

Schottky barrier and surface photovoltage induced by synchrotron radiation in GaP(110)/Ag

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(Received 17 April 1992; revised manuscript received 14 December 1992)

We measure the Schottky-barrier formation and the surface photovoltage induced by synchrotron radiation by complementing photoemission measurements with a Kelvin probe. This combined technique is applied to the Ag/GaP(110) interface, grown at room temperature. Large photovoltage shifts are observed up to high coverage. Based on decomposition of the Ga 3*d* core-level line shapes and surface photovoltage corrections, we conclude that the evolution of the Fermi level takes place during the deposition of about 15 Å, yielding a final Schottky barrier of 1.15 eV.

INTRODUCTION

The recent observation of surface photovoltage (SPV) induced by the photon beam in photoelectron-spectroscopy (PES) experiments on GaP and GaAs surfaces¹⁻³ has prompted renewed consideration of many results obtained by PES on metal-semiconductor interfaces in past years. For instance, the apparent Fermi-level movement upon metallization of GaAs at low temperature⁴ has been restudied both theoretically⁵ and experimentally.⁶ As for GaP, the Schottky-like behavior of metal-GaP interfaces proposed in 1987 (Ref. 7) on the basis of experimental data affected by SPV had been criticized by many authors.^{2,8,9} However, it should be noted that even new data taken on metal-GaP interfaces with awareness of SPV show a spread of values beyond the experimental errors.^{2,9,10} The underlying problem is that it is difficult to account quantitatively for SPV, especially in the lack of a sizable emission from the Fermi level, as in the case of clean semiconductor surfaces and for very low metal coverages. Probably, the data of Ref. 8 regarding metal-GaP interfaces are also affected by SPV shifts, as suggested by the broad range of initial band bending reported.

The real solution is to *measure* the SPV by using a Kelvin probe.¹¹ Mao and co-workers⁶ used a Kelvin probe combined with photoemission measurements for the first time. Their work clearly gives evidence of the SPV induced by synchrotron light and allows one to correct PES data for the SPV.

We present here a different use of a Kelvin probe associated with PES measurements which also allows one to account quantitatively for the SPV effect in every spectrum. This method offers several practical advantages, including greater simplicity, with respect to the previous one.⁶

We applied the method to the room-temperature-

grown interface GaP(110)/Ag. The value of the Schottky barrier precisely corrected for surface photovoltage is derived. The data are compared to other available results.

EXPERIMENT

The photoemission experiments were performed at the Laboratoire pour l'Utilisation du Rayonnement Electromagnétique (LURE) in Orsay using the undulator beam line SU(6). Moderately doped *n*-type GaP samples ($n = 5 \times 10^{17}$) were cleaved in a base pressure of 1×10^{-10} mbar. Good Ohmic contacts ensured an efficient electrical connection to the sample holder. Silver was sublimated using a tungsten filament at a rate of approximately 1 Å per minute, while the substrate was kept at room temperature. The pressure during Ag deposition was always below 6×10^{-10} mbar. Photoelectrons excited by $h\nu = 52$ eV were energy-analyzed by an angle-resolved hemispherical detector. In typical working conditions the overall resolution (checked with the line shape of the Fermi edge in a metal) was slightly better than 0.3 eV and it was mostly imputable to the electron analyzer. We used an angle of incidence of 45° and collected electrons at normal emission. The Fermi-level position in the spectra was determined by photoemission from a metallic sample.

The Kelvin-probe measurements were performed *in situ* after cleavage and also every time the surface was modified, i.e., after each Ag evaporation. A commercial Kelvin probe from Besocke Delta-PHI GmbH (Jülich), S model, was used. With this model the sample can be grounded and in this case the signal is extracted from the vibrating tip by means of a current-sensitive amplifier followed by a lock-in amplifier. The (fixed) operating frequency was about 180 Hz. The area of the vibrating tip was approximately equivalent to a circle of diameter 2.5 mm. As usual, the contact potential difference (CPD) be-

tween sample and reference tip was measured by means of a variable dc source and using the lock-in as a null-current meter.⁶ Another much larger dc voltage (20 V) was used to overcome the small CPD and generate a large signal in order to reproduce the sample-to-tip distance after a sample displacement. Since the method we employed for the Kelvin-probe measurements differs from the one reported in the literature,⁶ we would like to describe it in detail.

