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Growth of AlN Thin Film on Sapphire Substrates and ZnO Templates by RF-magnetron Sputtering

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AlN thin films were deposited on sapphire substrates and ZnO templates by rf-magnetron sputtering. Powder-sintered AlN target was adopted for source material. Thickness of AlN layer was linearly dependent on plasma power from 50 to 110 W, and it decreased slightly when working pressure increased from 3 to 10 mTorr due to short mean free path of source material sputtered from AlN target by Ar working gas. When N_2 gas was mixed with Ar, the thickness of AlN layer decreased significantly because of low sputter yield of nitrogen. AlN layer was also deposited on ZnO template. However, it showed weak thermal stability that the interface between AlN and ZnO was deteriorated by rapid thermal annealing treatment above 700°C. In addition, ZnO layer was largely attacked by MOCVD ambient gas of hydrogen and ammonia around 700°C through inferior AlN layer deposited by sputtering. And AlN layers were fully peeled off above 900°C.

Keywords : AlN, Sputtering, Protecting layer, Crystal quality

I. INTRODUCTION

Solid−state lighting industry is growing bigger and bigger now in general illumination field thanks to high−end white LED devices based on GaN growth technology. Main technology interest in LED industry is fabricating high performance LEDs at low cost and supplying high brightness LEDs at low price in order to penetrate into conservative general illumination industry [1−3]. GaN−related nitride semiconductors are typically grown on cheap sapphire substrates, which are thermally and electrically nonconductors, because GaN substrates are very expensive [4,5]. Therefore, horizontal−type LED structure with two upward contacts is inevitable, and this leads to heat generation due to current crowding in n−type GaN [6]. Since high brightness LEDs needs high density of current, fast heat dissipation is one of key issues in LED industry. Flip−chip process and laser lift−off (LLO) process have been adopted typically for fabrication of high−end commercial LEDs up to now to avoid the heat problem of nitride LEDs caused by sapphire substrates [7,8]. However, these two approaches need more fabrication steps, and it is one of main drawbacks to make high−performance LEDs cheaper.

Recently, alternative way such as chemical lift−off (CLO) has been studied by several research group [9,10]. After deposition of wet−etchable template layer on sapphire substrate, LED structure is grown

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on the template. This LED structure can be detached from sapphire substrate by wet etching. ZnO would be one of good candidates for CLO template because ZnO can be easily etched by acid and has wurtzite structure which is stable crystal structure of GaN, AlN, and InN [11]. In addition, good crystal quality of ZnO can be obtained by sputter deposition. However, ZnO layer is not stable in NH_3/H_2 ambient and its surface degradation occurs easily at high temperature by reaction with NH_3 under typical MOCVD growth conditions [12,13]. In this study, we deposited AlN protecting layers on ZnO templates and investigated their structural properties and thermal stability in N_2 ambient and NH_3/H_2 ambient at high temperature.

II. EXPERIMENTAL

AlN layers were deposited on c-plane sapphire substrates and ZnO templates by radio-frequency magnetron sputtering with various deposition parameters, such as substrate temperature, working pressure, plasma power, and input ratio of working gas. Powder-sintered targets of AlN and ZnO were adopted for source materials. Argon (6N) and nitrogen (6N) were used for working gases. Base pressure was below mid-10^{-6} Torr and working pressure was changed to 3, 5, 10 mTorr. In order to know dependence of plasma power on layer thickness, it was varied from 50 to 110 W. Target-to-substrate distance was fixed to 7 cm, and substrate was rotated to improve surface uniformity. Deposition time of AlN thin films were 2 hours, and typical deposition rate was 320 nm/hour at 90 W and 5 mTorr. Gas input ratio of Ar to N_2 was controlled from 0.3, 0.5, 0.7, 0.9, and 1 at constant total flow rate. All AlN layers in this research were deposited at room temperature. Rapid thermal annealing (RTA) treatment was carried out for all samples to improve crystal quality of AlN.

AlN thin films were also deposited on ZnO templates which were grown on sapphire substrates at room temperature. To see thermal stability of AlN layer on ZnO, the samples were thermally-treated with RTA system. RTA treatments were carried out at various temperatures from 500 to 1,000°C remaining other conditions fixed at 50 Torr and N_2 ambient. In addition, thermal and chemical stability of the samples were also investigated in typical MOCVD growth condition supplying NH_3 and H_2 gases because it was well-known that ZnO is very reactive with NH_3 and H_2 at high growth temperature and we expected AlN layer would act as protecting layer for ZnO template. The substrates were heated up to 500, 700, 900, 1,080°C, annealed for 2 min, and cooled down to room temperature.

