

Study of the effect of experimental conditions on atomic layer deposition of aluminum nitride films

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Abstract. AlN is an extremely chemically stable material that can withstand high temperature impacts and can be used as a coating against high temperature oxidation. In this paper, AlN films were grown on Si (111) substrates using pulsed chemical vapor deposition with a metal-organic source and ammonia as precursors followed by high-temperature in situ annealing and material physical characterization. The effects of temperature and plasma source on the AlN films were investigated, and it was concluded that the higher the temperature, the higher the growth rate of the AlN films and the lower the oxidation level. The plasma source pulsed mode showed higher growth rate and stronger aluminum signal, but its oxidation level was also higher. The plasma source normally open mode has a more desirable nitrogen signal.

Keywords: Aluminum nitride film, Pulsed Chemical Vapor Deposition, High temperature annealing.

1. Introduction

Aluminum Nitride (AlN) has a very high melting point and is an important material against high-temperature oxidation and has extremely important applications in military and aerospace fields involving resistance to high-temperature oxidation [1,2]. AlN films also have a good coefficient of thermal expansion and a thermal conductivity of up to 2.85 W/(cm·°C), making them excellent buffer layer materials [3,4]. In particular, physical vapor deposition is difficult to deposit uniformly for heteromorphs, including the inner and outer walls of tube shapes, so it is important to realize how nitride films can be achieved on the surface of complex heteromorphs [5,6].

The outstanding feature of ALD compared to other thin film preparation techniques is its self-limiting growth, a feature that allows ALD to prepare highly uniform films that can be used to deposit highly conformal coatings [7] and to achieve precise thickness control at the nanometer level. In the present experiments the deposition of AlN films was achieved using a self-built device and the characterization of the corresponding technical means was completed. In addition, the films grown by ALD under different conditions are different; for example, if the temperature is too low, insufficient reaction and multilayer condensation may occur, and if the temperature is too high, thermal decomposition and thermal desorption may occur, even within the ALD window (ALD window), and different temperatures may affect the quality of AlN films. Therefore, it is important to compare the aluminum nitride films prepared by ALD under different conditions. Usually ALD grows alumina all up to 300°C, but alumina nitride growth is more difficult and requires plasma-assisted growth (PE), thus avoiding its geometry requirements. In the present work, the study compares the nitride films prepared under different conditions and the quality of the corresponding films was examined by XPS. In addition, we performed in situ annealing of the samples to characterize the surface morphological changes.

2. Experimental procedure

During the experiments, silicon (111) was used as the substrate, and the wafers were treated with 1 % hydrofluoric acid for 1 min before the film deposition and were well washed with deionized water, the substrate was washed and dried, and then placed in a quartz tube and evacuated in less than 5 min. The AlN films were then grown by ALD and PE-ALD, respectively [8].

For the ALD growth of AlN films, trimethyl aluminum (TMA) was used as the aluminum source, ammonia as the nitrogen source, and argon (Ar) at 50 SCCM was used as the carrier gas for the deposition process at 400°C. The growth temperature was 400°C. Each ALD cycle is followed by 0.03 s of TMA pulse, 3 s of purge time, 3 s of 50 SCCM ammonia pulse, and 3 s of purge time, which is one cycle of ALD. 600 turns of AlN films are grown. After AlN film deposition, in situ annealing at 1100°C was performed [9].

Two comparative experiments were performed during the growth of AlN films by PE-ALD, with the control variables of temperature and plasma source mode, respectively. Trimethyl aluminum (TMA) was used as the aluminum source, nitrogen as the nitrogen source and carrier gas during deposition, and the nitrogen flow rate was set to 30 SCCM. Where the pulse time of TMA was 0.03 s and the purge time was 8 s. The number of growth turns was 300 turns. In the temperature comparison experiments, the growth mode of AlN was the nitrogen plasma source normally on mode with 100 W. The growth temperatures were controlled as room temperature, 300°C and 600°C. In the other set of comparison experiments, the growth temperature was kept at 300°C, and the mode of plasma was normally on and pulsed mode with 100 W power, respectively [10].

3. Sample Characterization

The test characterization of each sample was completed using X-ray photoelectron spectroscopy (XPS) with a monochromatized Al Kα1 X-ray source, and the crystallization of the annealed samples was analyzed using X-ray diffraction (XRD). The surface morphology and thickness of the aluminum nitride films were also characterized using scanning electron microscopy (SEM) measurements [11].

