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Sublimation Growth of AlN in Vacuum and in a Gas Atmosphere

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The growth of AlN crystals by sublimation technique is investigated. Two mechanisms of Al and N_2 transport from the source to the seed are distinguished – occurring predominantly via diffusion or via drift of the reactive species. Drift transport provides considerably higher growth rates compared to diffusive transport. The interplay of these mechanisms depends on temperature and gas pressure in the growth system. A theoretical model of AlN sublimation growth is developed allowing one to estimate the growth rate as a function of gas pressure and temperature. The theoretical predictions agree well with experimental observations obtained while growing AlN in the nitrogen atmosphere and in vacuum.

AlN is one of the promising materials suitable for fabrication of substrates with the lattice constants close to that of GaN. These substrates are commonly believed to improve crystalline quality of the group-III nitride heterostructures intended for various device applications. Sublimation growth is a traditional way to obtain bulk AlN crystals with acceptable growth rates [1, 2]. The development of this technique during the last decade stimulated research activity aiming to understand the basic mechanisms underlying the growth of AlN. In this paper, we report on the results of experimental and theoretical study of AlN crystal growth by sublimation technique.

The experiments were carried out in a sublimation sandwich system similar to that used for growth of high-quality SiC crystals [3]. The sandwich cell contained SiC substrate and AlN powder as the material source separated by a narrow clearance of 1 to 5 mm. The sandwich cell was placed into a special container with a temperature gradient zone where growth of AlN crystals on SiC substrate via Al and N_2 transport was initiated. The substrate temperature of 1700 to 2300 °C was maintained during the growth. The temperature difference between the source and the substrate was varied in the range of 1 to 5 K in the experiments. Both growth of AlN in nitrogen being under atmospheric pressure and in vacuum (with a background pressure of $\approx 10^{-4}$ Torr maintained in the container) are studied. In both cases AlN layers 60 to 80 μm thick of 10×10 mm^2 size were obtained.

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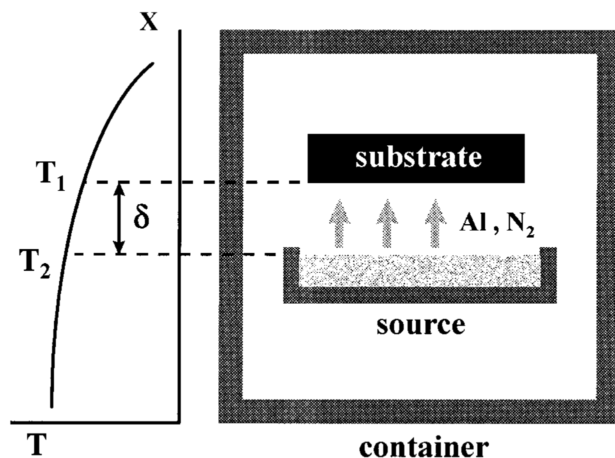

Fig. 1. Scheme of AlN growth by the sublimation sandwich method

The growth rate of AlN experimentally obtained in the nitrogen atmosphere at different temperatures is shown in Fig. 1. At 2300 °C it reaches a value of ≈90 μm/h while at lower temperatures it drops nearly exponentially. Under vacuum conditions comparable growth rates can be obtained at temperatures ≈350 to 400 K lower than those used for AlN growth in the nitrogen atmosphere (Fig. 2).

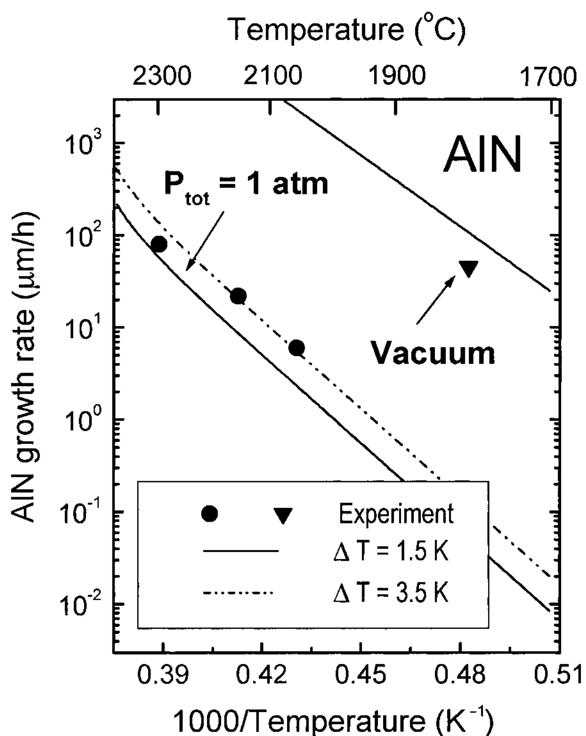

Fig. 2. AlN growth rate as a function of temperature (clearance $\delta = 4$ mm). Circles and triangle are the experimental data obtained while growing AlN in the nitrogen atmosphere and in vacuum, respectively. Lines present results of calculations using Eqs. (1) and (2)

