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TITLE: Au and Al SCHOTTKY BARRIER FORMATION ON GaAs (100) surfaces PREPARED BY THERMAL DESORPTION OF A PROTECTIVE ARSENIC COATING

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Summary

"Au and Al Schottky Barrier Formation on GaAs (100) Surfaces Prepared by Thermal Desorption of a Protective Arsenic Coating"

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Photoelectron spectroscopy has been used as a tool to investigate the initial stages of Schottky barrier formation on GaAs (100) surfaces. This is a popular technique that has been used by many researchers in the past to measure the band bending (or shift) of the valence band and conduction band (a measure of the Schottky barrier shift), while the Fermi level remains fixed at the system ground (i.e., the ground of the spectrometer). Metal deposition on a semiconductor surface can alter the Schottky barrier at the surface and pin the Fermi level near the middle of the energy gap. Extremely clean and crystallographically perfect surfaces are required in this study. Toward this end, a method of protecting the GaAs surface was employed which consists of capping the GaAs surface with a layer of As. Upon introduction into the high vacuum system the As is thermally desorbed, revealing a pure GaAs surface.

Our work was motivated by a previous study (Brillson et al.) on similarly capped specimens, which suggested that metal overlayers do not pin the Schottky barrier in GaAs. Barrier heights varied by as much as 0.75 eV between Al and Au overlayers. This large energy range is a striking result in view of the fact that a considerable number of prior studies on both (110) and (100) surfaces have found that all metals will pin within a narrow (0.25 eV) range at midgap. We repeated the measurements of Brillson on the identically doped samples used in their study using the two extreme range metals of Au and Al as overlayers. We found that the barrier height measurements on low doped n-type samples used in this work and in the previous work are affected by photovoltaic effects, even at room temperature. This was determined from taking spectra at a number of temperatures between 20 K and room temperature and looking for shifts. At room temperature there is still a non-zero slope to the photovoltaic shift. Photovoltaic shifts are seen normally below $\approx$ 250 K where the barrier height is sufficient to prevent thermionic emission of electrons from the bulk to the surface and thus shorting out the photovoltaic effect. The large, 0.85 eV, barrier in GaAS, however, raises this temperature to above 300 K. Heavily doped samples showed no photovoltaic effect.

With these techniques the Schottky barrier pinning between Au and Al was found to range within 0.25 eV. These remaining differences still need further investigation.

Au and Al Schottky Barrier Formation on GaAs (100) surfaces prepared by thermal desorption of a protective arsenic coating

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Soft x-ray photoemission spectroscopy has been used to investigate the initial stages of Schottky barrier formation on GaAs (100) surfaces prepared by the thermal desorption of an As cap. This work was motivated by a previous study [Brillson, et al., J. Vac. Sci. Tech. B 6 1263 (1988)] of identically grown and capped samples which reported "unpinned" Schottky barrier formation, with barrier heights falling over a wide range (0.75 eV) of energies. This large energy range is a striking result, as a considerable number of prior studies on both (110) and (100) surfaces have found that all metals will pin in a narrow (0.25 eV) range near midgap. Since Au and Al are the extremes of the larger 0.75 eV span of Schottky barriers, we have studied the deposition of these two metals. We found that the barrier height measurements on the low doped n-type samples used in this work and in the paper referenced above are affected by photovoltaic effects, even at room temperature. These photovoltaic effects cause shifts in the band bending which are an artifact of the measurement. We also performed measurements on more heavily doped samples, and the photovoltaic effects were removed. In addition, we point out that Au-Ga alloying makes the case of Au potentially misleading. With the photovoltaic effects

removed, and the Au-Ga alloying carefully accounted for, we found that the barriers heights for Au and Al differ by only 0.25 eV.

Introduction

It has recently been reported that a wide range (0.75 eV) of Schottky barrier heights could be obtained on the GaAs (100) surface prepared by MBE (ref.1). This is an extremely interesting result, which could be of great practical importance. However, the measurements have yet to be reproduced by any other group. Because of this, we have undertaken an independent study of identical GaAs samples, in the hope of confirming and understanding the previous work.

