Chemical structure of films grown by AlN laser ablation: an X-ray photoelectron spectroscopy study

I. STANCA[a,b]

[a]Department of Physics, University of Oradea, Oradea, 410087, Romania
[b]Department of Physics, Trinity College Dublin, Dublin 2, Ireland

We report on a study of the compositional and chemical properties of films deposited on silicon by excimer laser beam (Lambda Physik Compex 205, KrF, 248 nm wavelength, 25 ns pulse duration) of a ceramic AlN target. The ablation has been performed either in a vacuum or in the presence of a gas atmosphere. The effect of oxygen incorporation in the films on their chemical structure was investigated. The binding energy of the Al 2p, N 1s and O 1s core electrons indicates the formation of near-stoichiometric aluminum nitride in films grown in a vacuum (10^{-7}–10^{-5} mbar), whereas in films grown under an oxygen partial pressure of 0.1 mbar, only aluminum oxide formation was observed.

1. Introduction

A unique combination of material properties — dielectric, thermal, mechanical, optical, wear and corrosion resistance properties — makes AlN a material of choice for many applications as heat sinks, thin-film resistors, hard coatings and in the field of semiconductors. These applications require a severe control of the film purity since the AlN properties are easily affected by defects and contaminants. AlN films can be grown by several methods such as chemical vapor deposition, r.f. sputtering, and ion-beam sputtering. Due to the large chemical affinity of aluminum to oxygen, the major difficulty in depositing AlN films resides in the oxygen contamination control. AlN coatings have been successfully grown on aluminum by direct laser surface modification [1,2]. Pulsed laser ablation has recently attracted a great amount of interest owing to the congruent evaporation of compounds and the high deposition rates, and in this respect, high instantaneous growth rates can ensure a low impurity incorporation in the films [3]. Films of AlN have been deposited by laser ablation with either AlN [4, 5] or Al targets. In the latter case, the film growth must be carried out in a reactive N_2 or NH_3 atmosphere [6, 7, 8]. However, there have been few, if any, studies on the influence of oxygen on the structure and stoichiometry of laser-deposited AlN films. The purpose of this study, for which we present the preliminary results, is twofold: (1) to determine the composition and chemical structure of films grown on Si by laser ablation of an AlN target and (2) to determine the oxygen sensitivity of such structure in films deposited under different vacuum conditions during the process.

2. Experimental

2.1. Film deposition

AlN films were prepared in a high vacuum chamber by pulsed laser ablation of AlN ceramic. The target were ablated with a 248 excimer laser (23 ns pulse width) incident at 45° to the target normal. During deposition, the substrates were kept at 973 K. The films were grown at an instantaneous rate of 4.7×10^6 Å/s. Three sets of films were considered, labelled hereafter as A–C: two of them correspond to two vacuum levels of 1×10^{-7} mbar and 1×10^{-5} mbar (films A and B, respectively). The third set (C) was deposited under an O_2 pressure of 0.1 mbar. Table 1 summarizes the conditions of the AlN film growth. The other data displayed in the table are discussed below.

Table 1. Deposition parameters, film identification and XPS quantification results (see text for a definition of the different ratios).

	Film A	Film B	Film C
Deposition temperature	973 K	973 K	973 K
Pressure conditions	1×10^{-2} mbar vacuum	1×10^{-2} mbar vacuum	0.1 mbar O_2
Nt/Al	0.81	0.64	0.0
Ot/Al	0.23	0.50	1.90
Al(nitr)/Al(oxy)	9.00	3.00	0
Al(nitr)/Al(nitr)	0.86	0.82	-
O(oxy:hydro)/Al (oxy)	2.0	1.80	1.70

2.2. Film characterization

XPS measurements were performed with a Scienta Esca 200 spectrometer, equipped with a monochromatized AlKα (1486.6 eV) source. The working pressure was less than 1×10^{-7} Pa. The spectrometer was calibrated by assuming a binding energy (BE) of $Ag_{3}d_{5/2}$ at 368.27 eV with respect to the Fermi level. Detailed scans were recorded for Al 2p, N 1s, O 1s and C 1s core-level regions. The spectra were recorded with a resolution of 0.4 eV. After a Shirley-type background substraction, the raw spectra were fitted using a non-linear least-squares fitting

program adopting a Gaussian–Lorentzian peak shape. Quantification of the XP spectra was achieved by measuring the relative peak areas and then correcting them by atomic sensitivity factors [9]. A 4 keV Ar^+ beam was used to sputter-etch the films in-situ, and the in-depth atomic composition of the films was obtained by alternating sputter-etching and acquisition cycles. As a result of the electrical charging of the samples during the analysis, the XP spectra of the as-deposited films were shifted in binding energies. Therefore, as a second reference, the C 1s line relative to hydrocarbon contamination was set at 285 eV with respect to the Fermi level [10]. No energy shift correction was needed for spectra recorded from in-situ sputter-etched films A and B.

