

A METHOD OF PRODUCING HIGH QUALITY OXIDE AND RELATED FILMS ON SURFACES

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ABSTRACT

Aluminum oxide or aluminum nitride films were deposited on MBE grown GaAs(100) using a novel cryogenic-based reactive thin film deposition technique. The process involves the condensation of molecular oxygen, ammonia or other gases normally used for reactive thin film deposition on the substrate before the metal is deposited. The metal vapor is deposited into this layer and reacts with the molecular solid to form the desired compound or a precursor that can be thermally decomposed to generate the desired compound. The films produced by this method are free of impurities and the low temperatures can be used to control the film and interfacial structure. The process can be easily integrated with existing MBE-systems and on going research using the same apparatus suggests that photon or electron irradiation could also be used to promote the reactions needed to give the intended material.

INTRODUCTION

This paper discusses a new reactive thin film fabrication technique which has been used to deposit films like Al_2O_3 or TiN on a chemically reactive substrate like gallium arsenide. Chemical bonding and physical phenomena like wetting and nucleation play a central role in controlling interfacial structure and thin film morphology.¹ These phenomena can often thwart attempts to fabricate particular microstructures. Basic surface science research is providing an understanding of the underlying mechanisms of thin film growth and structure on an atomic scale and this knowledge can be applied to overcome fundamental problems like the formation of unwanted phases by solid state reaction. It is well-known that many metals react on contact with semiconductors or undergo grain boundary-assisted diffusion at low temperatures when deposited in the high quality vacuums.² This is, in part, due to the chemical activity of metal atoms and also due to the fact that the incident beams of atoms, ions, molecules or clusters are often sufficiently energetic to cause the chemical reaction.³ An obvious control strategy is the emplacement of an inert barrier layer to thermalize or neutralize the incoming species before they encounter the substrate. An implementation of this procedure is represented by the work of Waddill et al.⁴ who used Xe films to control the morphology of metal-semiconductor interfaces and their electrical properties. The same group also found that the removal of oxygen from high T_c superconductors when metals are deposited can be minimized by cluster

deposition into a Xe buffer layer.⁵ A condensed barrier layer can also be chemically active and serve as a reactive matrix for thin film growth. This new feature distinguishes this work from earlier efforts using condensed gas layers to modify thin film growth and, as we will discuss, provides some advantages that can be exploited in fabricating thin films.

The need for better methods of growing dielectric films on materials like gallium arsenide is motivated by the fact that compound semiconductors have comparatively poor native oxides.⁶ Silicon is an ideal material for microelectronics, in part, because SiO₂, an excellent dielectric, can be grown by thermal oxidation. SiO₂ films are an essential element of every microelectronic device. For gallium arsenide, the obvious oxides Ga₂O₃ and As₂O₃ are thermodynamically unstable, difficult to grow and have relatively poor morphology and electrical properties when compared to SiO₂. Usable As₂O₃ layers can be produced in an As-rich atmosphere and the losses of As encountered during device fabrication can be compensated by going off stoichiometry. There is a need for growing better dielectric materials on compound semiconductors or simplifying the growth process.

THIN FILM PREPARATION

The details of the cryogenic reactive deposition procedure have been described elsewhere (refs. 7 and 8). The work was done in a stainless steel vacuum system designed for surface and interfacial science studies and the experimental procedure is constrained by the nature of this apparatus. However, the concept is applicable to any ultrahigh vacuum system designed for thin film deposition and may also be applicable to systems with lesser quality vacuums. The apparatus and procedure are shown schematically in Figure 1 . A semiconductor wafer was mounted on a molybdenum plate that was heated from behind by a 0 to 30 watt ceramic button heater. The molybdenum plate was attached to an OFHC copper cold finger that was cooled using a flowing He cryostat (APD Cryogenics Helitran) that can reach 15 K when cooled with helium or 78 K when cooled with liquid nitrogen.

