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Growth of AlF_3 thin films on GaAs(1 1 0). Structure and chemical stability

L.I. Vergara [a,b,*], R.A. Vidal [a], J. Ferrón [a,b], E.A. Sánchez [c], O. Grizzi [c]

[a] *INTEC, Univ. Nacional del Litoral – CONICET, Güemes 3450, CC 91, 3000 Santa Fe, Argentina*
[b] *Facultad de Ingeniería Química, Santiago del Estero 2829, 3000 Santa Fe, Argentina*
[c] *Centro Atómico Bariloche – CNEA, Instituto Balseiro and CONICET, 8400 San Carlos de Bariloche, Argentina*

Abstract

The growth process of AlF_3 films on GaAs(1 1 0), from submonolayer coverage up to several layers, have been characterized by means of Auger electron spectroscopy (AES), ion sputter depth profiling, and direct recoiling spectroscopy with time of flight analysis (TOF-DRS). The chemical composition and the surface structure were studied for films grown at room temperature (RT) and after annealing the films up to 400°C.

The films grow stoichiometrically at RT and no ordering was found in this case. The post-annealing of the AlF_3 films produces a loss of fluorine, and a chemical reduction of aluminum with the appearance of a metallic phase. AES and TOF-DRS combined measurements show that while F atoms escape through the surface, metallic Al diffuse into the substrate substituting Ga atoms.

Keywords: Semiconductor–insulator interfaces; Gallium arsenide; Low energy ion scattering (LEIS); Auger electron spectroscopy

1. Introduction

The structure and chemical stability of insulator/semiconductor systems have attracted wide interest for the applications in MIS (metal–insulator–semiconductor) devices. For the case of III–V compound semiconductors group II fluorides have been used as insulating materials and epitaxial growth have been found at substrate temperatures above 250°C [1,2]. Although the trifluorides crystallize in a more complex structure (rhomboedric) as compared with the cubic fluorite structure of group II fluorides, AlF_3, and AlF_3/LiF alloy thin films are promising materials to be used as inorganic resists for nanometer-scale patterning in electron beam lithography [3–6]. In this work we report experiments of direct recoiling spectroscopy with time of flight analysis (TOF-DRS) and Auger electron spectroscopy (AES) performed to obtain information about the growth mechanism of AlF_3 onto GaAs(1 1 0) and to study the effects of post-deposition annealing of these thin films.

2. Experimental method

AlF_3 films were grown over a p-type GaAs(1 1 0) single crystal doped with Zn (1×10^{19} at/cm^3). The

* Corresponding author. Address: Instituto de Desarrollo Tecnológico para la Industria Química, Güemes 3450, 3000 Santa Fe, Argentina. Tel.: +54-342-455-9175; fax: +54-342-455-0944.

E-mail address: lvergara@intec.unl.edu.ar (L.I. Vergara).

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TOF-DRS measurements were conducted in a custom-made chamber working at 2×10^{-10} Torr. The TOF-DR spectra were acquired with Kr^+ ions at 5 keV. Both neutrals and ions scattered at 45° were detected by a channeltron electron multiplier located at the end of a 122 cm drift tube. The scattering geometry is depicted in the inset of Fig. 1. Kr projectiles were chosen instead of the more frequently used Ar or Ne because in these cases, for our experimental conditions, there is overlap of scattering and recoiling peaks. The absence of Kr projectiles single scattered at 45° from F or Al simplifies the peak identification and enhances the sensitivity to Al and F direct recoils (DR). These effects allow the use of very small incident currents (5–10 pA), thus preventing charging effects and film damage. On the other hand, heavy projectiles (Kr) incident on a low mass film do not give good time and depth resolutions, due to recoils generated from different surface locations. AES measurements were carried on a separated commercial surface analysis system (PHI 590A) with a base pressure in the 10^{-10} Torr range. Auger electrons were excited by 2 keV electron bombardment. An electron density as low as 30 μA/cm^2 was used in order to minimize electron induced desorption. Differentiated spectra of the Al^{3+} (51 eV), Al^0 (68 eV), F (647 eV), Ga (51–55 eV) and As (31 eV) Auger transitions were acquired with a single-pass cylindrical mirror analyzer, with an energy resolution of 0.6% and 2 eV peak-to-peak modulation amplitude. Ion sputter depth profiling was performed using 1.5 keV Ar^+ ions with a current density of 10 μA/cm^2. The angle of incidence of the ions is 54° with respect to the surface normal.