All thin films were characterized by field-emission scanning electron microscopy (FE-SEM) for structural properties such as surface morphology and layer thickness. And x-ray diffraction (XRD) measurements were carried out by Rigaku Model D/MAX-2500V/PC to see formation of AlN crystalline phase and improvement of crystalline quality.

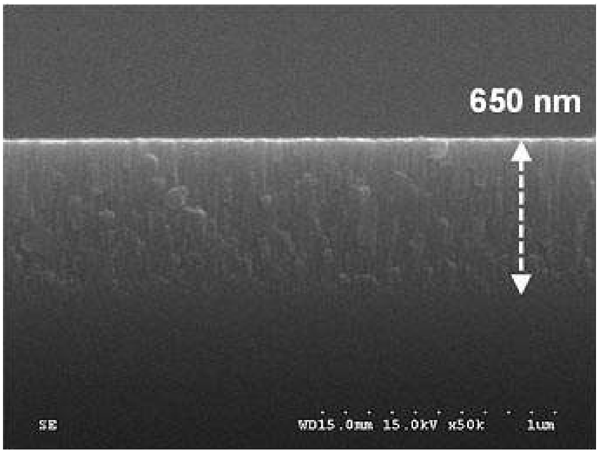

Figure 1. SEM image of AlN thin film with 650 nm thickness deposited on sapphire at room temperature. AlN layer was grown in the condition of Ar working gas and 90 W plasma power.

III. RESULTS AND DISCUSSION

Fig. 1 shows typical cross−sectional SEM image of AlN layer deposited on c−plane sapphire substrate at room temperature. AlN layer was 650 nm−thick deposited in condition of Ar working gas, 90 W plasma power, and 5 mTorr working pressure. AlN layer has smooth surface and no void in interface region between AlN layer and sapphire substrate, and the substrate was well−covered with AlN film. It means that this layer could be used as a protecting layer which guards ZnO against active species. Fig. 2 shows cross−sectional SEM images of AlN layers with plasma power of 50, 70, 90, 110 W at 5 mTorr. Thickness of AlN layer increased linearly with plasma power, 320, 510, 650, 830 nm, because more active Ar atoms would yield more sputtered−AlN amount. We also investigated effect of working pressure. Although it was not much changed, lower working pressure of 3 mTorr led to thicker AlN layer, and higher working pressure of 10 mTorr led to thinner AlN layer. Thin means that amount of AlN molecules which arrive at the substrate is determined by gas phase collision. Since AlN molecules experience more collisions under higher working pressure, less AlN species reach the surface and thinner AlN layer is deposited. In contrast, thicker AlN is deposited under lower working pressure because the number of collisions decreases.

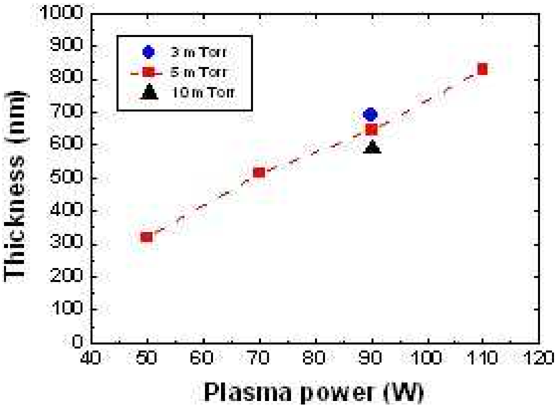

Figure 2. Thickness of AlN layers with plasma power of AlN target from 50 to 110 W and AlN layers under working pressure from 3 to 10 mTorr.

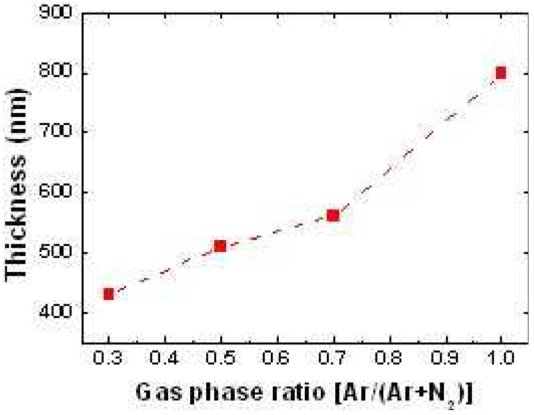

Figure 3. Thickness of AlN layers with gas phase ratio of Ar and N_2 ($Ar/(Ar+N_2)$) from 3 : 7 to 10 : 0.

