Applied Surface Science 315 (2014) 104–109

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

XPS analysis of AlN thin films deposited by plasma enhanced atomic layer deposition

P. Motamedi, K. Cadien*

Department of Chemical and Materials Engineering University of Alberta Edmonton, Alberta, Canada T6G 2V4

ARTICLE INFO

Article history:
Received 20 March 2014
Received in revised form 29 June 2014
Accepted 18 July 2014
Available online 27 July 2014

Keywords:
X-ray photoelectron spectroscopy
Atomic layer deposition
Aluminum nitride

ABSTRACT

X-ray photoelectron spectroscopy has been used to investigate the properties of AlN films deposited using a low temperature plasma-enhanced atomic layer deposition process. Aluminum, nitrogen and oxygen peaks were observed in the survey spectra. A thin layer of sputtered aluminum was used as a diffusion barrier, in order to distinguish between oxygen introduced during deposition and post-deposition. The results show no post-deposition oxidation. Furthermore, the samples were scanned at various depths, and the peaks were then deconvolved into the constituent subpeaks. The results show no Al–O–N bonding in the film. This result supports the models that propose that oxygen at low concentrations in AlN bonds exclusively to aluminum and forms planes of aluminum oxide octahedrons dispersed in the lattice.

1. Introduction

The wide band gap of AlN makes it a suitable candidate for several optoelectronic applications, including UV detectors and lasers. Moreover, excellent miscibility with similar III-N materials offers the potential of $Al_xGa_yIn_{(1-x-y)}N$ materials with adjustable band gap and lattice constant [1–5]. Integration of AlN as a dielectric in GaN-based devices is an intriguing possibility facilitated by the low lattice mismatch (~2.4%) of the two wurtizite structures [6]. AlN is also used in high power electronics due to its large dielectric breakdown field and high thermal conductivity [7]. The non-centrosymmetricity of the AlN wurtizite unit cell causes intrinsic polarization, making it a good choice for piezoelectric sensors and actuators [8,9]. The high velocity of surface acoustic waves (SAW) in AlN makes it a versatile material for various SAW devices, especially SAW receivers for harsh environments [10–12].

Atomic layer deposition (ALD) of AlN offers an attractive combination of advantages when compared to other deposition techniques such as metal-organic chemical vapor deposition and molecular beam epitaxy. Plasma-enhanced ALD (PEALD) of AlN can be accomplished at significantly lower temperatures, eliminating the problems associated with the difference in thermal expansion coefficient between the film and the substrate [13,14]. In comparison to reactive sputtering, ALD offers excellent conformality and scale-up potential, combined with precise thickness control. All of these features make ALD a fitting choice for future device applications [13,14].

Current AlN thermal ALD processes usually involve the use of halides or ammonia as precursors [15–20]. The use of halides poses environmental risks, as well as possible equipment and product corrosion problems. In this study we used nitrogen plasma and trimethylaluminum as precursors, to address the present concerns. PEALD has the intrinsic advantages over thermal ALD of a lower deposition temperature window. On the other hand, using nitrogen plasma instead of ammonia allows for injecting the desired amount of hydrogen ions into the reactor as the reducing agent, and significantly lowers the concentration of unwanted partially ionized variants of ammonia. This increases the efficiency and decreases the minimum dose time of the plasma dose step.

Regardless of the choice of precursors, low temperature deposition of III-nitrides by ALD is known to have many difficulties. The films are often reported to be non-stoichiometric or contain a large amount of impurities, especially oxygen [15,21–25]. In addition, AlN is known to form a passive oxide layer, when exposed to air [26,27]. The significant effect of oxygen impurity in AlN films has been demonstrated and investigated, especially for plasma processes [17,20,28]. The structural variations of AlN containing different amounts of oxygen has also been extensively studied [29–32]. It has also been demonstrated that small amounts of oxygen might significantly affect the electrical and optical properties of AlN [31,33–35]. Although generally considered to be detrimental in nature, this phenomenon can also be exploited to effect desirable alterations in the AlN structure and properties, provided the exact chemical environment and lattice distribution of oxygen atoms are known.

* Corresponding author. Tel.: +1 780 492 7380; fax: +1 780 492 2881.
E-mail address: kcadien@ualberta.ca (K. Cadien).

http://dx.doi.org/10.1016/j.apsusc.2014.07.105
0169-4332/

In spite of the prevalence of the problem, few studies have tried to systematically investigate the nature of oxygen impurity in ALD III-nitride thin films. In this paper we focus on the evaluation of PEALD AlN films using X-ray photoelectron spectroscopy, XPS, with a particular emphasis on the bonding of oxygen impurities in AlN. The approaches presented here is applicable to other nitride thin films.

2. Experimental

Depositions were carried out using a thin film deposition research system (ALD-150L, Kurt J. Lesker), which features thermal as well as remote plasma capabilities. Si (1 1 1) substrates were used for deposition. The substrates were cleaned with a standard buffered oxide etch cleaning procedure prior to deposition. During deposition the substrates were heated to 250 °C. An in situ spectroscopic ellipsometry apparatus by J.A. Woollam (M2000DI) allowed for precise control of the thickness.

Extensive experiments have been done to determine the optimal deposition parameters, and ensure they fall inside the limits of the ALD parameter window, and that the characteristic self-limiting regime of ALD deposition is achieved. The deposition consisted of four stages: 0.02 s trimethylaluminum dose, 7 s Ar gas purge, 10 s N_2/H_2 (19:1) plasma, followed by another 7 s Ar purge. The plasma power was set to 600 W. The carrier gas flow rate for the precursor was 40 sccm. The flow rate of forming gas and its carrier gas (Ar) were 60 and 100 sccm, respectively. The growth rate was 0.068 nm/cycle, as determined by spectroscopic ellipsometry.