Prior to the work of ref. 1, it had been found by many workers that the interfacial Fermi level position for metal-GaAs systems fell in a narrow energy range near midgap for either the (110) or (100) surface. The new result of the wide range of barrier heights was explained in terms of two factors. First, the high quality of the non arsenic rich MBE material used in ref. 1 resulted in a reduction of the density of electrically active near-surface defects, such as the As antisite (ref. 2,3). More importantly, in order to explain the inability of metal induced gap states (MIGS) (ref. 4-8) to pin the surface Fermi level at mid-gap, it was proposed that the (100) surface was terminated in an insulating reconstruction which would screen out these pinning states (ref. 9). This issue will be discussed in detail in a separate paper (ref. 10).

We have found that there are several complications to the measurement and analysis of the photoemission data taken during the deposition of Al and Au on these surfaces. We performed experiments on both $n=5x10^{16}$ cm^{-3} (as was used in ref .1) and on $n=5x10^{18}$ cm^{-3} doped material. In the $n=5x10^{16}$ cm^{-3} samples we found that there was a significant photovoltaic band flattening (ref. 11,12) *even at room temperature*. This photovoltage can occur because of the combination of the large n-type barrier height (≈0.85eV) and low doping ($5x10^{16}$ cm^{-3}) of the samples used here and in the n-type work of ref. 1. As will be

discussed, these photovoltage shifts can lead to errors in the band bending measurements for which it is difficult to correct. We do not find a large range of barrier heights, but instead a difference between the two metals of only 0.25 eV, which is quite similar to the values commonly reported in the literature, for example, in ref. 13. We see large shifts in the surface Fermi level during the metallization *only on the low doped samples which show the surface photovoltaic effect.* In addition to the photovoltaic problem, alloying between Au and Ga can complicate the extraction of band bending from the Au photoemission data.

Experimental

The photoemission experiments were performed on the grasshopper monochromator beamline III-1 at the Stanford Synchrotron Radiation Laboratory (SSRL), beamline U3C at the National Synchrotron Light Source (NSLS), and the monochromatized He discharge lamp at Stanford Electronics Laboratories (SEL). In the work at SSRL and SEL, data was taken using a Phi cylindrical mirror analyzer, while at NSLS, a VSW hemispherical analyzer was used. The GaAs was epitaxially grown at IBM on degenerately doped substrates, and was doped with 5 X 10^{16} cm^{-3} or 5 X 10^{18} cm^{-3} Si, and then given a protective coating of arsenic. These samples were prepared in the same laboratory as those of ref. 1 by the same technique and were believed to be as identical as possible. The wafers were shipped from IBM to Stanford under vacuum where they were stored in vacuum at approximately 2 X 10^{-7} torr. The samples were briefly (< 5min.) exposed to air while being indium bonded to a molybdenum sample holder and loaded into the analysis chamber. Photoemission spectra taken before annealing show a single As 3*d* peak and no Ga 3*d* emission, indicating that the arsenic cap was intact.

In order to remove the As coat, the samples were annealed by a resistively heated Ta filament mounted behind the Mo sample holder, and the temperature was monitored by a chromel-alumel thermocouple. In addition to the In bonding, the samples were held in the front by 4 small Pt clips. The heating cycles were typically a 15 min. ramp to the maximum temperature, which was held constant for 8 min. The maximum chamber

pressure during decapping was about 1 X 10^{-9} torr and was between 1 and 3 X 10^{-10} torr at the end of the 8 min. Details of the (100) surfaces produced in this way will be reported elsewhere (ref. 10). Au and Al depositions were made using resistively heated tungsten baskets, and the thicknesses were measured using a quartz oscillator thickness monitor. Au depositions were done at pressures in the low 10^{-10} torr range, and the Al depositions were done in the high 10^{-10} torr range.

Schottky Barrier Measurement using photoemission

Photoemission has been used extensively by many workers to measure band bending in semiconductors as a function of the deposition of various materials. This is typically done by monitoring the movement of electronic core levels, such as the As 3d and Ga 3d. The binding energy of these core levels will shift (bend) with the valence band and conduction band, while the Fermi level remains fixed with the system ground.

During our studies of the Schottky barrier formation, several difficulties became apparent. Since our samples were identical to those in ref. 1, these difficulties must have also been present in that prior work.

