PHYSICAL REVIEW B VOLUME 47, NUMBER 8 15 FEBRUARY 1993-II

Cryogenic growth of Al nitride on GaAs(110): X-ray-photoemission spectroscopy and inverse-photoemission spectroscopy

Ken T. Park and Y. Gao

Department of Physics and Astronomy, University of Rochester, Rochester, New York 14627-0011

(Received 6 July 1992)

We report on our recent studies of Al nitride growth on GaAs(110) formed by depositing Al onto a condensed ammonia overlayer on GaAs(110) at $T=90$ K using x-ray-photoemission spectroscopy and inverse-photoemission spectroscopy. We have also investigated the temperature dependence of the interface thus formed. The results show some limited amount of Al nitride formed at $T=90$ K even though the reaction is slow, but the overlayer mostly remains metallic until the substrate is heated up. Much of the reaction of Al with ammonia occurs at about $T=170$ K, above which the overlayer becomes insulating. The combined information from occupied and unoccupied states reveals new features of the interface formation, and is consistent with our previous synchrotron photoemission studies of $Al/NH_3/GaAs(100)$.

INTRODUCTION

There have been extensive experimental and theoretical investigations on metals dissolved in liquid ammonia because of a rich variety of physical behaviors associated with metal-nonmetal transitions in these systems.[1-11] A metal-NH_3 solution can be nonmetallic or metallic depending on the metal concentration, and there is a miscibility gap in the phase diagrams of many metal-NH_3 solutions in the intermediate range of concentrations over a broad range of temperatures and compositions.[6-9] These behaviors have been interpreted as being mediated by microscopic inhomogeneities,[10] or as a direct and necessary consequence of a metal-nonmetal transition of the "Mott-Hubbard" type.[11] Metal-nonmetal transition in the solid state has also been observed recently.[12] In this paper, we report our recent studies of the interface formation of $Al/NH_3/GaAs(110)$ using x-ray-photomission spectroscopy (XPS) and inverse-photoemission spectroscopy (IPES), in which we observed the metal-nonmetal transition of Al deposited on solid NH_3 from both the occupied and unoccupied electronic states. In addition, the potential significance of AlN in the microelectronics industry provides further motivation for this work: AlN is a primary candidate as an insulating and buffer layer in a metal-insulator-semiconductor (MIS) system based on GaAs because of the low density of states ($\leq 10^{12}$/eV cm^2) of the AlN/GaAs(110) interface.[13-15] The inability of native oxides of III-V semiconductors to protect the surface of the substrate from disruptions induced by metal deposition has hampered the application of these high electron mobility semiconductors, which is in sharp contrast to the remarkable success of Si- and SiO_2-based metal-oxide-silicon (MOS) technology since Frosh and Derrick's discovery that a thin layer of SiO_2 can effectively protect against the diffusion of most acceptor and donor impurities in *p-n* junctions.[16]

The conventional ways of fabricating AlN on GaAs are metal-organic chemical-vapor deposition (MOCVD),[17] ion implantation,[18-20] and reactive molecular-beam epitaxy.[21,22] We recently developed a method of growing AlN on GaAs(100) by evaporating Al on NH_3 condensed on GaAs(100) at 100 K. Using synchrotron photoemission spectroscopy, we investigated the formation of $Al/NH_3/GaAs(100)$ and observed, by examining the valence-band and core-level spectra, that Al reacted with the substrate neither at $T=100$ K nor after annealing to $T=450\,^{\circ}\mathrm{C}$.[23,24] Instead, the aluminum overlayer reacted with molecular ammonia to form an insulating Al nitride layer during heating of the sample from $T=100$ K to room temperature.

In this paper we report our recent investigation of the interface formation of $Al/NH_3/GaAs(110)$ using x-ray-photoemission spectroscopy and inverse-photoemission spectroscopy. One of the purposes of the investigation is to learn whether there is any fundamental difference between the cryogenic Al nitride formation on GaAs(100) and GaAs(110), which are polar and nonpolar surfaces, respectively. Our XPS spectrometer allows us to observe the evolution of deep core levels such as N 1*s* to follow the changes of NH_3 during the interface formation. The evolution of the unoccupied electronic states of $Al/NH_3/GaAs(110)$ during the interface formation is followed by using IPES, in which the temperature dependence of the metal-nonmetal transition is observed from the reaction between molecular ammonia and Al. These investigations provide us with a more complete picture of the growth of Al nitride on GaAs at cryogenic temperatures.