METHOD

The starting point is that a (relative) measurement of work function (WF) can be performed either by PES or with a Kelvin probe: In the former case WF is related to the cutoff of the secondary electron distribution (SED). In the present context the main difference between these two techniques is that in the case of photoemission (from a semiconductor) the WF measurement is potentially affected by SPV induced by the beam, whereas in the case of the Kelvin probe, the SPV is simply not present. The usual assumption that the electron affinity of a semiconductor is not changed by illumination⁶ seems reasonable. Unlike Ref. 6, we did *not* put the Kelvin-probe tip in the beam position: Therefore, we did not measure the beam-induced SPV *directly*. There are many practical advantages in having the tip away from the beam. First, there is no necessity to perform PES at grazing incidence. Second, there is no need to be concerned with the sample illumination being the same with and without the tip. Third, the problem of photoemission current possibly affecting the CPD measurement is completely eliminated. Finally, the whole operation is easier to perform.

As shown in Fig. 1, we first calibrate the apparatus for the work-function measurement (PES+Kelvin probe) with a metal [panel (a)]. We obtain in this way the work function of the sample W_{met} relative to the work functions of the electron analyzer (PES) and the reference electrode (Kelvin probe). Next, we study a semiconductor [panel (b)] and in this case we allow for a SPV induced by the beam in PES. As a consequence, PES and Kelvin probe no longer yield WF values equally shifted with respect to the metal calibration, the difference being just the precise *measurement of the SPV shift*. The result can be used to correct the apparent positions of peaks in photoemission spectra. Of course, these spectra should be collected with the same photon flux as the SED spectrum, but this is by no means a limitation. Every time a parameter affecting the photon flux (grating, photon energy, slits) is varied, it is sufficient to collect a spectrum of SED cutoff in addition to the spectra of interest. Even the exponential decrease of beam intensity in storage rings is not a problem since the beam lifetime is much larger than the acquisition time.

The above-mentioned procedure (SED cutoff and Kelvin-probe measurements) should be repeated after any change in surface conditions is made—for instance, after gas exposure or metal evaporation. In fact, any surface change may bring in new values of band bending, work function, and SPV shift.

The viability of the method can be tested by applying it to two metals: in fact, the two work functions should

differ by the same amount when measured by both PES and Kelvin probe. We verified that this is indeed the case with thick layers of Ag and Au evaporated onto a GaP substrate. We measured $W_{\text{Au}} - W_{\text{Ag}} = 0.90$ eV with both techniques to within 25 meV.

The sensitivity of the CPD determination with the Kelvin probe in our experimental conditions was 5–10 meV and the reproducibility was excellent. However, in real life the error is definitely larger due to a number of reasons. First, of all, it is well known that a cleaved surface exhibits non-negligible variations of the work func-

