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The effect of temperature and conversion rate on the AlN microstructure synthesized by direct nitridization

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Aluminum nitride (AlN) thin film has been synthesized by the direct nitridization of aluminum with heated NH_3 gas. The infrared heating with focusing capability was adopted as a heat source and the reaction zone was constantly translated by controlling the sample stage. The metallic Al layer was deposited on the amorphous fused silica glass substrate using a thermal evaporation system at 3.0×10^{-6} Torr and the temperature profile of the reaction zone could be arbitrary chosen by varying the focal length of the IR reflector in the range of 600 ~ 800 °C. The polycrystalline AlN thin film was obtained with <100 nm thickness in a single step and the thickness of the AlN layer could be increased by the iterated steps. The morphology and the crystalline quality of the AlN thin film have been characterized by the XRD, SEM, and EDS analyses.

Key words: AlN thin film, Direct nitridization, IR heater, Directional solidification.

Introduction

Aluminum nitride (AlN) which has high melting point (2200 °C) and thermal conductivity (285 W/m·k) for high temperature applications has been emerged as material of new-generation substrate due to wide band gap (6.2 eV), a thermal expansion coefficient that matches well with that of silicon, high electric breakdown field (1.8×10^6 V/cm), and high electron thermal velocity (1.85×10^5 m/s) [1-3].

AlN single crystals are commonly grown by sublimation method or solution growth with flux because of its high melting temperature. Currently the most efficient and commercial sublimation method is the physical vapor transport (PVT) method where the raw materials at the bottom of the growth chamber evaporate and the transported gaseous phases recrystallize around seed surface located at the upper part of the chamber. While sublimation method enables the formation of a large crystal, its major weakness is the difficulty of achieving reproducibility, due to the numerous factors affecting control of the growth rate and quality [4-6]. Since the wafering of AlN single crystal comprises many batch-type processes including slicing, grinding, lapping, and chemical mechanical polishing (CMP), the whole AlN wafering process is costly and time consuming. Also a stable native hydroxide surface layer could be formed upon exposure to ambient air or water during wafering processes. As an effort to avoid the wafering processes and acquire a necessary thickness of the AlN layer with crystal quality for the active layer deposition, homo- [7, 8] or hetero-epitaxial [9] growth have been attempted using AlN, sapphire, or SiC substrates.

In this study, direct nitridization method combined with directional solidification was tried to synthesize the AlN thin film, which has advantage of simple chemical reaction at much lower reaction temperature than the methods mentioned above.

In the directional solidification, the growth behavior of crystals is limited in one direction and the growing speed, temperature, and reaction zone width can independently controlled. In particular, the large temperature gradient (ΔT) is a key parameter to induce nucleation and one-sided growth by increasing the mobility of atoms due to strong one-way heat transfer [10, 11]. The infrared heater composed of 1kW halogen lamp and ellipsoidal Au-coated reflector with focusing capability was used in this study to form a constant and high temperature gradient. 2-dimensional Al thin film was directly nitrided with NH_3 gas and the converted AlN grain growth was controlled by directional solidification with the aid of IR heater which formed a narrow hot zone with very high temperature gradient.

Experimental

Thin Al layer with the thickness was deposited on the

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amorphous fused silica glass by thermal evaporation system using Knudsen cell and high purity aluminum metal (99.999%). The fused silica substrates were cleaned before deposition with ultrasonic cleaner in acetone, ethanol, and DI water for 10 minutes. Since the diffusion coefficient of nitrogen in AlN and molten Al is 2.63×10^{-25} m^2/s and 3.9×10^{-8} m^2/s at 660 °C [12], respectively, the deposited Al layer was limited less than 100 nm. When the AlN layer is firstly formed on the surface, nitrogen cannot come into contact with the inner Al without cracking the surface nitride layer due to extremely low diffusion coefficient of nitrogen in AlN.

