STRUCTURAL CHARACHTERIZATION OF ALN THIN FILMS OBTAINED ON SILICON SURFACE BY PE-ALD

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Abstract: The aim of this study is to investigate the hydrogen impregnations in AlN thin films deposited using plasma-enhanced atomic layer deposition technique. As of date, there is an apparent gap in the literature regarding the matter of hydrogen impregnation within the AlN layers. Hydrogen is a frequent contaminant and its content has detrimental effect on the quality of resulted layer, which is why it is relevant to investigate this particular contaminant and try to eliminate or at least minimize its quantity. Within the films hydrogen commonly forms amino or imide types of bonds ($–NH_2$, -NH). There is only a handful of analytical methods enabling the detection of hydrogen. This particular study comprises two of them – Fourier-transform infrared spectroscopy (FTIR) and second ion-mass spectrometry (SIMS). XPS analysis has also been included to examine the surface nature and structural imperfections of the grown layer.

Keywords: atomic layer deposition, aluminum nitride, thin films, fourier-transform infrared spectroscopy, hydrogen impregnations, x-ray photoelectron spectroscopy.

INTRODUCTION

Aluminum nitride is a semi-conductive material with wide band gap (6,2 eV), its crystalline structure forms a hexagon akin to the mineral known as wurtize (zinc sulfide), thus AlN is often called a wurtize-phased material. This material can boast high thermal resistance in inert atmospheres [1].

Thin films of aluminum nitride (AlN) have seen an increase in popularity lately, due to the promising characteristics and properties of this material such as already mentioned wide band gap, excellent mechanical properties, high electrical resistance, high chemical stability, high breakdown voltage, low temperature for deposition and a potential for piezoelectricity [2]. A low deposition temperature of AlN renders it advantageous over other materials with piezoelectric properties as zinc oxide or zirconate titanate since it allows it to be utilized in conventional silicon monolithic systems where low temperature process is a requirement [3]. A low deposition temperature (under 400 °C) of AlN is also a reason why this material is a suitable option for post-processing of the integrated circuits. There are also records of AlN being implemented in surface acoustic wave filters and bulk acoustic wave [4].

Atomic layer deposition (ALD) is a subtype of CVD methods for obtaining thin films in vapor phase. Certain advantages of ALD over its analogues make it a more attractive choice for thin film fabrication process. Those advantages include the possibility of the precise control over the film growth and staged process with purging session between each stage allows to keep the chamber clean from waste components which occur after each precursor introduction. ALD also shows a lot of promise in energy conversion technologies and semiconductor manufacturing process [5]. Atomic precision of ALD is essential for application in nanoelectronics. For the last several years ALD has been proving itself to be a relatively cheap method with great scalability and precision necessary for high-quality thin film fabrication at the nanoscale level.

However, there still seems to be a lack of adequate and comprehensive studies when it comes to impurities in AlN thin films obtained by ALD and other methods [7, 8]. This particular papers attempts to bring some contribution to filling the gap in that area.

PREPARATION OF THE SAMPLES

In this work we obtained AlN thin films using plasma enhanced atomic layer deposition (PE-ALD) on silicon substrates. Deposited films then have been analyzed using FTIR, XPS and SIMS instruments.

Prior to deposition silicon substrates with dimensions of 1x1x0,1cm and (100) orientation were cleaned in isopropanol. Each individual ALD cycle comprised of the next steps: 1) injection of TMA (0,06sec), 2) purge 10sec, 3) flow of N_2/H_2 (20 sccm) and activate plasma (40 sec), 4) purge 5sec

The total amount of such ALD cycles was 1100 and this converts into resulting thickness of approximately 70 nm. The temperature of deposition was chosen to be 250 °C which is within the AlN ALD window. The energy of plasma was 300W. The annealing was implemented at 1000 °C for duration of 1 hour, however, for 10 minutes of this hour the temperature was increased to 1250 °C.

