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Investigation of structure of AlN thin films using Fourier-transform infrared spectroscopy

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Abstract

This study focuses on structural imperfections caused by hydrogen impurities in AlN thin films obtained using atomic layer deposition method (ALD). Currently, there is a severe lack of studies regarding the presence of hydrogen in the bulk of AlN films. Fourier-transform infrared spectroscopy (FTIR) is one of the few methods that allow detection bonds of light elements, in particular - hydrogen. Hydrogen is known to be a frequent contaminant in AlN films grown by ALD method, it may form different bonds with nitrogen, e.g. amino (–NH2) or imide (–NH) groups, which impair the quality of the resulting film. Which is why, it is important to investigate the phenomenon of hydrogen as well as to search for the suitable methods to eliminate or at least reduce its quantity. In this work several samples have been prepared using different precursors, substrates and deposition parameters and characterized using FTIR and additional techniques such as AFM, XPS and EDS to provide a comparative and comprehensive analysis of topography, morphology and chemical composition of AlN thin films.

Keywords: thin-films, aluminum nitride, Fourier-transform infrared spectroscopy, hydrogen impurities, structural analysis.

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1. Introduction

Aluminum nitride is a wide band gap semiconducting material with covalent bonds, which has a hexagonal crystalline structure that is an analog of the structure of zinc sulfide known as wurtzite. This material is resistant to high temperatures in the inert atmospheres [1].

Thin films of aluminum nitride (AlN) are gaining a lot of attention lately, due to the excellent characteristics of this material such as wide band gap, remarkable mechanical properties, high chemical stability, high electrical resistance, high breakdown voltage, low deposition temperature and impressive piezoelectric properties [2]. Another advantage of AlN thin films in comparison to other piezoelectric materials such as lead zirconate titanate and zinc oxide is the possibility of their integration in traditional silicon monolithic systems, for synthesis of which a low temperature deposition processes is demanded [3]. A low deposition temperature (below 400 °C) of AlN makes it a compatible material when it comes to post-processing of the integrated circuits. Also, it seems to be a promising candidate for bulk acoustic wave filters and surface acoustic wave [4].

Atomic layer deposition (ALD) is a vapor phase method used for obtaining thin films of different materials. ALD has established itself as a promising technique in semiconductor manufacturing process and technologies for energy conversion [5]. For application in nanoelectronics it is crucial to have atomic precision in materials manufacturing. Over the last several years ALD proved to be a relatively cheap and scalable method which provides the necessary precision of the atomic layer for fabrication of films at the nanoscale level [6].

But there is still a lack of study regarding contaminations in AlN obtained by various methods [7, 8]. This paper in particular aims to fill the gap in knowledge of preparation AlN thin films grown by ALD.

Infrared reflectance is a spectroscopic non-destructive techniques providing information on the nature of chemical bonds. By evaluating the intensity of light dispersed from and through a sample, NIR reflectance spectra can be employed to quickly define material's properties without changing the sample.

Another technique that allows detection of light elements is Secondary ion-mass spectrometry (SIMS). In this work it was employed in time-of-flight mode, the sputtering of the film was conducted using Ar cluster. As a result, we managed to create 3D profile images for certain elements in the bulk of the film. The depth of the sputtering was around 200nm (the density of the AlN layer is around 70nm).