There were several reports that some amount of N_2 addition to working gas could improve crystal quality of nitride semiconductors deposited by sputtering and it also affected residual stress by changing stoichiometry of nitride semiconductors [14,15]. Fig. 3 shows effect of gas phase ratio on AlN thickness. All layers were deposited at room temperature, and N_2 gas was mixed with Ar gas. Flow rate of Ar gas was controlled to maintain total flow rate not changed.

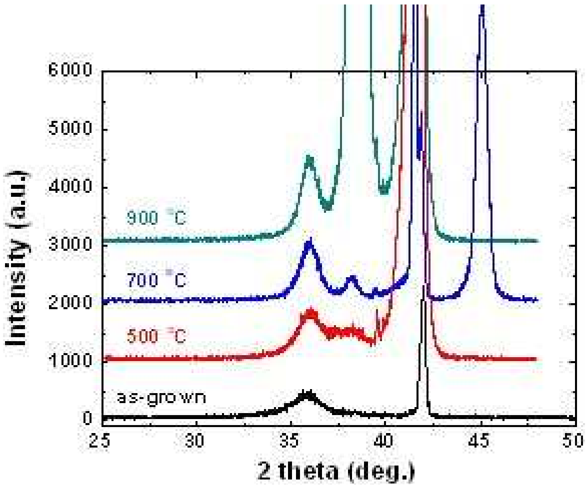

Figure 4. XRD $\omega/2\theta$ scan results of AlN layers grown on c−plane sapphire at room temperature after RTA treatment at 500, 700, 900°C for 2 min.

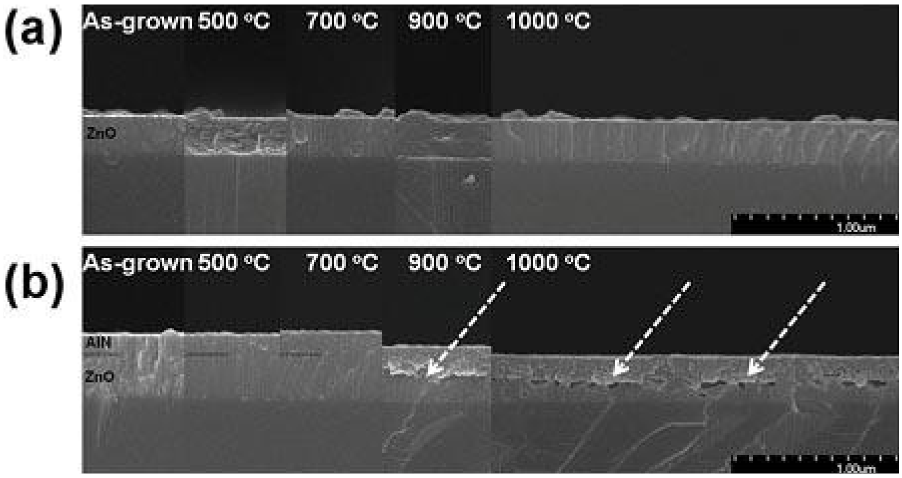

Figure 5. SEM cross-section images of (a) ZnO templates and (b) AlN layers on ZnO templates before and after RTA treatment at 500, 700, 900, 1,000°C in N_2 ambient. Some voids were formed at the interface region as pointed by several white arrows.

Gas phase ratio in this graph means the fraction of Ar gas flow rate to total flow rate. As shown in Fig. 3, thickness of AlN layer decreased to 800, 560, 510, 430 nm in case of Ar input fraction of 1.0, 0.7, 0.5, 0.3, respectively. This result was caused by smaller sputter yield of nitrogen than argon because nitrogen atom is lighter than argon atom.

Fig. 4 shows x-ray diffraction (XRD) ω/2Θ scan results of AlN layers grown directly on c-plane sapphire at room temperature after RTA treatment at 500, 700, 900°C. Only two peaks, AlN (0002) around 35.8° and Al_2O_3 (0006) around 41.7°, were detected from as-grown AlN layer deposited at room temperature, which means AlN layer was well-oriented along [0001] direction. And AlN (0002) peak became stronger at higher RTA temperature which means the crystal quality of (0002) phase was getting improved. However, extra peaks at 37.5 and 45 o from AlN (101) phase and Al metal (200) phase, respectively, were also observed at high temperature. This indicates AlN layers deposited on sapphire substrates were not single crystalline even though as-grown AlN film was oriented along [0001] direction to some degree due to the crystallographic information of sapphire substrate after thermal treatment.