Photovoltaic Band Flattening at Room Temperature

As we stated above in the experimental section, we set out to study samples which were as identical as possible to those used in ref. 1. The first wafer we studied was made to the specifications of the earlier investigators, and was an n-type epi-layer doped with $5x10^{16}$ cm^{-3} Si. We studied the deposition of several different metals on samples taken from this wafer and found that the photoemission peaks moved around significantly, suggesting that there was a great deal of movement in the surface Fermi level with metal deposition. Eventually we realized that the large shifts in the photoemission peaks were not due to movement of the dark Fermi level, but rather to photovoltaic band flattening (ref. 11,12) caused by electron-hole pair formation in the depletion region. This was at first surprising, since the calculations (ref. 11) indicated that there should be no photovoltaic effect at room temperature, even for doping as low as 1 x 10^{16} cm^{-3}. The calculations of

ref. 11 were made for a typical barrier height of 0.65 eV, and showed that there will be a photovoltaic shift in the spectra for temperatures at or below 250K. Above this temperature, thermionic emission of electrons from the bulk to the surface will prevent the development of a large photovoltage, and the measurements will give the true, dark band bending. The difference is that the n-type barrier height in our case is closer to 0.85 eV. This is important because the barrier height appears exponentially in the equations of ref. 11 along with the temperature. The effect of this barrier height difference will be roughly to shift the temperature dependence by a factor of 0.85/0.65, meaning that the onset of the photovoltaic effect will occur closer to 327K, or 54C. A simple way to check for photovoltages at room temperature is to take spectra as a function of temperature and look for shifts. A plot of the change in the As 3d peak position with temperature (whose shift represents the apparent change in barrier height due to the photovoltaic band flattening) is given in fig. 1. This reversible shift during cooling and warming conclusively shows the surface photovoltage at 25C. Although our temperature measurement was not calibrated for this temperature range, the dependence is similar to that predicted by ref. 11.

This effect can partially explain the wide range of initial positions for the Fermi level reported in ref. 1. In UHV, the sample will tend to equilibrate to room temperature slowly through the last 50C or so. Depending on how long the sample was allowed to cool, the measured Fermi level position can vary over a range of a few tenths of an electron volt. To a lesser extent, the barrier height measurements will depend on the photon energy and flux used (ref. 11). This could lead to a problem which would result in an incorrect final barrier height determination even if the photovoltage is shorted out at high coverages. For example, valence band spectra taken using a low flux of low energy photons will create fewer electron-hole pairs and have a relatively small photovoltaic shift. The initial clean surface Fermi level position could be obtained by comparing the valence band maximum from such a spectra to a Fermi edge reference. If this Fermi level starting point is then assigned to a clean core level spectra which is taken at a higher flux of higher energy

photons and contains a larger photovoltage, then the difference between the two photovoltages will carry over as an error in the final barrier height determination, even if the highest coverage contained no photovoltage.

By way of summarizing this section, photoemission spectra from low doped samples are unreliable unless extreme care is taken to measure the photovoltage accurately and account for it. However, it makes far more sense to simply do the experiments on more heavily doped material.

Aluminum and Gold Schottky Barriers

Of the barrier heights reported in ref. 1, Au is the most different from previous reports of metal contacts on GaAs. We have studied Au deposition on both $n = 5 \times 10^{16}$ cm^{-3} and $n = 5 \times 10^{18}$ cm^{-3} doped layers. The raw As 3d data is shown for the low doped sample in figure 2a, and the heavily doped sample in figure 2b. The most striking difference is of course the large shifts seen in the early coverages for the lower doped sample. The band bending is plotted as a function of coverage in figure 3. We find that the final band bending value is reached by the 2 ML coverage for the low doped case, and by the 1 ML coverage in the heavily doped case. The total change in barrier height for the low doped case is only 0.15 eV, while in the lightly doped case, the change is a substantial 0.35 eV. Note that this difference in energy is just what we measured for the photovoltaic band flattening in fig. 1. In the case where the photovoltage is important, the larger shifts occur when the deposition "shorts out" the photovoltage by providing an alternate electrical path from the surface to ground. This shorting out process will depend on the exact details of sample mounting and overlayer morphology and could vary from experiment to experiment.

The measurements of ref. 1 indicated that additional Fermi level movement occurs up to higher Au coverages, even above 10Å. Although this is not the case in our experiments, it is true that the centroid of the Ga 3d peak continues to shift to higher kinetic energy, the direction which indicates increased band bending on n-type. This can be seen

for the heavily doped Ga 3d spectra in figure 4. This shift led to reports of anomalously high barrier heights in earlier work on cleaved GaAs(110) (ref. 14). These reports of high barrier heights were subsequently proven incorrect as is documented extensively in ref. 15. The reason for this shift is not band bending, but rather the formation of Au-Ga alloys when the Au reacts with the GaAs. In figure 5, the true band bending is compared to the band bending obtained by simply following the centroid of the Ga 3d. This shift is the reason for the incorrect high barrier heights reported in reference 14, and also strongly resembles the barrier height vs. Au coverage curves of reference 1. Such shifts do not occur in the As 3d's as can be seen from fig. 2b (see also ref. 15).

