correspond to the real Fermi level position, i.e., after correction for surface photovoltage.

p-type substrates, which apparently were widely separated (1 eV) before the SPV correction, almost coincide now (within 100 meV). The drop in E_F typically observed at LT on low-doped *n*-type substrates which accompanies the appearance of metallicity at the interface, and that was often considered³ as experimental evidence for the metal-induced gap state (MIGS) model, disappears after SPV correction. Even considering the difficulty in measuring precisely the SPV at low coverages, our data clearly reveal that the Fermi level is pinned in a unique position for *n*- and *p*-type samples before the actual drop occurs. The drop, as well as the previous flat band conditions, are simply an artifact of the measurement technique. Experiments on GaP(110) surfaces with other metals (reactive and unreactive) confirm the generality of these conclusions, which are also in agreement with results reported recently by Waddill et al. for Bi on low-

doped GaAs(110) at LT¹⁹ and those of Mao et al. for Ag/

D. Temperature cycling experiments

GaAs(110).14

Here we investigate for a fixed metal coverage the effects of changing the temperature of the sample. Similar experiments were recently performed on LD-GaAs samples by Vitomirov *et al.* and Waddill *et al.*,^{4,5} and led these authors to propose a new model, the dynamic coupling model (DCM), which invokes tunneling of electrons from the bulk semiconductor through the depletion region into the metal. These authors concluded that the position of E_F changed progressively with T over a quite wide energy range, between flat band conditions and positions near midgap. Moreover, the Fermi level position was found to be reversible even in the absence of morphological changes due to temperature varia-



FIG. 5. Effect of temperature change on the magnitude of SPV, for a 15 Å indium layer on GaP(110), as evident from the core level (left) and valence level (right) spectrum, for *n*- as well as *p*-type substrates.

tions, such in the case of Ti on GaAs. This finding led us to examine the temperature-dependent Fermi level movement in the unreactive In/GaP(110) system.^{7,15} Our core and valence level results are shown in Fig. 5. The interface was grown at LT up to metal coverages of 60 Å; the substrate was then warmed up to 300 K, spectra were recorded, at this temperature, and again after recooling to 100 K. It is well known that indium spontaneously forms clusters at RT on GaP(110), while a much more laminar growth occurs at low temperature. In order to exclude morphology changes we focus first on the process of cooling down from 300 to 100 K. This is the process described in Fig. 5, for p-type (top) and ntype (down) substrates. The intensity and shape of the Ga(3d) and In(4d) core levels corroborate the absence of important changes in morphology during the process of cooling down. The energy of these peaks undergoes significant shifts, however. The substrate core levels (Ga3d) from *n*-type samples are shifted by around 0.5 eV to lower kinetic energies; the shift for the *p*-type substrate is 0.4 eV in the opposite direction. Therefore, if we derived the band bending changes only from such peaks, we would conclude that

upon cooling E_F moves up to 0.5 eV towards flat band conditions, similarly to what was reported for low temperature experiments on low-doped GaAs(110) by Weaver's group.⁴ A complete analysis of the data in Fig. 5, based on the observed SPV shifts in the Fermi edges shown on the righthand side, demonstrates that such a conclusion would be erroneous. A shift of approximately the same magnitude and sign than that of the semiconductor core levels is observed on the In 4d core levels and on the Fermi edge of the deposited metal. Moreover, a simple comparison of these Fermi edges from In with the gold reference for E_F (see Fig. 5) reveals the existence of a surface photovoltage (SPV), and a change of its magnitude as the temperature is lowered from 300 to 100 K.