To understand the general trends in AlN sublimation growth we apply a model accounting for low sticking of N_2 molecules to AlN surface (N_2 sticking/evaporation coefficient as a function of temperature was extracted in a recent work [4] using independent experimental data on free evaporation of AlN in vacuum). Obviously low N_2 sticking results in considerable suppression of the growth/evaporation rate of AlN at low temperatures. In the case of AlN growth in the nitrogen atmosphere (with the total pressure P_{tot}), where Al vapor is very diluted by nitrogen, the kinetics of nitrogen adsorption becomes less important, and the growth rate can be approximated by the expression

$$V_{\mathrm{g}} = \frac{M_{\mathrm{AlN}}}{\varrho_{\mathrm{AlN}}} \frac{D}{RTL} \left(K_2^{1/2} - K_1^{1/2}\right) / P_{\mathrm{tot}}^{1/2} \,. \tag{1}$$

Here M_{AlN} and ϱ_{AlN} are the molecular mass and the density of AlN, respectively, D is the diffusion coefficient of Al in N_2, R is the gas constant, K_1 and K_2 are the equilibrium constants of the reaction of AlN formation from the gaseous Al and N_2 referred to the temperatures of the seed (T_1) and of the source (T_2), respectively. The growth rate calculated using Eq. (1) for a temperature difference $\Delta T = T_2 - T_1$ of 1.5 to 3.5 K agrees well with the experimental data obtained.

A detailed analysis shows that in the case of AlN growth in vacuum, the transport of Al and N_2 inside the sandwich is not longer controlled by species diffusion. Instead, stoichiometric evaporation of group-III and group-V species occurs at the source, and the gaseous species drift from the source to the substrate as a uniform gas stream (the existence of such transport mode was mentioned in [5]; a more detailed discussion on our model will be done in a separate paper). As a result, the growth rate becomes considerably larger than that observed in the nitrogen atmosphere,

$$V_{\mathrm{g}} = \frac{M_{\mathrm{AlN}}}{\varrho_{\mathrm{AlN}}} \frac{(\lambda K_2)^{1/3} - (\lambda K_1)^{1/3}}{(\alpha_2\beta_2)^{-1} + (\alpha_1\beta_1)^{-1}} \,, \qquad \lambda = 2\, \frac{(\alpha_2\beta_2)^{-1} + (\alpha_1\beta_1)^{-1}}{(\tilde{\alpha}_2\tilde{\beta}_2)^{-1} + (\tilde{\alpha}_1\tilde{\beta}_1)^{-1}} \,. \tag{2}$$

Here N_{A} is the Avogadro number, $\beta_j = (2\pi M_{\mathrm{Al}} R T_j)^{-1/2}$ and $\tilde{\beta}_j = (2\pi M_{\mathrm{N_2}} R T_j)^{-1/2}$ are the Hertz-Knudsen factors of Al and N_2 referred to the temperature T_j, α_j and $\tilde{\alpha}_j$ are the respective sticking coefficients referred to the temperature T_j (for Al we accept $\alpha_1 = \alpha_2 = 1.0$), M_{s} is the molar mass of the s-th species (s = Al, N_2). Comparison of the measured growth rate with that calculated using Eq. (2) is also shown in Fig. 2. One can see that growing of AlN in vacuum allows one to decrease the growth temperature by $\approx$350 to 400 °C compared to growing in the nitrogen atmosphere kept the same value of the growth rate.

The AlN growth rate as a function of total gas pressure in the container calculated for different temperatures is shown in Fig. 3. It is seen that at low temperatures the growth rate decreases with pressure as $P_{\mathrm{tot}}^{-1/2}$ in accordance to Eq. (1). At higher temperatures deviation from this law occurs related to a change of the transport mechanism from diffusive to the drift one.

In conclusion, growth of AlN crystals by sublimation technique is studied both theoretically and experimentally. Two mechanisms of Al and N_2 transport from the source to the seed are distinguished, occurring predominantly via diffusion or via drift of the reactive species. The drift mechanism of transport provides a considerably higher growth rate compared to the diffusive one. The interplay of the transport mechanisms

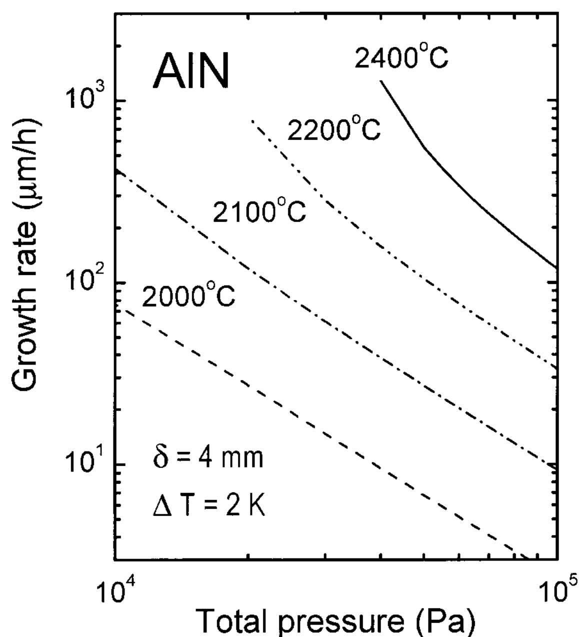

Fig. 3. Growth rate of AlN as a function of gas pressure in the container calculated for different temperatures of the substrate

depends on temperature and gas pressure in the growth chamber. A theoretical model of AlN sublimation growth is developed accounting for kinetic limitation of the growth and evaporation rates due to low N_2 sticking to the AlN surface. The model allows the easy estimation of AlN growth rate as a function of temperature and gas pressure. The theoretical predictions obtained by the model agree well with experimental observations.

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