A simple consistent picture emerges. Surface plasmons are damped above the interband transition in Au and Cu. The effect is seen as a rather clear image of the electron energy-loss function in the spectrum of light emitted from tunnel junctions. The findings are in harmony with surface-enhanced Raman spectroscopy data.

The authors are grateful to A. Adams, P. K. Hansma, J. R. Kirtley, and J. C. Tsang for helpful discussions and to them and D. L. Mills for preprints. The present work was supported by the United Kingdom Science and Engineering Research Council.

[1] J. Lambe and S. L. McCarthy, Phys. Rev. Lett. 37, 923 (1976).

[2] N. Kroó, Zs. Szentirmay, and J. Felszerfalvi, Phys. Status Solidi (b) 102, 227 (1980).

[3] J. R. Kirtley, T. N. Theis, and J. C. Tsang, Phys. Rev. B 24, 5650 (1981).

[4] N. Kroó, Zs. Szentirmay, and J. Felszerfalvi, Phys. Lett. 88A, 90 (1982).

[5] A. Adams, J. C. Wyss, and P. K. Hansma, Phys. Rev. Lett. 42, 912 (1979).

[6] B. Laks and D. L. Mills, Phys. Rev. B 20, 4962 (1979).

[7] C. Kittel, *Introduction to Solid State Physics* (Wiley, New York, 1976), 5th ed, p. 350.

[8] P. Nozières and D. Pines, Phys. Rev. 113, 1254 (1959).

[9] A. Adams and P. K. Hansma, Phys. Rev. B 23, 3597 (1981).

[10] P. B. Johnson and R. W. Christie, Phys. Rev. B 6, 4370 (1972).

[11] N. E. Christensen and B. O. Seraphin, Phys. Rev. B 4, 3321 (1971).

[12] H. Ehrenreich and H. R. Philipp, Phys. Rev. 128, 1622 (1962).

[13] C. J. Powell, J. Opt. Soc. Am. 60, 78 (1970).

[14] H. Raether, *Excitation of Plasmons and Interband Transitions by Electrons*, Springer Tracts in Modern Physics Vol. 88 (Springer-Verlag, Berlin, 1980).

[15] T. E. Furtak and J. Reyes, Surf. Sci. 93, 351 (1980).

[16] B. Pettinger, U. Wenning, and H. Wetzel, Surf. Sci. 101, 409 (1980).

[17] U. Wenning, B. Pettinger, and H. Wetzel, Surf. Sci. 70, 49 (1980).

[18] H. Wetzel and H. Gerischer, Chem. Phys. Lett. 76, 460 (1980).

[19] I. Pockrand, Chem. Phys. Lett. 85, 37 (1982).

Initial Adsorption State for Al on GaAs(110) and Its Role in the Schottky Barrier Formation

R. R. Daniels, A. D. Katnani, Te-Xiu Zhao,[a] and G. Margaritondo
Department of Physics, University of Wisconsin, Madison, Wisconsin 53706

and

Alex Zunger
Solar Energy Research Institute, Golden, Colorado 80401, and Department of Physics, University of Colorado, Boulder, Colorado 80309

(Received 13 July 1982)

Synchrotron-radiation experiments were performed at ultralow (< 0.1 monolayer) coverages to test the weakly-interacting-cluster model for Al adsorption on GaAs(110). The evolution of the Al 2*p* peak revealed *two* different submonolayer adsorption states, one below and one above 0.1 monolayer coverage, as predicted by the model. These results demonstrate that experiments at ultralow coverages are crucial to the understanding of the Schottky barrier formation.