The Ga 3d electrons taken at hv=80 eV have a kinetic energy of ≈55 eV and therefore a very short escape depth of ≈5Å. Because of this, the Ga 3d signal comes almost entirely from Ga atoms in Au-Ga alloy clusters on the surface. By going to very low kinetic energies, we can increase the escape depth to roughly 30Å and get significantly more signal from the bulk GaAs. Spectra taken at a constant final state (CFS) kinetic energy of 3 eV are shown in figure 6. Whereas the photoemission spectra are taken by fixing the photon energy and counting electrons as a function of the electron kinetic energy, the CFS spectra are taken by fixing the kinetic energy and counting electrons as a function of photon energy. The spectra are interpreted similarly, with the higher kinetic energy features corresponding to the low photon energies in the CFS spectra. Because of this, the spectra come out reversed. At the kinetic energy of 3 eV, the increased escape depth of the electrons means that the measurement samples a greater depth into the material. This increased bulk sensitivity results in a spectrum which can clearly be separated into a component from the Ga atoms in the GaAs (which give the band bending), and a component which is from Ga atoms which are incorporated in the Au-Ga alloy and dominate the surface sensitive photoemission spectra at high coverages. This spectra shows clearly that the continued shift of the Ga 3d centroid is due to an alloying effect rather than true band bending.

In figure 7, we show the band bending vs. coverage curves which result from experiments which do not have photovoltaic shifts, and for which chemistry and alloying are carefully accounted for. As indicated, we find only a 0.25 eV difference in barrier height for Al and Au, which is in sharp contrast to the 0.75 eV reported earlier. While we have discussed possible reasons for the difference in the Au barriers, we have yet to address the 0.25 eV difference in the Al case. The most likely candidate is the presence of photovoltaic band flattening. While Au is known to form leaky diodes, even at very low temperatures (ref. 16), Al seems to remain unshorted even at high coverages. In fact this low temperature work (ref. 16) shows that the bands remain flat due to photovoltages at the highest Al coverages. In the present room temperature case, a smaller effect could explain the difference. In any case, the photovoltaic effect casts serious doubt on any claim of unusually low barrier heights measured by photoemission on low doped samples.

Summary and Conclusions

Although the prior workers (ref. 1) reported a range in barrier heights of as much as 0.75 eV for Al and Au, we find a difference of only 0.25 eV for the 2 metals. Our study of n-type samples which were doped with the same density as was used in ref. 1 showed that there is a significant photovoltage due to the photoemission measurement. The low doped samples which show the photovoltaic effect were the only samples which showed large shifts in the apparent Fermi level position. We point out that the Au experiments have the additional complication that the Ga 3d continues to shift beyond the coverage at which the Fermi level stabilizes, giving the false impression of increased band bending on n-type.

From this we must conclude that the differences between the results reported here, and those reported in ref.1 are due to differences in interpreting core level shifts caused by photovoltaic effects and chemistry.

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Figure Captions.

Fig. 1- The photovoltage as a function of temperature for the clean surface as monitored by the As 3d shift. The circles are taken while the temperature is decreasing. The x's are taken upon reheating to show the reversibility of the effect. This is a simple method of checking for photovoltages at room temperature.

Fig. 2- As 3d vs Au coverage for (a) lightly and (b) heavily doped n-GaAs. Note that the shifts are completed at coverages below 3ML. The larger shifts in the lightly doped case are due to the shorting out of the photovoltage by the Au overlayer.