Synthesis of AlN thin film

The deposited Al specimen was placed inside the quartz tube chamber while maintaining the minimum contact with the ambient air atmosphere to avoid the oxidation. After purging the quartz tube chamber with NH_3 gas, nitridization reaction proceeded in the very narrow hot zone of the Al layer while injecting heated NH_3 gas to the hot zone region at a constant rate. With the custom-built IR heater consisting of a halogen lamp and ellipsoidal Au-coated reflector (Fig. 2(a)), narrow hot zone with the width ~3 mm could be obtained up to 1100 °C. The infrared radiation emitted from the tungsten filament was focused at the hot zone of the sample which located at a focal point of the ellipsoidal reflector. The temperature was monitored with the k-type thermocouple near the hot zone and the translation of the specimen stage was controlled in the range between 0.01 mm/min to 9.99 mm/min using the step motor. The temperature profile at the hot zone showed very steep temperature gradient ~350 °C/mm as shown in Fig. 2(b). NH_3 gas was heated to 650 °C using a heating tape (DHT102040LD, OMEGA) around the stainless steel tube and injected into the quartz tube chamber at a flow rate of 0.1 mL/min. The detailed specifications of the IR heating apparatus used in this study are shown in Table 2.

The temperature and translation speed of the hot zone are the critical parameters for forming the AlN thin film using the IR heater. The effect of both parameters on the morphology and the preferred orientation of the AlN grains were investigated separately using SEM (JOEL JSM-6400), FE-SEM (JEOL JSM-7610F/Philips XL30SFEG), and XRD (Regaku D/max-3C).

Since the thickness of the AlN layer was limited less than 100 nm in this study due to the difficulty of nitrogen diffusion through the converted AlN surface, repeated deposition and conversion was conducted with the same condition to increase the AlN layer thickness. Also the improvement of the homogeneity and continuity of the hetero-epitaxial layer was expected as the crystal or thin film grown on the substrate moves away from the fused silica substrate [13, 14]. The stacked AlN thin films synthesized by repeated deposition method were observed using FE-SEM to confirm the improved morphological change.

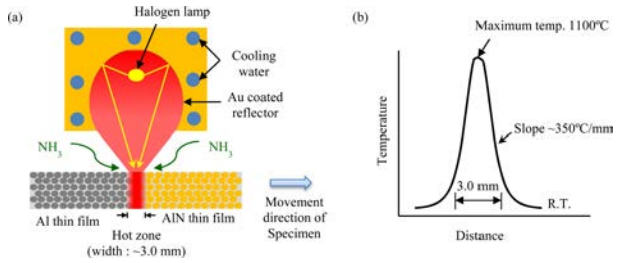

Fig. 1. Schematic drawing of the (a) custom-built IR heater consisting of 1kW halogen lamp and specimen stage located at the focal points of the ellipsoidal Au-coated reflector and (b) temperature profile of the hot zone formed by the focused IR irradiation.

Table 1. Specification of the custom-built IR heater system.

Experimental parameter	Conditions
Beam width	About 3.0 mm
Gas temperature	650 °C
Gas flow rate	0.1 mL/min
Heating temperature	Max. 1100 °C
Hot zone translation speed	0.01 ~ 9.99 mm/min

Results and Discussion

The effects of temperature at the reaction zone

The temperature profile of the custom-built IR heater at the reaction zone could be controlled to have a different heating width and temperature distribution by adjusting the IR lamp position and the input power. Also the reaction time was optimized by adjusting the translation speed of the specimen stage, which was fixed at 0.08 mm/min of a relatively low speed. The microstructural features including nucleation and the grain growth were analyzed by SEM and XRD. The average grain size of AlN thin films increased to 0.5 μm, 1.0 μm, and 1.5 μm as the temperature of the hot zone increased to 550 °C, 600 °C, and 650 °C, respectively as can be seen in Fig. 2. As the hot zone temperature exceeded above the melting point (660.3 °C) of Al, AlN phase was not observed due to the evaporation of the deposited Al thin layer (Fig. 2(d)). The elemental distribution and the morphologies of AlN phase synthesized on the fused silica glass substrate at 650 °C were analyzed using FE-SEM (JEOL JSM-7610F) and EDS. EDS data in Fig. 3 shows high contents of silicon and oxygen since the incident electron beam easily penetrated the thin AlN layer (<100 nm). AlN thin films formed on fused silica glass substrate at 650 °C slightly lower than the melting