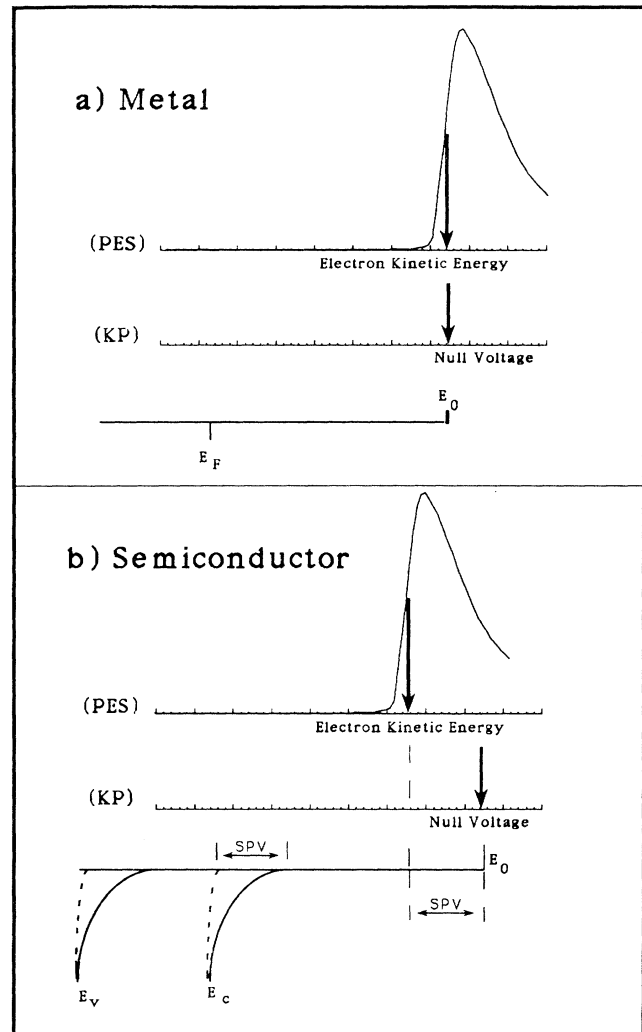


FIG. 1. Schematic view of the method for measuring surface photovoltage by PES+Kelvin probe. Calibration with a metal is shown in panel (a): the work-function values obtained by PES and Kelvin probe are pointed out by the arrows. Panel (b) shows instead the case of a semiconductor with a surface photovoltage induced by synchrotron radiation: The Kelvin-probe measurement yields the real shift with respect to the metal, while in PES there is an additional shift due to SPV. Reference is made to an *n*-type sample, whose space-charge region is sketched in the bottom part of the figure, with and without SPV. E_0 is the vacuum level; E_v and E_c are the band edges.

tion from point to point, presumably due to cleavage defects.¹² Both the Kelvin-probe tip and the synchrotron-radiation beam average these fluctuations over a certain area which is not the same because the tip is larger than the area probed by PES. Nevertheless, in our experience this problem is greatly reduced provided the sample position is carefully reproduced during an experimental cycle. Other sources of errors are related to the presence of clusters, as we will discuss later on.

In conclusion, we evaluate the error associated with a single SPV determination as ± 50 meV. However, in comparing results obtained with different techniques [for example, Schottky barriers by PES + Kelvin probe and by BEEM (ballistic electron emission microscopy) (Ref. 10) or electrical measurement], we think that a more conservative error bar of ± 100 meV should be used.

LIMITS OF THE METHOD

The above-mentioned method suffers from a serious limit with *inhomogeneous* surfaces, as in the case of a growth by islands, in the sense that its application either requires great care or is totally hampered.

Roughly speaking, one can assume that in this case the surface is composed of two different parts *A* and *B* with areas S_A and S_B and work functions W_A and W_B . In such a nonuniform situation, PES and the Kelvin probe do not measure precisely the same parameter as in the case of homogeneous surfaces. The SED cutoff in PES is determined by the area with lower WF, while the Kelvin probe measures a value falling between W_A and W_B , somehow dependent upon the space-charge regions at and around the *A* and *B* regions. For the sake of simplicity we can assume that a Kelvin probe measures just the average of W_A and W_B with weights S_A and S_B , as in the case of patches on a metallic surface.¹³

Obviously, any system is homogeneous both before the evaporation process (clean surface) and after a certain coverage, when a continuous film is developed on the surface. In between these boundaries, there is a range of coverage in which patches with WF W_A on a substrate with WF W_B are present. A criterion for estimating the extent of this range is provided by the persistence of surface components in the spectra of substrate core levels. When the surface component disappears, upon overlayer deposition, then the system can be considered homogeneous.

The case of Ag deposited on GaP(110) at room temperature is a very peculiar one. First, clusters certainly dominate the growth morphology.^{2,8,9,14} Second, the surface component in the Ga 3*d* core level survives up to very large coverages,^{9,14} and indeed it can be identified in *all* our spectra, the last coverage being 50 Å. However, there is a fortuitous circumstance that compensates for these unfavorable premises: The work functions of Ag and clean-cleaved *n*-type GaP(110) are *very close*.¹⁵

Therefore, the *work-function inhomogeneity* in Ag/GaP(110) is expected to be small, in spite of the nonuniform growth. Then, the above-mentioned method can be applied to the present case, as we will discuss both in the next section and in the Appendix.