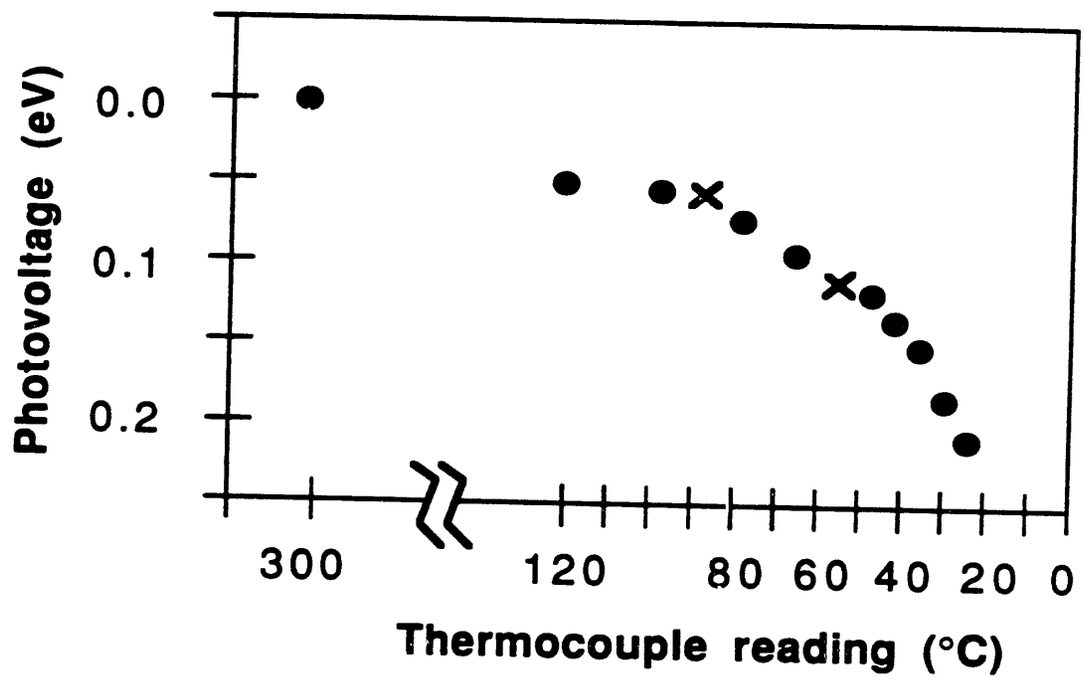
Fig. 3- Plot of the Schottky barrier height vs. Au coverage for the light and heavily doped case. The large shifts and different starting position of the low doped case is due to the photovoltaic shift, and its subsequent removal by Au deposition.

Fig. 4- The Ga 3d spectra corresponding to the As 3d in figure 2. Note that the centroids of the spectra continue to shift at coverages which are higher than the band bending saturation coverage. This is due to the formation of clusters of Au-Ga alloy.

Fig. 5- Band bending vs. Au coverage as determined correctly (solid squares) or by following the Ga 3d centroid (unfilled squares). The additional "band bending" determined by the Ga 3d centroid is due to the changing chemical environment of Ga in the Au-Ga alloy.

Fig. 6- Constant final state (CFS) Ga 3d spectrum for 10ML of Au. In this spectrum, the kinetic energy is set at 3 eV, and the photon energy is varied. The spectra come out reversed from left to right when compared to the photoemission spectra in figure 4. Otherwise, this is similar to the 80 eV photoemission spectra with the difference that the spectrum is far more bulk sensitive due to the reduced inelastic scattering at low kinetic energies. With this greater bulk sensitivity, the Ga 3d signal from Ga atoms can be clearly separated from the shifted Ga 3d in the Au-Ga alloy.

Fig. 7- Band bending vs. Al and Au coverage determined for the heavily doped samples. In the absence of photovoltaic effects there are no large shifts with coverage and the difference between the two metals is only 0.25 eV.