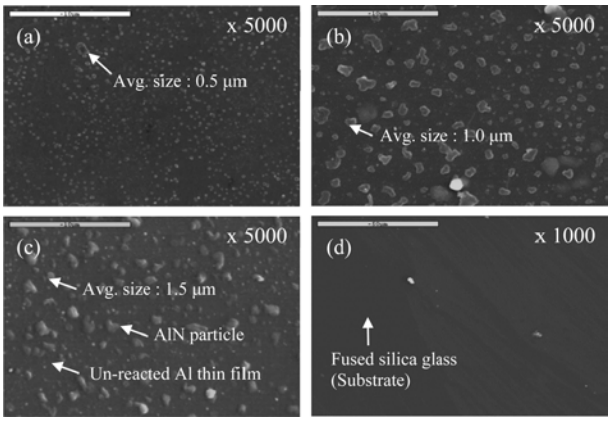

Fig. 2. SEM images of AlN thin films synthesized on fused silica substrate by IR heating temperature of (a) 550 ºC, (b) 600 ºC, (c) 650 ºC, and (d) 700 ºC. The average particle size was increased with increasing heat treatment temperature.

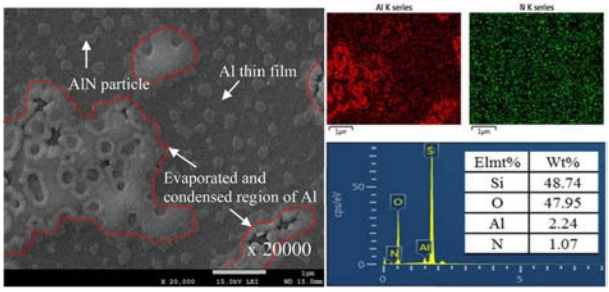

Fig. 3. SEM image and EDS data of AlN thin film synthesized on fused silica substrate at 650 ºC. The red dotted regions show the evaporated and condensed regions of Al.

point of Al were partially melted and condensed due to the non-uniformed thickness of Al thin films deposited by thermal evaporation system. T. Okada et al. also reported that the non-nitirided Al regions in the vicinity of converted AlN region were melted and condensed by the nitridization reaction heat of Al, which is having a large exothermic reaction [12].

AlN thin films synthesized at different temperatures were examined with XRD (Fig. 4). The overall XRD peak intensities were weak due to the small mass of the AlN phase. AlN phase was detected in the specimens heat treated above 550 ºC and the XRD peak intensities increased with temperature up to 650 ºC. AlN thin film synthesized at 700 ºC showed the amorphous peak of the fused silica glass substrate due to the evaporation of thin Al layer.

Hexagonal-AlN structure generally forms the close-packed plane along the c-axis in the order ABAB···, which can lower the interface energy than the other stacking sequences during crystal growth. In this experiment using the focused IR heater as a heat source, the synthesized AlN phase showed the preferred a-axis orientation with (1000) plane parallel to the amorphous substrate surface. C. S. Oh reported that the growth of AlN under NH_3 atmosphere using the conventional resistive heating method could provide

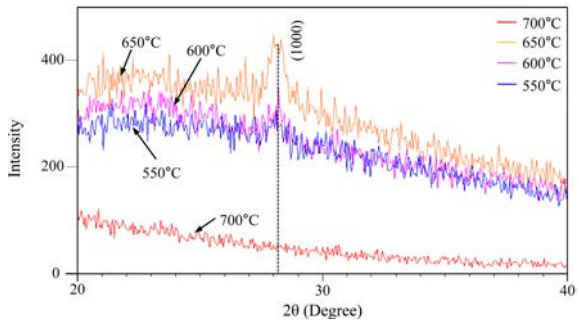

Fig. 4. XRD patterns of AlN thin films heat-treated at 550 ºC, 600 ºC, 650 ºC, and 700 ºC on the fused silica substrate.

sufficient time for reaction between N_2 gas with Al, leading to c-axis growth [15]. NH_3 gas can be decomposed with the mixture of N_2 and H_2 above 200~300 ºC under atmospheric pressure and the decomposed N_2 gas from NH_3 gas is more reactive than the normal N_2 gas [16]. Since the 2-D growth technique of AlN thin film using the focused IR heater in this experiment exhibited the very rapid growth rate of 4.8×10^3 μm/h, the AlN phase exhibited [1000] growth direction.