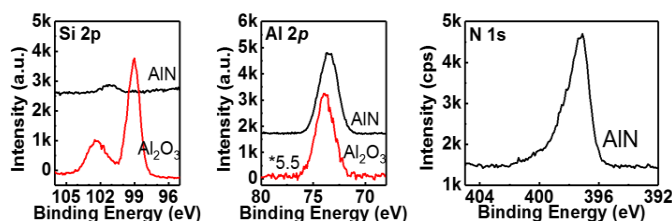


Fig. 1 XPS patterns of Si2p, Al2p, N1s of AlN/Si samples with and control samples of Al2O3/Si

Fig. 1 shows the XPS patterns of Si2p, Al2p, and N1s in the AlN/Si sample and the control sample Al2O3/Si. Both samples were calibrated with Si2p (Be = 99.0 eV), which was used to observe the changes in the relative positions of the Al peaks in both samples. For the Si2p mapping, a trace signal of the substrate Si2p bulk peak was present in the AlN/Si sample. For the Al2p mapping, there is a significant peak position difference between the two samples, the bonding mode of Al in the Al2O3/Si sample is Al-O, and the bonding mode of Al in the AlN/Si sample is Al-N, because the electronegativity of O is stronger than that of N, therefore, the binding energy of the Al2p peak in the AlN/Si sample is smaller than that of the Al2p peak in the Al2O3/Si sample. Also, the signal of N1s was observed in the AlN/Si samples [12].

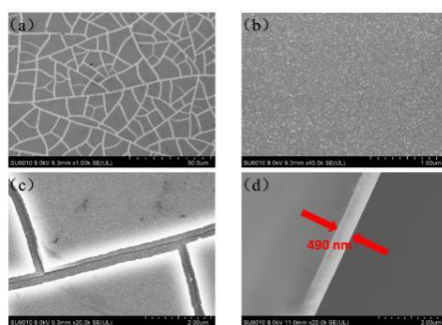


Fig. 2 SEM images of AlN/Si sample surface and cross section

The SEM images of the surface and cross-section of the AlN/Si sample are given in Fig. 2, and the low magnification images of the surface of the AlN/Si sample are given in Fig. 2(a), where

microcracks were generated by the tearing of the AlN film on the surface of the AlN/Si sample, while no tearing of the AlN film was observed in the unannealed treated AlN/Si sample, which indicates that the micro cracks were generated probably due to the amorphous transformation of the AlN film to the crystalline state during the annealing process at 1100°C [13], and the lattice mismatch between the AlN film and the substrate Si(111) during the crystallization process. High magnification images of the non-cracked part of the surface of the AlN/Si sample and the cracked part of the surface are given in Fig. 2(b) and Fig. 2(c), respectively. Some research groups have reported that certain stresses are released from the substrate by artificially creating holes and defects on the substrate to better match the aluminum nitride lattice and thus better epitaxy of aluminum nitride crystals, but this method is obviously an unnatural stress release. However, this method is obviously unnatural stress release and the lattice match is lower than that of cracked aluminum nitride films after annealing, thus this phenomenon in this experiment reveals that the annealed aluminum nitride films may have the potential to be used as a substrate buffer layer for aluminum nitride epitaxy growth. Fig. 2(d) gives the cross-sectional SEM image of the surface part of the AlN/Si sample, the interface between the substrate Si and AlN film is clearer, and the thickness of the AlN film is measured to be about 490 nm, so we can know that the growth rate is about 0.8 nm/turn when the AlN film is grown by ALD method[13].

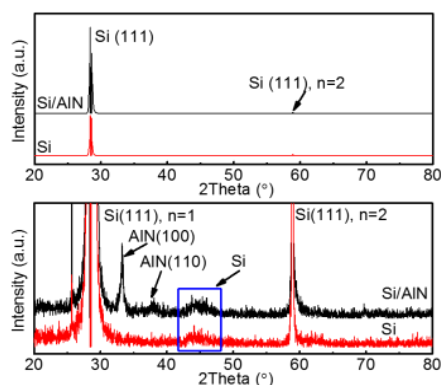


Fig. 3 XRD patterns of AlN sample and control sample Si

The XRD patterns of the AlN/Si sample and the control sample (111) Si are given in Figure 3. Since the detection depth of XRD is large, much larger than the thickness of the films grown in this experiment, the strongest signal is concentrated in the substrate Si(111) plane, so we enlarged the vertical coordinate of the XRD pattern and ignored the intensity of this signal. By comparative analysis, the signals of AlN(100) and AlN(110) were observed, so this is a good indication of the better crystallinity of the aluminum nitride films obtained in this experiment. From Fig. 2, we had thought that the cracks on the surface of the sample should be due to the crystallization process caused by the lattice mismatch between the aluminum nitride film and the substrate, and now the conclusion that the aluminum nitride film crystallized well after annealing, as derived from Fig. 3, confirms our previous speculation to some extent [14].

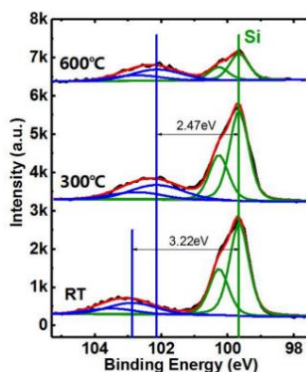


Fig. 4 XPS patterns of Si_{2p} of AlN/Si samples at room temperature (RT), 300°C and 600°C

Fig. 4 shows the XPS patterns of experimental samples of aluminum nitride films grown at room temperature, 300°C and 600°C. Using the substrate Si2p bulk peak (BE = 99.6 eV) as a calibration, and after splitting the peak fit, we can see that the signal intensity of the Si bulk peak is decreasing as the growth temperature increases. The difference between the Si2p bulk peak and the Si2p oxide peak is 3.22 eV when grown at room temperature, while this difference decreases to 2.47 eV when grown at 300°C and 600°C as the experimental temperature increases [15].