PACS numbers: 79.60.-i, 68.55.+b, 73.40.-c

The traditional theoretical models described the Schottky barrier (SB) as the result of a charge redistribution between a metallic adlayer and a bulk semiconductor.[1] In contrast, modern experimental studies[2-9] have revealed that, in many cases, the barrier is already formed at *atomic* metal-adatom coverages (~1 Å), where the overlayer need not be metallic. These studies were performed on adlayers as thin as 0.1–1 Å while the more traditional thicknesses occurring in devices are ~10^3 Å. Their results have focused considerable attention on the local chemical bonds,[3] localized defects,[7] and the interface geometry.[10] Following these experiments, current theoretical models[11-13] analyze the SB properties in terms of strong chemisorption bonds between an epitaxial adlayer and the semiconductor.

We investigated the SB formation at an even earlier stage by examining the prototypic interface GaAs(110)-Al at *ultralow coverages of* 10^{-2} Å using synchrotron-radiation photoemission. We found that the adsorption state for Al at such ultrathin coverage is *distinctly different* from those that prevail at coverages of 0.1–1 Å. The crucial importance of this novel ultralow-coverage Al adsorption state is highlighted by Fig. 1 which shows the adatom-induced shift of the interface Fermi level E_F in the gap of GaAs. From Fig. 1 we see that about 50% of the SB height $E_c - E_F$ is already established at a coverage of 0.07 Å where the ultralow-coverage adsorption state prevails.

The existence of an ultralow-coverage Al adsorption state is revealed by a 0.3–0.55-eV shift of the Al $2p$ peak to lower binding energies, over and above the band bending, upon increasing the coverage from 0.05 to 0.2 monolayer. This shift is consistent with Zunger's prediction[14] that the ground state at submonolayer coverages (and low temperature) involves Al_n molecular clusters which interact only weakly with the substrate, rather than a strongly chemisorbed, ordered metallic adlayer.[11-13] At ultralow coverages where the statistical probability of adatom-adatom encounter vanishes, the adatoms are dispersed and in a different adsorption state, whereas at large coverages a bulklike metallic overlayer is formed. This picture is also consistent with the notorious failure to establish a molecular-beam-epitaxy (MBE) growth of Al on GaAs at conventional MBE temperatures (~600 °C),[15] despite the excellent lattice matching. Recent experiments[16] have indicated that this results from an anomalously large (and hitherto unexplained) surface mobility of the weakly bonded Al species to the surface, leading to a preferential dendritic cluster formation of Al. This motion could be quenched at −5 °C, leading for the first time to a successful MBE growth on the (110) face.[16]

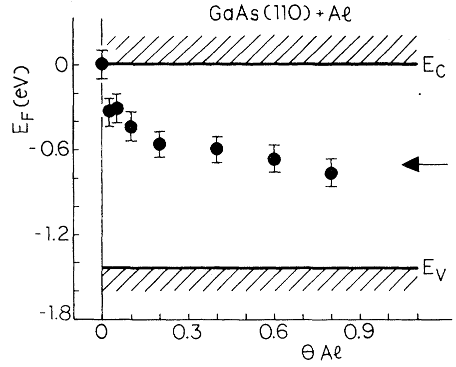

FIG. 1. Shift of the interface Fermi energy, E_F, as a function of the nominal Al overlayer thickness in monolayers (1 monolayer ≃ 1.4 Å). E_v and E_c denote the valence- and conduction-band edges of the substrate. The arrow shows the asymptotic position of E_F. Notice the rapid evolution of the Schottky barrier, $E_c - E_F$.

Experiment and theory, therefore, agree in emphasizing the crucial importance of the early adsorption state (<0.1 monolayer) for Al on GaAs(110)—and for metals on semiconductors in general. To our knowledge, however, no experimental study of this state exists in the literature. Previous experiments provided partial tests of the cluster model[14] at intermediate or large coverages but no test at ultralow coverages. Even at intermediate coverages the results were not conclusive. Photoemission and low-energy electron-diffraction[10] experiments did clarify the nature of the intermediate-coverage adsorption state for Al on GaAs(110) after annealing—but that of the unannealed interface remained unexplained.

