



Citation	Sina sadeghpour, Frederik Ceyskens, Robert Puers, (2016), Crystalline growth of AlN thin films by atomic layer deposition Journal of Physics: Conference Series, 757 (2016), 012003
Archived version	Author manuscript: the content is identical to the content of the published paper, but without the final typesetting by the publisher
Published version	http://iopscience.iop.org/article/10.1088/1742-6596/757/1/012003/meta
Journal homepage	http://iopscience.iop.org/
Author contact	sina.sadeghpour@esat.kuleuven.be phone number + 32 (0)16 325309

(article begins on next page)



Crystalline growth of AlN thin films by atomic layer deposition

S Sadeghpour, F Ceysens and R Puers

ESAT-MICAS, KU Leuven, Leuven, Belgium

E-mail: sina.sadeghpour@esat.kuleuven.be

Abstract. Aluminum nitride (AlN) thin film was grown by plasma enhanced atomic layer deposition using trimethylaluminum and ammonia precursors. A method was found to have crystalline thin film AlN with almost zero thickness variation and a truly one layer deposition of atoms per each cycle of the process. The growth rate saturated at $\sim 1 \text{ \AA}/\text{cycle}$, and the thickness was proportional to the number of reaction cycles. The preferred crystal orientation, uniformity of the nucleation and the surface roughness of the grown AlN were investigated. X-ray diffraction (XRD), atomic focused microscopy (AFM) and scanning electron microscopy (SEM) were carried out to analyze the crystallinity and properties of the films.

1. Introduction

Aluminium nitride (AlN) is a piezoelectric material with high band gap ($\sim 6.2 \text{ eV}$) [1], high thermal conductivity [2], high electric resistance ($10^{13} \Omega \text{ cm}$), as well as low expansion at high temperatures [3]. It is a good candidate for many applications such as surface acoustic wave (SAW), high frequency resonators for electronic and sensing applications. The advantage of AlN with respect to other piezoelectric materials is its possibility to be deposited in a CMOS compatible process. Plasma enhanced atomic layer deposition (PE-ALD) is one of the more advanced methods of thin film growing at low temperature, between 150 to 300°C. ALD is a type of chemical vapor deposition based on sequential, surface-adsorption limited reactions. In ALD, gaseous precursors and oxidisers are applied to the substrate in separate pulses and every pulse at most a complete monolayer is adsorbed. Therefore, in each pulse a single layer of atoms is deposited.

ALD deposition of AlN has already been demonstrated based on using trimethylaluminum (TMA) or aluminum chloride (AlCl_3) as the aluminum source [4, 5]. The use of TMA as the aluminum precursor results in higher deposition rates and lower doses to achieve saturation [6], which means more uniform nucleation on the surface of the substrate in the first cycle of the deposition. This will cause a higher crystallinity when growing AlN.

In this paper, we report the crystalline growth of AlN thin films by PE-ALD using TMA and ammonia (NH_3) as the aluminum and nitrogen source, respectively. Different parameters such as temperature, pressure, pulse time and the effect of substrate were investigated. Also, the effect of annealing on the crystallinity after deposition of the AlN thin film is presented. Although the characteristics of ALD-deposited AlN were already investigated [7–9], to our knowledge the combination of parameters for growth of crystalline AlN thin films by ALD discussed here has not been extensively studied before.

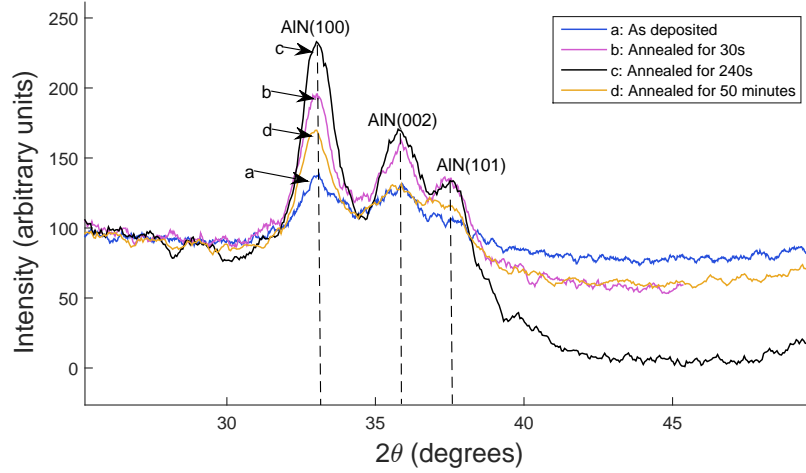


Figure 1. XRD pattern of AlN grown by the first recipe, as-deposited and annealed at 900°C for different duration, shows polycrystalline hexagonal structure.