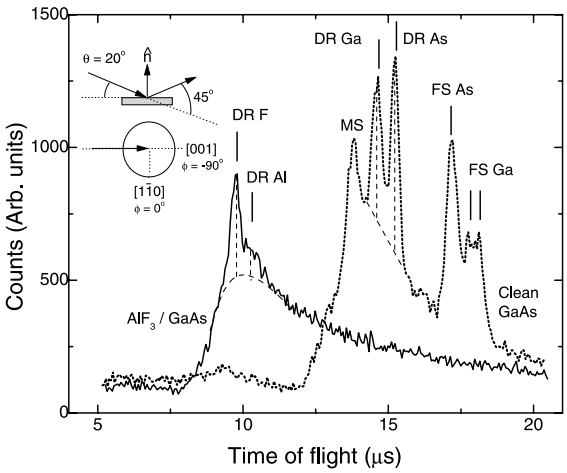

Fig. 1. TOF spectra measured for a clean (···) and an AlF_3-covered GaAs(1 1 0) surface (—). The film evaporation time was 300 s. The calculated position for DR for As, Ga, F, and Al, and forward scattering (FS) for As and Ga are displayed in the figure. The peak labeled MS comes from multiple scattering sequences. A schematic diagram with the TOF-DRS geometry and the angle definitions are also shown. The dashed lines under the DR peaks represent the background used to obtain the peak intensities.

The substrate was cleaned by two different methods: grazing bombardment (<2°) with 20 keV Ar^+ ions and annealing at 500°C for TOF-DRS measurements, and 1 keV Ar^+ ion bombardment and annealing at 500°C for AES measurements. We have already shown, [7] through TOF-DRS [8] and LEED measurements [9], that both methods are effective to remove impurities, yielding very smooth and ordered surfaces. Fluoride depositions were performed 'in situ' from a Knudsen cell charged with anhydrous AlF_3 (CERAC Inc., Milwaukee, Wisconsin, EEUU, 99.5%). The cell was carefully degassed and shuttered to avoid sample contamination. UHV conditions were kept throughout the evaporations with chamber pressures in the 10^{-10} Torr range.

3. Results and discussion

In Fig. 1 we show the TOF spectra for the clean GaAs surface and after an AlF_3 evaporation of 300 s with the sample at room temperature (RT) and the Knudsen cell at 550°C, corresponding roughly to a film thickness of ~3 ML. The calculated position for the direct recoiling and forward scattering peaks are included in the figure. A projectile incidence angle of 20° was chosen to reduce shadowing and focussing effects during the incident and exit trajectories [8]. In the spectrum corresponding to the clean surface we can identify Kr projectiles scattered (in the forward direction) through a single collision with either Ga or As atoms (labeled FS) and Ga and As atoms produced as recoils in single collisions (labeled DR). The peak labeled MS comes from multiple

scattering sequences. The structures related to Ga are broader due to the presence of two isotopes with similar abundance (40% and 60%). In the zone corresponding to the lighter recoils (7–12 μs), only a broad and low intensity peak is observed. This peak comes from surface recoiling processes plus some Al remaining from previous evaporations and oxygen contamination (less than 3% of a monolayer). During evaporation, the peaks coming from the substrate decrease and new ones, due to F and Al DR are detected. Upon saturation of the Al and F DR, we observe a complete disappearance of the single scattering events (narrow peaks) coming from the substrate (see the first spectrum of Fig. 3a), suggesting that the GaAs surface is completely covered by the aluminum fluoride film. In order to investigate possible crystallographic structures in the film we performed several analysis of the ion beam angular dependence. In Fig. 2 we show the azimuthal angular dependence of the DR peak intensities of F and Al in the evaporated film, and of As for the clean GaAs surface. To obtain these intensities we subtract a smooth background (Fig. 1) and integrate the counts for five channels around the peak maximum. From the peak intensities and the corresponding recoiling cross sections we obtain an elemental composition that is close to the stoichiometric one. While the As peak intensity for the clean surface shows minima along the main crystallographic axes of the (1 1 0) surface, related to stronger shadowing along these directions [8], the Al and F DR peaks do not show any structure at all. The same result is obtained for other incident angles showing the absence of any crystalline order in the fluoride film surface grown at RT.

