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Growing aluminum nitride films by Plasma-Enhanced Atomic Layer Deposition at low temperatures

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Abstract. Aluminum nitride films have been grown by Plasma-Enhanced Atomic Layer Deposition method. It was found that at temperatures of 250 °C and 280 °C increase of the plasma exposure step duration over 6 s, as well as increase of reactor purge step duration over 1 s does not affect the growth rate, however, it affects the microstructure of the films. It was found that crystalline aluminum nitride films deposit with plasma exposure duration over 10 s and the reactor purging over 10 s. When the temperature drops the increase of reactor purge step duration and plasma exposure step duration over 20 s is required for crystalline AlN film growth.

1. Introduction

Aluminum nitride (AlN) is a material with a large band gap (6.2 eV) [1], high chemical inertness and thermal conductivity (320 W/m·K) [2]. AlN thin films are promising for the production of cold cathodes [3-5], buffer layers [6], dielectric and passivation coatings [7-9] as well as in the creation of gas sensors [10, 11], UV LEDs and photodetectors [12, 13].

Various methods of synthesis are used for AlN growth: chemical vapor deposition (CVD) [14], plasma-enhanced chemical vapor deposition (PECVD) [15], magnetron sputtering (MS) [16], molecular beam epitaxy (MBE) and atomic layer deposition (ALD) [17].

Plasma-Enhanced Atomic Layer Deposition method (or PEALD) is particularly interesting because it allows high precision control of film thickness and drastic reduction of the synthesis temperature by increasing the reactivity of the reagents. Furthermore, with regard to the deposition of aluminum nitride films, PEALD allows usage of nitrogen-hydrogen plasma as a nitrogen source, as alternative to ammonia, which is toxic and explosive gas.

Conventionally, atomic layer deposition method is utilized to grow amorphous films of aluminum nitride. The aim of our study was to obtain crystalline films at substrate temperatures less than 300 °C, which is important for creating passivation coatings for elements of micro- and nanoelectronics.

2. The experiment

PEALD TFS-200 device, manufactured by Beneq (Finland) was used for the deposition of AlN films. The operating frequency of the RF generator was 13.56 MHz. All experiments were performed at HF radiation power (W) of 200 W. Films were grown on a monocrystalline silicon substrate (111).

After loading the substrates into the reactor, a roughing pump was used to decresase pressure below 10 Pa. Then, nitrogen feed was turned on for ventilation of reactor chamber and the reactor itself. The nitrogen flow rate through the reactor chamber (R_k) was 200 cm^3/min, and 300 cm^3/min through a reactor (R_r).While maintaining constant values of R_k and R_r, the reactor was heated up to temperatures (T) ranging from 150 to 280 °C. 60 minutes after reaching the temperature, the surface of the substrate

was treated by the plasma of mixture of hydrogen (R_{H2} = 80 cm^3/min) and nitrogen (R_{N2} = 20 cm^3/min) gases for 1 minute. The plasma of this gas mixture was used as the nitrogen source in a cyclic film deposition process. This is followed by a cyclic process of feeding the reactants in the reactor (Figure 1). Trimethylaluminum (TMA) was used as aluminum source. Evaporator with TMA was kept at a temperature of 18 °C. TMA feed pulse duration (τ_{TMA}) of experiments in “F-series" was 0.3 s, and in “M-series" – 0.05 s. Duration of reactor purging phase after the step of treatment the substrate with the vapor of TMA (τ_{PUR}) varied from 1 to 30 s, and the duration of exposure of the substrate stage to plasma gas mixture of hydrogen and nitrogen (τ_{PE}) varied from 3 to 30 s. Duration of reactor ventilation phase after plasma exposure (τ_{PR}) in all experiments was 10 s.

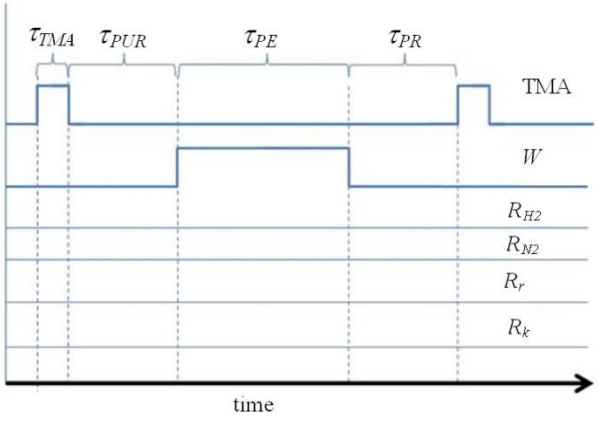

Figure 1. Illustration of the deposition process.