EXPERIMENT

The experiment was carried out at the surface-science laboratory at the University of Rochester. The x-ray-photoemission spectrometer consists of a VG XR2E2 high-power x-ray source operated at the Mg $K\alpha$ line ($h\nu=1253.6$ eV) and a VG ADES 500 angle-resolved electron energy analyzer mounted on a two-axis goniometer. The energy resolution of the XPS spectrometer was 1.2 eV, resulting from the convolution of the natural width of 0.68 eV of the Mg $K\alpha$ line[25] and the resolution of 1.0 eV chosen for the hemispherical energy analyzer. The low-energy–high-brightness electron gun for inverse-photoemission spectroscopy was built according to an existing design.[26,27] The bandpass photon detector was constructed by putting a CaF window in front of two microchannel plates (MCP's) in tandem, with 400 Å of KBr evaporated on the first MCP.[28,29] The combination of the CaF window and the KBr coating sets the energy of photon detection at $h\nu = 9.8$ eV. The energy resolution of the inverse-photoemission spectrometer was measured to be ~0.9 eV from the 10–90 % onset at the Fermi edge of a 10 Å layer of Cr on a GaAs(110) crystal.

An n-type Si-doped ($n_d = 1\times10^{18}$ cm^{-3}) GaAs single crystal from Crystal Specialties was cut into 3×4×30-mm bars along the [110] direction, and the bars were bromine etched to remove surface stress from cutting. The sample was cleaved *in situ* until a flat, mirrorlike surface was obtained. The sample was cooled with a TRI Model 225 liquid-helium-flow cryostat, and liquid nitrogen was used to lower the sample temperature to $T = 90$ K. To ensure good thermal and electrical conductivity, we applied a gallium-indium alloy between the sample and sample holder, and the sample holder was dipped in a gallium bath installed on the cryostat. The temperature of the sample was monitored by thermocouples mounted on the cryostat and gallium bath, and the temperature varied from $T = 90$ to 300 K during the experiment. The time for the sample to cool down from ambient temperature to $T = 90$ K was minimized to about 10 min, which is important for reducing contamination from the ambient atmosphere during cooling. Ammonia was administered into the vacuum chamber through a precision leak value while the temperature of the GaAs sample was held at about $T = 90$ K, and the dosage was determined by ion gauge reading and timing. Aluminum was evaporated from a resistively heated W basket with an average rate of 2 Å/min, and the thickness of Al was monitored by a quartz-crystal thickness monitor. The base pressure of our UHV system was in the 10^{-11}-Torr range.

The experimental procedure is the following: first, we took spectra of the clean surface of GaAs(110) at room temperature, then lowered the sample temperature to about 90 K. Once the sample was cooled down, we condensed ammonia on GaAs(110) and evaporated aluminum at low temperature. After the Al evaporation, we raised the sample temperature to $T = 170$, 220, and 270 K. At each stage, we took XPS and IPES spectra to study the interface formation.

RESULTS AND DISCUSSIONS

Figure 1 shows the Ga 3d core-level energy distribution curves (EDC's) taken with the Mg $K\alpha$ line for various stages of Al nitride growth on GaAs(110) at cryogenic temperatures. The EDC's have been normalized to the same height for visual clarity, and the centroid of each peak is marked by a short bar. The background of each spectrum was determined by fitting a smooth polynomial to both ends of the spectrum, and this background has been subtracted in the EDC's presented in the figure. The binding energies of all the spectra are referred to that of the cleaved GaAs(110) surface at room temperature. The treatments of the EDC's of other core levels are similar unless otherwise specified.

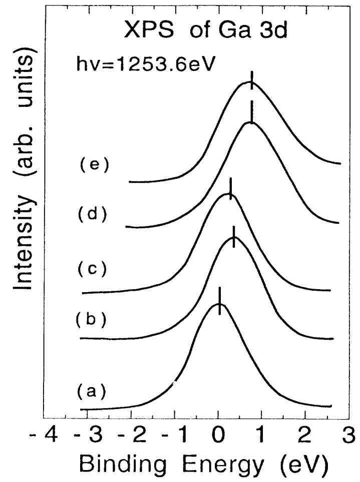

FIG. 1. Ga 3d x-ray-photoemission spectra for Al nitride growth on GaAs(110). From the bottom up: (a) clean GaAs at room temperature; (b) clean GaAs at $T = 90$ K; (c) after exposure of 20 L of NH_3 at $T = 90$ K; (d) after 2 Å of Al deposition at $T = 90$ K; (e) after 10 Å of Al deposition at $T = 90$ K.

