Mater. Res. Soc. Symp. Proc. Vol. 1068 © 2008 Materials Research Society 1068-C03-05

Molecular Beam Epitaxy of AlN Layers on Si (111)

Jean-Christophe Moreno, Eric Frayssinet, Fabrice Semond, and Jean Massies
CRHEA-CNRS, rue Bernard Gregory, Valbonne, 06560, France

ABSTRACT

In this work, aluminum nitride (AlN) thin films are epitaxially grown by Molecular Beam Epitaxy (MBE) on silicon substrates in order to fabricate thin film bulk acoustic resonators (TFBARs). Using atomic force microscopy, scanning electron microscopy and X-ray diffraction, we study the quality of AlN films as a function of different silicon surface preparation techniques. Finally, acoustic picosecond measurements are presented.

INTRODUCTION

In recent years, AlN thin films have attracted much attention for optoelectronic and acoustic applications [1-4]. AlN is potentially a very interesting material because it is a high-band gap piezoelectric semiconductor material having a high cohesive energy and furthermore it is compatible with the silicon technology. Present AlN-based FBAR filters are fabricated with AlN films that are deposited by sputtering [5, 6]. Although sputtered AlN films are polycrystalline, films having a thickness above 1 µm are sufficiently well oriented that the piezoelectric coupling (Kt^2) is close to the value expected for bulk single crystals. Nowadays the wireless telecommunications development needs to handle higher frequencies where submicron AlN films would be required. However, the degradation of the quality of submicron AlN films deposited by sputtering as well as the related increases of insertion losses is reported and seems to be a limiting factor to further increases operating frequencies. On the other hand epitaxial AlN thin films are expected to behave like bulk single crystals and their quality is not expected to depend a lot with the film thickness.

During the last 10 years, an efficient growth process has been developed at CRHEA about the epitaxy of group III-nitride on silicon substrates [7]. Although mainly dedicated to the fabrication of GaN-based transistor devices, this has resulted in the ability to grow smooth epitaxial AlN films on silicon substrates. So, we propose to use epitaxial AlN thin films grown on silicon substrates to realize advanced high frequency bulk acoustic wave devices for filtering and time reference (oscillators) applications.

EXPERIMENT

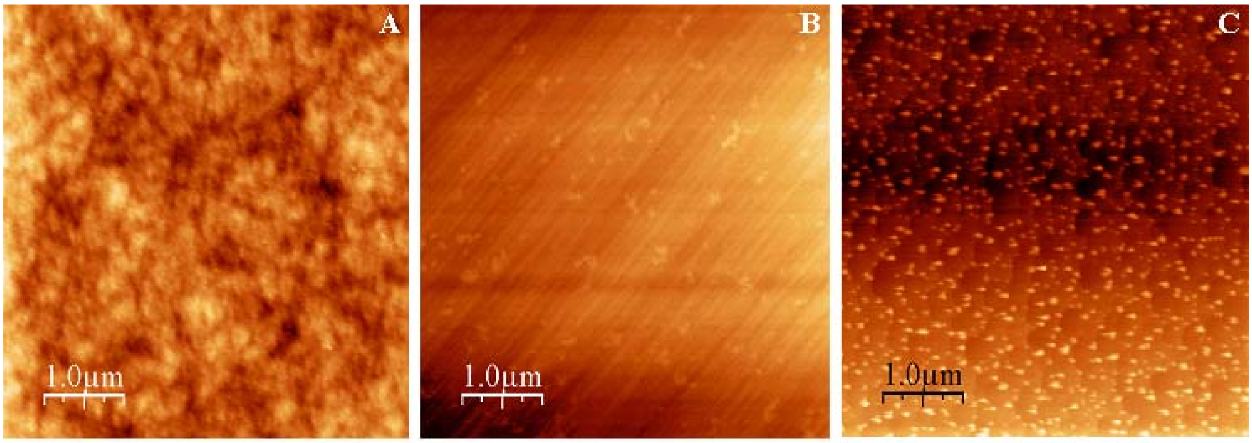
AlN epitaxial films are grown on 2” silicon (111) wafers. Obviously in the silicon technology, the (111) surface orientation is much less used than the (100) but it turns out that the hexagonal surface symmetry of (111) orientation is more appropriate to grow the AlN wurtzite phase. Also, using such surface orientation only one AlN polarity is grown, actually only the Al-polarity can be grown, and no inversion domains are usually observed. Three different silicon surface preparation techniques are assessed in this work. The first one consists in an *ex-situ* standard chemical cleaning followed by an H-passivation using a diluted HF solution with a subsequent de-ionized water rinsing [8, 9]. Then wafers are loaded in the MBE growth chamber. The second surface preparation involves high temperature (1200°C) hydrogen annealings in a chemical vapor deposition reactor prior loading wafers in the MBE growth chamber. This surface preparation, like the first one, results in an oxide-free and H-terminated Si(111) surface. Before growth, the H-passivation is removed *in-situ* by a thermal annealing at about 600°C for about ten minutes and then the well known 7x7 surface reconstruction appears as observed by reflection of high energy electron diffraction (RHEED). Concerning the third surface preparation called Ultra High Vaccuum (UHV) thermal annealing, “as received” substrates covered by native oxide are directly taken from the box and loaded in the outgassing chamber where wafers are heated up to about 500°C during several hours. After outgassing, samples are transferred inside the growth reactor and the native oxide is removed in-situ using several thermal flashes up to 900°C. Upon cooling, the 1x1-7x7 surface reconstruction transition appears around 830°C. In all cases the 7x7 surface reconstruction is the starting point of the AlN epitaxy. Ammonia is used as the N-precursor. The silicon substrate temperature is monitored using a calibrated pyrometer and it is maintained at 900°C during the AlN growth. 250 nm thick AlN films are grown and the surface morphology of the growth front as well as the crystalline quality is followed *in-situ* by RHEED during the growth. Also the growth rate as well as the thickness of AlN films is monitored using a home-made reflectometry set-up.