Our work utilized a molecular beam epitaxy (MBE) grown GaAs(100) wafer approximately 1 cm x 1 cm which was cleaned and pre-etched using established methods or As capped. The As capped wafers were heated to 585 C to evaporate the capping layer. Ordered gallium arsenide surfaces require special sputter etching and annealing treatments. The specific procedures used normally produce gallium rich surfaces.⁹ RHEED (reflection high energy electron diffraction) and photoemission data were used to establish the nature of the surface before the dielectric films were fabricated.

The substrates were heated and sputter etched at room temperature to prevent the cold trapping of impurities on the cold finger. During the cool-down to liquid nitrogen or helium temperatures, the button heater was used to keep the sample above 150 K to prevent condensation of significant amounts of residual gases like CO or water. When the cold finger and cryostat were cold, the heater power was turned off to allow the wafer to cool down quickly. In the case of the reaction to form Al₂O₃, a jet of gaseous oxygen was directed on to the wafer using a needle doser while the temperature of the GaAs sample was held at 46-49 K. Aluminum vapor was then directed on to the sample from a resistively heated W basket at a rate of about 2 Å/ min. The thickness of the Al was monitored using a quartz crystal microbalance. For the attempt to grow AlN, an ammonia film was first condensed and Al was then evaporated into it.