Figure 1(a) is a Ga 3d EDC at room temperature which is typical of a clean surface. Figure 1(b) is the spectrum of the same surface taken at $T = 90$ K. As the temperature decreases from room temperature to 90 K, there is a peak shift of about 0.3 eV toward the higher binding-energy side [Figs. 1(a) and 1(b)]. We attribute this shift to the probable contraction of the lattice spacing by cooling or physisorption of a small amount of foreign atoms on the surface. This physisorption, if any, is well below the sensitivity of detection of our XPS spectrometer, since we checked the full range of the XPS spectrum from a binding energy of 0–1000 eV and could not identify any contaminant, particularly carbon and oxygen. We rule out the possibility that the photovoltaic effect causes the peak shift, since the intensity of our x-ray source is too small (order of 10^{12}/cm^2 s),[25] and the doping density of our sample is too high for the photovoltaic effect.[30–34] The condensation of 20 L NH_3 (1 L$=10^{-6}$ Torr s) at $T = 90$ K shifts the Ga 3d core level back to the lower binding-energy side by 0.2 eV [Fig. 1(c)]. Interestingly, the same phenomenon was observed in our previous synchrotron radiation photoemission study on Al/NH_3/GaAs(100),[23] indicating that it is quite general for GaAs surfaces. Similar peak shifts are also observed for the As 3d core level (not shown), and these peak shifts suggest movement of the Fermi level toward the center of the band gap. This movement may result from the reaction between Ga and some of the nitrogen released from NH_3 to form a postulated $GaAs_{1-x}N_x$ compound, or from new interface states generated near the conduction-band minimum (CBM), which will be further discussed in the

IPES part of our measurements. The thickness of molecular ammonia is estimated to be about three monolayers (ML) by measuring the attenuation of the intensities of Ga 3*d* and As 3*d* core-level EDC's.

Subsequent deposition of 2 and 10 Å of Al at $T=90$ K produced noticeable peak broadening and peak shifts toward higher binding energies [Figs. 1(d) and 1(e)]. These changes cannot be due to reactions between Al and GaAs because it would have resulted in releasing free Ga on the surface. Free Ga would lead to a shifted Ga 3*d* component with $\Delta\text{BE}\sim 1$ eV on the lower binding-energy side of the Ga 3*d* core-level EDC,[35] which could easily have been resolved by our XPS spectrometer. Instead it is likely that the peak shift of both Ga 3*d* and As 3*d* is the signal of enhanced nitrification of the substrate upon deposition of Al, which was also observed on Al/NH_3/GaAs(100).[23] A similar role of alkali metals as catalysts was observed by Soukiassian *et al.*[36]

Raising the temperature of the sample ignites the reaction between the aluminum and the ammonia. The evolution of Ga 3*d* EDC's during the study of temperature dependence is shown in Fig. 2 in the order of increasing substrate temperature: (a) Ga 3*d* EDC at $T=90$ K, (b) at $T=180$ K, (c) at $T=230$ K, and (d) at $T=270$ K. As we heated the sample up to 270 K [Fig. 2(d)], we observed a continuous peak shift of Ga 3*d* toward the lower binding-energy side and finally to its clean surface position. Because similar peak shift and broadening are also found in As 3*d* core-level EDC's, we exclude the possibility that these are caused by exchange between Ga and Al. Instead, they imply that band bending is reduced by annealing the sample to near room temperature. Further support for this assertion is the absence of any observable amount of free Ga signature on the lower binding-energy side of the 3*d* spectra throughout the temperature study. Compared with our previous studies on Al/NH_3/GaAs(100),[23] GaAs(110) exhibits very similar behaviors in its core-level spectra (Ga 3*d* and As 3*d*), indicating that the surface orientation of the substrate does not significantly affect the nitrification by molecular ammonia.

Our argument for the formation of Al nitride instead of a Ga-Al exchange is further supported by the Al 2*p* core-level EDC's shown in Fig. 3. Figures 3(a) and 3(b) show the Al 2*p* spectra after the evaporation of 2 and 10 Å of Al on the sample, respectively. The peak broadening on the lower binding-energy side in Fig. 3(b) is likely due to the greater metallic characteristic at the 10 Å aluminum coverage than at the 2-Å coverage, when the overlayer is too thin to be metallic. As the sample temperature is raised to $T=170$ K [Fig. 3(c)], a large decrease is observed in the intensity on the lower binding-energy side, resulting in a peak shift of $\Delta\text{BE}\sim 0.9$ eV toward the higher binding energy. This peak shift of Al 2*p* is likely caused by the formation of Al_xN_x in the overlayer, indicating that the initially metallic aluminum overlayer has reacted with molecular ammonia to become an insulating Al-nitride layer. Also, the observed peak shift of Al 2*p* is consistent with the peak shift of $\Delta\text{BE}=1.1-1.3$ eV in the formation of AlN reported by Taylor and Rabalais.[20] After the sample is further heated up to $T=270$ K [Figs. 3(d) and 3(e)], the peak shifts back to the lower binding-energy side, indicating annealing of the substrate.