RESULTS AND DISCUSSION

3.1 FOURIER-TRANSFORM INFRARED SPECTROSCOPY DATA

Infrared reflectance is a spectroscopic non-destructive analysis allowing to study the nature of the chemical bonds. We used FTIR in the reflectance mode in which the intensity of the dispersed light from the sample is presented on the graph as a function of the wavelength. By evaluation the peaks and dips of the intensity we can make draw some conclusion on the type of chemical bonds existing in the sample. FTIR reflectance spectrum of AlN on silicon is given in fig 1.

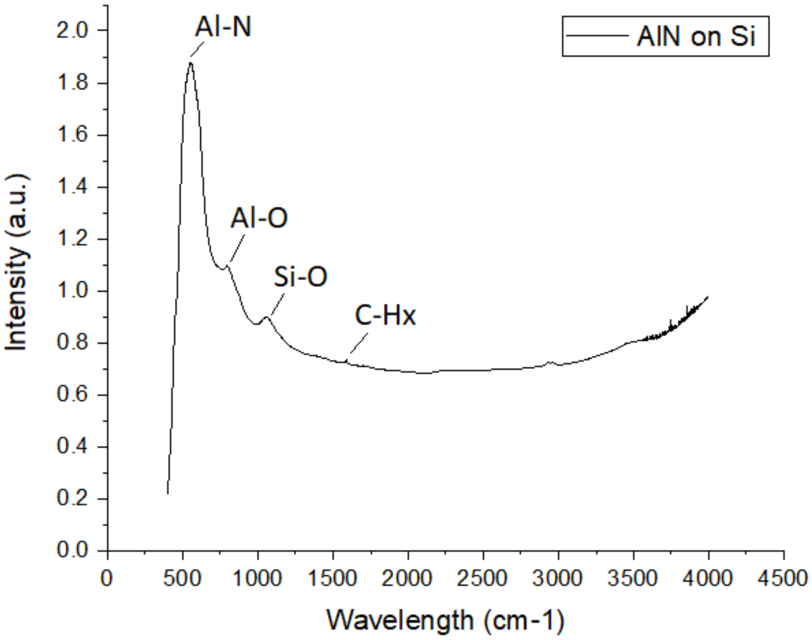


Figure 1: Raman spectra of AlN on Si substrate

The most intensive peak at ~615 cm-1 is attributed to Al–N, vibration mode A1(TO); less intensive peaks at 735 cm-1 and ~1100 cm-1 are assigned to ν(Al–O), vibration mode Al–O and to Si-O vibration mode ν(Si–O) correspondingly [9, 10]. There is also a barely visible peak at ~1500eV which is according to [11] corresponds to C-H bonds. Given our initial goal to detect hydrogen within the AlN films, this peak is of particular interest.

3.2 SECONDARY ION-MASS SPECTROMETRY

Unlike FTIR and XPS, SIMS is a destructive technique and relies on sputtering a crater on the sample with high energy ions, after which by collecting the ejected (secondary) ions distribution profiles of the elements in the depth of the sample are created. SIMS is extremely sensitive method and allows detecting all elements (including hydrogen). However, quantization in SIMS is complicated and requires the use of the standards which are not always available especially for less common materials. The quantization of hydrogen is further complicated by the fact that it is picked up by analyzer not only from the sample but also from atmosphere, even under high-vaccum. In this study SIMS was used in time-of-flight mode, the sputtering of the film was conducted using oxygen gun. 3D profile distribution for chosen elements in the bulk of the film are given in the Figure 2. The depth of the crated ~200nm (the density of the AlN fiilm is around 70 nm).