RESULTS AND DISCUSSION

The photoemission part of the experiment consisted in collecting spectra of the valence band (VB), Ga 3*d* core level, and secondary electron distribution cutoff after cleavage and following each Ag deposition. Although it would have been desirable to investigate also the P 2*p* core level, we studied Ga 3*d* alone since in this way we avoided a change of grating and were able to keep the photon energy constant (52 eV), thereby eliminating possible sources of error.

Figure 2 shows a set of Ga 3*d* core levels for increasing thicknesses of deposited silver. The inset shows instead the VB line shape of the clean surface as measured in normal emission. Since the data analysis yielding the height of the Schottky barrier only requires the spectra reported in Fig. 2, the whole set of VB spectra as a function of coverage is not shown here.

A major problem in this kind of spectroscopy concerns the core-level line shape since in general it contains other contributions in addition to the bulk term. As a rule, core levels of surface atoms as well as segregated or alloyed atoms exhibit chemical shifts with respect to core levels of bulk atoms. On the other hand, only the bulk

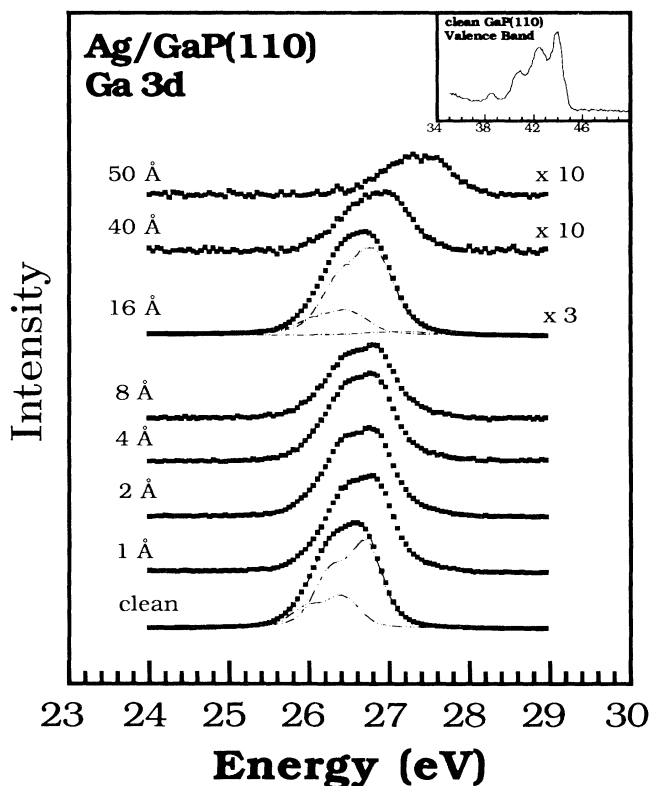


FIG. 2. Set of Ga 3*d* core levels as measured in photoemission for increasing Ag coverage with the following conditions: $h\nu = 52$ eV, angle of incidence 45° , normal emission. The results of a least-squares deconvolution fit are reported for the clean surface and the 16-Å coverage. The inset shows the valence-band line shape for the clean surface, in the same experimental conditions.

term is relevant in the present study since its kinetic energy tracks band-bending variations. As a consequence, the Ga 3d line shapes of Fig. 2 must be deconvolved into different components. We performed such a deconvolution by means of a computer program, making use of a least-squares algorithm. The program fits a core-level component with a convolution of a Gaussian and a Lorentzian and allows one to substitute the Lorentzian with a Doniach-Sunjic line shape.²⁰ The fitting was based on general ideas and starting values of the parameters taken from the abundant recent literature on the subject.^{8,9,14,20,21} The results were quite satisfactory. As an example, line-shape deconvolutions for the clean surface and for a coverage of 16 Å are reported in Fig. 2. In the former case only a second component (due to the surface) in addition to the main bulk component is needed to obtain a very good fit. The chemical shift with respect to the bulk term is 0.3 eV, in agreement with previous works.^{21,22} On the other hand, a third extra component clearly develops on the low-binding-energy side of the spectrum as soon as Ag is deposited, even at submonolayer coverages.⁹ Therefore, we confirm the small but detectable reactivity of Ag with GaP already reported by other authors, using photoemission^{8,9} as well as Auger line-shape analysis.²³ As to the surface component, it survives up to very large coverages, in agreement with Refs. 9 and 14. This is a consequence of the growth by three-dimensional (3D) clusters that leaves part of the surface uncovered.