We performed a time-dependence study of Al/NH_3/GaAs(110) at $T=90$ K in order to determine whether the above-observed changes in EDC's resulted from the change in the substrate temperature alone. During a period of time similar to that for the

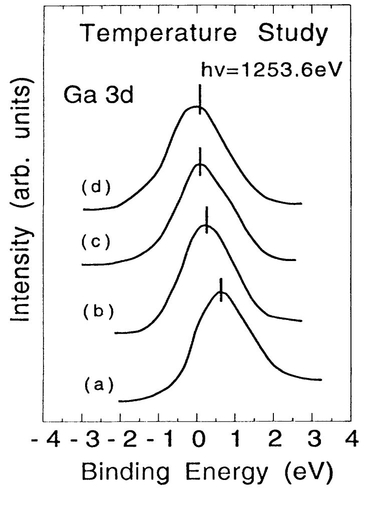

FIG. 2. Ga 3*d* x-ray-photoemission spectra for temperature dependence of Al nitride on GaAs(110). From the bottom up: (a) after 10 Å of Al deposition at $T=90$ K; (b) the same surface at $T=180$ K; (c) the same surface at $T=230$ K; (d) the same surface at $T=270$ K.

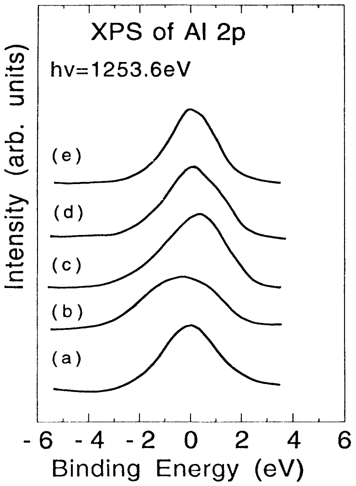

FIG. 3. Al 2*p* x-ray-photoemission spectra for Al nitride growth on GaAs(110). From the bottom up: (a) after deposition of 2 Å of Al on NH_3/GaAs(110) at $T=90$ K; (b) after deposition of 10 Å of Al on NH_3/GaAs(110) at $T=90$ K; (c) after annealing the same surface to $T=170$ K; (d) after annealing the same surface to $T=220$ K; (e) after annealing the same surface to $T=270$ K;

temperature-dependence studies (Fig. 3), the Al 2*p* core-level peak shifted toward the higher binding-energy side by about 0.5 eV, but no peak shift toward the lower binding-energy side nor peak broadening was observed. Thus we conclude that the observed peak shift of 0.9 eV toward the higher binding-energy side in the temperature-dependence study may not be solely due to the increase in the sample temperature. Instead, photogenerated low-energy electrons, resulting from the inelastic scattering of photoelectrons, may also have contributed to the formation of Al nitride and the observed peak shift in Fig. 3.[37]

The nitrification of Al on GaAs(110) can be studied further by examining the evolution of N 1*s* core-level EDC's (Fig. 4). After the exposure of 20 L NH_3 to the sample, a N 1*s* core-level peak related to physisorbed molecular ammonia similar to that found by Bozso and Avouris was observed [Fig. 4(a)].[38] The deposition of 2 and 10 Å of aluminum on molecular ammonia resulted in significant peak broadening of N 1*s* [Figs. 4(b) and 4(c)], especially on the higher binding-energy side. It is not difficult to see that there is more than one component in the N 1*s* core-level EDC's (marked with arrows). Although we could not resolve clearly all the components because of the limited resolution of our XPS spectrometer, we performed a quantitative peak decomposition with the following simple assumptions: (1) the peak width in Fig. 4(a) is a single-component Gaussian which is associated with NH_3; and (2) the peak position of NH_3 does not change before dissociation.