The present experiments were performed by use of the technique described, for example, in Ref. 2. Photoemission spectra were taken on freshly cleaved and Al-covered GaAs substrates. The samples were n type, Te doped, with $n = 10^{18}$ cm^{-3}. The spectra were taken in the valence-band/Fermi-level energy region and in the regions of the Al $2p$, Ga $3d$, and As $3d$ core levels. The photon energy was selected to enhance the surface sensitivity by minimizing the photoelectron escape depth. Al depositions ranging from $\frac{1}{40}$ to 50 monolayers were obtained by evaporating Al from a W basket. The depositions were controlled and monitored with a shutter and a calibrated quartz crystal monitor. Typical deposition rates were 0.3–20 monolayers/min. Several refinements of the experimental procedure were required to perform experiments on ultrathin overlayers. For example, the pressure had to be constantly kept in the 10^{-11}-Torr range and the averaging time per spectrum was increased in some cases to more than 90 min.[17] The cleaved substrates were rejected unless they had a flat-band configuration, free of Fermi-level pinning by extrinsic clean-surface states, e.g., by cleavage-step states.[9]

Figure 2 shows Al $2p$ spectra corresponding to the three different Al adsorption states on GaAs(110). We see that the Al $2p$ peak shifts in energy by several tenths of an electronvolt as the coverage increases from 0.05 to 1 monolayer. The shift is *over and above* the shift caused by the Al-induced band bending (see Fig. 1). To eliminate band-bending effects, each peak in Fig. 2 was shifted by an amount equal to the difference in band bending between the corresponding interface and the thick-Al interface. The band bending was deduced for each Al coverage from the shift of the metal-covered-surface Ga $3d$ peak with respect to the clean-surface Ga $3d$ peak. The evolution from the ultralow-coverage adsorption state to the intermediate-coverage adsorption state is shown in more detail in Fig. 3. Most of the shift occurs for coverages between 0.05 and 0.2 monolayer while the spectra stay nearly constant at coverages above 0.2 monolayer (and until the evolution towards bulk Al starts). An exact determination of the Al $2p$ shift from 0.025–0.05 monolayer to 0.1–0.2 monolayer is made difficult by the low signal-to-noise ratio. Experiments on several interfaces enabled us to estimate the upper and lower limits for this shift to be 0.55 and 0.3 eV after correction for the band bending.

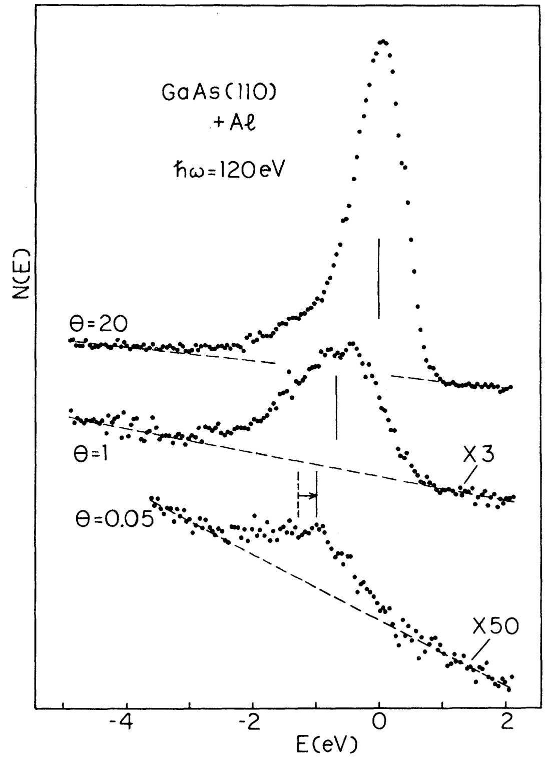

FIG. 2. Photoemission spectra of the Al $2p$ core level, illustrating the three different Al adsorption states as a function of coverage. The top spectrum corresponds to bulk Al, and the zero of the energy scale is set to coincide with this bulk-Al peak. The band-bending correction is very small for the monolayer-coverage peak, while for the 0.05-monolayer spectrum it is illustrated by the vertical dashed and solid straight lines. The shift (over and above the band bending) between the bottom and middle peaks demonstrates that two different adsorption states occur for Al, one below and one above ~0.1 monolayer coverage. The dashed lines show the estimated secondary-electron background by linear interpolation.