One point we would like to comment on is the choice of the linewidth in the deconvolution fit. We fixed the Lorentzian width at 0.18 eV, in agreement with the literature.^{8,14,21} As to the Gaussian width, in the case of the clean surface the best fits were obtained with a value (0.37 eV) definitely larger than expected on the basis of the experimental resolution (<0.3 eV). We believe this finding reflects *surface-potential inhomogeneities*, as already observed at GaP cleavage surfaces.¹² Interestingly, the Gaussian widths of all Ga 3d components become up to 50 meV larger upon Ag deposition. This result seems very sound since by keeping the same linewidth of the clean surface, the ratio of the surface-to-bulk components *increases* upon metal coverage (which is physically unacceptable), and the only way to let it decrease is to increase the (Gaussian) linewidth. Incidentally, changing the width of the *reacted* component alone does not help, because of its small contribution to the total core-level emission. A possible explanation of this effect is again in terms of small *surface-potential inhomogeneities* in the intercluster region.²⁴ The effect is rather small, being of the order of 50 meV, and is not relevant for the peak positions, which are almost independent from this parameter. However, the ratio of the surface-to-bulk components depends *significantly* upon the choice of the linewidth. Since the latter can only be *estimated*, reliable attenuation curves for the surface and reacted components cannot be derived from the data. We believe this is the first case, in photoemission spectroscopy, in which *limits* of the core-level line-shape analysis of *intrinsic* type (not due to poor statistics) are observed and reported.

In conclusion, the deconvolution fit allowed us to ex-

tract the bulk term from the Ga 3d core-level line shape. The “apparent” band-bending variation upon Ag coverage was then inferred. In the particular case of Ag, we realized *a posteriori* that the error we would have made by taking the Ga 3d line shape as a whole instead of its bulk component would have been negligible. However, we believe this is not true in general, as recognized by many authors^{8,9,14} as well as proved by our own preliminary data on Au/GaP.

Due to the fact that at room temperature Ag grows by 3D clusters on GaP(110), the application of the above-mentioned method based on PES and a Kelvin probe for measuring a SPV shift is problematical, since we are dealing with an *inhomogeneous* surface. Moreover, there is evidence that part of the surface remains uncovered even at the largest investigated coverages. However, as we have already mentioned, the work functions of Ag and cleaved GaP are practically identical. Therefore, the variation of the work function across the surface is expected to be small and in this case the PES and Kelvin-probe techniques do measure the same physical parameter in spite of the nonuniform growth. Indeed, we have verified with Kelvin-probe measurements that the same compensating voltage is required for the clean surface and after Ag depositions larger than about 30 Å. The Kelvin-probe results are discussed in detail in the Appendix.

In Fig. 3 the SPV corrections to the Ga 3d core-level positions are reported as a function of coverage. The