AlN film refractive index (n) and thickness (h) was measured by spectral ellipsometer SE-800 (Sentech, Germany).The growth rate of the film was evaluated as the ratio of its thickness to the quantity of deposition cycles.

Chemical composition of the grown film was evaluated infrared absorption spectra obtained using FTIR spectrometer FSM-1201 (Infraspek Ltd., Russia).

Film phase composition was studied using X-ray diffractometer Smart Lab (Rigaku, Germany).

3. Result discussion

Studies of aluminum nitride film deposition processes at low temperatures (150 °C) shown (Figure 2) that, ceteris paribus(τ_{PE} = 10 s, τ_{PR} = 10 s) increasing the duration of reactor purging step (τ_{PUR}) leads to a decrease in film growth rate (V).The most significant changes of V are observed at τ_{PUR}<10 s, after which the dynamics of the growth rate declination becomes slower. Presumably, growth rate is reduced due to efficiency of physically adsorbed TMA molecules removal from the substrate surface.

This assumption is supported by the fact that V drops not only because of τ_{TMA} decrease, but also due to an increase in temperature of the substrate.

At low temperatures (150 °C), the dependence of the growth rate on the duration of the plasma exposure is of extreme nature (Figure 3). Presumably, increasing value of τ_{PE} from 3 to 10 s raises the proportion of TMA radicals and molecules adsorbed on the substrate surface and engaged into chemical interaction with plasma particles; as a result, the growth rate increases. In our opinion, increase in growth rate at temperatures of 250 and 280 °C is also caused by these reasons.

However, the deposition process at temperatures well below the decomposition temperature of $Al(CH_3)_3$ (230 °C), in particular at a temperature of 150 °C, complete chemical conversion of TMA does not occur. Therefore, some of the CH_x (where $0 \le x \le 3$) radicals can be overgrown into the bulk of the film, making it amorphous and less dense.

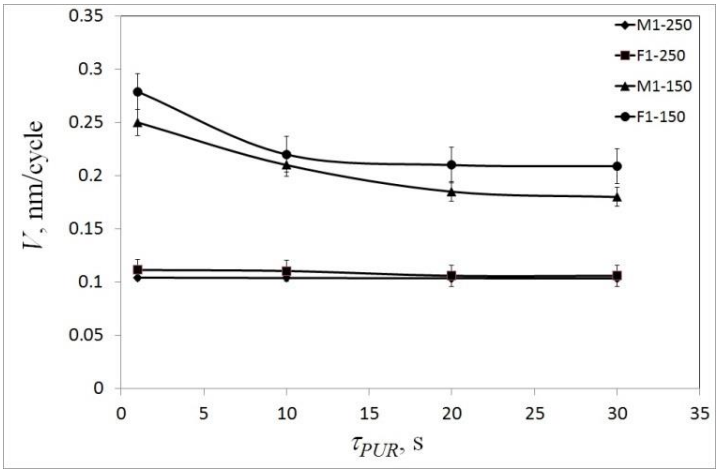

Figure 2. Dependence of film growth rate on the duration of post TMA treatment purge: τ_{PE} = 10 s; τ_{PR} = 10 s; F1-150 – T = 150 °C, τ_{TMA} = 0.3 s; F1-250 – T = 250 °C, τ_{TMA} = 0.3 s; M1-150 – T = 150 °C, τ_{TMA} = 0.05 s; M1-250 – T = 250 °C, τ_{TMA} = 0.05 s.

With increase of plasma exposure duration from 10 to 30 s efficiency of plasma exposure continues to increase, resulting in a reduction of CH_x radical fraction and in increase of density of the film. As a result of density increase, the rate of film growth decreases.