Photovoltage (eV)
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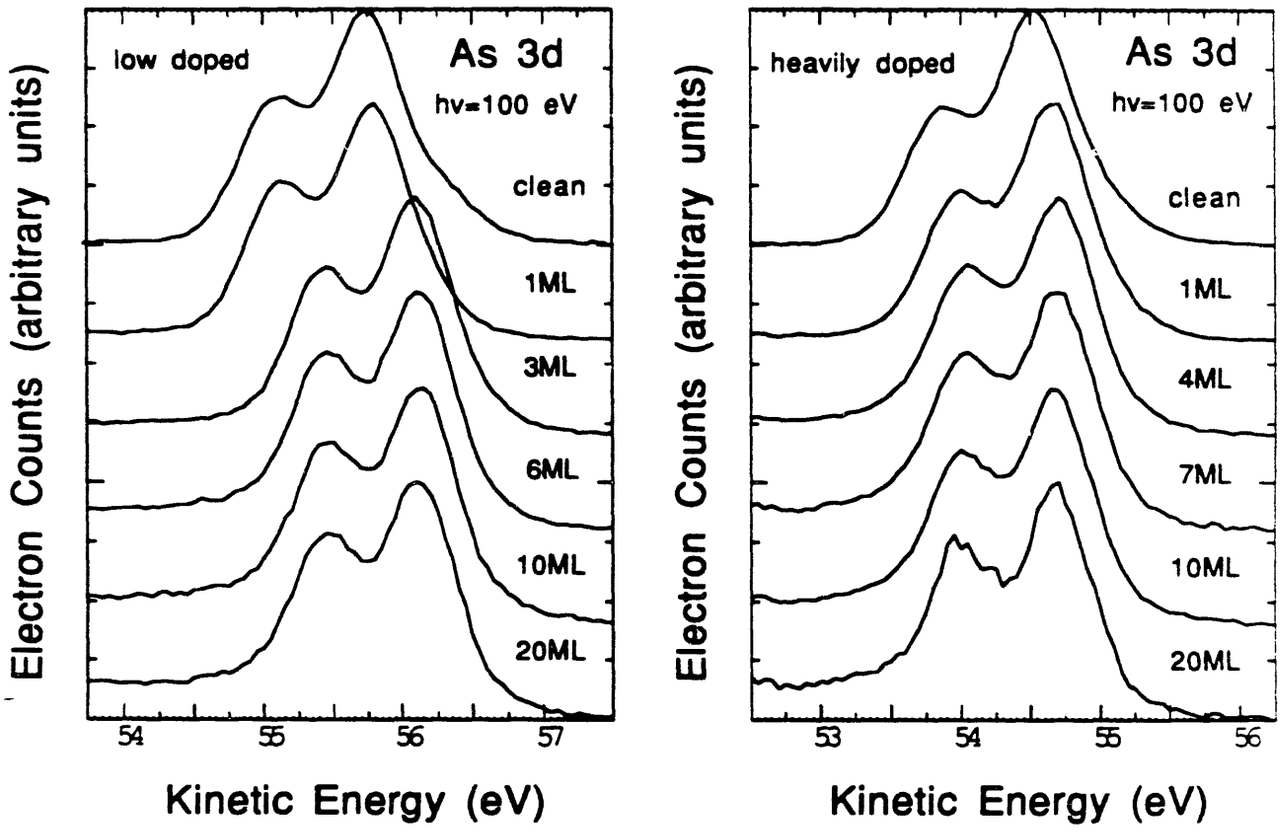
0.1
0.2
300
120
80
60
40
20
0
Thermocouple reading (°C)