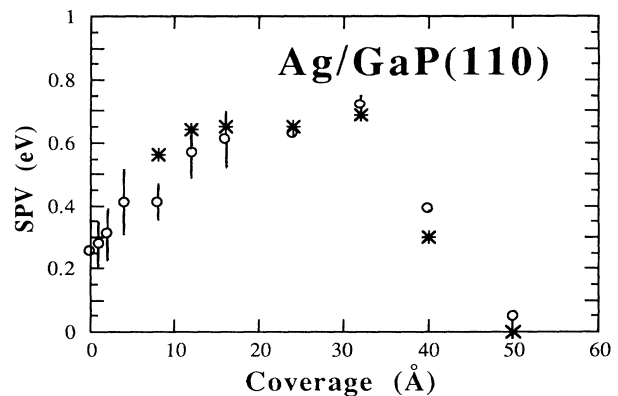


FIG. 3. Surface photovoltage shifts as measured with a Kelvin probe for various Ag coverages on GaP(110) (open circles). All data points are affected by an error of the order of ± 50 meV (not shown). The error bar reported for some points instead accounts for uncertainties originating from surface inhomogeneities. In particular, the upper extreme of the error bar represents raw SPV as measured with the method based on PES and Kelvin probe, while the lower extreme accounts for surface inhomogeneity, as described in the text. The extent of the error bars is the same as the “deviation” of Fig. 5, and the data point is tentatively drawn in the middle of each bar. The asterisks represent instead the SPV directly inferred from the shift of the Fermi level with respect to the metallic value, in photoemission spectra. Within the errors, the two sets of data (circles and asterisks) are in agreement.

open symbols are calculated according to the method described in the previous section. The error bars account for uncertainties due to surface inhomogeneities, as discussed in the Appendix. The solid symbols instead are directly derived from the Fermi-level displacement with respect to the metallic value. Whenever the comparison is possible, the agreement is very good, implying that the approximations made to account for surface inhomogeneity are indeed sensible. We emphasize the importance of using a Kelvin probe for measuring SPV shifts, since this is the *only* viable method in the case of clean surfaces and very low metal coverages (monolayer and submonolayer regimes).

Figure 3 shows that the magnitude of SPV is strongly coverage dependent. For the clean surface the SPV shift amounts to 0.25 eV, against a band bending of 0.50 eV, as measured in the present work and in previous ones.¹⁷ Therefore, we can say that in our experimental conditions the SPV of the clean surface was certainly relevant but not saturated. We anticipate that the subsequent increase of SPV upon Ag coverage almost tracks the Fermi-level movement in the forbidden gap (see Fig. 4). The data analysis shows that a complete flattening of the bands is never achieved. We conclude that, except for the clean surface, the *residual band bending* rather than the SPV is approximately constant during the interface formation. Figure 3 also shows that the SPV in GaP(110)/Ag vanishes at fairly large coverages (larger than ~ 40 Å) in agreement with Refs. 1 and 2. This finding is probably related to the persistence of core-level signals characteristic of the surface up to high coverages. Both phenomena are indicative of the peculiar growth morphology already discussed.

In Fig. 4 the evolution of the Fermi level with Ag deposition is reported. In particular, the solid circles

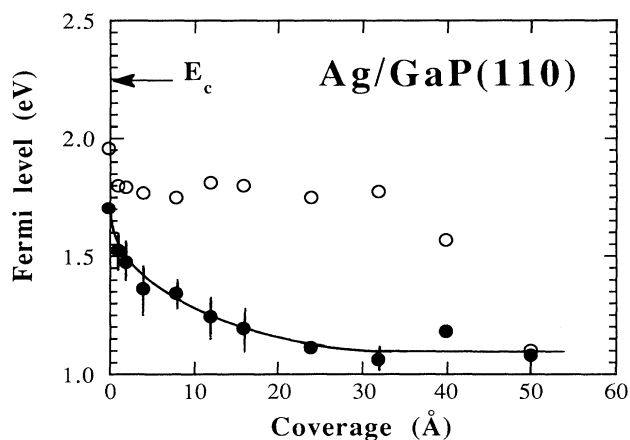


FIG. 4. Fermi-level evolution at Ag/GaP(110) upon Ag coverage. Open circles are obtained without accounting for the SPV-induced shifts, the initial value being inferred by linear extrapolation of the valence-band edge. Solid circles are instead obtained by correcting the previous values for the SPV shifts reported in Fig. 3. The energy scale is referenced to the top of the valence band. The arrow indicates the bottom of the conduction band. The solid line is a guide for the eye.

represent the experimental data corrected for SPV (see Fig. 3), while the open circles represent the results without SPV correction.