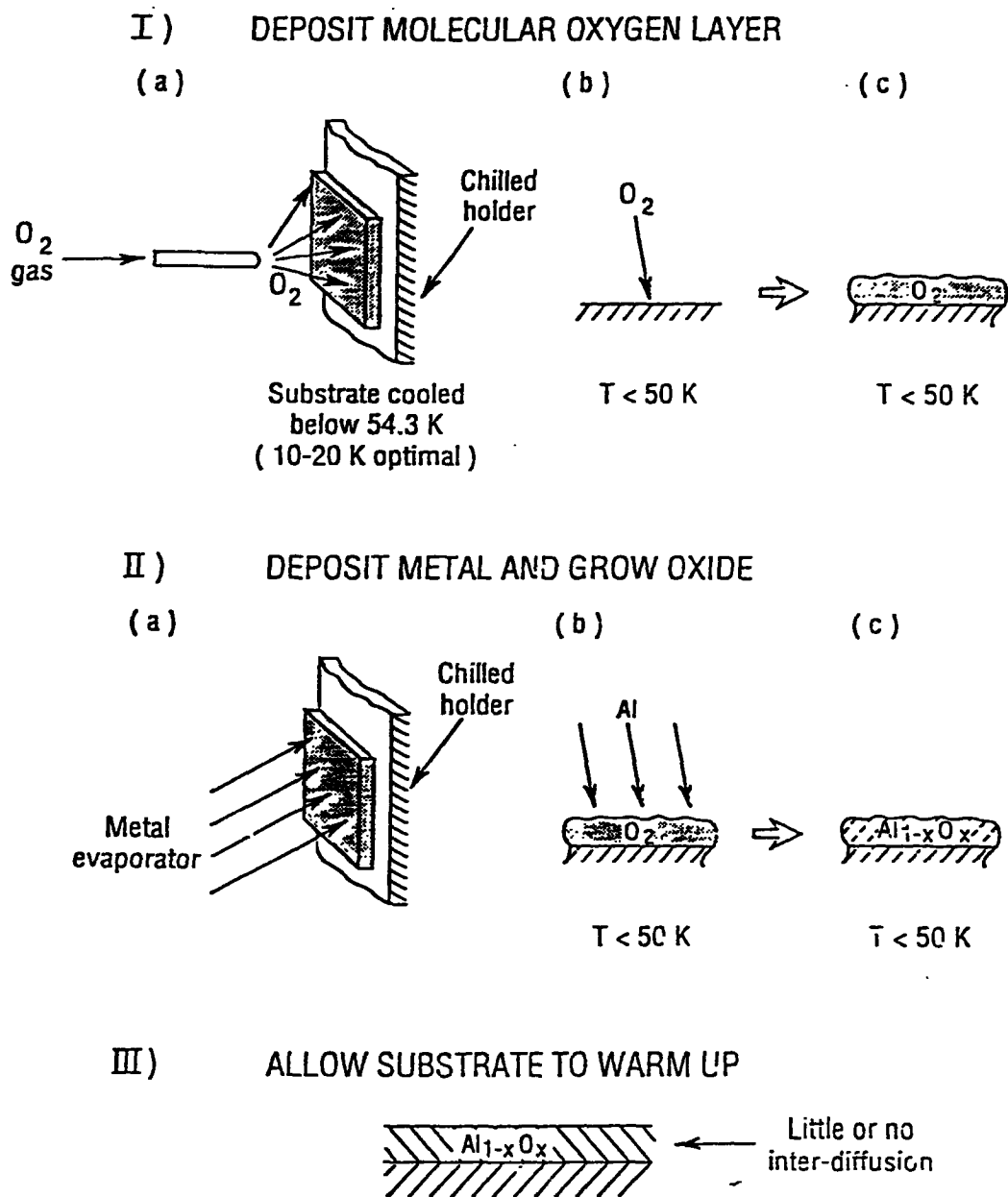


Figure 1. Schematic Diagram of the Thin Film Deposition Process

RESULTS AND DISCUSSION

Photoemission was used to characterize the thin metal compound layers formed on GaAs(100). The photoemission experiments have been reported elsewhere^{7,8} but will be summarized here. In both cases to be illustrated, the Al inorganic compounds were formed on GaAs(100) below room temperature. It is well known that most metals react with an impurity free gallium arsenide surface and form metal arsenides or gallium alloy layers near the interface. Compound semiconductors are especially susceptible to solid state reaction because some of their surfaces contain both anions and cations.¹⁰ Most metals (Al, Cu or Au) used as conductors react with gallium arsenide. Evidence of substrate disruption can be seen in core level photoemission data which is sensitive to the chemical state of the photo-ionized atom.¹¹ Specifically, the core level binding energy is related to the chemical state of the atom and, provided other factors are the same, the atoms in a number of different atomic environments will generate components that can be isolated in the spectra. Photoemission was used as a probe of thin film growth and composition because it is a more direct means of studying layers as thin as a monolayer and is more sensitive than Rutherford backscattering.¹² Since the films are nowhere near the thickness required for device fabrication, the work described here establishes the scientific feasibility of the concept and further work is needed to make a technologically useful dielectric film.

For the growth of Al₂O₃ films on GaAs(100), the experiment consisted of three steps: (1) the condensing molecular O₂ on the surface, (2) vapor deposition of Al into the solid O₂ and (3) the heating of the sample to remove excess O₂.

In figures 2 and 3, we show valence band and core level data for the formation of aluminum oxide on GaAs(100) at 49 K. The results for the clean surface (Figure 2) are similar to those reported in many papers.¹³ The valence band maximum (VBM) was found 0.42 eV below the Fermi level which indicates the surface is pinned. The photoelectron energies of the features shown in the experimental data are referenced to the VBM. Close examination of RHEED pattern, valence band photoemission spectra and the Ga 3d/As 3d ratios which were 0.48 indicates this surface is the gallium-rich (4x6) surface.

After the sample was cooled to 49 K, a jet of O₂ was directed on the sample and a thin O₂ film condensed on the sample surface. The triple point of O₂ is near 54 K and the vapor pressure at the critical point is 1.1 torr.¹⁴ Being close to the critical point for O₂, limited the thickness of the O₂ layer to that of a weakly chemisorbed monolayer. Additional cooling would condense a much thicker O₂ layer. However, the thickness of O₂ was sufficient to make a thin layer of aluminum oxide and very thin layers are frequently made by MBE. O₂ has a distinct valence electronic structure which is reflected in the photoemission spectra of the valence band. After the deposition of O₂, the valence band shows peaks identified by Frankel et al.¹⁵ with the 3σ_g (13.6, 11.2 eV), the 1π_u (9.8 eV) and the 1π_g (5.2 eV) molecular orbitals. The addition of Al vapor causes the reaction to form an aluminum oxide that can be identified on the basis of the Al 2p core level shift (Figure 3) as an amorphous Al₂O₃.¹⁶ The molecular photoemission features disappear and are replaced by a broad peak about 6-8 eV binding energy which is also seen when metallic Al surfaces are oxidized.