At coverages between 1 monolayer and 20 monolayers the Al $2p$ spectra show the well-known evolution towards a bulk Al $2p$ peak[4,6] (see Fig. 2). The Ga $3d$ and As $3d$ spectra exhibit an intensity decrease but no shift beyond the band bending nor line-shape change during the early stages of metal coverage. Above 0.4 monolayer the Ga $3d$ peak has a high-energy component due to free Ga atoms released by replacement interactions between the adatoms and the substrate.[4,6,18]

In summary, the following empirical conclusions are deduced from our experimental data. The GaAs(110)-Al interface formation occurs in *three* different stages corresponding to different Al adsorption states. The last stage is the well-

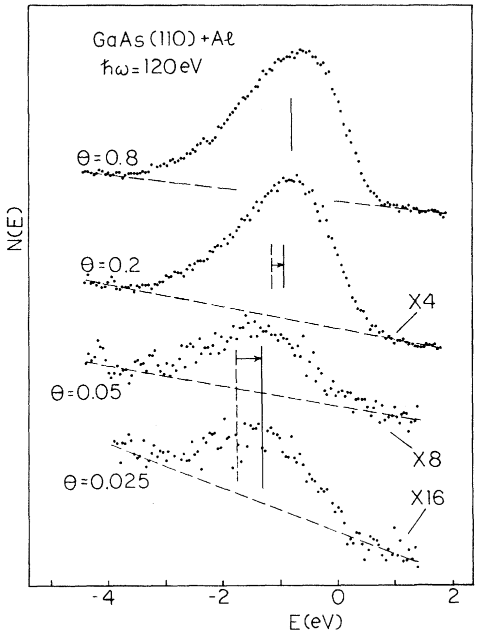

FIG. 3. Evolution from the initial Al adsorption state to the intermediate Al adsorption state. The energy scale is again referred to the bulk-Al peak.

known formation of bulk Al accompanied by replacement interactions.[4,6] The second stage occurs at coverages between 0.1 and several monolayers and is also accompanied by replacement interactions. The Al $2p$ peak for the second stage is asymmetric and it could be the superposition of two different peaks corresponding to Al atoms in different environments. During the first stage the Al $2p$ binding energy has the largest value and there is no direct evidence for replacement interactions. The evolution from the first to the second stage occurs between 0.05 and 0.2 monolayer coverage. The establishment of the interface parameters, i.e., of the Schottky barrier height, is very rapid and occurs mostly during the first stage and the transition to the second stage.

The sign and the magnitude of the observed Al $2p$ shift between the first and second stages are consistent with the predictions of the weakly-interacting-cluster model.[14] Furthermore, the model correctly predicts the overlayer thickness range for the transition between the first and the second stages (and the evolution after the second stage as discussed in Ref. 14). These results are of general importance to the theory of the Fermi-level-pinning defects and of the processes leading to their formation.[7] Furthermore, they suggest a natural source for the surface energy required by different models of SB formation, e.g., to create defects,[7] to overcome activation barriers for the formation of new compounds,[3] and in general for chemical exchange reactions,[10] or to promote the anomalously large surface migration.[16] The thermal and condensation energies of Al appear far too small to overcome these barriers,[14] but the heat released upon Al cluster formation (~3 eV) is sufficient to activate a rich variety of surface reactions.

These experiments were supported in part by the U. S. Office of Naval Research. We are grateful to Ed Rowe and to the entire staff of the University of Wisconson Synchrotron Radiation Center (supported by the National Science Foundation under Grant No. DMR 76-15089) for their invaluable technical help.