3. Results and discussion

3.1. Film composition

The element depth-concentration profiles of film A, obtained by XPS depth profiling, are shown in Fig. 1. Regardless of surface contaminants such as carbon (and silicon, not shown), the amounts of which decreased in the bulk to reach noise levels, the film composition was uniform throughout the film thickness. Table 1 lists the mean values of the total atomic ratio of nitrogen to aluminum (N_t/Al_t) and of oxygen to aluminum (O_t/Al_t) throughout the film thickness. The atomic film composition, except in the surface layers, can be globally expressed as $AlN_{0.81}O_{0.23}$.

The same procedure was applied to check the film composition in films B and C, and the results are displayed in Table 1. The global atomic composition of films B can be written as $AlN_{0.64}O_{0.50}$. In film B, oxygen was more abundant than in film A, at the expense of nitrogen, and

film C consisted of almost only aluminum and oxygen, the amount of nitrogen incorporated being very low (1 at.%).
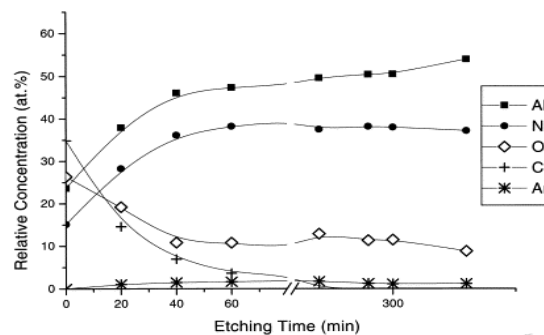

Fig. 1. Element depth concentration profiles of film A.

3.2. Film chemical structure

The chemical structure of the films was determined by examining the Al 2p, N 1s and O 1s core-level spectra. Fig. 2 and Fig. 3 show the Al 2p spectra obtained from the original surface of film A and from a sputter-etched surface of the same film, respectively. Both spectra are given together with the results of a least-squares fit analysis, as they are composed of several components corresponding to Al with different chemical states. The major contribution that resulted from the peak deconvolution is centered at 74.1 eV in the original surface spectra. Such a BE value is consistent with that of Al 2p in Al---N bonds [11], whereas the small peak at a higher BE is assigned to Al in oxide-like bondings, although centered at a BE value (74.7 eV) lower than that reported for bulk Al_2O_3 (~75.5 eV)[12].
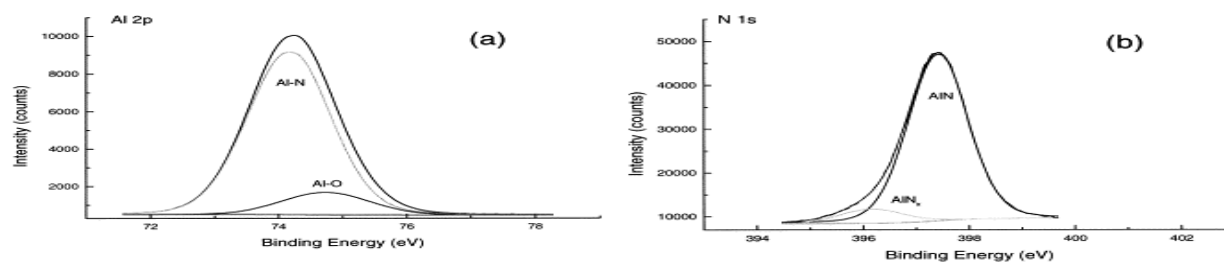

Fig. 2. (a) Al 2p and (b) N 1s core-level spectra from the original surface of film A.