There are a number of ways to make a sapphire film and the films produced have a variety of morphologies and compositions. A challenging problem with a material like gallium

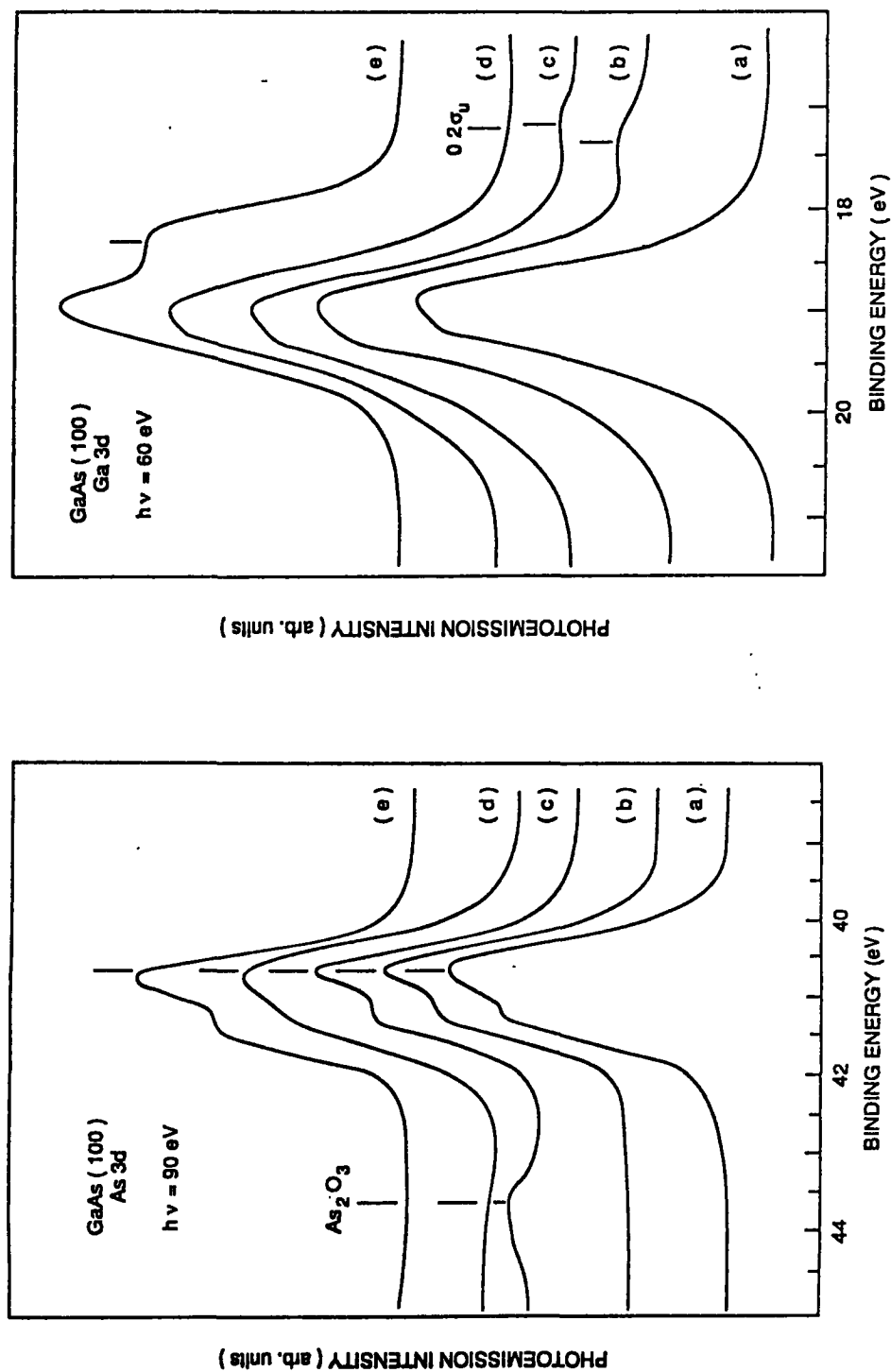


Figure 3. As 3d and Ga 3d core level photoemission spectra for the reactive deposition of Al into solid oxygen. For both figures (a) represents GaAs(100), (b) the same surface covered by O_2 , (c) the same surface after the deposition of 2A of Al, (d) 10 A of Al A and (e) shows the effect of depositing 10 A of Al on GaAs(100) at 300 K.