figure 1



Figures 2a and 2b

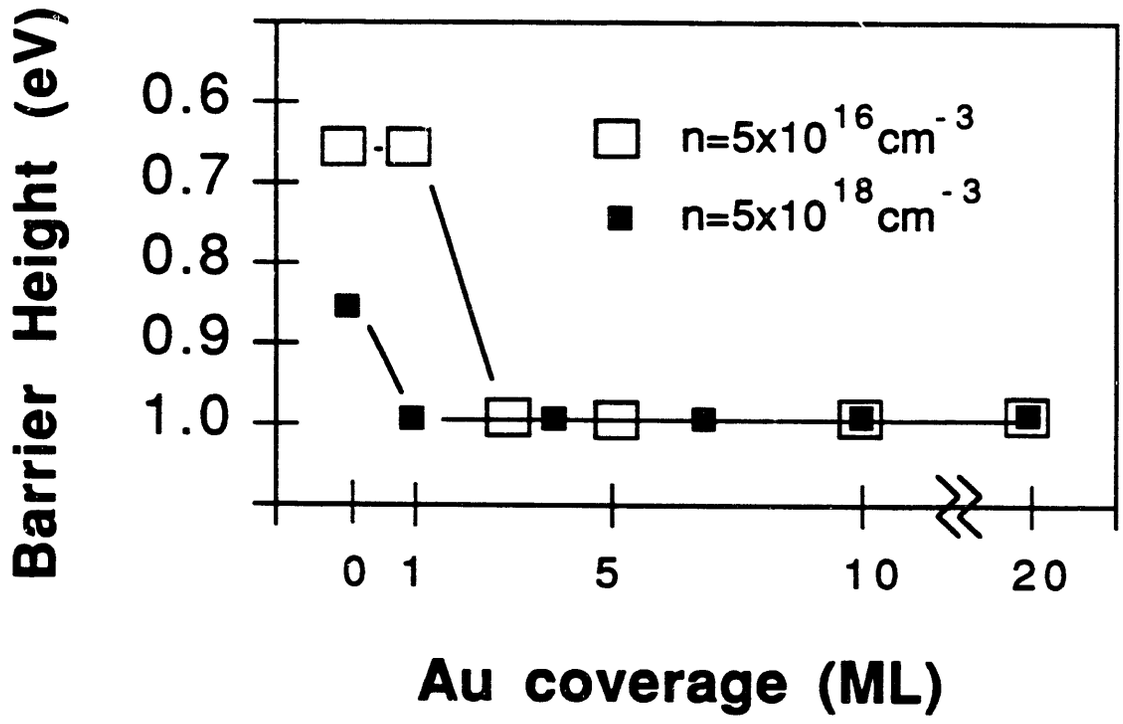

Barrier Height (eV)
0.6
0.7
0.8
0.9
1.0
n=5x10^16cm^-3
n=5x10^18cm^-3
0
1
5
10
20
Au coverage (ML)