2. Experimental details

(100) Si wafers were cleaned using Piranha and Hydrofluoric acid sequentially. The reason that plasma is used in the process is to reduce the reaction temperature of ammonia, which is around 550°C, to less than 300°C in order to prevent from the decomposition of TMA, which occurs above 300°C [10].

Several deposition experiments were done by our SENTECH PE-ALD machine, which can be divided in two different recipes. The second recipe is the improved version and will be discussed in section 3. Furthermore, the effect of the substrate and bottom electrodes on crystallization were investigated by using Si(100) and glass substrates and sputtered Ti on Si. Actually, it was shown that Ti works promising as an electrode for crystalline AlN growing [11].

The deposition rate of the grown AlN by PE-ALD were calculated by dividing its thickness to the number of deposition cycles. The thickness of the grown AlN layer was measured by reflectometry in at least ten points of each sample and was confirmed by cross section scanning electron microscopy (SEM) of the deposited AlN. Then the thickness variation was calculated by comparing the measured thickness in different points on the sample. The crystallinity and surface roughness of the grown film was investigated by X-ray diffraction (XRD) measurement and atomic force microscopy (AFM), respectively.

3. Results and discussion

3.1. First recipe

For the first experiment, the AlN was deposited on a 3" Si(100) substrate at 300°C using nitrogen as carrier and purging gas, and TMA and ammonia as aluminum and nitrogen source, respectively. The power of the plasma was set to 200 W and the flow rates of the ammonia and nitrogen were set to 40 and 50 sccm, respectively. Each cycle of the deposition process consists of a 30ms TMA pulse, purging the reactor with nitrogen for 4 seconds, exposure to NH₃ plasma for 15 seconds, and purging again for 8 seconds. To keep the plasma chamber clean of TMA during the TMA pulse, the shutter between plasma and reactor chamber was opened only through NH₃ plasma exposure. This cycle was repeated 2000 times to reach to a reasonable thickness in order to make the XRD measurement possible.

The averaged measured thickness is equal to 84 nm, which means that the grow rate is equal

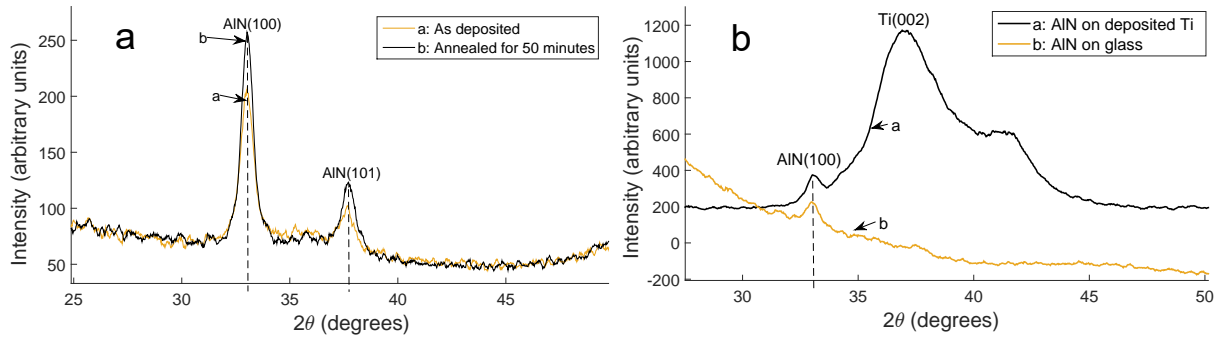


Figure 2. XRD pattern of AlN grown by the second recipe, as-deposited and annealed at 900°C on (a)Si and on (b)Ti and glass substrate.

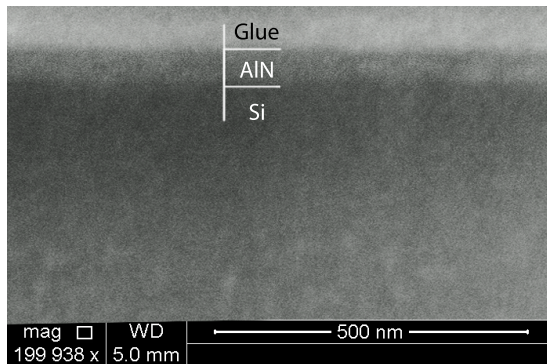


Figure 3. Cross-sectional SEM-image of a 100nm AlN film on Si(100), deposited by the second recipe