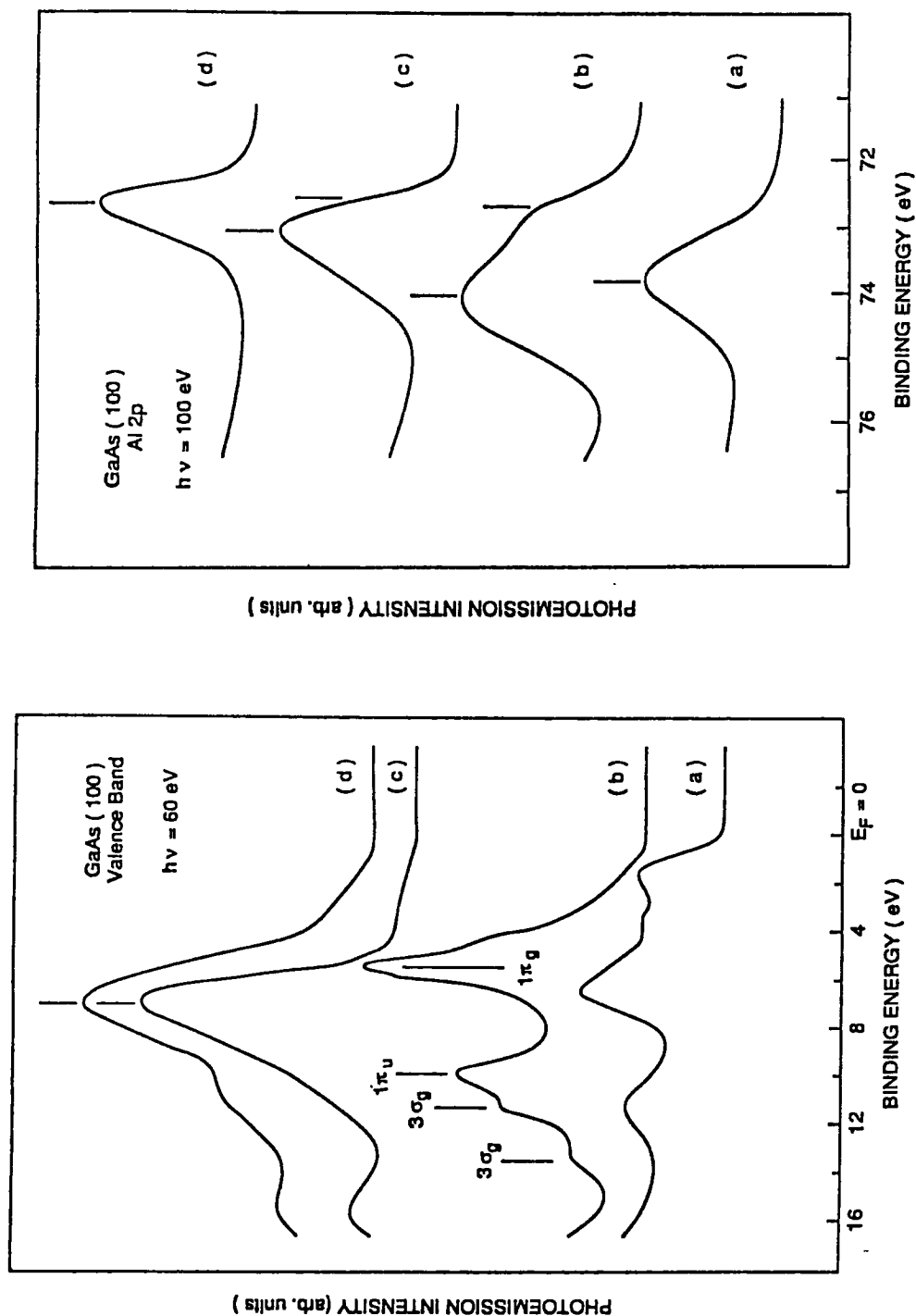


Figure 2. Valence and Al 2p core level photoemission spectra for the reactive deposition of Al into solid oxygen. For the valence band spectra (a) represents GaAs(100), (b) the same surface covered by O_2 , (c) the same surface after the deposition of 2 Å of Al, and (d) shows the surface upon warming to 300 K. For the Al 2p spectra (a) shows the Al oxide formed by depositing 1 Å of Al, (b) 2 Å of Al (c) the effect heating to 300 K and (d) the Al 2p spectrum for aluminum.

arsenide is the fact that the substrate can react with the incoming species that make the thin film. Alternative methods of making Al_2O_3 films include oxidizing predeposited aluminum films, reactive evaporation, plasma-assisted chemical vapor deposition from metal organic precursors (PCVD), laser ablation of Al_2O_3 and radio frequency sputtering of Al_2O_3 target. All of the above techniques have drawbacks that can be largely eliminated by our new technique. For example, the plasmas generated by sputtering and PCVD heat and damage fragile substrates.

The Ga 3d and As 3d core level photoemission data in Figure 3 show nature of the dielectric/GaAs interface during the growth process, provide clues concerning the adhesion of the dielectric and indicate the extent of reaction between the dielectric and gallium arsenide. Extensive interdiffusion is seen when aluminum is deposited on the substrate and is evidenced in the spectra by the development of a second Ga 3d core level component (curve 3(e)) at lower binding energy that can be associated with an intermixed Al-Ga phase. An Al_2O_3 layer produced by the oxidation of a predeposited Al film would have a Ga oxide impurity that might decompose when heated. It is emphasised at this point that the aluminum oxide/GaAs(100) interface prepared by cryogenic reactive deposition lacks the Ga-Al phase seen when Al is directly deposited on GaAs. A small peak is seen about 3.1 eV above the As 3d peak. This component is due to a small amount of As_2O_3 that is produced by the reaction of arsenic with the atomic oxygen liberated during the