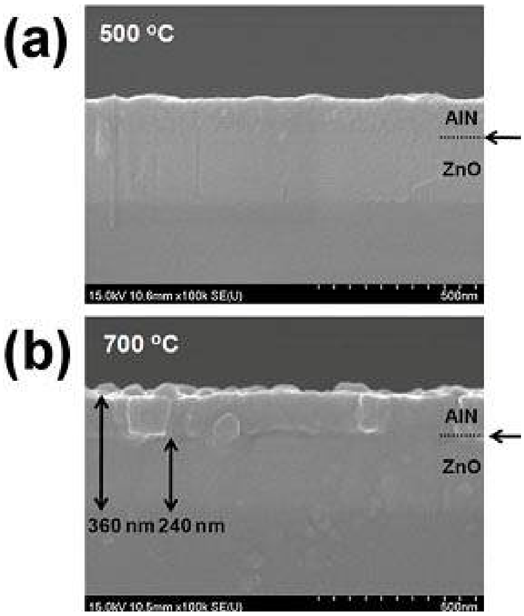

Figure 6. SEM cross-section images of (a) as-grown AlN on ZnO template (b) and AlN on ZnO template which was treated at 500 and 700°C in typical growth ambient of MOCVD. The interface between AlN and ZnO layers were clearly observed after thermal treatment (as pointed on the right side by black arrow).

Although the crystalline quality of AlN layer should be improved for growth of LED structure, however, we checked probability of AlN protecting layer for ZnO template because the template could be covered

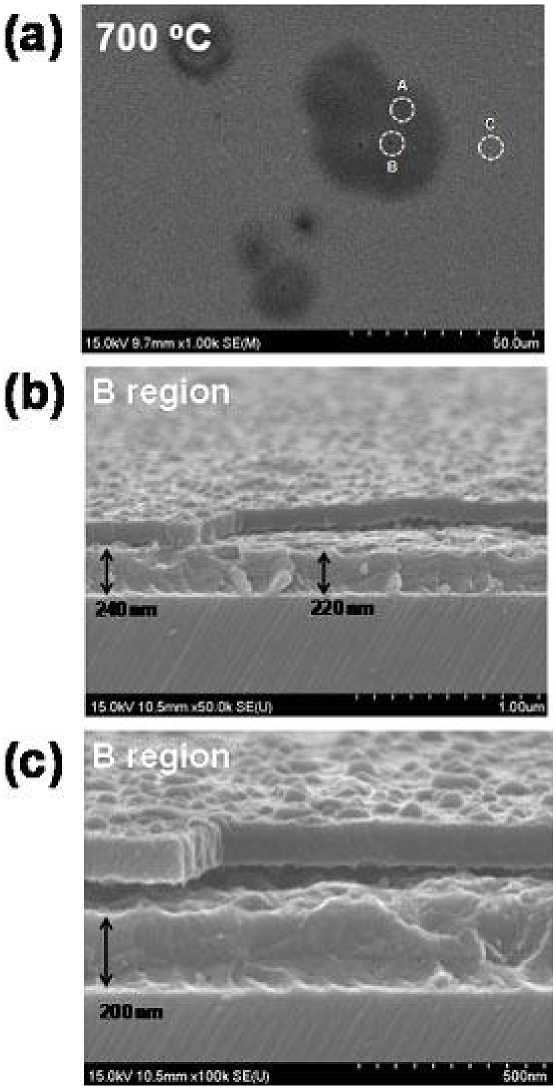

Figure 7. (a) SEM surface image of AlN layer on ZnO template after 700°C (×1000) thermal treatment in MOCVD chamber and (b), (c) cross-section images of B region in (a).

completely with AlN layer. AlN layer was deposited on ZnO template which was grown on sapphire substrate. ZnO template was grown at room temperature in Ar ambient, and AlN layer was also deposited at room temperature in Ar ambient with plasma power of 90 W. Cross-sectional SEM images of ZnO templates and AlN layers on ZnO before and after RTA treatments were shown in Fig. 5(a) and (b). Thickness of ZnO template and AlN layer were 230 nm and 130 nm. As shown in Fig. 5(b), the interface between two layers of as-grown film and RTA treated films at 500 and 700°C was not distinguishable, and it indicates that AlN layer was well-deposited without void. However, AlN layers on ZnO templates showed remarkable changes after RTA treatment at 900 and 1,000°C, while ZnO layers didn't show any other difference after RTA treatment even at 1,000°C. As shown in Fig. 5(b), the interfaces were deteriorated and voids appeared around the interface, resulting that total thickness was reduced. It is well-known that AlN layer is stable under NH_3 and H_2 at low temperature. Assuming voids were generated at the interface between ZnO and AlN, it can be inferred that thickness of ZnO template decreased significantly, which indicates that ZnO layer accompanying AlN was not thermally-stable while ZnO layer is thermally stable up to 1,000°C. It is presumed that low adhesion of AlN to ZnO and difference of thermal expansion coefficient between AlN and ZnO caused that result. However, further study is needed to elucidate the reason why ZnO with AlN was not stable at high temperature.