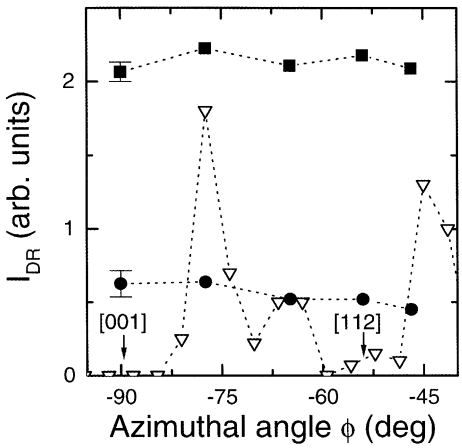

Fig. 2. Azimuthal angle dependence for DR yields of F (-■-) and Al (-●-) obtained at $\theta = 20°$ for a RT as grown sample. The As (-▽-) DR intensity measured at $\theta = 8°$ for the clean substrate is also shown.

Whenever the crystalline epitaxial growth is possible the quality of the film can be improved by increasing the atom mobility. This could be accomplished in two ways, by post-annealing the aluminum fluoride film and by growing the film over a heated substrate. In this work we present results obtained after annealing the films at temperatures ranging from RT up to 400°C. The growth on heated substrates will be discussed elsewhere.

In Fig. 3a we show the evolution of TOF-DRS with the annealing temperature starting with a film thinner (about one monolayer) than the one shown in Fig. 1. Each spectrum was taken after 1 min of annealing at the temperature shown in the figure. We observe the gradual change of the TOF-DRS spectrum, from the one corresponding to an as-grown AlF_3 thin film to a spectrum with major GaAs features. This sequence was taken at a random orientation of the sample, other measurements performed along the main channels show similar behavior. At the same time the F DR peak decreases drastically while the Al one is practically unchanged. In Fig. 3b we show the evolution of the AES spectra with annealing temperature. In the Auger system, the Knudsen cell is located closer to the sample, a condition that for the same temperature and evaporation times produces films slightly thicker than those used in the TOF-DRS setup. The RT AES spectrum reveals two major peaks corresponding to oxidized aluminum (51 eV) and fluorine (647 eV). The small peak at 68 eV corresponds to metallic Al, a byproduct of the primary electron irradiation. In order to prevent the accumulation of this undesirable effect we worked with extremely low electron beam densities and each spectrum, along the annealing process, was acquired in a different previously not bombarded spot. In this way we ensure that the me-

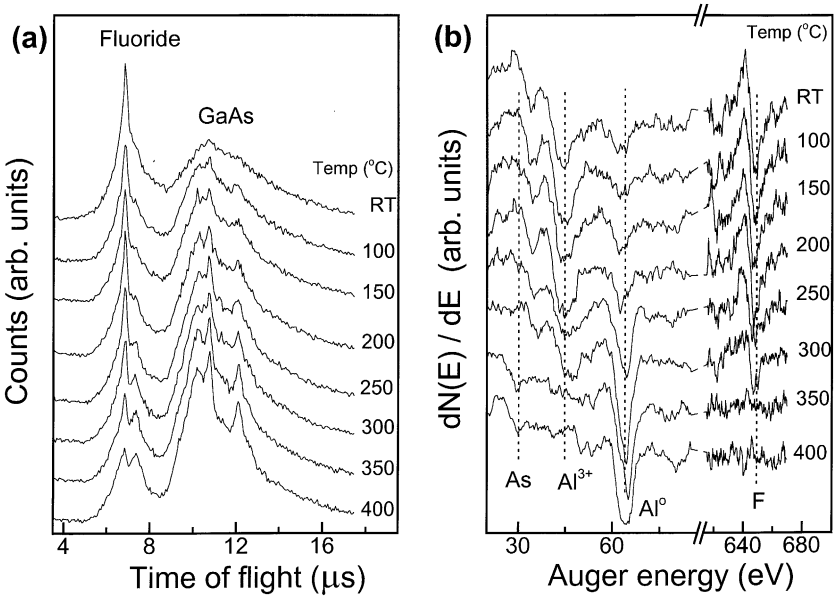

Fig. 3. (a) Evolution of TOF-DRS spectra with post-annealing temperature. The first spectrum corresponds to an AlF_3 film after 100 s evaporation time at RT (~1 ML). (b) Evolution of AES spectra with post-annealing temperature.

tallization of the film, pointed out by the increase in the Al AES peak at 68 eV, is due to the annealing process. From the Auger spectra evolution it is clear that, in addition to the Al reduction there is a loss of fluorine, also observed in the DRS spectra evolution. In comparing the evolution of the spectra for both techniques we can extract more useful information about the annealing process. For AES the F detection limit is reached for annealing temperatures around 300°C, while for TOF-DRS it is still detected up to 400°C. Since AES provides information from several layers below the surface while TOF-DRS just from the surface, the above result implies that fluorine is being evaporated during the annealing. Fluorine diffusion to the bulk would be characterized by just the inverse behavior, i.e. F detection limit would be reached first for TOF-DRS and then for AES. Another interesting result coming from the AES measurements is the appearance of a small As Auger signal along with the absence of a Ga signal, characteristic of the GaAs (1 1 0) surface. This difference is consistently observed through various experiments, and cannot be attributed to different electron escape depths [10].