reaction of O_2 with Al. This peak is reduced when the O_2 is used up and the Al reacts with As_2O_3 to form Al oxide and free As. We interpret the core level data as indicating that a relatively pure amorphous Al_2O_3 film with a sharp dielectric/GaAs(100) interface can be grown at temperatures of 50 K by the cryogenic reactive evaporation technique. The small scale modification of the gallium arsenide surface shows that there is bonding between the dielectric material and gallium arsenide. Aluminum oxide layers of useful thickness could be grown on a thin O_2 barrier film by co-deposition of aluminum and O_2 or by pulsed deposition of the two reactants separately.

The other dielectric deposited on GaAs(100) by the cryogenic reactive evaporation technique was aluminum nitride. CV measurements by Mizuta et al.¹⁷ suggest that the interface density of states ($< 10^{12} \text{ /eVcm}^2$) is small between AlN and GaAs(100) making it a candidate for GaAs metal-insulator-semiconductor (MIS) system. AlN is also used as a capping material for gallium arsenide. AlN can be grown by a variety of techniques including but not limited to metal organic chemical vapor deposition (MOCVD), ion implantation of nitrogen into Al films and reactive molecular beam epitaxy. We attempted to grow AlN using cryogenically condensed ammonia.

Ammonia can be condensed on the surface at liquid nitrogen temperature (77 K) . The same procedures were used in this case as in the earlier experiment to make aluminum oxide. The chemistry of aluminum and ammonia is more complicated because a number of compounds can be formed between Al and ammonia or its fragments NH_2 and NH . Figure 4 shows valence band and Al 2p data for the reaction of Al with solid NH_3 on GaAs(100). Like O_2 , the condensation of NH_3 changes the valence band region. Peaks at -7.0 and -12.2 eV binding energy are assigned to the NH_3 3a₁ and 1e orbitals, respectively. We exposed the surface to 20 L of NH_3 and based on the reduction in the intensity of the Ga and As 3d core levels estimate the thickness of the molecular film as being 3 monolayers.