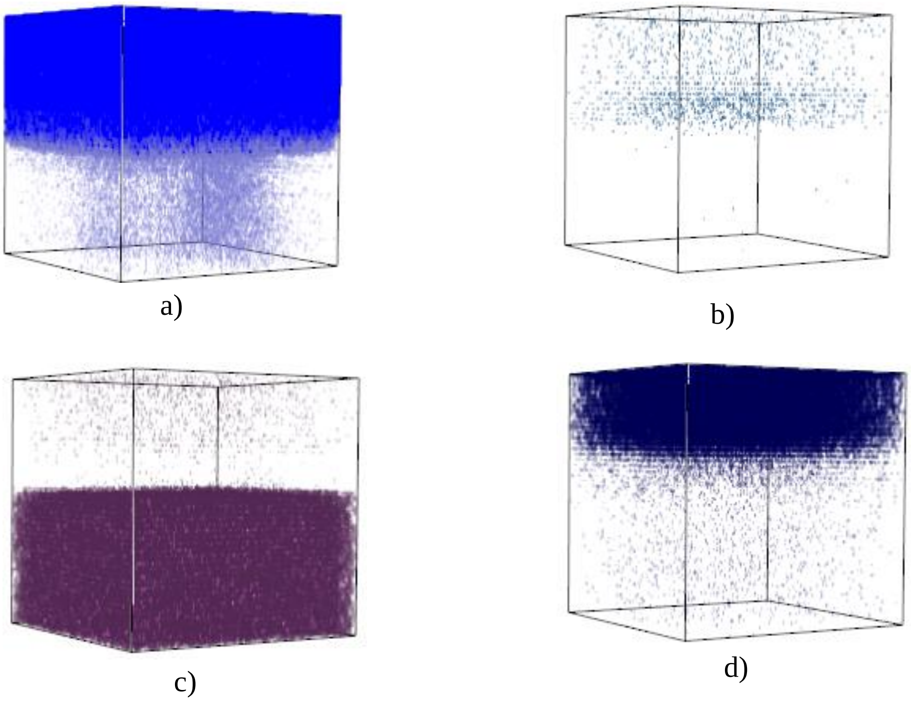

a)
b)
c)
d)

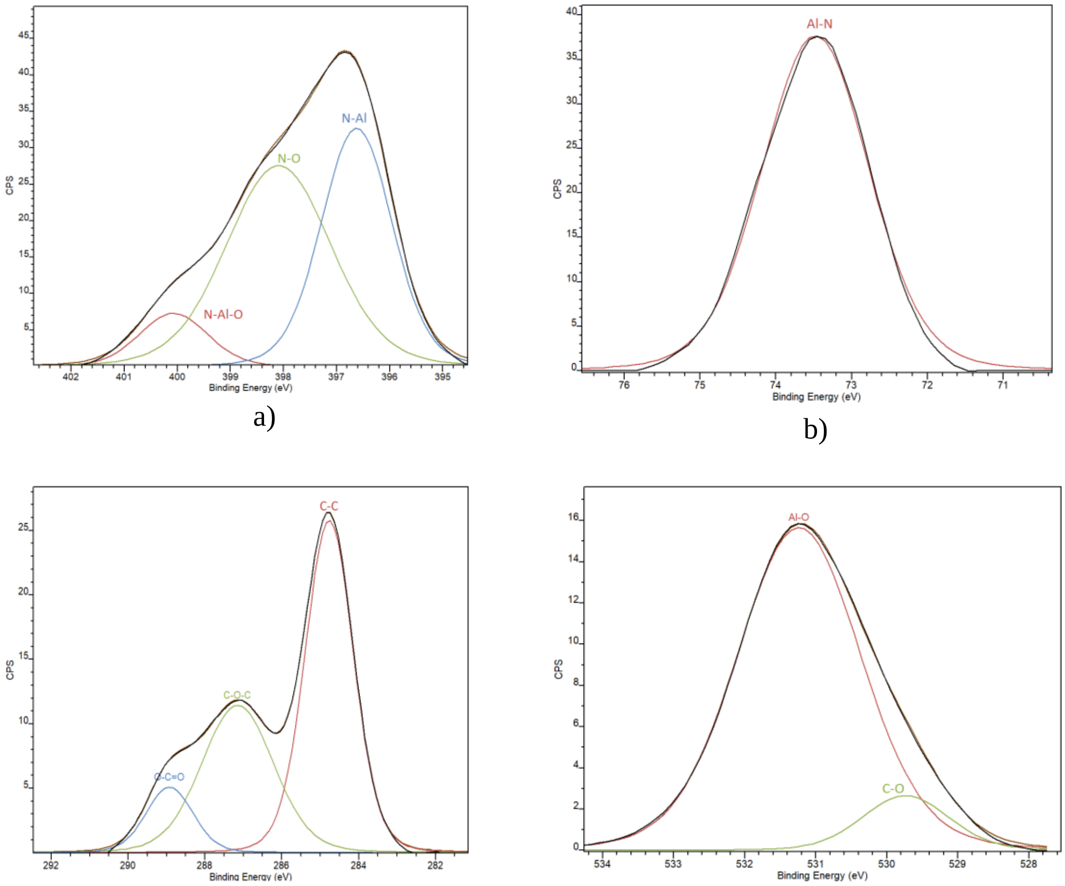
Figure 2: SIMS 3D profiling images of: a) Aluminum, b) Nitrogen, c) Silicon, d) Hydrogen.

