AES characterization and depth profiles measurements of AlN thin films on SiO₂ substrates

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ABSTRACT :

Depth profiles measurements of the elements Al, Si, N and O were determined using Auger electron spectrometry during ion etching of an AlN C.V.D. thin film deposited on an amorphous silica substrate. The Auger spectra collected at various time intervals showed the presence of Al-O, Si-O and Si-N chemical bondings in the interphase AlN/SiO₂. This result indicates that the growth of an AlN thin film on a silica substrate begins by a strong oxidation of aluminium which involves a partial nitridation of silicon.

I. INTRODUCTION

Aluminium nitride is a semiconductor III-V compound presenting a large forbidden band (gap ~ 6.2 eV) [1,2]. It is also a piezoelectric material. Another interesting property of AlN is the very high rate of acoustic waves propagation ($v_s=6\text{km/sec}$) [3,4]. It is also a refractory compound which is stable up to 2400°C [5]. The oxidation kinetics are low at temperatures below 1200°C. The thermal emissivity of this compound suggests its utilization as a source of positive ions which could replace the iridium metal for doping semiconductors via ion implantation [6]. AlN can be used also as a good insulating material, as well as a passivating coating for other semiconducting materials [7].

Another interesting property is the high thermal conductivity of AlN, slightly higher than 1W/cm K at T=300K [8]. This material is often used in a massive solide state; thin films are generally employed for optical and electronical applications.

The chemical vapour deposition (C.V.D) is currently used for AlN thin films deposition [8,9]. AlN thin films have been deposited by C.V.D processes or by other techniques on various substrates like Si, SiC, Al₂O₃, SiO₂, etc...[4,7,10,11].

In a previous paper [10], we have reported a detailed study of the C.V.D deposition of AlN coatings on SiC substrate. This first study was followed by depth profile analyses of AlN-SiC interphases which were carried out by Auger spectrometry measurements during ion etching of the C.V.D. coating [13]. It has been observed that oxygen was present at the interphase AlN-SiC.

In this paper, we report results obtained by A.E.S depth profile measurements of the interphase AlN-SiO₂, between an AlN C.V.D. coating and a silica substrate.

II. EXPERIMENTAL

II.1 AlN thin films elaboration on SiO₂ substrate.

The first step of this work was the SiO₂ substrate preparation. First, a 50µm SiC coating was deposited on a graphite pellet using the thermal decomposition of Tetramethylsilane [Si(CH₃)₄] in a hot wall C.V.D reactor designed in the laboratory [14,15]. Then, the SiC coatings were carefully polished (optical grade) and oxidized in the following experimental conditions :

Temperature T=1483 K

Oxygen pressure : 83.10³ Pa

Oxidation time : 16 hours.

This oxidizing treatment resulted in the formation of an amorphous silica coating. The thickness of this SiO₂ layer was about 500nm as indicated by ellipsometry measurement.

Then we deposited an AlN layer of about 200 nm thickness on this amorphous silica in a hot wall-reactor according to the conditions which were previously reported [13,16,17]. The reactant gas used for the AlN layer elaboration were AlCl₃ and NH₃ mixed in nitrogen, in the following conditions :

$$D_{\text{NH}_3}/D_{\text{AlCl}_3} \# 1, D_{\text{N}_2}/D_{\text{AlCl}_3} \# 550.$$

Where D is the gas flow rate.

The total pressure and the temperature were respectively fixed at 130 Pa and 1273 K.

II.2 A.E.S. depth profiles measurement

The AlN layer was etched by argon ion sputtering with an ion accelerating voltage fixed at 3 kV. Under the same sputtering conditions used in this work, we measured previously the etching rate which was obtained for AlN samples having thicknesses which were measured by ellipsometry. The etching rate generally obtained on AlN layers was 15 ± 2 Å/min. A.E.S. measurements were performed in the crater formed by ion sputtering at different sputtering times.

Some spectra were recorded in a low kinetic energy range, between 25 and 550 eV. These spectra were obtained with primary electron accelerating voltage fixed at 3 kV.

Other spectra were collected in the kinetic energy range : 1370 - 1400 eV for the Al KLL Auger transition. In this case the primary electron energy was fixed at 5 kV.

III. RESULTS

Figure 1 shows the Auger spectra recorded during argon ion sputtering of the interphase AlN-SiO₂. During the first 90 minutes etching time, all the recorded spectra were similar to that obtained

after 60 min. These spectra showed the peaks due to Al LVV, N KLL and O KLL Auger transitions. The presence of oxygen (~ 5% atomic concentration) was detected in the AlN deposit.