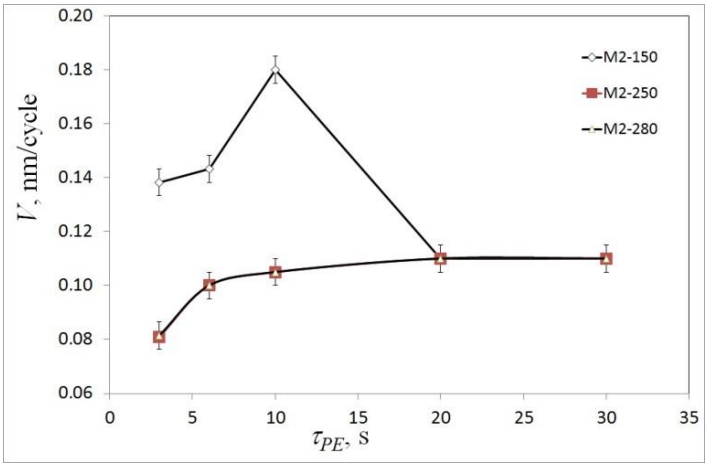

Figure 3. The dependence of film growth rate on the duration of plasma exposure step: τ_{TMA} = 0.05 s, τ_{PUR} = 30 s, τ_{PR} = 10 s; M2-150 – T = 150 °C, M2-250 – T = 250 °C, M2-280 – T = 280 °C.

As a confirmation of the density change assumption, we can employ the results of the study of dependence of refractive index (n) on the film deposition conditions. It is known that for AlN film refractive index value varies within the range from 1.9 to 2.1; it decreases as crystallinity and, therefore, the density, lowers.

As shown in Figure 4, in case of high-temperature processes (250 and 280 °C), increase of plasma exposure to 6 s leads to the increase of n from 1.9 to 1.97, after which significant changes of the refractive index substantially does not occur. This fact indicates that the most significant changes in the microstructure of AlN films occur at τ_{PE} < 6 s. Under the low-temperature process conditions (150 °C), with the duration of plasma exposure of 10 s deposited films have low values of refractive index, which indicates their amorphousness and low density. Increasing τ_{PE} to 20 s and more allows

growing films with a refractive index of about 1.9, which can be regarded as films of aluminum nitride, in contrast to those obtained at lower values of the plasma exposure duration.

It is important to note that the samples grown at 150 °C and τ_{PE} < 20 s and τ_{PUR} < 30 s almost completely lack IR absorption band with maximums at 670-675 cm^{-1} and 600-610 cm^{-1} [15], responsible for the vibrations of the Al-N.

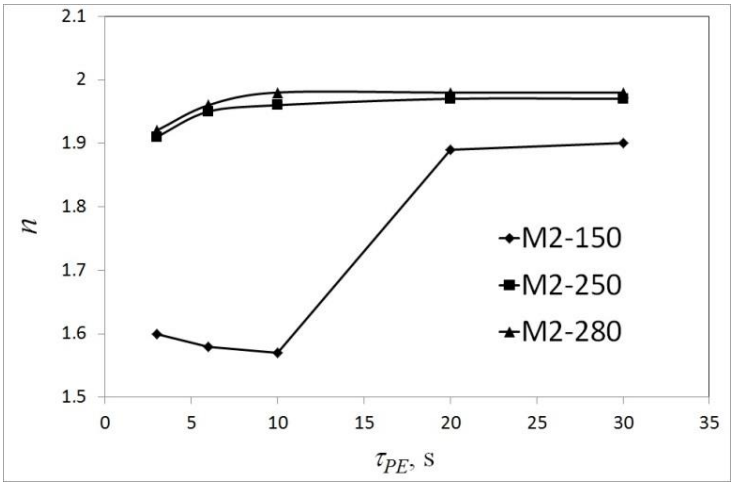

Figure 4. Dependence of the refractive index on the plasma exposure stage duration: τ_{TMA} = 0.05 s, τ_{PUR} = 30 s, τ_{PR} = 10 s; M2-150 – T = 150 °C, M2-250 – T = 250 °C, M2-280 – T = 280 °C.

As shown in Figure 5, the maximum of the IR absorption spectrum in the wavenumber range of 400-1000 cm^{-1} increases with increase in substrate temperature and duration of purging and plasma exposure steps. These results correlate well with changes in the values of the refractive index of the deposition conditions, and show the way to an increase in the crystallinity of the AlN films.