It appears from Fig. 4 that the development of the Schottky barrier (SB) for Ag on GaP(110) takes place over a coverage of about 15 Å, in substantial agreement with Ref. 25. Should this behavior be confirmed with other metals on GaP(110), the result would imply an important difference between the GaAs and GaP cleaved surfaces. In fact, it is well known that in metal/GaAs(110) interfaces the final value of the SB is attained at less than one monolayer.²⁶ This was indeed one of the key points supporting the defect model.²⁶ A marked difference between GaAs and GaP in this respect might be indicative of a different activation energy for defect formation and possibly different mechanisms of Fermi-level pinning in the two cases.

Figure 4 shows that after an initial movement terminating at about 15 Å, the Fermi level is stable, within the experimental errors, even at the highest investigated coverages. This result agrees with Ref. 9, while it is at variance with Ref. 2. However, in consideration of the large error inherent to core-level spectroscopy at coverages larger than, say, 30 or 40 Å, it is not surprising that different authors reach slightly different conclusions. The important point is that a global inspection of Fig. 4 strongly suggests that (i) the SB formation for Ag on GaP(110) terminates at about 10–15 Å, and (ii) any further movement of the Fermi level at coverages larger than about 30 Å is *uncertain*, probably spurious, and at any rate does not affect the SB height. In this respect we disagree with the conclusions of Ref. 2.

As to the important issue of the SB height, its value is determined by the band-bending variation upon metal coverage and also by the initial position of the Fermi level (E_F) which in our case is $E_F - E_V = 1.70 \pm 0.05$ eV. This value derives from an evaluation of E_V by linear extrapolation of the leading edge of the VB (inset of Fig. 2) and is already corrected for the SPV-induced shift and the instrumental broadening. The latter correction, which we estimate to be 0.1 eV, is necessary because this broadening introduces a systematic shift to larger kinetic energies of the VB edge.^{8,27} Incidentally, the E_F determination does not require such a correction for the obvious reason that the instrumental broadening does not shift the inflection point of a curve. The initial positions of E_F were consistently the same within the experimental error for three cleaves of the same bar. The above-quoted value is also in agreement with previous determinations.^{16,17}

In conclusion, we obtain for the SB of Ag on GaP(110) the following value: 1.15 ± 0.05 eV. We stress again that the above-quoted error only accounts for the reproducibility of the measurement, while a larger error ($\sim \pm 0.1$ eV) would better account for systematic errors when comparing results obtained with different techniques. We wish to point out that the above-reported value (1.15 eV) is in excellent agreement with the value (1.1 eV) already published by some of the authors²⁵ before the relevance of the SPV effect in photoemission with powerful light sources was recognized. However, this is not surprising

since the value of Ref. 25 was obtained with the photons emerging from a bending magnet of Adone in Frascati. Adone being a first-generation storage ring, the photon flux was sufficiently low to make the SPV effect irrelevant. As to the comparison with other data, there is a reasonable agreement with the BEEM result,¹⁰ that is, 1.27 eV. We do disagree instead with the datum of Ref. 2 (1.5 eV). It is difficult to reconcile the latter result with the present data. In Ref. 2 the initial value of the Fermi-level evolution is derived by Ga 3*d* core-level spectra of both *n*-type and *p*-type samples at low temperature, in a quasisaturated SPV condition, without resorting to valence-band extrapolation.²⁸ The error inherent in such a method should be carefully analyzed.

Other data based on PES are either in surprising agreement with the present result (1.23 eV from Ref. 8) or in partial disagreement (1.37 eV of Ref. 9). In these works the SPV was not accounted for, either through lack of awareness⁸ or because it was estimated to be negligible (although not measured).⁹ Finally, the present result is in very good agreement with the only measurement of SB height on thick Ag/GaP interfaces (1.20 eV) obtained by photoresponse.²⁹

CONCLUSIONS

We measured SPV shifts induced by the synchrotron-radiation beam in photoemission measurements with a Kelvin probe. We applied this method to study the room-temperature-grown Ag/GaP(110) interface. Problems brought about by lack of homogeneity along the surface are discussed: The approximations made to overcome them are accounted for by a *larger* error bar affecting the SPV measurements in a certain coverage range. However, these problems do not affect the main physical results presented. By using a deconvolution program to extract the bulk component from the Ga 3*d* core level and correcting for the SPV, we were able to follow the band-bending changes induced by Ag coverage. While in such a system the SPV shifts are relevant up to a coverage of about 50 Å, the Fermi-level movement ends after deposition of about 15 Å. The final Schottky-barrier height is 1.15 eV, in good agreement with results obtained with different techniques which are not affected by SPV.