A very noticeable change in the Auger spectra occurred after about 90 min of ion etching : the O KLL signal intensity began to increase, and the N KLL intensity began to decrease. At this point, a shoulder observed at the high energy side of the Al LVV transition indicated the presence of silicon.

After 160 min etching the Auger spectrum indicates the presence of SiO₂.

Figure 2 shows the variations of P/B (peak to background ratios) for the N KLL, O KLL, Al KLL and Si KLL signals with increasing argon etching time of the interphase layer. This figure shows that the thickness of the interphase between the AlN layer and the SiO₂ substrate is larger than 500 Å. Indeed the interphase region, containing Al, Si, O and N elements was observed between about 100 and 150 min argon etching (between 150 and 225 nm).

Chemical states informations from Al LVV and Si LVV position and lineshapes in the interphase AlN-SiO₂ are submitted to very high uncertainty due to the overlapping of these Auger peaks and their satellites.

Therefore, we tried to obtain chemical bonding informations from the Al KLL and Si KLL high kinetic energy transitions. We present in figure 3 two Al KLL transition observed during ion sputtering at different times : 60 and 140 min etching.

This figure 3 shows that the Al KL₂₃L₂₃ transition is shifted at lower kinetic energy in the interphase region (140min etching), when compared with the Al KL₂₃L₂₃ transition recorded in the AlN layer (1). This shift of ~ - 2 eV, can be attributed to the change in chemical bonding of Aluminium from Al-N major bonding in the AlN layer to Al-O bonding in the interphase [18].

The oxidation of Aluminium in the interphase region can be explained, considering that the Al₂O₃ free energy of formation is lower than the SiO₂ free energy of formation. The presence of oxidized aluminium was also previously found in the AlN/SiC interphase [10] due to the superficial oxidized layer on the SiC surface.

Figure 4 shows the Si KL₂₃L₂₃ lineshapes observed for the AlN/SiO₂ interphase (1) and for the SiO₂ substrate (2). In the interphase the Si KL₂₃L₂₃ peak position is shifted at a higher kinetic energy than in SiO₂. This shift of about 1.5eV is not enough large to be attributed to a change from Si-O (SiO₂) bondings to Si-N (Si₃N₄) bondings. Indeed, the shifts generally observed between Si KL₂₃L₂₃ for SiO₂ and Si KL₂₃L₂₃ for Si₃N₄ have a magnitude of about 4 eV [18]. Therefore, we attribute the 1.5 eV positive shift for the Si KL₂₃L₂₃ in the AlN/SiO₂ interphase region to the presence of Si-O and Si-N bondings.

Finally, we can conclude that the high temperature C.V.D growth of an AlN layer on a SiO₂ substrate in the conditions described above (experimental section) begins by an oxygen transfer from the SiO₂ substrate to aluminium coming from the gaseous precursor. Consequently, some Si-N bondings are created in the

interphase AlN/SiO₂ .

IV. CONCLUSION

This work has demonstrated the presence of oxidized aluminium in the interphase between an SiO₂ and an AlN coating. Due to the oxidation of aluminium, the presence of mixed Si-O and Si-N bondings was revealed by the Si KL₂₃L₂₃ peak lineshape observed in the interphase region.

Our results confirm the initial oxidation of aluminium when nitride is C.V.D deposited on a silicon oxide layer. The initially deposited AlN thickness of about 200 nm appears to be built of about 150 nm pure AlN and about 750 nm interphase region containing Al-O and Si-N bonds. On the basis of these results associated with other results previously reported, [13] it is obvious that a careful elimination of oxygen from the surfaces of silicon compounds substrates (for example SiC or Si₃N₄) should be made to obtain interphases without oxidized aluminium.

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Figure 1 : Auger spectra recorded in the range 25-550eV for various Argon etching times.

Figure 2 : Variation of P/B (peaks to background ratios) for the N KLL(1), O KLL(2), Al KLL(3) and Si KLL(4) signals with etching times in the interphase AlN/SiO₂.

Figure 3 : Al $KL_{23}L_{23}$ Auger position transition recorded in the AlN layer (1) - in the AlN/SiO₂ interphase after 140 min Ar⁺ etching (2).

Figure 4 : Si $KL_{23}L_{23}$ Auger transitions recorded in the AlN/SiO₂ interphase after 140 min Ar⁺ etching (1) - in the SiO₂ substrate after 160 min Ar⁺ etching (2).