As explained later, for some samples metallic aluminum was coated on top of the PEALD AlN layer in order to protect the AlN and to permit the high resolution XPS spectrum of Al2p to be used as a reference. After ALD deposition these samples were transferred under high vacuum to an interconnected sputtering chamber where a 3-nm thick layer of aluminum was deposited via DC magnetron sputtering at 200 W, 2 mTorr and at room temperature.

A Kratos AXIS Ultra X-ray photoelectron spectroscopy (XPS) was used to study the chemical structure of the 50 nm thick films, using Al (1486.69 eV) X-ray source at 50° incidence angle. An argon ion gun (4 keV) was used to probe the depth of the samples. The etch rate was experimentally determined to be ~2 nm/min.

3. Results and discussion

Fig. 1 shows the results of the XPS survey scans for an uncoated sample. As evident in Fig. 1a, aluminum and nitrogen are present at the surface. In addition, a considerable amount of carbon is observed, which is characteristic of uncleaned surfaces. The most noteworthy feature of this spectrum is the prominent oxygen peak, taller than those of aluminum and nitrogen. In order to calculate the atomic ratio of the four elements, high-resolution scans were performed on the areas around the peaks O 1s, N 1s, C 1s, and Al 2p. Calculating the area under the four peaks, and applying the relative sensitivity factors of 2.930, 1.800, 1.000, and 0.537 for the above peaks in the mentioned order gives the atomic ratios reported in Table 1. As seen, equal amounts of oxygen and nitrogen exist at the surface. In Fig. 1b, the survey spectrum of the sample after 20 min of argon ion etching, reveals three differences with Fig. 1a: (1) carbon peak intensity has dropped to a very low value; (2) oxygen peak shows a significant drop in intensity, yet still shows a noticeable presence; (3) some argon atoms are embedded in the film, indicating argon is being implanted by the sputter cleaning process. Following the procedure described above, the atomic ratio of the four elements has been calculated and reported in Table 1.

The amount of carbon in the film is very low and indicates that, despite the low temperature of deposition, no significant

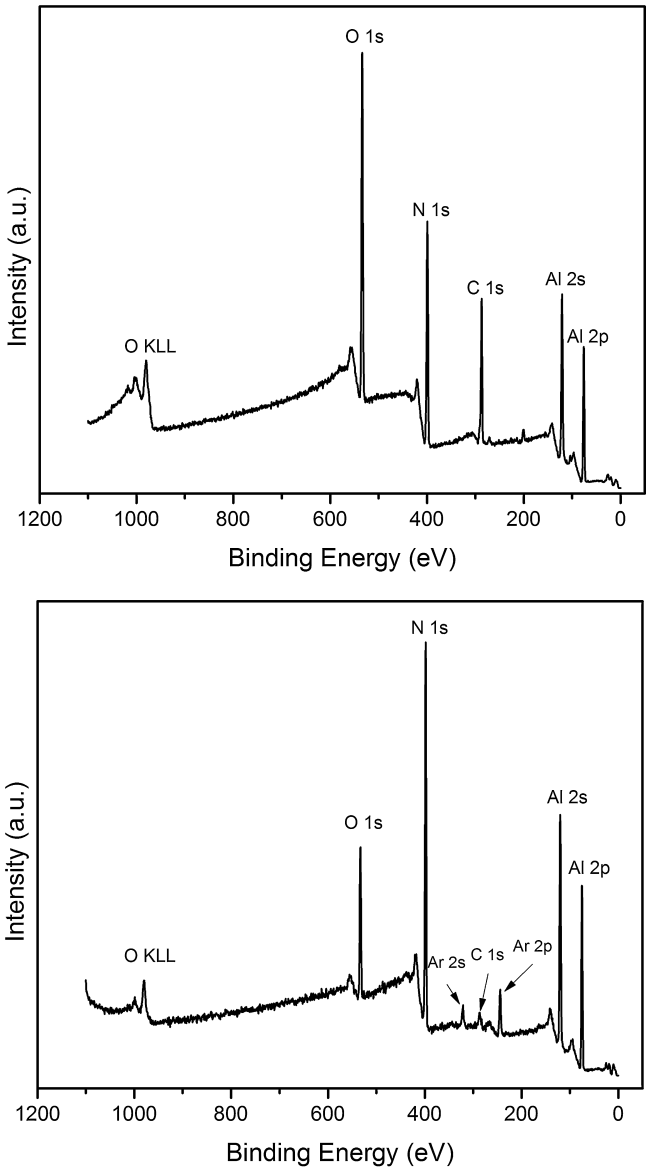

Fig. 1. Survey scan of the uncoated sample (a) before etching and (b) after 20 min of etching.

incorporation of carbon containing ligands from the precursors has occurred. If methyl groups from the precursor were trapped in the film, this would give rise to a large amount of carbon [36]. The lower amount of oxygen, compared to the surface, shows that a significant portion of it is the result of atmospheric oxidation, not the deposition process itself. The surface of the AlN film is prone to oxidation, and various forms of oxides and hydroxides have been reported to form on the surface, depending on the environment [37–40]. The higher than expected amount of aluminum might be the result of preferential argon ion sputtering which has been reported for III-nitrides [41].

An important question concerns the nature of the oxygen impurity inside the film, as well as its possible chemical interaction with aluminum and nitrogen. A high resolution XPS scan of the Al 2p peak reveals the nature of the aluminum bonding. Fig. 2 shows the comparison of the Al 2p peaks for the uncoated sample before and after 20 min of etching. The center of the peak shifts from 75.4 to 74.9 eV. It should be noted that the center of the C 1s peak was observed at 286.3 eV throughout all the readings, whenever carbon was detected. Thorough analysis of the two