2. Preparation of the samples

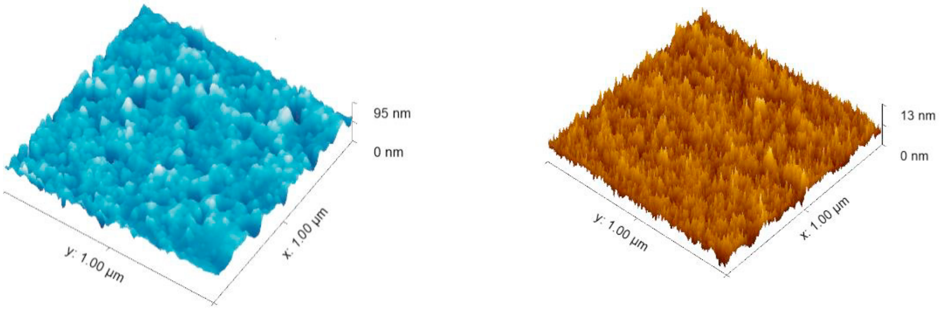
In this work we obtained AlN thin films using plasma enhanced atomic layer deposition (PE-ALD) on silicon substrates and highly oriented pyrolytic graphite (HOPG). Obtained films have been analyzed using AFM, XPS, EDS methods.

In total 634 ALD cycles have been performed which translates into thickness of approximately 40nm (1cycle ≈ 0,629 Å). The temperature of deposition was 250 °C. The energy of plasma was 300W. The sequence of each cycle consisted of following steps: 1) introduction of TMA (0,06sec), 2) purge 10sec, 3) initiate flow of N2/H2 (20 sccm) and enable plasma (40 sec), 4) purge 5sec. Annealing duration was of 1h, 10min of which under 1250 °C, the rest 50 min under 1000 °C. Silicon substrates with (100) orientation and dimensions of 1x1x0,1cm are polished to atomic thickness and were cleaned with isopropanol prior to deposition.

3. Results and discussion

3.1. Atomic force microscopy

In order to investigate surface morphology and topography of the films obtained we utilized atomic force microcopy technique in tapping mode. AFM images are given in fig. 1.



a) b)

Figure 1. AFM imgaes of: a) AlN on Si substrate, b) AlN on HOPG

Average rougness (Ra) has also been calculated. For AlN on Si its values equals to 12.5 Å and for AlN on HOPG – 9.7 Å. Which suggests that the films grown on HOPG have more uniform topography and therefore better quality.

3.2. Fourier-transform infrared spectroscopy data

FTIR reflectance spectrum of AlN on HOPG is given in fig 2.

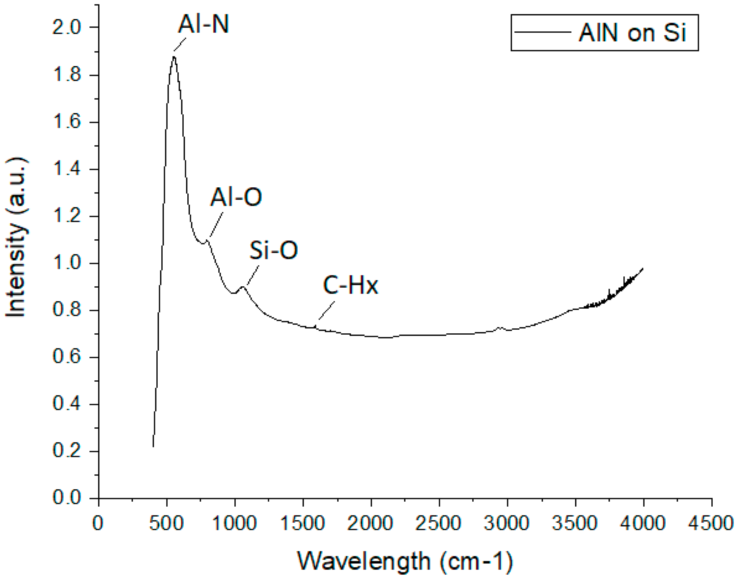


Figure 2. FTIR spectra for AlN on HOPG

The major peak at ~615 cm^{-1} is assigned to Al–N, vibration mode A1(TO); smaller peaks at 735 cm^{-1} and ~1100 cm^{-1} are attributed to ν(Al–O), vibration mode Al–O and to Si-O vibration mode ν(Si–O) correspondingly [9, 10]. There is also a slightly visible peak at ~1500eV which is according to [11] corresponds to C-H bonds. This peak is of particular interest since FTIR used in this work mostly to detect the presence of hydrogen.