The result of the curve fitting of Fig. 4(c) with the above assumptions is presented in Fig. 5. Component 1 is from the molecular ammonia as presented in Fig. 4(a). Component 2, which is located about 1.1 eV higher than component 1, is believed to be the molecular nitrogen peak.[39] The increase in component 2 as the amount of deposited Al increases, by comparison to a similar decomposition of Fig. 4(b) (not shown), indicates that this peak results from the dissociation of the molecular ammonia by the deposition of aluminum. This peak quickly disappears as the substrate is heated to $T=170$ K, while the molecular ammonia peak sharply decreases, indicating that N_2 from dissociated NH_3 can easily leave the surface. We can rule out the possibility that peak broadening and a new component on the higher binding-energy side result from the formation of Al nitride, since it would have resulted in a peak shift toward the lower binding-energy side due to the charge transfer from Al to the nitrogen atom. This is also supported by our previous observation of valence-band spectra, where NH_3 molecular orbitals can be clearly identified.[23] Component 3 is about 1.0 eV lower compared to the molecular peak, and survives the annealing to $T=170$ K and higher. This peak also grows as more aluminum is deposited on the ammonia overlayer, and it is speculated to be $GaAs_{1-x}N_x$ or $Al_{1-x}N_x$ but not yet AlN, since the binding energy of AlN is reported to be about 2 eV lower than that of NH_3.[20]

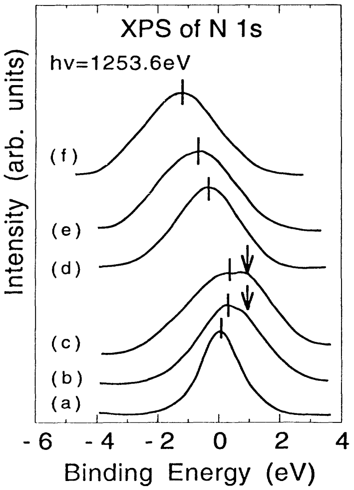

FIG. 4. N 1*s* x-ray-photoemission spectra for Al nitride growth on GaAs(110). From the bottom up: (a) after exposure of 20 L of NH_3 at $T=90$ K; (b) after 2 Å of Al deposition at $T=90$ K; (c) after 10 Å of Al deposition at $T=90$ K; (d) after annealing the same surface to $T=170$ K; (e) after annealing the same surface to $T=230$ K; (f) after annealing the same surface to $T=270$ K.

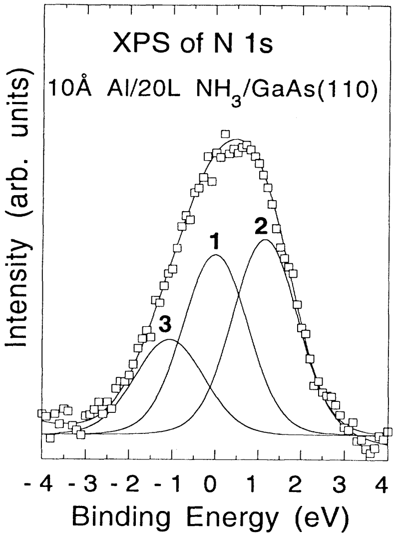

FIG. 5. Core-level fitting of N 1*s* peak at 10 Å $Al/NH_3/GaAs(110)$ at $T=90$ K. The data points (open squares) are the identical data presented in Fig. 4(c), and the fitted data are also shown in lines. The component 1 represents the EDC for molecular ammonia, the component 2 that for molecular nitrogen, and the component 3 that for $GaAs_{1-x}N_x$ or $Al_{1-x}N_x$.

The temperature study of N 1*s* EDC's [Figs. 4(d)–4(f)] exhibits N 1*s* behavior consistent with our assertion that the formation of Al nitride accelerates after the sample temperature increases to $T=170$ K. As we heat up the sample to $T=170$ K, the peak shifts to the lower binding-energy side by $\Delta BE \sim 0.4$ eV [Fig. 4(d)]. Combined with the peak shift of the Al 2*p* core-level EDC's toward the higher binding-energy side [Fig. 3(c)], this peak shift of N 1*s* indicates an increase in the formation of the Al-nitride overlayer, and the peak shift results from the lower electronegativity of Al compared to that of nitrogen atoms. The continuous peak shift toward the lower binding-energy side [Figs. 4(d)–4(f)] reflects the continuation of the formation of Al nitride and the dissociation of molecular ammonia into NH_x as the sample is heated, and it is consistent with the binding energy of 397.3 eV for AlN (Ref. 20) and 398.5 eV for NH_x compared with 400.1 eV for molecular ammonia.[38]

As the temperature increases, the unreacted NH_3 and gaseous molecular nitrogen escape from the surface. We observe a reduction of about 50% in the peak intensity after heating up to $T=270$ K. This reduction provides us with an indication of the degree of Al nitridation during heating. The thickness of the formed Al_xN_{1-x} is estimated to be ≤ 4 Å, assuming that all the nitrogen left on the sample reacts with part of the deposited aluminum to form the Al-nitride layers.