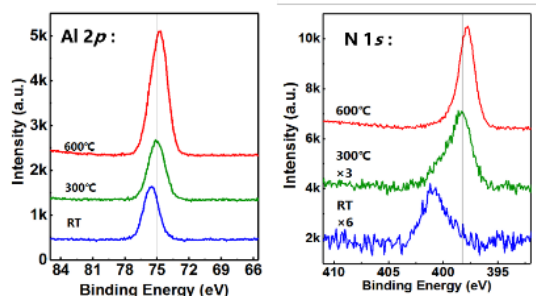


Fig. 5 XPS patterns of Al 2p and N 1s of AlN/Si samples at room temperature (RT), 300°C and 600°C

Fig. 5 shows the XPS patterns of the experimental samples of aluminum nitride films grown at room temperature, 300°C and 600°C. We can see that there is a strong signal of Al2p and N1s in the experimental samples, and the signal intensity is getting stronger with the increase of the experimental temperature. And as seen in Fig. 4, the signal intensity of the substrate Si2p bulk peak (Be= 99.6 eV) becomes weaker and weaker with the increase of the experimental temperature. Since XPS is a surface-sensitive material analysis technique, it indicates that a large amount of Al and N elements are present on the surface of the sample, and the film grows faster and the peak of Al2p and the peak of N1s have less binding energy as the temperature increases under the same experimental conditions. At room temperature, the peak shape of nitrogen element changes more obviously and its oxidation degree is the highest. Combining the above analysis, we can infer that the higher the temperature, the faster the growth rate of the aluminum nitride film and the lower the degree of oxidation at the same time, under the same other experimental conditions[16].

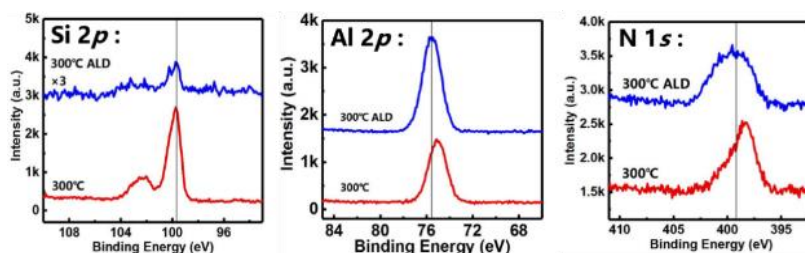


Fig. 6 XPS patterns of Si2p, Al2p and N1s in aluminum nitride films in normally open and pulsed modes of plasma sources

Fig. 6 shows the XPS patterns of the experimental samples of aluminum nitride films grown at 300°C in the normally open and pulsed modes of the plasma source, respectively. From Fig. 6 we can see that the substrate Si2p signal is weaker in the pulsed mode of the plasma source, and since XPS is a surface-sensitive material analysis technique, it can be concluded that the film growth rate is faster in the pulsed mode under the same experimental conditions. After calibrating the samples and comparing the peaks of Al2p in both modes, it can be seen that the Al signal is weaker in the normally open mode of the plasma source, but the peaks are small and less oxidized. And comparing the peaks of N1s in both modes, it can be seen that the nitrogen signal in the normally open mode of the plasma source is more desirable [17].

4. Conclusion

a. AlN films were successfully prepared by plasma-enhanced chemical pulse vapor deposition and annealed at 1100°C. After annealing, a relatively strong signal of aluminum nitride and a weak signal of substrate were detected by XPS, and good crystallinity of aluminum nitride films was obtained by XRD patterns, and micro-cracks were observed on the surface of aluminum nitride films by SEM.

b. In addition, the behavior of stress release after annealing that appeared in the experiments might be applied to the substrate buffer layer of epitaxially grown aluminum nitride. AlN films were also successfully prepared by the technique of pulsed chemical vapor deposition. and compared the growth results of AlN films at different temperatures and different plasma source modes.

c. The results from XPS show that the higher the temperature, the higher the growth rate and the lower the oxidation of AlN films under the same experimental conditions. The growth rate in the pulsed mode of plasma source is higher and the aluminum signal is stronger, but its oxidation degree is also higher. while the plasma source normally open mode has a more desirable nitrogen signal.

d. AlN has the characteristics of high thermal conductivity, high temperature resistance, radiation resistance, acid and alkali resistance, high strength and high hardness, etc., which has a wide application prospect in military industry. This paper provides a reference for the growth mode and parameter setting of atomic layer deposition of aluminum nitride thin film[18].

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