Effects of Growth Conditions on AlN Layer Grown by Ga-Al Liquid Phase Epitaxy

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We developed an original liquid phase epitaxy technique that uses Ga-Al solution to grow AlN on surface nitrided sapphire substrates. In this paper, effects of temperature, solution composition, and N₂ gas flow rate on the growth of AlN layer were investigated. The AlN layer grown in the solution with higher Al content and higher growth temperature tended to dissolve into the solution, thus, the AlN layers exhibited inhomogeneous surface. The growth rate had a maximum at 60 mol%Al and at 1673 K for solution composition dependence and growth temperature dependence, respectively. On the other hand, the growth rate monotonically increased with increasing N₂ gas flow rate. Based on these results, growth mechanism and rate-determined step of this liquid phase epitaxy process were discussed. [doi:10.2320/matertrans.M2016413]

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1. Introduction

AlGaN-based light-emitting diodes (LEDs) can be used as various light sources emitting from 3.4 to 6.0 eV by controlling the ratio of AlN to GaN. Especially, AlGaN-based deep ultraviolet LEDs are expected as a substitute for mercury lamps for sterilization, water purification and curing. AlN has high ultraviolet transparency, high thermal conductivity, and small lattice mismatch with AlGaN, therefore, AlN is one of the best substrate materials for the AlGaN-based LEDs. A number of groups fabricate bulk AlN single crystal using a sublimation method^{1–3)} and an alumina reduction method^{4–6)}. Recently, Kumagai *et al.*⁷⁾ and Kangawa *et al.*⁸⁾ grew AlN single crystal by the hydride vapor phase epitaxy method and Li₃N solution growth method, respectively, using bulk AlN as a seed crystal fabricated by the sublimation method. Bockowski *et al.* fabricated AlN crystals from Al melt at high temperature up to 2000 K and high N₂ pressure of order of 1 GPa without seed crystal⁹⁾. Their AlN crystals have very low threading dislocation density and impurity concentration. However, fabricating larger diameter AlN bulk crystal at a reasonable cost has not been achieved yet. Recently, P. Wu *et al.* reported the AlN growth method using vaporized Al and nitrogen gas as source materials^{10,11)}. Some groups fabricated AlN by nitridation of metallic Al^{12–14)}. These techniques are simple, however, fabrication of high quality AlN bulk crystal have not been reported. On the other hand, template growth of AlN single crystal on sapphire substrates has been also investigated by many researchers to obtain larger-diameter and lower-cost substrates. AlN has large lattice mismatch with sapphire, therefore, a few techniques to control the growth at the interface between AlN layer and sapphire substrate were reported^{15–17)}. In our group, we had developed a method for fabricating high-quality AlN thin films by nitriding sapphire under controlled conditions^{18,19)}. Using the nitrided sapphire substrate as a template, DC-pulsed sputter deposition^{20,21)} and RF reactive sputtering techniques^{22,23)} have been investigated. Recently, authors have developed the Ga-Al liquid phase epitaxy (LPE) technique on the nitrided sapphire substrate, and have successfully grown 1.2-μm-thick AlN layer at 1573 K under normal pressure of N₂ gas for 5 h^{24,25)}. The full

width at half maximum values of X-ray rocking curves for (0002) and (10–12) were 90 and 392 arcsec, respectively²⁶⁾. Moreover, we clarified that the polarity inversion of the AlN layer was caused by oxygen incorporation at the initial stage of the AlN solution growth^{27,28)}, and oxygen plays an important role for the LPE growth.

In this study, the effects of solution composition and growth temperature on the AlN growth were studied to optimize the LPE process. Moreover, at the optimized temperature and solution composition, the effect of flow rate of N₂ gas on the AlN growth was also studied. Based on these results, growth mechanism and rate-determined step of the LPE process were discussed.

2. Experimental Method

Experimental details and a schematic of the facility for the Ga-Al LPE technique were described in the previous paper²⁴⁾. An alumina crucible containing the Ga-Al flux was set in a furnace at a homogeneous temperature zone. Inner diameter of the crucible was 50 mm. The Ga-Al flux was poured into the crucible to a height of 60–70 mm. The nitrided c-plane sapphire substrates^{18,19)} (11 mm × 10 mm) were immersed into the Ga-Al solution, and subsequently, N₂ gas containing oxygen ($P_{O_2} = 10^{-6}$ bar) was injected into the solution directly through the alumina tube during the AlN growth. Inner diameter of the alumina tube was 4 mm. The growth temperature and solution composition were varied from 1473 to 1773 K and from Ga-20 mol%Al to Ga-80 mol%Al, respectively. Here, Ga-*x* mol%Al indicates a Ga-Al alloy containing Al of *x* mol%. The LPE growth process was conducted at each growth temperature with a N₂ gas flow rate of 20 sccm for 5 h. Finally, the N₂ gas flow rate was varied from 10 to 100 sccm at the optimized temperature and solution composition.