The deposition of 10 Å of Al causes the NH_3 features to shift about 0.8 eV to higher binding energy. Unlike O_2 , the peaks are not disrupted and we conclude that NH_3 is retained

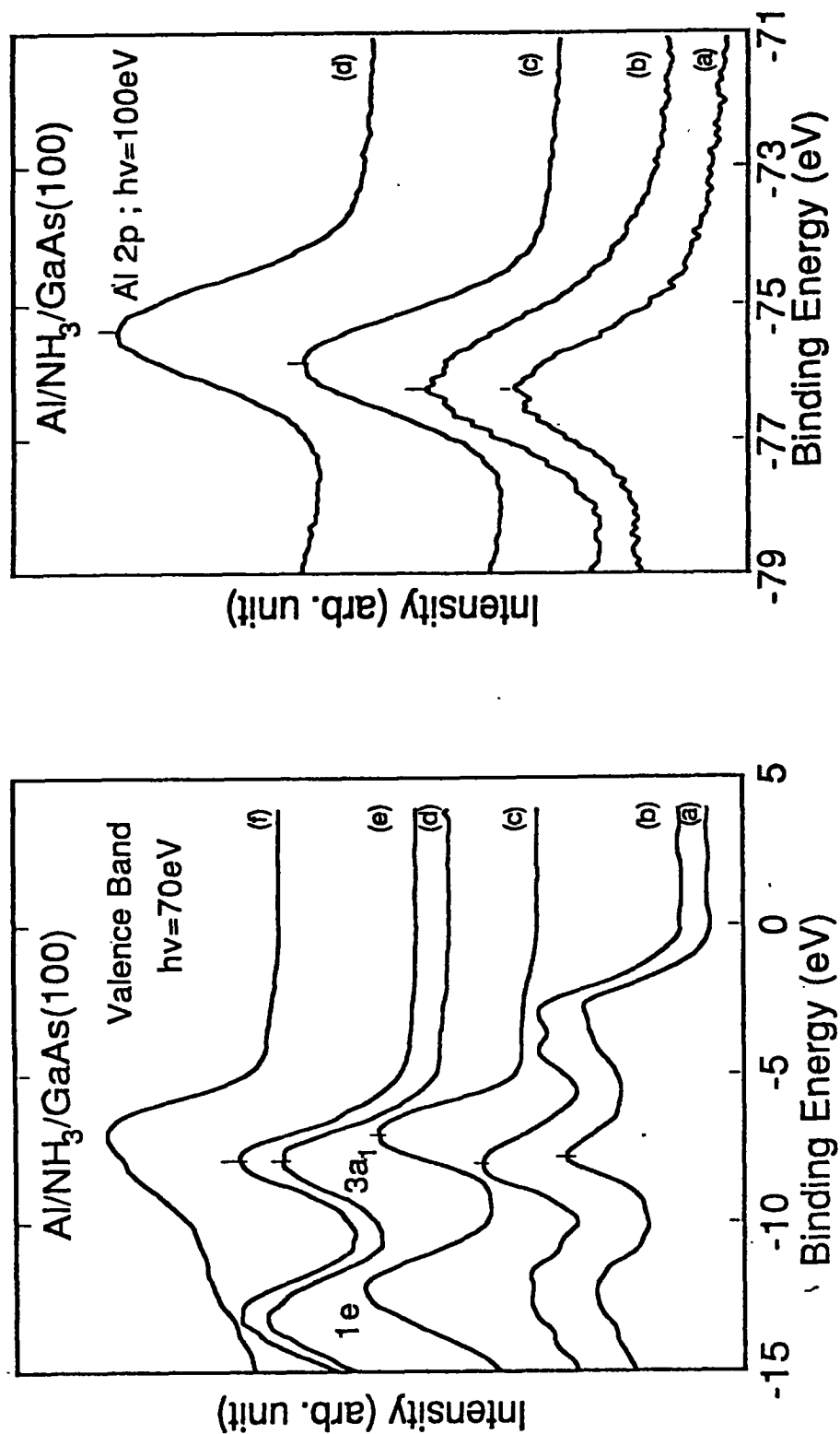


Figure 4. Valence and Al 2p core level photoemission spectra for the reactive deposition of Al into solid ammonia. For the valence band spectra (a and b) represent GaAs(100), (c) the same surface covered by NH₃, (d) the same surface after the deposition of 10 A of Al, (e) 20 A of Al and (f) shows the surface upon warming to 300 K. For the Al 2p spectra (a) shows the Al-NH₃ phase formed by depositing 10 A of Al, (b) 20 A of Al (c) the effect heating to 300 K and (d) 600 K (300 C).

as a bonded species in the Al-NH₃ compound. The deposition of a further 20 Å of Al caused no changes in the valence band. Large scale changes are seen in the valence band when the sample is heated by allowing the cold finger to return to room temperature. The NH₃-related features disappear and a large broad feature peaking near -5.5 eV binding energy is seen. The shape of the valence band is the same as that obtained for AlN. There is a threshold temperature for AlN formation between 78 and 300 K. The large Al 2p core level (Figure 4) shift (2-3 eV) indicates that Al is chemically bonded to the NH₃. Thus a Al(NH₃)_x precursor or adduct forms at low temperatures. Heating is required to decompose this to form the nitride, but as will be briefly discussed in the conclusion, processing using energetic photon or electron beams should also provide a method of generating this compound.

The As 3d and Ga 3d core levels show changes that reinforce the conclusions drawn from the valence level data and provide information about the AlN/GaAs(100) interface. The As 3d core level is broadened and the surface core level component is reduced when NH₃ is condensed. This can be connected with the chemisorption of the ammonia and the elimination of unsaturated (dangling) surface bonds. After 10 Å of Al are deposited, the As 3d again broadens. This may be due to the formation of AsN or AlAs depending on whether hydrogen , an NH_x fragment or nitrogen is released during the insertion of Al into NH₃ or Al reaches a reaction site at the interface. The Ga 3d peak is also broadened but on the higher not lower binding energy side which is seen when Al is