3.3. Secondary ion-mass spectrometry

3D SIMS images are given in fig. 3.

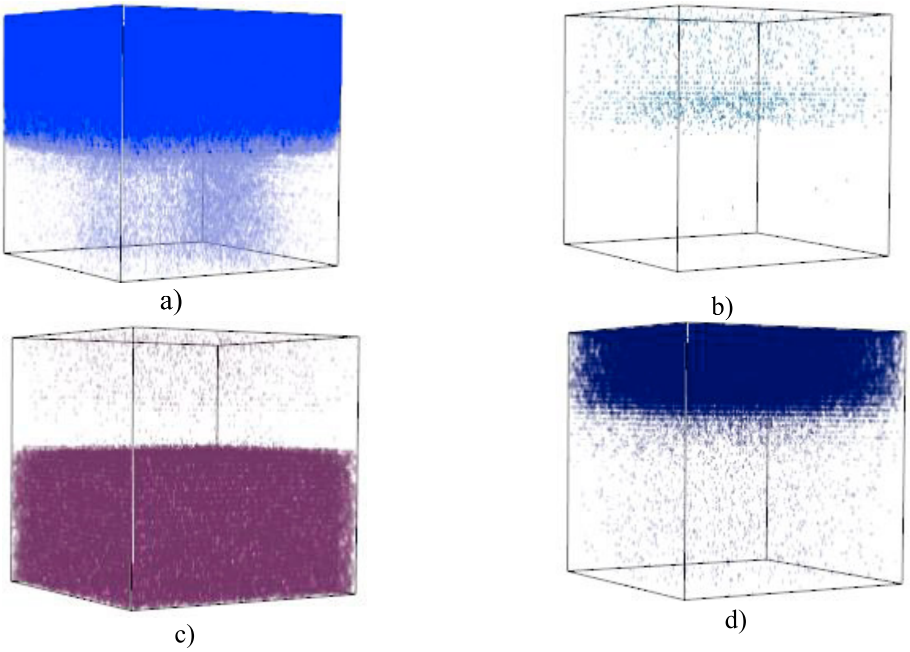

a)
b)
c)
d)

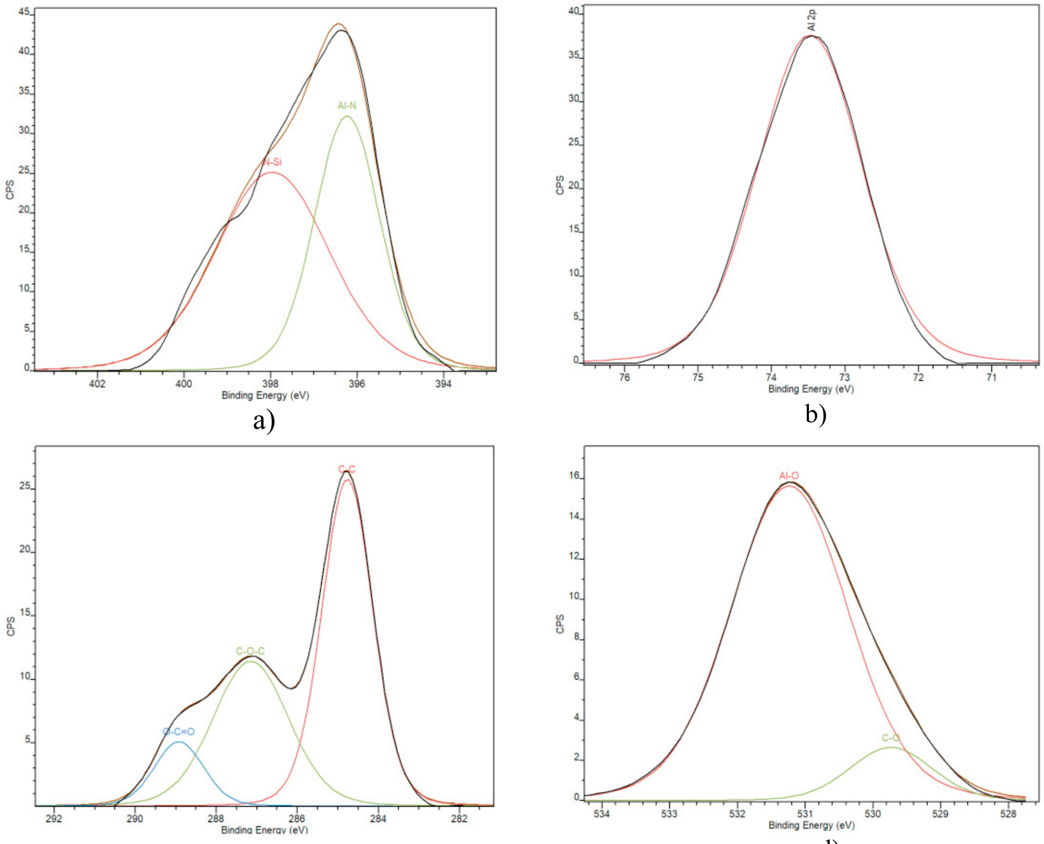
Figure 3. SIMS 3D profiling images of: a) Aluminum, b) Nitrogen, c) Silicon, d) Hydrogen.