figure 3

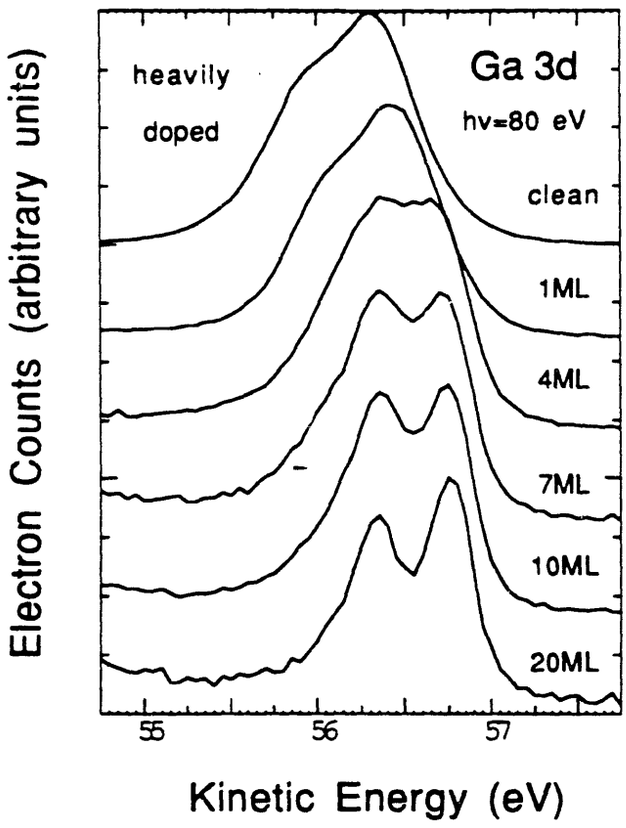


fig.4

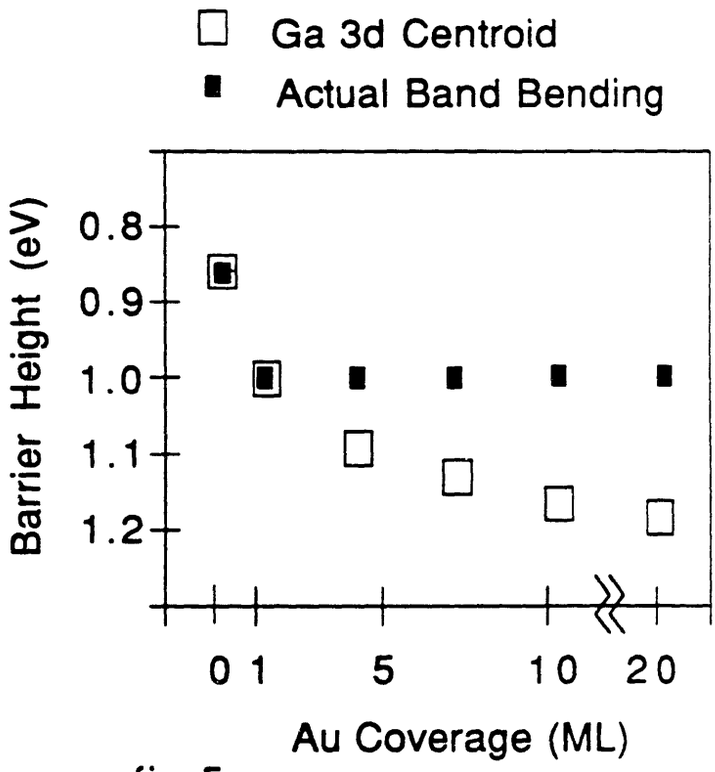


fig.5

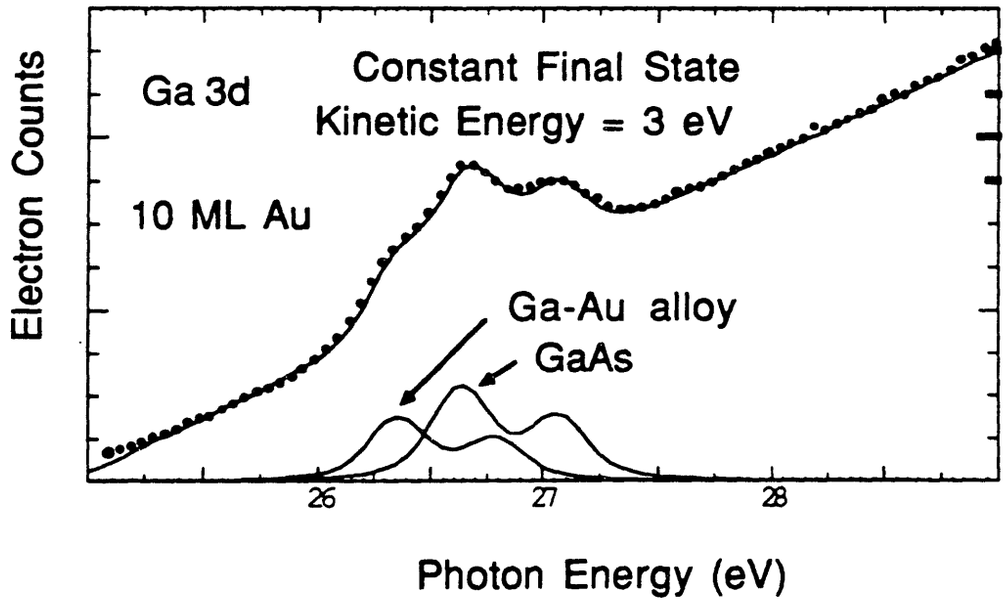


fig. 6

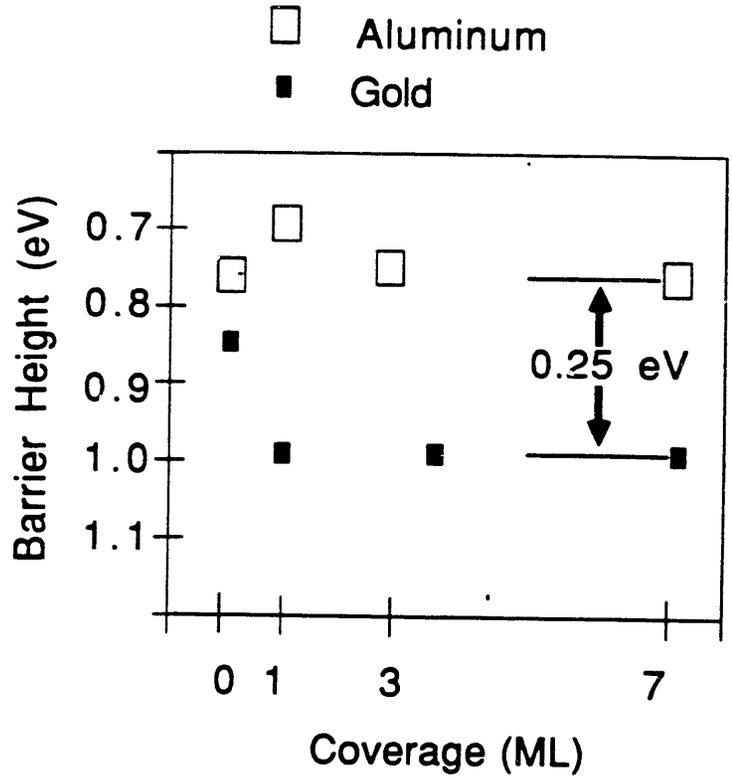

Aluminum
Gold
Barrier Height (eV)
0.7
0.8
0.9
1.0
1.1
0.25 eV
0
1
3
7
Coverage (ML)

fig. 7

END

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