While the XPS core-level spectra demonstrate the process and temperature dependence of the $Al/NH_3/GaAs(110)$ interface formation, our inverse-photoemission studies provide a clear picture of the evolution of the unoccupied electronic states and the metal-insulator transition associated with the nitrification of Al. Figure 6 displays the inverse-photoemission spectra at four different experimental stages: (a) clean surface at room temperature, (b) after 1 L exposure of NH_3, (c) after 20 L exposure of NH_3, and (d) after deposition of 10 Å of Al. The energy of the inverse-photoemission spectra was measured from Fermi level of the sample.

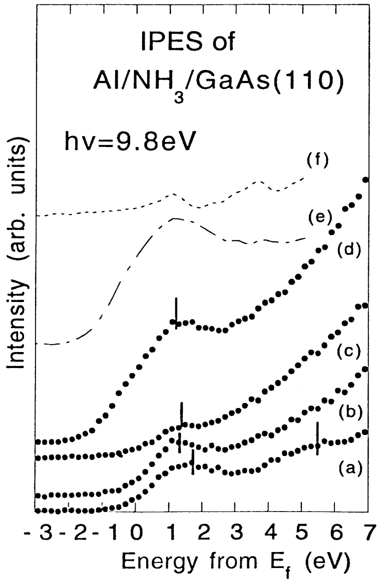

FIG. 6. Inverse-photoemission spectra at four different experimental stages. From the bottom up: (a) clean GaAs at room temperature; (b) after exposure of 1 L of NH_3 at $T=90$ K; (c) after exposure of 20 L of NH_3 at $T=90$ K; (d) after deposition of 10 Å of Al on $NH_3/GaAs(110)$ at $T=90$ K; (e) difference curve between (c) and (d); (f) difference curve between (a) and (b).

We present the spectrum of a clean surface of GaAs(110) at room temperature [Fig. 6(a)], which has been similarly observed by many others.[40,41] We observe two main peaks, one at $E=1.7$ eV and the other at $E=5.6$ eV above the Fermi level. We believe that the former represents the empty surface states of the substrate, which is very sensitive to the condition of the surface, and increases or decreases significantly upon the subsequent deposition of insulating or metallic overlayers. The broad feature centered at $E=5.6$ eV reflects the transition into conduction bands,[41] which will quickly disappear after we deposit overlayers. We also notice the tailing of the conduction-band minimum into the Fermi level, indicating that some surface states, likely due to the imperfect cleave of the sample, exist in the band gap.

The condensation of 1 L NH_3 (≤ 0.2 ML) in Fig. 6(b) introduced two peaks at $E=1.2$ and 3.7 eV, respectively [Fig. 6(f)]. We believe that these two peaks represent new interface states generated during the nitrification of the substrate, rather than empty molecular states of ammonia, since the lowest unoccupied molecular state of ammonia is $4a_1$, whose energy is expected to be around $E=15.4$ eV or 0.58 hartree.[42] The 1.2-eV peak may also be due to a shift of the 1.7-eV peak of the clean surface [Fig. 6(a)] toward the Fermi level, which is consistent with our earlier suggestion in the XPS study that the nitrification of the substrate reduces band bending toward the center of the band gap. Upon further condensation of 20 L of NH_3, the inverse-photoemission spectrum shows a strongly suppressed peak at $E=1.2$ eV, confirming the presence of a thick insulating layer [Fig. 6(c)]. After the deposition of 10 Å of Al on the sample,

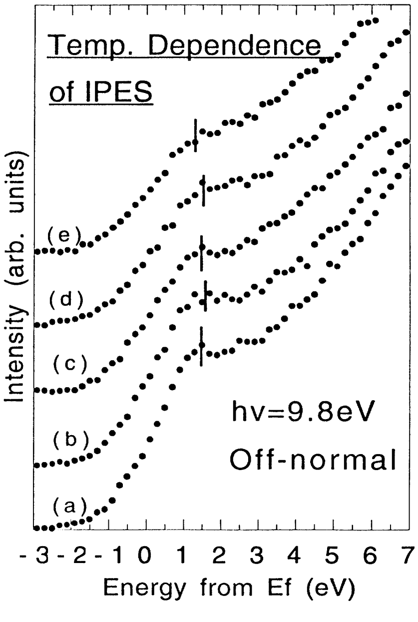

FIG. 7. Inverse-photoemission spectra for temperature dependence of Al nitride on GaAs(110). From the bottom up: (a) 10 Å $Al/20$ L $NH_3/GaAs(110)$ at $T=90$ K; (b) the same surface at $T=150$ K; (c) the same surface at $T=200$ K; (d) the same surface at $T=230$ K; (e) the same surface at $T=270$ K.