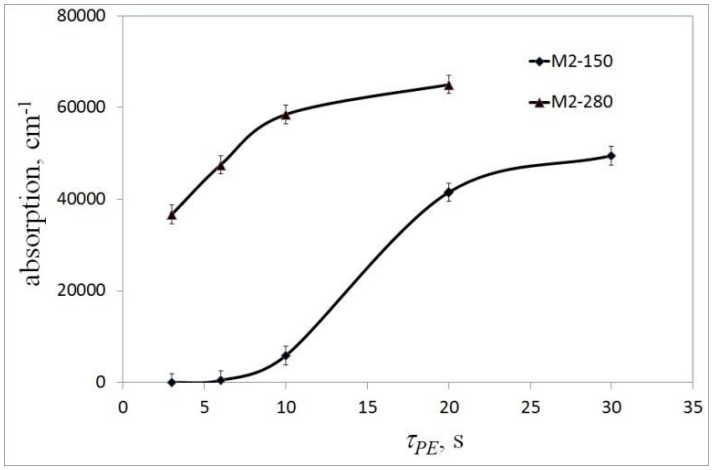

Figure 5. The dependence of the infrared absorption on the plasma exposure duration: τ_{TMA} = 0.05 s, τ_{PUR} = 30 s, τ_{PR} = 10 s; M2-150 – T = 150 °C, M2-280 – T = 280 °C.

In X-ray diagrams of samples with IR absorption coefficient of more than 55 000 cm^{-1} distinct reflexes, typical of aluminum nitride, were present (Figure 6). It should be noted that the crystallites in aluminum nitride films synthesized at a temperature of 280 °C, predominantly had a hexagonal polytype. At the same time, films obtained at a temperature of 250 °C, were formed by crystallites of

the cubic modification. Samples with IR absorption coefficient of less than 55 000 cm^{-1} no X-ray reflections was observed.

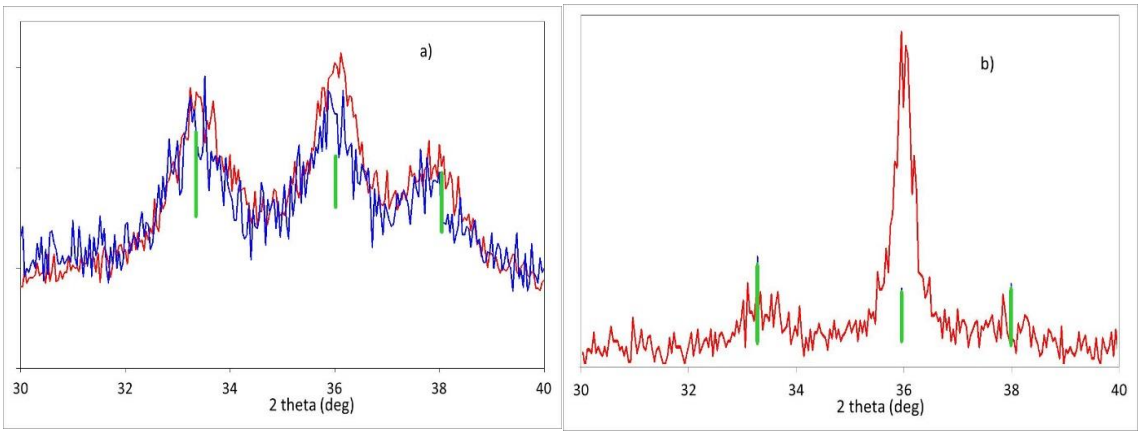

Figure 6. The XRD patterns of aluminum nitride film samples grown at temperatures of 280 °C (a) and 250 °C (b); τ_{TMA} = 0.05 s, τ_{PUR} = 20 s, τ_{PE} = 20 s, τ_{PR} = 10 s.

Thus, it was found that the aluminum nitride films that have a refractive index greater than 1.9 and having a spectrum of infrared absorption bands responsible for Al-N bonds, deposit at a rate not more 0.10±0.02 nm/cycle. Herewith, it was found that at temperatures of 250 °C and 280 °C increase of the plasma exposure step duration over 6 s, as well as increase of reactor purge step duration over 1s does not affect the growth rate; however, it affects the microstructure of the films. It was found that crystalline aluminum nitride films deposit with plasma exposure duration over 10 s and the reactor purging over 10 s. When the temperature drops the increase of τ_{PE} and τ_{PUR} over 20 s is required for crystalline AlN film growth.

4. Conclusion

The results of the investigation of the dependence of the refractive index, coefficient of IR absorption, XRD, and the growth rate on the deposition conditions showed that crystalline AlN film can be obtained by plasma-enhanced atomic layer deposition at temperatures less than 300 °C, and the film growth rate does not exceed 0.12 nm / cycle.

Acknowledgments

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