This change in SPV can be easily understood considering that the change in substrate temperature will in general change interface morphology and electron-hole recombination rate. When no significant morphology changes occurs, the only important factor will be the recombination rate; this is what happens for In/GaP(110) upon cooling, and thus, the substantial decrease of the electron-hole recombination rate will cause the increase of SPV observed in the photoemission spectra, such as demonstrated in calculations for GaAs.⁸ When the morphology changes significantly with temperature, as happens usually in systems with a high tendency to cluster at RT, both factors must be considered; for such systems, warming up an interface grown at LT frees extensive areas of the semiconductor surface (which tends to increase SPV), but simultaneously increases the surface electron-hole recombination rate (which tends to reduce SPV). Thus, the SPV values achieved upon warming up in such systems will not be reproduced when the interface is recooled. The change in SPV observed here is therefore the factor responsible for the shifts observed on the semiconductor and metal levels, and hence, of the apparent band bending changes with temperature. Once the energies from Fig. 5 are corrected by the SPV, we find that the position of E_F within the semiconductor gap of both n- and p-type samples



FIG. 6. Effect of increasing metal coverage on the magnitude of the SPV, for indium deposited on GaP(110) at low temperature. The right panel shows the effect of warming this layer to room temperature, subsequent cooling to 100 K, and the deposition of a new layer of In onto the sample, on the size of the SPV.

does not move upon change of temperature.

We have represented in Fig. 6 the evolution of SPV for the In/GaP(110) interface, including changes in SPV due to increasing metal coverages for a given temperature (100 K), and changes due to temperature cycling for a given coverage (60 Å In). The energy distance $\Delta = \Delta_n + \Delta_n$ between the Fermi edges from In on n- and p-type samples serves to visualize, simultaneously for both doping types, the magnitude of the SPV (filled triangles). The same distance (Δ) between *n*- and *p*-type samples, but measured on the metal (In 4d) and semiconductor core levels (Ga 3d), is also shown in Fig. 6 (squares and circles, respectively). The figure shows clearly that for metal coverages high enough to measure the SPV by PES, the influence of the coverage and of the substrate temperature on the Ga(3d) energies can be explained almost entirely by the SPV; discrepancies (including n- and p-type contributions) between metal and semiconductor levels are always found to be less than 200 meV. In the second panel of Fig. 6, the 60 Å layer was warmed up to room temperature, with a slight increase of the SPV. This layer, having been grown at low temperature, is quite laminar and therefore facilitates surface discharging and reduces SPV^{6,15,19}; the magnitude of SPV is therefore quite small at the beginning of the temperature cycle. Upon warming to 300 K some minor enhancement of the SPV occurs; however, the biggest effect is cooling down to 100 K, where near flatband conditions are apparently restored; only upon new evaporation at LT, which covers the semiconductor surface. is the SPV decreased again (see Fig. 6). If we had started the temperature cycle at lower coverages, before the apparent drop in the E_F diagram occurs for *n*-type substrates, the surface photovoltage would have been higher. This would mean that upon warming and re-cooling, the temperatureindued differences in the SPV would have been very similar, because of overlayer clustering. The overall behavior would therefore have been similar to that presented in Fig. 6. We thus would have obtained very similar values of SPV for the starting and final points of the T cycle; a situation that, again, would resemble the experimental findings of Ref. 4.

E. Conclusions

In view of the similarities with previous results for GaAs, it seems plausible to generalize our conclusions about the temperature dependence of E_F movement to other metal/ III-V semiconductor interfaces. The interpretation of the temperature-cycling results for GaAs in terms of the present results would also explain the difference in behavior which were observed between systems with and without morphology changes. Recently, Chang et al.20 have carried out photoemission experiments at different substrate temperatures on clean GaAs(100) surfaces. These also support our present conclusions about the influence of surface photovoltage. In these experiments, the absence of any overlayer eliminates any changes in morphology or chemistry which may produce irreversible effects. These authors reported a reversible shift (0.75 eV) of the valence-band edge with temperature (for T between 60 and 550 K).²⁰ Our own experiments on low-doped GaAs(110) samples, reported elsewhere,²¹ confirm the conclusions from the GaP(110) and GaAs(100) experiments and support their extrapolation to previous published work. Finally, recent experiments at very low coverages on low-doped Ag/GaAS(110) interfaces, in which the Kelvin probe method and synchrotron radiation are combined, fully support our above conclusions for the temperature dependence, and extend them to the low coverage regime.14

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