In the clean surface spectrum, the same contributions are again present at 74.3 and 75.2 eV, together with a new, though weak, peak located at 72.8 eV. The latter corresponds to metallic Al and is believed to be an artifact resulting from an ion-induced decomposition of the nitride during the ion-etching. Additional information about the chemical structure of the A films is provided by the N 1s spectra analysis. Fig. 2 and Fig. 3 show the N 1s spectra obtained from the original surface and from the inner layers of the films, respectively. The spectrum from the original surface consists of a major contribution centered at 397.6 eV. The peak deconvolution gave another

component at 396.2 eV. The first BE matches very well with that of N 1s in the Al---N bonds, corresponding with the characteristics of the Al 2p spectra. The small contribution shifted to a 1.4 eV lower BE has various interpretations in the literature devoted to nitrides, and assignment of a contribution in this spectral region is not direct. Many authors assign a N 1s peak below the nitride to an oxynitride (see, for example, Ref. [13]). If so, this contribution should be associated with the oxidized species in the Al 2p spectrum, i.e. the latter should comprise a component midway between the BEs in AlN and in Al_2O_3. This could be the case for the virgin surface

of the present films, but it was no more true for the inner layers [Fig. 2 and Fig. 3]. Furthermore, the N 1s low BE peak was found on both spectra, with the same weight relative to the nitride peak, although the oxidized species appeared at different BEs in the Al 2p spectra. In the Al 2p spectrum from the etched film, the position of the Al---O bond matched very well with that in Al_2O_3. Thus, in the light of this discussion and at this point of our work, we agree with other authors [14] who associate the low BE N 1s line with a substoichiometric nitride phase (AlN_x in N 1s spectra). What further supports this assignment is that the relative ratio of this peak to the nitride peak remained unchanged by varying the base vacuum level to produce films A and B. In this respect, details about the evolution of the film chemical structure with the pressure conditions will be considered later.
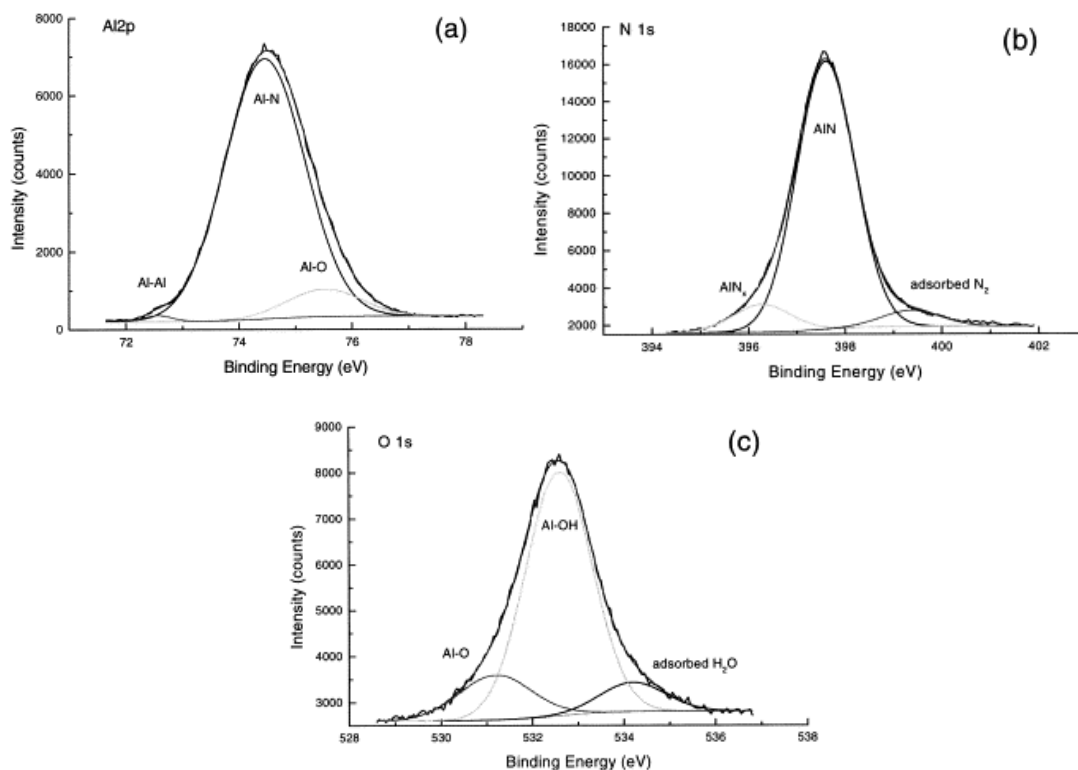

Fig. 3. (a) Al 2p, (b) N 1s and (c) O 1s spectra from a sputter-etched surface of film A.