3. Results

3.1 Effects of temperature and solution composition on AlN growth

Figure 1 shows the surface morphologies of the AlN layers grown under each condition observed using a 3D laser microscope. The AlN layers with smooth surface grew uniformly

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on the substrates using Ga-20 mol%Al at 1573 K, Ga-40 mol%Al at 1473 K and 1573 K. Fringe patterns on these surface were caused by thickness distribution of the AlN layer. Details of the fringe patterns were explained in the previous paper²⁴. The AlN layer with rough surface grew on the substrate using Ga-40 mol%Al at 1673 K because of the adhesion of three dimensional AlN crystal grains. Figure 2 shows a surface image of the AlN layer grown from Ga-40 mol%Al at 1673 K taken using a SEM. For other growth conditions, the AlN layers exhibits inhomogeneous surface caused by partial dissolution of AlN layer into the solution. The inhomogeneous surface did not indicate that the AlN grew by island growth mode. The AlN grew by film growth mode and dissolved into the solution simultaneously at difference position on the template, therefore, inhomogeneous surface appeared. The AlN layer tended to dissolve into the solution with higher Al content of solution and higher growth temperature.

Figure 3 shows (a) solution composition dependence at 1573 K and (b) temperature dependence of the growth rate of AlN layer. The growth rate was evaluated from the thickness of the AlN layers except for the dissolved area. All samples were grown for 5 h. The growth rate has a maximum at 60 mol%Al as shown in Fig. 3(a). The growth rate has a maximum at 1673 K using 20 mol%Al solution as shown in Fig. 3(b). Thus, the growth rate exhibits non-monotonous be-

havior with growth temperature and solution composition.

3.2 Effects of N₂ gas flow rate on AlN growth

From the result mentioned above, the AlN layer with smooth surface successfully grew from Ga-40 mol%Al at 1573 K. With this condition, effect of the N₂ gas flow rate on the AlN growth was studied. Figure 4 shows the surface morphologies of the AlN layers grown for N₂ gas flow rates of (a) 10 sccm, (b) 20 sccm, (c) 50 sccm, and (d) 100 sccm. The

Fig. 1 Surface morphologies of the AlN layers grown under each condition observed using a 3D laser microscope.

Fig. 2 Surface image of the AlN layer grown from Ga-40 mol%Al at 1673 K taken using a SEM.

Fig. 3 (a) Solution composition dependence of the growth rate of AlN layer at 1573 K. (b) temperature dependence of the growth rate of AlN layer.

Fig. 4 (a) Surface morphologies of the grown AlN layers provided N₂ gas at a flow rate of (a) 10 sccm, (b) 20 sccm, (c) 50 sccm and (d) 100 sccm observed using a laser microscope.

AlN layers covered overall surface of the substrates except for 10 sccm. Figure 5 shows the effect of the N_2 gas flow rate on the AlN growth. The growth rate monotonically increased with increasing N_2 gas flow rate.

4. Discussions

As explained in the introduction, oxygen incorporation on the nitrided sapphire substrate at the initial stage of the LPE growth is necessary for polarity inversion and uniform growth²⁸⁾. Taking into account the oxygen incorporation, possible elementary steps of the LPE process are as follows, and the schematic of growth mechanism of the LPE process is shown in Fig. 6.

Step 1: Dissolution of nitrogen and oxygen gas into the solution

Step 2: Transport of dissolved nitrogen and oxygen atoms to the substrate

Step 3: Oxygen incorporation on the surface of substrate at the initial stage of growth

Step 4: AlN formation from the dissolved nitrogen and Al on the substrate

The dissolved nitrogen and oxygen in the solution are consumed by formation of Al_2O_3 and AlN as in a form of 3-dimensional nucleation in the solution using the higher Al content solution at higher temperature. This yields inhomogeneous growth of AlN layer as presented in Fig. 1, which results in the non-monotonous behavior in the growth rate as

Fig. 5 Provided N_2 gas flow rate dependence of growth rate the AlN layer.

Fig. 6 Schematic of growth mechanism of the LPE process (a) in the lower Al content solution at lower temperature (b) in the higher Al content solution and/or at higher temperature.

presented in Fig. 2. Thus, the growth process window is limited, and the optimized solution composition and temperature are 40 mol%Al and 1573 K, respectively. Using the optimized condition, increasing N_2 gas flow rate helps not only to supply nitrogen and oxygen, but also to agitate the solution. This leads to the increase in the growth rate as presented in Fig. 5. Therefore, we considered that rate-determining step under the optimized condition was elementary Step 1 or Step 2.

5. Conclusions

Effects of growth conditions such as temperature, solution composition and N_2 gas flow rate on the LPE growth of AlN were studied to optimize the growth condition and to understand the growth mechanism. The optimized solution composition and growth temperature were 40 mol%Al and 1573 K. The nitrogen and oxygen supply onto the nitrided sapphire substrates controls the growth rate under the optimized condition.

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