The effects of hot zone movement speed

AlN thin films were synthesized at various conditions to verify the possibility of a rapid and continuous production process at different temperature and the movement speed of hot zone using the focused IR heater. The temperature of the deposited Al thin film should be high enough and the hot zone should secure an enough time to react with N_2 gas [17-19]. When the translation speed of the hot zone was faster or slower than an optimum range, the temperature of the hot zone did not reach the reaction temperature or the evaporation of the deposited Al occurred, respectively. The combination of the correlated temperature and translation speed of the hot zone was investigated through trial and error method to find an optimum range as shown in Table 2. These results showed that the temperature controlled by the focused IR heater was a more dominant factor than the translation speed of the reaction zone in this experiments.

Fig. 5 shows the SEM images of AlN thin film synthesized at relatively fast 5.0 mm/min and extremely slow 0.08 mm/min translation speed of the hot zone. As the translation speed of the hot zone increased, morphological defects including the exposed substrate region formed by Al evaporation and re-condensated Al cluster increased. At extremely slow translation speed of the hot zone condition, most of the sample surface was covered with AlN phase except the evaporated and re-condensated Al region. Although direct nitridization of Al was successful at low translation speed of the hot zone with temperature lower than the melting point of Al, the occurrence of the Al cluster formed by

Table 2. The combination of the hot zone translation speed and the temperature required for direct nitridization of Al.

Hot zone translation speed (mm/min)	Heating temperature (°C)
1.0	650 ± 4
2.0	683 ± 3
3.0	728 ± 3
4.0	751 ± 4
5.0	778 ± 4

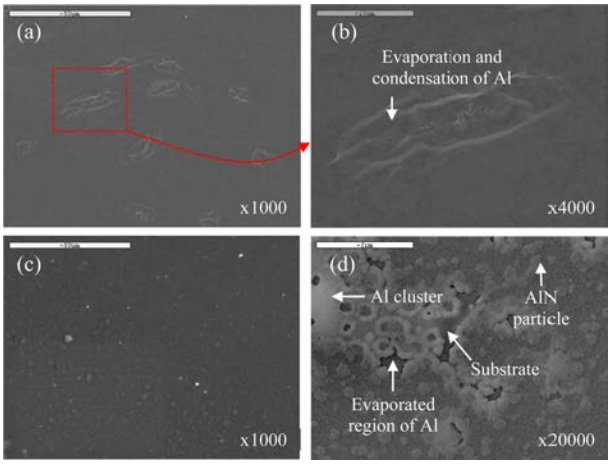

Fig. 5. SEM images of AlN thin film synthesized at different hot zone translation speed of (a),(b) 5.0 mm/min and (c),(d) 0.08 mm/min, showing the different morphology appearance including condensation and evaporation of Al.

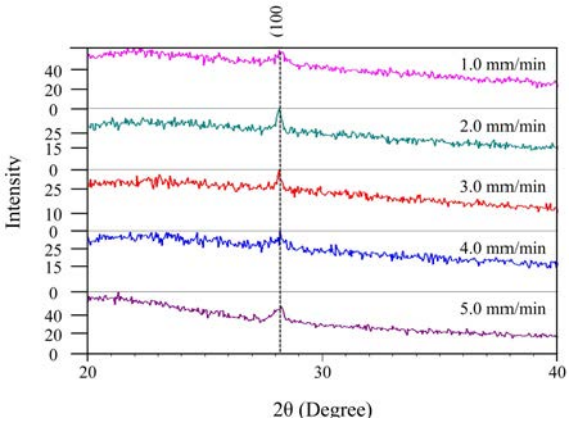

Fig. 6. XRD patterns of the thin films synthesized by respective hot zone translation speed, showing the major AlN (100) peaks with different intensity and crystallinity.

evaporation and re-condensation of Al due to the long duration time of the hot zone could not be avoidable. To avoid the evaporation of Al from the hot zone, the duration time of the hot zone at a specific temperature could be shortened by increasing the translation speed of the hot zone. As the translation speed increased, the temperature of the hot zone should be increased to secure the enough thermal energy to convert the Al into AlN. As the translation speed and the temperature of the hot zone increase, the windows for direct