deposited and we conclude that AlAs has not formed at this stage of film growth. These changes are more pronounced after 20 Å of Al are deposited. In addition, at the 20 Å Al coverage, a small Ga 3d component associated with the Ga-Al phase begins to be seen. Heating the surface to 300 K, reverses some of the changes in the substrate seen when Al is inserted in to the NH₃ layer. The width of the As 3d decreases and the shape is comparable to that seen for a clean surface. The Ga 3d peak remains broadened and indicates that the GaN phase at the interface is stable at 300 K.

Both the Al oxide and AlN layers were heated to temperatures just below the threshold for GaAs substrate disruption and both films proved to be stable as evidenced by the lack of changes in the photoemission spectra.

SUMMARY AND CONCLUSIONS

From surface sensitive photoemission studies, we conclude that stable dielectric layers can be grown on a compound semiconductor by reactive deposition into cryogenically condensed molecular solids. In the specific examples, Al oxide and Al nitride were formed by reaction with O₂ at 49 K and NH₃ between 78 and 300 K. We believe the technique can be scaled up to make coatings of useful thicknesses and point out that the fabrication of these films under novel conditions provides an opportunity to make such films with morphologies that vary from those produced by more widely used techniques. Work has continued at Brookhaven using condensed molecular solids. Intense EUV and soft x-ray beams have been directed into condensed mixtures of gases like diborane and ammonia to produce coatings whose spectroscopic properties resemble boron nitride.¹⁸ Work is also proceeding using metal organics like tri-methyl aluminum to make compounds like AlN. We feel that condensed molecular films might play a role in advanced EUV and x-ray lithographic processes because molecular solids can be used to enhance etching and selective thin film deposition. The technique also has promise for depositing coatings like aluminum oxide on polymer surfaces for use as a protective layer. Another area that deserves closer examination is the use of this

process to deposit dielectric films on oxide surfaces like $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ for use in planar tunneling junctions.

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