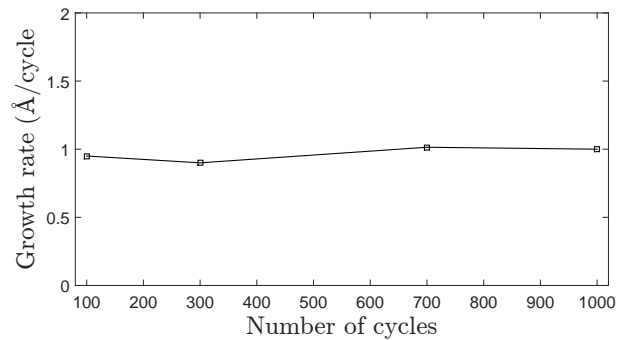


Figure 4. Growth rate of AlN film as function of cycles' number, deposited by the second recipe.

to 0.42 Å/cycle. This is even less than 1 Å/cycle, which means that the deposition is not truly one layer of atoms per cycle. It is reasonable to suppose that the incomplete reaction of NH_x to methyl groups of TMA as well as nonuniform nucleation on the surface of the substrate in the early cycles are the two main reasons of the low growth rate. This nonuniform growing leads to random nano crystallization, which was proven by XRD measurement of the grown AlN. Figure 1 shows the existence of two (100) and (002) crystal orientations of AlN in equal density. The figure also shows the beneficial effect of annealing at 900°C for varying periods. Longer annealing time doesn't have a significant effect on the crystallization. A short annealing time is shown to be superior to longer times, which is confirming the benefits of rapid thermal annealing (RTA) claimed in literature [12]. The thickness variation by this recipe is above 10 percents.

3.2. Second recipe

In order to eliminate the problem of nonuniform nucleation, after the cleaning process with HF and Piranha, all wafers were put again in Piranha for 10 minutes to cover the whole surface with OH groups. A uniformly hydroxylized starting surface appeared critical for obtaining strongly crystalline layers. This can be understood out of the need for hydroxyl groups to react with TMA during the ALD process, a reaction in which the hydrogen of the hydroxyl group is replaced

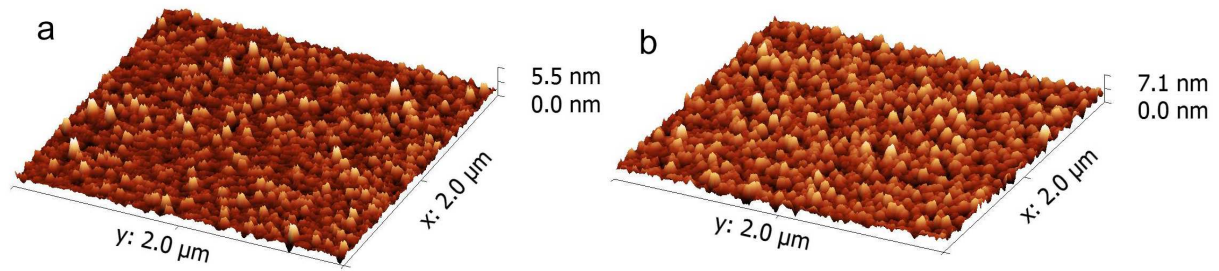


Figure 5. Surface morphology of the deposited AlN by PE-ALD on (a) Si and (b) sputtered Ti, which was measured by AFM.

with Al. Furthermore, during the ALD reaction cycles, the TMA molecules were trapped in the reactor chamber for a few seconds by closing the throttle after the pulse to increase the incubation period. This process modification aimed at causing a higher probability of nucleation on surface of the substrate. Also, the exposure time of the substrate to NH_3 plasma was increased to obtain a sufficient removal of methyl groups of deposited TMA molecules, which leads to less carbon contamination of the deposited AlN [13]. The temperature was decreased to 280°C in order to prevent the decomposition of TMA and obtain a self limiting growth of AlN.

The second recipe was repeated for 1000 cycles and each cycle includes $2 \times (40\text{ms TMA pulse with closed throttle to trap the atoms, waiting for 10 seconds while the throttle is kept close, purging for 10 seconds with fully open throttle})$, 20 seconds of NH_3 plasma exposure, and again purging for 10 seconds. The power and pressure of the plasma in this process were kept at 200W and 70Pa, respectively. The thickness of the grown AlN was 100nm, which demonstrates a growth of $1 \text{ \AA}/\text{cycle}$. This is clear evidence of strong nucleation of deposition of a full atom layer per cycle. Figure 3 shows the cross-section image of the grown AlN film, which has been obtained by focused ion beam (FIB) etching and cross-section SEM in the same time. As shown in figure 4 the growth rate is almost constant with respect to the number of cycles. The thickness variation by this recipe is less than 1 percent.

Figure 2 shows the XRD pattern and the effect of annealing of the grown AlN on a Si(100) substrate, on borosilicate glass, and on sputtered Ti on Si. It is shown that the (100) orientation of AlN has a peak significantly higher than the previous recipe and also, the substrate does not have a remarkable effect on the preferred orientation of the grown AlN, but has an effect on the quality of the film and surface morphology. Figure 5 proves this fact by showing the AFM result of the deposited AlN on Si and Ti. The absolute value of the surface roughness of 100nm thick AlN deposited on Si and Ti is 0.35 nm and 0.71 nm, respectively.