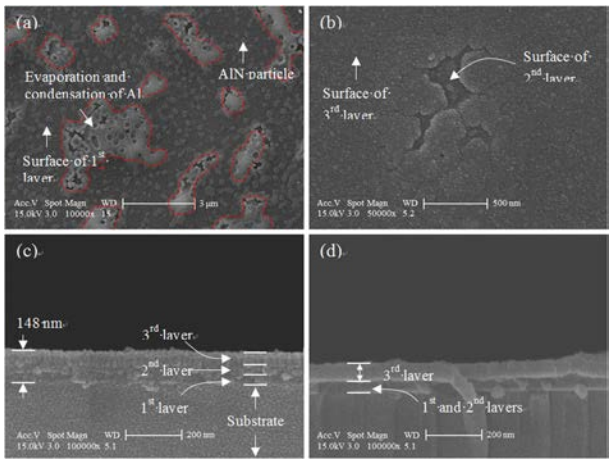

Fig. 7. SEM images of the (a) first layer, (b) third layer, (c) cross-sectional image of AlN film synthesized by the repeated processes, and (d) cross-sectional image of defect region due to the evaporation of Al.

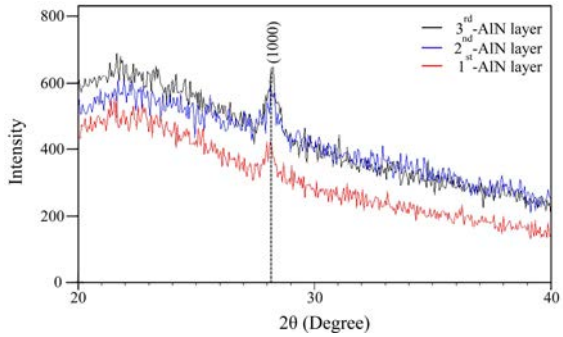

Fig. 8. XRD patterns of AlN thin films showing the increased intensity of AlN (100) plane with the repeated processes.

nitridization of Al became narrow and various defects appeared as can be seen in Fig. 5. However, XRD data in Fig. 6 shows that AlN phase were grown in a-axis direction at all the experimental conditions despite of the different morphologies such as Al cluster and heterogeneous region.

The effects of repeated deposition

Since the single layer of AlN thin films synthesized in this study showed poor crystallinity with the thickness less than 100 nm, the multilayer AlN films were synthesized by the repeated processes involving the deposition of Al layer and direct nitridization, expecting improved the crystallinity and larger thickness.

The multilayer AlN films were analyzed by FE-SEM (Philips XL30S FEG). Fig. 7(a) shows that the surface of the 1st-AlN layer containing evaporated and condensed regions. However, the surface of 3rd-AlN layer in Fig. 7(b) exhibited improved morphology with less defects. The cross-sectional image in Fig. 7(c) showed the uniform layer thickness of about 150 nm. Although the region with the reduced thickness due to the uneven growth process was found occasionally as in Fig. 7(d), multi-layer AlN films could be obtained by the

repeated process with less defects than single layer AlN film.

The improvement of crystallinity of AlN phase with the iterated processes was confirmed by XRD analysis. The peak intensity of AlN (100) plane increased with the number of repeated deposition process as in Fig.8.

Conclusions

AlN thin films were synthesized using the direct nitridization method with the focused IR heater as a heat source by reacting NH_3 gas with Al thin films. The reaction region with approximately 3.0 mm width was controlled with different translation speed and temperature, enabling a continuous process as an alternative to the batch type conventional process which takes a long time for single crystal growth and wafer processing. Al thin films were directly nitrided under the controlled hot zone conditions by directional solidification. The morphology and the defects of the grown AlN films were characterized with XRD, SEM, and EDS. The AlN films showed polycrystalline nature with (100) preferred orientation and the various defects depending on the growth parameters. The combination of the translation speed and the temperature of the hot zone was critical to suppress the defect formation by the regional Al evaporation and re-condensation. The thickness of the single AlN layer was limited less than 100 nm due to the limited diffusion coefficient of nitrogen into AlN and the total thickness of the AlN film could be increased by the repeated process with improved surface crystalline nature.

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