In the N 1s spectrum from the inner layers of the films [Fig. 3(b)], beside the contributions described above, a new feature appeared that is believed to be an artifact of the ion-etching, as for Al 2p. Such a peak, at 399.3 eV, can be assigned to physisorbed molecular nitrogen [15]. None the less, in spite of the ion-induced dissociation, the stoichiometry of the aluminum nitride, N(nitr)/Al(nitr) in Table 1, was still found to be high (0.86) and approaching the bulk AlN value.

In summary, in A films, Al and N atoms were in major part involved in nitride-like bonds. However, the atomic ratio of Al engaged in Al---N bonds to Al engaged in Al---O bonds, Al(nitr)/Al(oxy) in Table 1, increased only slightly after surface ion-cleaning (7 versus 9), which indicates that most of the oxygen in the original surface arose from adventitious contaminants introduced while handling the sample.

Regarding the oxide contribution to the Al 2p spectrum, its location differs, as can be seen, for the original surface and for the layers underneath it. One explanation can be found in the different phase structure of the oxide at the topmost layers and inside the film. Many studies have shown that in aluminum oxide, low oxidation states such Al^{+1} and Al^{+2} can be found, with a BE lower than that relative to Al^{+3} [16]. Such states would be consistent with an amorphous character of the aluminum oxide, as indicated by Ref. [17].

The O 1s spectrum from the sputter-etched surface of a film A is shown in Fig. 3(c). The spectrum is peaked around 532.5 eV and curve fitting gave also two other components of minor intensity at 531.2 and 534.2 eV. These BE values correspond well with three oxygen species OH^- (in Al---OH bonds), O^{2-} (in Al---O bonds) and molecular H_2O physically adsorbed, respectively [9 and 18]. Therefore, from the O 1s spectrum lineshape, it is clear that the oxidized states of Al consisted mostly of hydroxylated Al. It is in fact commonly established that alumina easily hydrates under ambient moisture exposure. In the present films, the atomic ratio of O to Al involved chemically in oxide-like bonds, $O_{(oxy+hydro)}/Al_{(oxy)}$ in Table 1, is found to be equal to 2, which fairly describes the boehmite phase ($Al_2O_3.H_2O$) of hydrated aluminium oxide. In contrast with what is generally reported for bulk alumina, in the present films hydration did not concern

only the very surface layers. The hydroxylate states of Al were also observed in the inner regions of the films. This difference may be due to different permeation characteristics of the films, certainly in correlation with the film morphology and hence the defect density.

Let us consider now the evolution of the Al 2p, N 1s and O 1s spectra with the pressure conditions in the deposition chamber. The results of the curve fitting of the spectra recorded from sputter-etched films B and C are given in Table 1 and can be compared to those from film A. It can be seen that the Al---O bondings gained in weight relatively to Al---N bondings in film B, and in film C, they were the only bonds in which Al was involved. The total O-to-N atomic ratio (O_t/N_t, which can be calculated from Table 1) increased from 0.28 in films A to 0.78 in films B. Correspondingly, the Al(nitr)/Al(oxy) ratio decreased from 9 to 3. However, the stoichiometry of the nitride did not change significantly in films B with respect to films A.

However, the O 1s spectrum analysis for the various film deposition conditions also provided information about water origin in the films. It was found that the O 1s spectrum lineshape did not change significantly from films A to C. The spectra can be described with the same components, with almost the same relative weight, indicating that oxygen was bonded in the same chemical states irrespective of the vacuum or pressure conditions of the film growth. This result indicates that the aluminum oxide, formed in the films during their deposition, hydrated during the post-deposition sample handling, by taking up moisture from the environment.

4. Conclusions

The chemical and compositional properties of films deposited by laser ablation of AlN target have been investigated. The laser technique promises to be useful for highly stoichiometric aluminum nitride deposition. However, as was found from this study, in spite of a high instantaneous growth rate for which low contamination levels might be expected, the use of a pulsed laser did not make the aluminum nitride films immune from oxygen incorporation. The present results show the great sensitivity of the films to oxygen-containing environments. Only under low residual oxygen pressure, could aluminum nitride be grown. In this case, in spite of the formation of a hydrated oxide phase as a by-product, a near-stoichiometric aluminum nitride phase was obtained. For films grown in oxygen atmosphere, only oxide films were obtained. At this point, it is not clear whether the oxide formed between consecutive pulses or originated from an oxidized target. Work is in progress to elucidate, via in-situ diagnostics, the mechanisms of oxidation of aluminum nitride films.

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*Corresponding author: istanca@uoradea.ro