---

[a] On leave from the China University of Science and Technology, Hefei, China.

[1] E. H. Rhoderic, *Metal-Semiconductor Contacts* (Clarendon, Oxford, 1978).

[2] J. E. Rowe, G. Margaritondo, and S. B. Christman, Phys. Rev. B 15, 2195 (1977); G. Margaritondo, J. E. Rowe, and S. B. Christman, Phys. Rev. B 15, 5396 (1976).

[3] L. J. Brillson, Phys. Rev. Lett. 40, 360 (1978); L. J. Brillson, C. F. Brucker, N. G. Stoffel, A. D. Katnani, and G. Margaritondo, Phys. Rev. Lett. 46, 838 (1981).

[4] L. J. Brillson, R. Z. Bachrach, R. S. Bauer, and J. McMenamin, Phys. Rev. Lett. 42, 497 (1979).

[5] L. J. Brillson, G. Margaritondo, and N. G. Stoffel, Phys. Rev. Lett. 55, 667 (1980).

[6] P. Skeath, I. Lindau, P. Pianetta, P. W. Chye, C. Y. Su, and W. E. Spicer, J. Electron. Spectrosc. 17, 259 (1979); P. Skeath, I. Lindau, P. W. Chye, C. Y. Su, and W. E. Spicer, J. Vac. Sci. Technol. 16, 1143 (1979).

[7] W. E. Spicer, I. Lindau, P. Skeath, C. Y. Su, and P. Chye, Phys. Rev. Lett. 44, 420 (1970).

[8] R. Z. Bachrach, J. Vac. Sci. Technol. 15, 1340 (1978); R. Z. Bachrach and R. S. Bauer, J. Vac. Sci. Technol. 16, 1149 (1977).

[9] A. Huijer, J. Van Laar, and T. L. Van Rooy, Surf. Sci. 102, 264 (1981), and 62, 472 (1977).

[10] C. B. Duke, A. Paton, R. J. Meyer, L. J. Brillson, A. Kahn, D. Kanani, J. Carelli, J. L. Yeh, G. Margaritondo, and A. D. Katnani, Phys. Rev. Lett. 46, 440 (1981); A. Kahn, L. J. Brillson, A. D. Katnani, and G. Margaritondo, Solid State Commun. 38, 1269 (1981).

[11] J. R. Chelikowsky, S. G. Louie, and M. L. Cohen, Solid State Commun. 20, 641 (1976); J. R. Chelikowsky and M. L. Cohen, Phys. Rev. B 20, 4150 (1979).

[12] D. J. Chadi and R. Z. Bachrach, J. Vac. Sci. Technol. 16, 1159 (1979).

[13] E. J. Mele and J. D. Joannopoulos, Phys. Rev. Lett. 47, 1094 (1979).

[14] A. Zunger, Phys. Rev. B 24, 4372 (1981).

[15] R. Z. Bachrach, R. S. Bauer, P. Chiaradia, and G. V. Hansson, J. Vac. Sci. Technol. 19, 335 (1981).

[16] G. A. Prinz, J. M. Ferrari, and M. Goldberg, Appl. Phys. Lett. 40, 155 (1981).

[17] Even at these low pressures it is necessary to check that long exposures do not influence the band bending [W. Gudat, D. E. Eastman, and J. L. Freeouf, J. Vac. Sci. Technol. 13, 250 (1976)]. Repeated tests on the Ga $3d$ peak did not reveal any effect of this kind.

[18] In contrast to our results and to those of other authors (Refs. 4 and 6), A. Huijser, J. Van Laar, and T. L. Van Rooy, Surf. Sci. 102, 264 (1981), did not detect this component. We did not observe the dependence on surface quality of the exchange reaction, suggested by those authors as a possible explanation for this discrepancy. Our results suggest instead that their sensitivity to the Ga $3d$ signal (~10%) might be too low to detect the free-Ga component for submonolayer coverages.