More details about the growth parameters are reported elsewhere [7].

DISCUSSION

Before to assess the AlN epilayer quality, we carried out an AFM study of silicon substrate surfaces depending on the surface preparation technique used. Images displayed in Fig.1 show how looks like the silicon surface morphology just before to initiate the growth. Actually, for those images silicon substrates are taken out of the growth reactor once a well-developed 7x7 surface reconstruction is observed by RHEED. Using a wet H-passivation (Fig.1-A), although the surface is very smooth, terraces and step edges are hardly seen. Some features likely related to mechanical polishing are observed suggesting that almost no silicon has been etched away during the wet chemical treatment. On the other hand, the high temperature hydrogen annealing surface preparation method leads to a very smooth surface with clearly resolved terraces and straight monolayer height step edges. Polishing features are removed suggesting that some material has been etched away during the H_2 high temperature process. Concerning the last surface preparation method involving ultra-high vacuum (UHV) thermal annealings of “as received” silicon substrates, we do see many small islands having typically a density of 10^9 cm^{-2}. Also terraces and step edges are clearly seen but they do not form a straight regular network. Actually, it turns out that step edges are pinned by the small islands leading to the formation of terraces having an irregular shape. In agreement with the interpretation of features seen on the RHEED pattern, it is believed that islands are SiC crystallites but so far we were not able to confirm that by cross-section TEM images. It is suggested that carbon impurities are trapped in the native oxide and once this last one is thermally removed *in-situ* inside the growth reactor, carbon species being less volatile they do form Si-C bonds at the silicon surface.