As was expected we have a dense distribution of aluminum atoms and less so of nitrogen in the AlN layer (fig 2a and fig. 2b). Low intensity of nitrogen atoms is due to the fact that measurement was performed in a positive mode, whereas the bulk of nitrogen secondary ions are negative by nature. In addition, D. Cao et al. [16] claim that annealing of AlN in the nitrogen atmosphere might improve the quality of the layer and thereby increase the amount of nitrogen atoms.

Once the sputtering beam has breached the AlN layer, no more aluminum is picked up, instead we can observe the dense distribution of Si atoms belonging to the substrate (fig 2c). The hydrogen 3D profile is presented in fig 2d. Since SIMS detector collects not only atoms emitted from the surface but also from the atmosphere it is next to impossible to tell how much of the hydrogen exactly belongs to the AlN layer. However, at the very least we can reasonably presume that main part of it exists in the AlN layer and not in the substrate, given the drastic decline in its concentration once the AlN layer is breached.

3.3 X-RAY PHOTOELECTRON SPECTROSCOPY (XPS) DATA

XPS analysis is given here to provide additional information on the nature of the chemical bonds, mostly on the surface since x-ray penetrates first 7-10 nm of the layer, no sputtering was used. The fitting was done in CasaXPS software. The whole spectrum was shifted to center C1s (C-C bond) at 284.8 eV.



a) b) c) d)

Figure 3: XPS elemental spectra for AlN on Si: a) N1s, b) Al2p, c) C1s, d) O1s

The nitrogen peak (fig. 3a) can be deconvoluted into three subpeaks with binding energies of 396,6eV, 398eV and 400 eV. The tallest of them at 396,6 eV refers to N-Al bond and the other two are ascribed to N-O and N-Al-O correspondingly [12].

Aluminum exhibits just one high-intensity peak (fig.3b) at ~73,5 eV which is precisely the binding energy of Al-N accoridng to literature [13, 17], which goes along well with the data of the nitrogen peak.

Carbon is an invebitable contaminants in form of carbon (fig.3c) and oxygen(fig.3d) are also presented. Carbon forms a triplet of peaks at 284,8eV; 286,5eV and 288,5 eV which are attributed to C-C; C-O-C and O-C=O correspondingly. Oxygen doublet consits of peaks at 529,8 eV (C-O) and 531eV (Al-O) [14, 15].

CONCLUSION

This paper’s aim was to study chemical structure of AlN thin films obtained by ALD on silicon substrates. To achieve this goal such analytical methods as FTIR, SIMS and XPS were utilized. FTIR analysis detected C-Hx bond proving the hydrogen presence in the AlN layer, the hydrogen contamination has further been confirmed by the SIMS method in the 3D distribution hydrogen profile. XPS method showed the presence of oxygen and carbon impregnations. However, when it comes to the AlN structure, all three methods showed rather promising results - Al-N bond was detected by FTIR and XPS whereas SIMS analysis provided a dense concertation of aluminium atoms in the film. In summary, it can be said that the overall quality of the deposited layer is reasonable and contaminations level are within the norm for AlN layers obtained using ALD. However, impurities should be further investigated and the methods for their elimination should be developed. High-temperature annealing is reportedly a good tool for improving the crystallinity of the films and removing undesired and defective bonds by the process of diffusion and atomic rearrangement.

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