Fig. 6 shows cross-sectional SEM images of AlN layers deposited on ZnO templates after thermal treatment at 500°C (Fig. 6(a)) and 700°C (Fig. 6(b)) in typical condition of MOCVD for GaN which is NH_3/H_2 ambient. As shown in Fig. 6(a), AlN layer didn't show any change at interface. However, the interface between ZnO and AlN was clearly observed and a part of AlN layer was also slightly detached from ZnO template as shown in Fig. 6(b). This result was very similar to the case of 900 and 1,000°C RTA treatment in Fig. 5(b). The sample which was thermally treated with NH_3 and H_2 at 700°C in MOCVD chamber showed different morphology, while 500°C annealing sample didn't show any difference. As shown in low magnification SEM image (×1000) of Fig. 7(a), round-shaped area was observed and it was uniformly distributed on the whole surface. There were three types of region, bright area (C), dark area (A), dark area with black spot (B) at the center of dark circle. Region C and A showed same morphology, but AlN layer in region A showed slight detachment from ZnO template and AlN layer was fully delaminated from ZnO template in region B as shown in Fig. 7(b). It is also notable that thickness of ZnO in region B was a little reduced to 220 nm which was probably caused by the reaction of ZnO and NH_3. And much thinner ZnO with 200 nm and AlN delamination was clearly observed in Fig. 7(c). AlN layers were fully peeled off at 900 and 1,080°C thermal treatment in MOCVD chamber. These results mean ZnO surface was not perfectly protected by AlN layer even though AlN was well-deposited as confirmed by SEM measurement. Therefore the reason why AlN layer was not adequate for protecting layer on ZnO should be elucidated for clear understanding. In addition, the growth condition for single crystalline AlN layer should be optimized at higher substrate temperature.

IV. CONCLUSIONS

Continuous AlN thin films were deposited on sapphire substrates and ZnO templates by rf-magnetron sputtering. The thickness of AlN layer was linearly dependent on plasma power from 50 to 110 W, and lower working pressure led to faster deposition rate. When N_2 gas was mixed with Ar gas as working gas, layer thickness was remarkably reduced due to smaller sputter yield of nitrogen. These AlN layers were adopted as protecting layers on ZnO templates which are very reactive in NH_3 and H_2 ambient. However, ZnO template accompanying AlN layer was not thermally-stable and didn't not act as a protecting layer.

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RF 마그네트론 스퍼터링법을 이용하여 사파이어 기판과 ZnO 박막 위에 증착한 AlN 박막의 특성분석

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먼저 RF 마그네트론 스퍼터링법을 이용하여 사파이어 기판 위에 AlN 박막을 증착하였다. AlN 공급원으로는 분말소결된 AlN 타겟을 적용하였다. 플라즈마 파워를 50에서 110 W로 증가시켰을 때 AlN 층의 두께는 선형적으로 증가하였다. 그러나 동작압력을 3에서 10 mTorr로 증가시켰을 때는 동작기체인 아르곤 양이 증가함에 따라 AlN 타겟으로부터 스퍼터링되어 나온 AlN 입자들의 평균자유행정의 거리가 감소하기 때문에 AlN 층의 두께는 약간 감소하였다. 질소 기체를 아르곤과 섞어주었을 때는 질소의 낮은 스퍼터링 효율에 의해서 AlN의 두께는 크게 감소하였다. 다음으로는 ZnO 형판 위에 AlN를 증착하였다. 그러나 700도 이상의 열처리에 의해서 AlN와 ZnO의 계면이 약간 분리되어 계면의 열적 안정성이 낮다는 결과를 얻었다. 게다가 스퍼터링으로 증착한 AlN 박막의 나쁜 결정성으로 인하여 700도에서 MOCVD의 반응기 기체인 수소와 암모니아에 의해서 AlN 밑의 ZnO 층이 분해되는 현상도 관찰하였다. 그리고 900도 이상에서는 ZnO가 완전히 분해되어 AlN 박막이 완전히 분리되었다.

주제어 : AlN, 스퍼터링, 보호층, 결정성

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