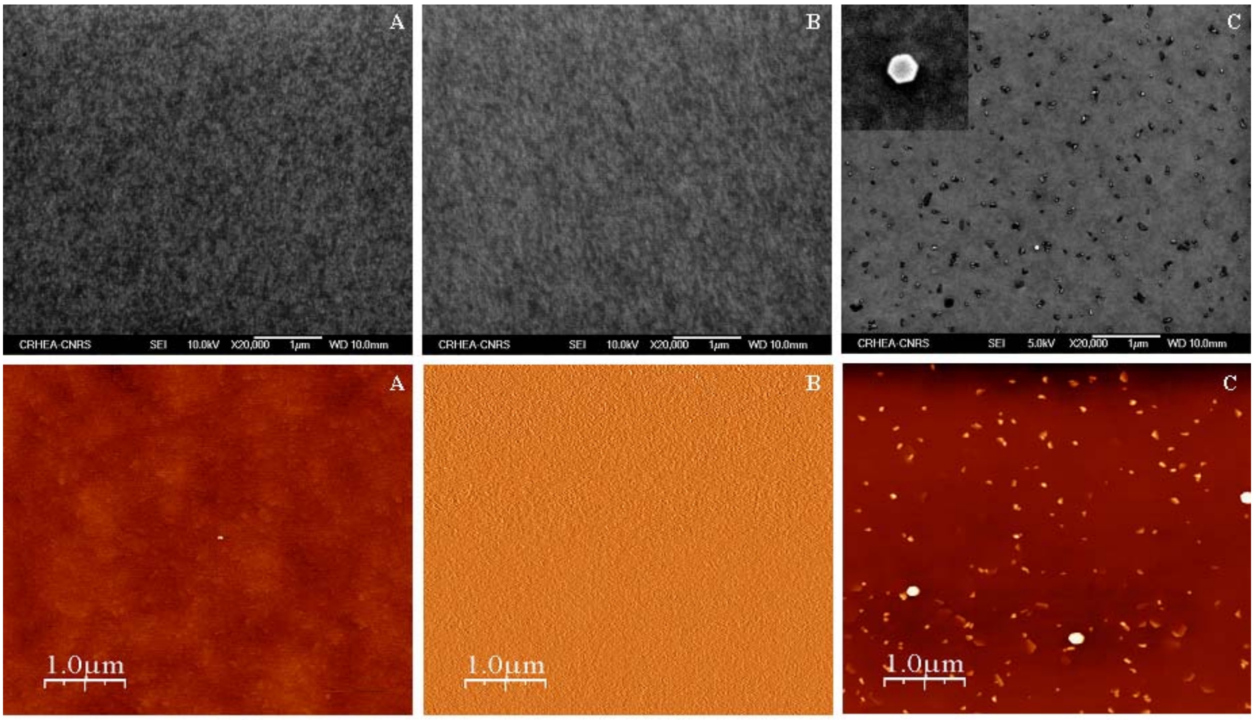
AFM and SEM images of 250 nm thick AlN layers are shown in Fig.2. Using « as received » Si substrates followed by UHV thermal annealings (Fig. 2-C) result in a poor AlN surface morphology as shown by the presence of many islands. These islands are likely AlN grains nucleated on top of the biggest SiC islands seen on the silicon surface prior to the growth. Some islands are perfectly aligned along the growth axis and an almost perfect hexagonal shape emerge from the surface (as shown in the inset) but most of them are tilted and inclined top facets are emerging from the surface. On the other hand, growth on H-terminated surfaces, prepared either by wet etching or either by hydrogen annealings, results in smooth AlN surface morphologies (Fig. 2-A and 2-B).



RMS = 3,4 Å RMS = 2,3 Å RMS = 9,5 Å

Fig.1: AFM pictures showing (111) oriented Si surfaces after different surface treatment A) after a wet H-passivation, B) after a CVD H_2 high temperature annealing, C) after an UHV annealing

Due to the huge thermal expansion coefficient mismatch between AlN and silicon, AlN epilayers usually exhibit a high tensile strain. By measuring the curvature of 2” wafers before and after the growth, strain calculations are carried out using the Stoney formula [10]. Results are summarized in Tab.1. All layers are in tensile strain but surprisingly the amount of strain depends strongly on the substrate surface preparation method used.



RMS = 2,6 Å RMS = 7,9 Å RMS = 22,5 Å

Fig.2: SEM (up) and AFM (down) images of AlN surfaces epitaxially grown by MBE on silicon. A) after a wet H-passivation, B) after a CVD H_2 high temperature annealing, C) after an UHV annealing

Si(111)	**Strain (MPa)**
UHV annealing	610
wet H-passivation	998
CVD H_2 high temperature annealing	1342

Tab.1: Strain in AlN layers.

The structural properties of these three layers have been assessed by X-ray diffraction. The full width at half maximum of the (002) peak is very similar for all the samples, around 1200 arcseconds (see Fig. 3). This result suggests that the morphological improvement of the treatments doesn't affect the material structure, and the impact of the defects is reduced in a very local scale in comparison with the matrix. The (302) peak, which give information on the edge-dislocations density, can't be measured owing to its low intensity (4% of (002) peak intensity). However, enhancements of the piezoelectric coefficient d_{33} and of electromechanical coupling factor Kt^2 are expected with such low values compared to films obtained by sputtering [11, 12]. The acoustic wave speed in the [001] direction (along the growth axis) is measured by acoustic picoseconds. There are not many differences between these three samples. The acoustic wave speed is around 11700 m/s, which is the best value ever reported to our knowledge. On sputtered AlN, this value range in between 9000 and 11000 m/s [13].