ACKNOWLEDGMENTS

We would like to thank P. Mahowald for the computer program used in the data analysis.

APPENDIX

The result obtained with the Kelvin probe are shown in Fig. 5, where variations of the compensating voltage with respect to the initial value 0.450 ± 0.010 V are reported as a function of Ag coverage. These data confirm that the clean and Ag-covered GaP surfaces have identical work functions, within the experimental accuracy. Figure 5 also shows that for intermediate coverages the WF of the system, as measured by a Kelvin probe, is larger than the initial and final values, the deviation being on the average 100–150 meV. In principle, this behavior can be ex-

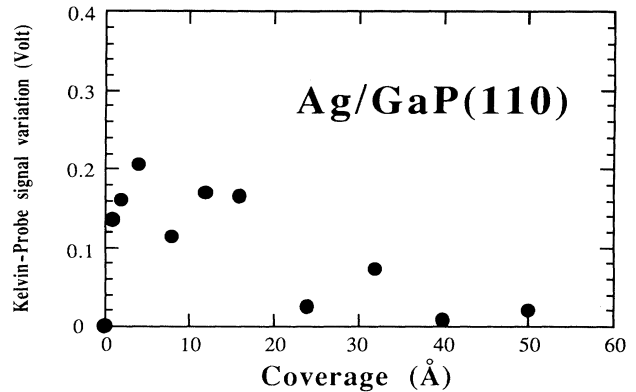


FIG. 5. Variations of the Kelvin-probe signal (compensating voltage) with respect to the initial value 0.450 ± 0.010 V at Ag/GaP(110), for various coverages. Initial and final work functions are the same within the experimental accuracy.

plained by two different physical mechanisms. The first reason is a *larger* WF in clusters of Ag than in bulk Ag.³⁰ The second one is a possible variation of the surface potential in the intercluster region.²⁴ We think the first hypothesis is more likely, since an evaluation of the latter effect shows it cannot account for the results of Fig. 5. In fact, although a numerical calculation has recently shown that in general the depletion length *along the surface* is smaller than in the perpendicular direction,²⁴ we estimate that in our case the depletion length is much larger than the average cluster distance (perhaps with the exception of the submonolayer regime, which is not at issue here).³¹ Furthermore, from the above-reported analysis of the spectral linewidths, we conclude that surface-potential inhomogeneities in the intercluster region are only of the order of 50 meV throughout the investigated coverage range.

At any rate, within the limits of the present article the physical origin of the 100–150-meV deviation of Fig. 5 is irrelevant. The important point is that for coverages between 1 and 30 Å the system is actually inhomogeneous. In these conditions a Kelvin probe measures an effective work function, intermediate between the one of the clusters and the one of the bare substrate. On the other hand, PES measures the lower WF and in addition its value can be *further decreased* by a SPV shift. This analysis leads to the following conclusions: (i) By treating the Ag/GaP system as if it were homogeneous, one *overestimates* the SPV; (ii) the *maximum* error in this case is given just by the deviation plotted in Fig. 5, namely, 100–150 meV in the range 1–30 Å; and (iii) the real SPV shift falls between an upper bound calculated by completely ignoring the lack of homogeneity and a lower bound obtained by fully subtracting the results of Fig. 5 from the previous value to correct the data. The correctness of these conclusions can be easily verified by comparing the SPV shifts obtained in this way with the SPV values directly given by the shifts of the Fermi edge in photoemission spectra with respect to the Fermi edge of a metallic sample (see Fig. 4). In our case this comparison is meaningful only for coverages larger than 8 Å.

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