In Fig. 4 we show the azimuthal angular dependence of the F, Al, Ga and As DR peak intensities for the AlF_3 sample annealed at 400°C. We first note that the ratio of the F/Al intensity is different from that obtained at RT (Fig. 2),

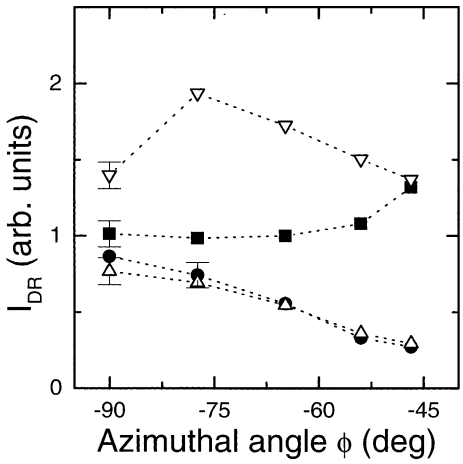

Fig. 4. Azimuthal angle dependence for DR yields of F (-■-), Al (-●-), Ga (-△-) and As (-▽-) corresponding to a post-annealed ($T = 400$°C) fluoride film. The incident angle was set at $\theta = 20°$.

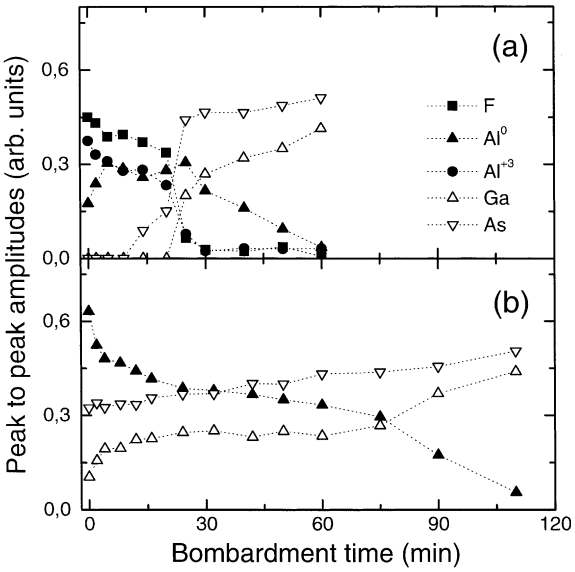

Fig. 5. AES depth profiles corresponding to AlF_3 film grown at (a) RT, and (b) post-annealed at 400°C.

showing a strong decrease in the F intensity. The interesting result here is the similar azimuthal dependence shown by the Ga and Al peaks. This result has been complemented by measurements of the incidence angle dependence of the F/Al DR yield ratio (not shown) that present an enhancement of this ratio for grazing incidence ($\theta < 10°$) and for grazing exit trajectories ($\theta > 35°$). This suggests that fluorine is, after the annealing, preferentially located on the top of the fluoride film.

In Fig. 5 we show the AES ion sputter depth profiles for: (a) an as-grown RT AlF_3 thin film, and (b) an AlF_3 thin film post-annealed at 400°C. The profiles clearly show that aluminum diffuses into the bulk when the temperature of the film is increased. Moreover, the complementary behavior of Al and Ga is in agreement with the azimuthal dependences observed in TOF-DRS (see Fig. 4) and suggests that Al is replacing Ga atoms. In fact, while As Auger yield is detected from the beginning of the profile, Ga yield increases simultaneously with the Al decrease. This behavior is observed twice along the profile b. At the very surface, where the Al concentration is maximum, and when the diffusion front is reached by the ion profiling. The replacement of Ga atoms by Al ones is already known in semiconductor technology where Al is commonly used as GaAs dopant or from GaAs/AlAs multilayer technology [11,12].

4. Conclusions

We have used TOF-DRS and AES to study the growth of AlF_3 on GaAs(1 1 0) at RT and their chemical stability and surface structure after annealing the films from RT up to 400°C. We found that AlF_3 shows no surface structure when grown at RT. Several changes occur when the film is annealed at temperatures above 100°C: (i) the film is depleted of F simultaneously with the reduction of Al; (ii) F preferentially locates over Al; (iii) while the loss of F is produced through evaporation, Al diffuses into the bulk; (iv) Al diffuses replacing Ga atoms.

Acknowledgements

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