In our experiments, the plasma power lower than 100W and plasma pressure higher than 100Pa lead to insufficient removal of methyl groups, causing deposition of low quality porous AlN. Figure 6 shows the XRD pattern of the grown AlN on Si(100) by the second recipe, but with plasma pressure and power equal to 150 Pa and 100W respectively. As shown, no crystalline phase was observed from the XRD pattern.

In each cycle of the ALD process one layer of either Al or N atoms is deposited, which means that the deposition units are atoms. As shown in figure 1 and 2, the dominant crystal orientation of the grown AlN thin film is (100); it is in contrast with [14], in which the preferred crystal orientation is (002) whenever the growth unit is atoms instead of Al-N dimer.

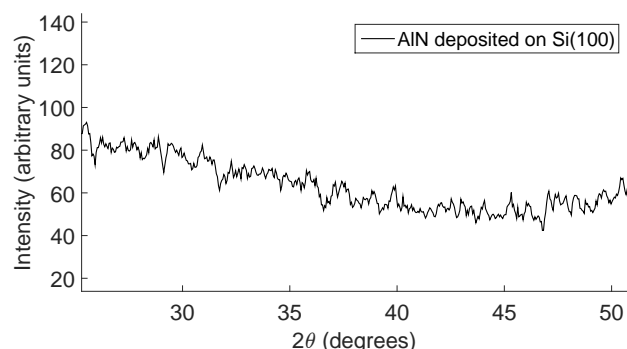


Figure 6. XRD pattern of AlN grown by the second recipe on Si(100), at plasma pressure and power equal to 150 Pa and 100 W, respectively.

4. Conclusions

In this study, we have deposited crystalline AlN thin films at 280°C with zero thickness variation and constant growth rate with respect to the number of reaction cycles. It was found that the incubation period and dose of the TMA precursor strongly influence the crystallinity. Also, in the improved recipe a higher exposure time to the NH₃ plasma is used to increase the removing of methyl groups and improve the crystallization of the grown film. Furthermore, it was shown that the substrate type (Si(100), glass or Ti on Si(100)) does not have significant effect on the preferred crystal orientation, but has effect on surface roughness and grain size. The most important output of this study is the observation that crystalline growth of AlN thin film by PE-ALD is mostly dependent to the uniform nucleation of atoms at the primary cycles of the process, which we enhanced by ensuring a hydroxylated starting surface and by increasing the incubation times.

Acknowledgements

This research was made possible by Frederik Ceyskens research fellowship from FWO-Flanders and has received funding from the European Union's Seventh Framework Programme (FP7/2007-2013) / ERC grant agreement n 340931, Thalys.

References

- [1] Motamedi P and Cadien K 2015 *J. Cryst. Growth.* **421** 45-52
- [2] Goerke S et al 2015 *Appl. Surf. Sci.* **338** 35-41
- [3] Figge S, Krncke H, Hommel D and Epelbaum B 2009 *Appl. Phys. Lett.* **94** 101915
- [4] Perros A, Hakola H, Sajavaara T, Huhtio T and Lipsanen H 2013 *J. Phys. D: Appl. Phys.* **46** 505502
- [5] Lee Y, Kang S 2004 *Thin Solid Films* **446** 227231
- [6] Ozgit C, Donmez I, Alevli M and Biyikli B 2011 *J. Cryst. Growth.* **335** 51
- [7] Van Bui H, Wiggers F B, Gupta A, Nguyen M D, Aarnink A A, de Jong M P and Kovalgin A Y 2015 *Journal of Vacuum Science & Technology A* **33** 01A111
- [8] Leskel M, Ritala M 2002 *Thin solid films* **409** 138-146
- [9] Alevli M, Ozgit C, Donmez I, Biyikli N 2011 *J. Cryst. Growth.* **335** 51-57
- [10] Puurunen R, Lindblad M, Root A and Krause A 2001 *Phys. Chem. Chem. Phys.* **3** 1093-1102
- [11] Doll J, Petzold B, Ninan B, Mullapudi R and Pruitt B 2010 *J. Micromech. Microeng.* **20**
- [12] Cao D, Cheng X, Xie Y, Zheng Li, Wang Z, Yu X, Wang J, Shenc D and Yua Y 2015 *RSC Adv.* **5** 37881-37886
- [13] Bosund M, Sajavaara T, Latinen M, Huhtio T and Lipsanen H 2011 *Applied Surface Science* **257** 7827-7830
- [14] Ishihara M, Li S J, Yumoto H, Akashi K, Ide Y 1998 *Thin Solid Films* **316** 152-157