As expected, we have a dense distribution of aluminum atoms and less so of nitrogen in the surface of the sample (fig 3a and fig. 3b). According to [16] annealing of AlN in the nitrogen atmosphere might improve the quality of the layer and therefore increase the amount of nitrogen atoms.

Once the sputtering beam has broken through the AlN layer, no more aluminum is detected, instead we can observe the dense distribution of Si atoms of the substrate (fig 3c). The hydrogen 3D profile is given in fig 3d. Since SIMS detector picks up not only atoms emitted from the surface but also from the atmosphere it is nearly impossible to tell how much of the hydrogen exactly belongs to the AlN layer. Nevertheless, we still can reasonably assume that at least part of it resides in the bulk of the AlN layer, given that there is almost none of the hydrogen in the substrate.

3.4. X-ray photoelectron spectroscopy (XPS) data

To provide comprehensive analysis of chemical composition X-ray photoelectron spectroscopy (XPS) method was utilized. Fitted elemental high resolution spectra are presented in fig. 4.



a) b)

c) d)

Figure 4. XPS elemental spectra for AlN on Si: a) N1s, b) Al2p, c) C1s, d) O1s

The nitrogen peak (fig. 4a) consists of two subpeaks of binding energies of 397eV and 398,3eV. The bigger suppeak at 397eV is one belonging to Al-N bond and the smaller one is ascribed to N-Si [12].
Aluminum has just one intense peak (fig.4b) at ~73,5 eV which is exacly the binding energy of Al-N accoridng to literature [13], which perfectly correlates with the data of the nitrogen peak
Peaks of unavoidable contaminants in form of carbon (fig.4c) and oxygen(fig.4d) 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].

4. Conclusion

In this paper AlN thin films have been deposited using PE-ALD equipment on two different substrates – silicon and HOPG. Surface analysis of the samples using AFM indicated that AlN layer on HOPG has a more uniform topography as compared to the one on silicon. Chemical structure of the samples obtained has been thoroughly studied using such techniques as FTIR, SIMS and XPS. FITR analysis showed the presence of Al-N bonds which was also confirmed by XPS analysis. Hydrogen has also been detected by FTIR in the form of C-Hx bonds. Using data obtained by SIMS method with Ar cluster, 3D profiles of the aluminum, nitrogen, silicon and hydrogen have been generated which provided information on distribution of these elements in the stratum of the sample. As a result of this study we have confirmed the presence of nitrogen in the bulk of the AlN layer using several methods while at the same time providing a comprehensive analysis of AlN thin films obtained by PE-ALD.

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