we observe a large increase in the states around the Fermi level and a smooth, free-electron-like density of states, which are the indications of the thin film of metallic aluminum which one expects to see. The difference curves of (e) and (f) are also shown in Fig. 6 for visual clarity of the changes in the spectra after the exposure of 1 L of NH_3 and aluminum evaporation.

The temperature study of the IPES data shows the transition from a metallic Al layer to an insulating Al-nitride layer. As we continuously heat up the sample from $T=100$ up to 270 K, the emission onset near the Fermi level becomes less steep, and the free-electron-like density of states steadily disappears, leaving behind the much less structured spectrum [Figs. 7(a)–7(c)]. This featureless behavior and the large decrease in the density of states near the Fermi level may be rationalized by noting that the formation of Al_xN_{1-x} takes place during the warmup to room temperature, and the formed insulating overlayer is amorphous. In addition, charging up in the insulating layer smears out the spectra, resulting in a smooth rise near the Fermi level rather than clearly displaying the conduction-band minimum of Al_xN_{1-x}.

CONCLUSIONS

We have studied the interface formation of $Al/NH_3/GaAs(110)$ using x-ray-photoemission and the inverse-photoemission spectroscopy. We have found that the nitrification of GaAs(110) is very similar to that of GaAs(100) after examining the core-level EDC's of the substrate. Our results from N 1*s* core-level EDC's confirm our previous suggestion that the nitrification of the substrate is enhanced by the deposition of aluminum. The formation of Al nitride is observed in the N 1*s* and Al 2*p* core-level EDC's and the inverse-photoemission spectra. Especially, Al 2*p* core-level EDC's and the inverse-photoemission spectra reveal the metallic-to-insulating transition of the overlayer. Also, with finer temperature control, we are able to observe the formation of Al nitride at $T=170$ K and above. It appears that above $T=90$ K there is no threshold temperature for the formation of Al nitride to take place, although the reaction to form Al nitride at $T=90$ K is slow, and probably kinematically limited. Finally, the interaction between the aluminum overlayer and the substrate is minimal, and little or no free Ga is observed throughout the experiment.

ACKNOWLEDGMENTS

The research was supported in part by the New York State Science and Technology Foundation under Grant No. RDG 90185 and by National Science Foundation Grant No. DMR-8913880. The authors acknowledge the contribution from T. Balasubramanian at the early stage of constructing the electron gun for IPES. Dr. J. D. Tobin and Dr. B. Knapp generously offered the drawings of the electron gun. Suggestions of Dr. P. D. Johnson about the construction of the MCP bandpass photon detector are also gratefully acknowledged.

---

[1] N. F. Mott and E. A. Davis, *Electronic Processes in Noncrystalline Materials* (Clarendon, Oxford, 1979).

[2] M. H. Cohen and J. C. Thompson, Adv. Phys. **17**, 857 (1968).

[3] J. C. Thompson, J. Solid State Chem. **54**, 308 (1984).

[4] P. S. Hsu, C. B. Zimm, and W. S. Glaunsinger, J. Solid State Chem. **54**, 346 (1984).

[5] D. Smith, B. E. Williamson, and P. N. Schatz, Chem. Phys. Lett. **131**, 457 (1986).

[6] P. D. Schettler and A. Patterson, J. Phys. Chem. **68**, 2865 (1964).

[7] *Metal-Ammonia Solutions,* edited by J. J. Lagowski and M. J. Sienko (Butterworths, London, 1970).

[8] H. Teoh, P. R. Antoniewics, and J. C. Thompson, J. Phys. Chem. **75**, 399 (1971).

[9] *Solutions Metal-Ammoniae,* edited by G. Lepoutre and M. J. Sienko (Benjamin, New York, 1964).

[10] M. H. Cohen and J. Jortner, J. Phys. Chem. **79**, 2900 (1975).

[11] N. F. Mott, J. Phys. Chem. **84**, 1199 (1980).