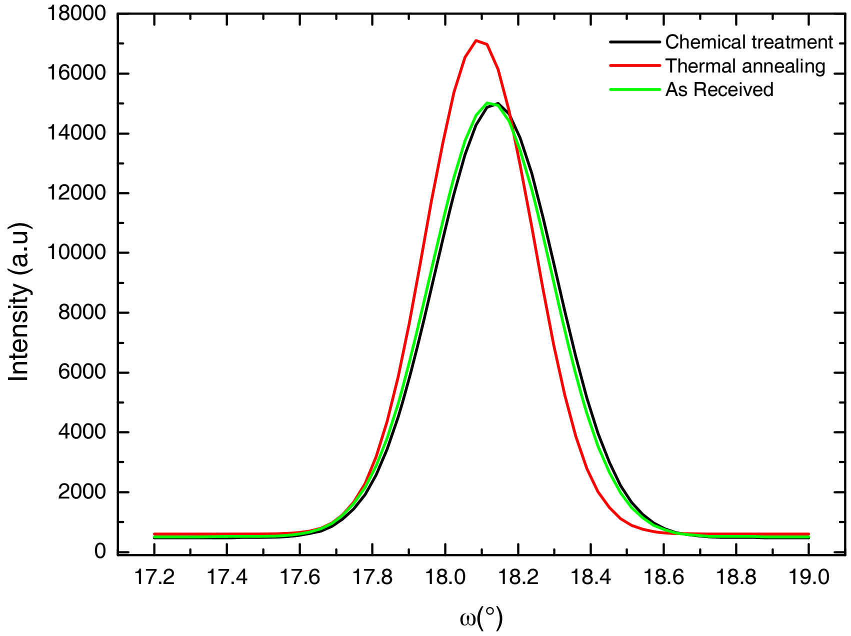


Fig.3: XRD rocking curve of (0002) peak of AlN layers grown on different silicon substrate preparations

CONCLUSIONS

250 nm thick AlN films grown by MBE on silicon (111) substrates using different surface preparations are studied. MBE allows to grow much better crystalline quality AlN layers than those grown by sputtering and depending on the surface substrate preparation very flat defect free AlN surfaces could be obtained. On the other hand a huge tensile strain is usually measured in those AlN thin films grown by MBE and this strain is strongly dependent to the silicon surface preparation. Moreover, structural properties and acoustic wave speed values suggest that high operating frequency BAW devices could be fabricated using AlN thin films grown by MBE.

ACKNOWLEDGMENTS

The authors thank P. Emery (ISEN, Lille, France) for acoustic picosecond measurements and want to acknowledge STMicroelectronics which support this work within the project Nano2013.

REFERENCES

[1] Y. Taniyasu, M. Kasu, T. Makimoto, Nature 441 (2006) 325
[2] C. Caliendo, Appl. Phys. Lett. 92, 033505 (2008)
[3] J. Olivares, E. Iborra, M. Clement, L. Vergara, J. Sangrador and A. Sanz-Hervás, Sensors and actuators A 123-124 590 (2005)
[4] V. Cimalla, J Pezoldt and O. Ambacher, J. Phys. D: Appl. Phys. 40 (2007) 6386-6434
[5] M.A. Dubois, P. Muralt, Appl. Phys. Lett. 74, 3032 (1999)
[6] K.H. Chiu, J.H. Chen, H.R. Chen, R.S. Huang, Thin Solid Films 515 (2007) 4819-4825
[7] F. Semond, Y. Cordier, N. Grandjean, F. Natali, B. Damilano, S. Vézian, J. Massies, Phys. Stat. Sol. (a) 188, (2001) 501.
[8] V. A. Burrows et al., Appl. Phys. Lett. 53, 998 (1988)
[9] J. Wang et al., Microelectronic Engineering 56 (2001) 221-225
[10] P. H. Townsend, D. M. Barnett, T. A. Brunner, J. Appl. Phys., 62 (1987) 4438-4444
[11] F. Martin et al., J. Vac. Sci. Technol. A 2004/22(2)/361
[12] H.P. Loebl et al., Materials Chemistry and Physics 79 (2003) 143-146
[13] Private communication