[12] S. L. Qiu, C. L. Lin, L. Q. Jiang, and Myron Strongin, Phys. Rev. B **39**, 1958 (1989).

[13] M. Mizuta, S. Fujienda, T. Jitsukawa, and Y. Matsumoto, in *Gallium Arsenide and Related Compounds,* edited by W. T. Lindley (Institute of Physics, Bristol, 1987), p. 153.

[14] S. Fujienda and Y. Matsumoto, Jpn. J. Appl. Phys. **27**, L296 (1988).

[15] S. Fujienda, Y. Mochizuki, and Y. Matsumoto (unpublished).

[16] E. H. Nicollian and J. R. Brews, *MOS Physics and Technology* (Wiley, New York, 1982).

[17] K. Tsubouchi, and N. Mikoshiba, IEEE Trans. Sonics Ultrason. Ind. Eng. Chem. **SU-32**, 634 (1985).

[18] N. Lieske and R. Hezel, J. Appl. Phys. **52**, 5806 (1981).

[19] M. Gautier, J. P. Duraud, and C. Le Gressus, J. Appl. Phys. **61**, 574 (1987).

[20] J. A. Taylor and J. W. Rabalais, J. Chem. Phys. **75**, 1735 (1981).

[21] S. Yoshida, S. Misawa, Y. Fujii, S. Takada, H. Hayakawa, S. Gonda, and A. Itoh, J. Vac. Sci. Technol. **16**, 990 (1979).

[22] H.-U. Baier and W. Monch, J. Appl. Phys. **68**, 586 (1990).

[23] Ken T. Park, Jianming Cao, Y. Gao, G. W. Wicks, and M. W. Ruckman, J. Appl. Phys. **70**, 2623 (1991).

[24] M. W. Ruckman, Jianming Cao, Ken T. Park, Yongli Gao, and G. W. Wicks, Appl. Phys. Lett. **59**, 849 (1991).

[25] H. Felner-Feldegg, U. Gelius, S. Wannberg, A. G. Nisson, E. Basilier, and K. Siegbahn, J. Electron Spectrosc. **5**, 643 (1974).

[26] J. Knapp, Ph.D. thesis, University of Wisconsin–Madison, 1988.

[27] N. G. Stoffel and P. D. Johnson, Nucl. Instrum. Methods A **234**, 230 (1985).

[28] P. D. Johnson and S. L. Hulbert, Rev. Sci. Instrum. **61**, 2277 (1990).

[29] Recep Avci, Qing Cai, and Gerald Lapeyre, Rev. Sci. Instrum. **60**, 3643 (1989).

[30] M. H. Hecht, Phys. Rev. B **41**, 7918 (1990).

[31] I. M. Vitomirov, G. D. Wadill, C. M. Aldao, S. G. Anderson, C. Capasso, and H. Weaver, Phys. Rev. B **40**, 3438 (1989).

[32] G. D. Wadill, Tadahiro Komeda, Y. N. Yang, and J. H. Weaver, Phys. Rev. B **41**, 10 283 (1990).

[33] S. Chang, I. M. Vitomirov, L. J. Brillson, D. F. Rioux, P. D. Kirchner, G. D. Pettit, J. M. Woodall, and M. H. Hecht, Phys. Rev. B **41**, 12 299 (1990).

[34] A. Bauer, M. Prietsch, S. Molodtsov, C. Laubschat, and G. Kaindl, Phys. Rev. B **44**, 4002 (1991).

[35] Y. Gao, C. P. Lusignan, M. W. Ruckman, and Myron Strongin, J. Appl. Phys. **67**, 7148 (1990).

[36] P. Soukiassian, H. I. Starnberg, T. Kendelewicz, and Z. D. Hurych, Phys. Rev. B **42**, 3769 (1990).

[37] Steven G. Anderson, Y. Chen, J. M. Seo, and J. H. Weaver, Phys. Rev. B **43**, 9621 (1991).

[38] F. Bozso and Ph. Avouris, Phys. Rev. B **38**, 3937 (1988).

[39] M. Grunze, C. R. Brundle, and D. Tomanek, Surf. Sci. **119**, 113 (1982).

[40] D. Straub, M. Skibowski, and F. J. Himpsel, Phys. Rev. B **32**, 5237 (1985).

[41] B. Reihl, T. Riesterer, M. Tschudy, and P. Perfetti, Phys. Rev. B **38**, 13 456 (1988).

[42] W. L. Jorgensen and L. Salem, *The Organic Chemist's Book of Orbitals* (Academic, New York, 1973).