Thermodynamics for Fabricating AlN/alon/sapphire Double Epitaxial Layers as an Advanced Substrate for Blue/Ultraviolet Optical Devices

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In blue/ultraviolet light emitting devices, the importance of initial growth of the nitrides of Group III has been pointed out, because density of crystal dislocation is highly related to the light emitting effectiveness. Therefore, fabrication of appropriate substrates has received considerable practical concern to yield crystal-defect-free growth of the nitrides. Recently, the present authors have proposed the growth of AlN on a γ-aluminum oxynitride spinel (alon) buffer layer to decrease the lattice mismatch at a sapphire substrate/AlN interface. To make this process possible, it is necessary to establish the chemical potential diagram of the Al-N-O system including alon. However, no experimental data on the standard Gibbs energy of formation of alon are currently available due to the experimental difficulties. The present study aims to experimentally determine the thermodynamic stability of alon. For this purpose, equilibrium compositions of the N_2-CO gas mixture coexisting with alon-Al_2O_3-graphite were measured at temperatures above the eutectoid decomposition temperature of alon. Based on the obtained results, the standard Gibbs energy change of the carbothermal nitridation reaction of Al_2O_3 to form alon has been determined. Subsequently, the thermodynamic stability of alon has been discussed.

Figure 1 shows the Gibbs energy, ΔG^M, the entropy, ΔS^M, and the enthalpy, ΔH^M, of mixing for the Al_2O_3-AlN system as a function of mole fraction of AlN. The mole fractions of AlN having a minimum for ΔG^M exist in the single-phase region of alon. The enthalpy and the entropy of mixing exhibit positive values in the whole composition range and a maximum at the mole fraction of AlN where alon is saturated with AlN.

Figure 2 shows the three-dimensional chemical potential diagram of the Al-O-N-C system as a function of the activities of oxygen (P_{O2}), nitrogen (P_{N2}) and carbon (a_c) at 2000 K. The Gibbs energy of formation of AlN obtained in the previous study[1] has been used for the construction of the diagram. Intercompounds (Al_2OC, Al_4O_4C, Al_5C_3N) and a solid solution formed between Al_2OC and AlN, were ignored for the construction of the diagram due to the lack of the reliable thermodynamic data. In the diagram, the phase stability region of alon is defined by the gray-colored space.

Figure 3 presents the phase stability diagram of the Al-O-C-N system by using two axes of P_{CO} / P_{N2} and temperature under the condition of $a_c = 1$ and $P_{CO} + P_{N2} = 1$. Based on this diagram, alon can be synthesized with controlling its non-stoichiometry. By using the obtained results, AlN/alon/sapphire double epitaxial layers as an advanced substrate have been successfully fabricated, which will be separately presented in this conference by the present authors.

Reference

[1]W. Nakao, H. Fukuyama and K. Nagata, *J. Am. Ceram.*, in print.

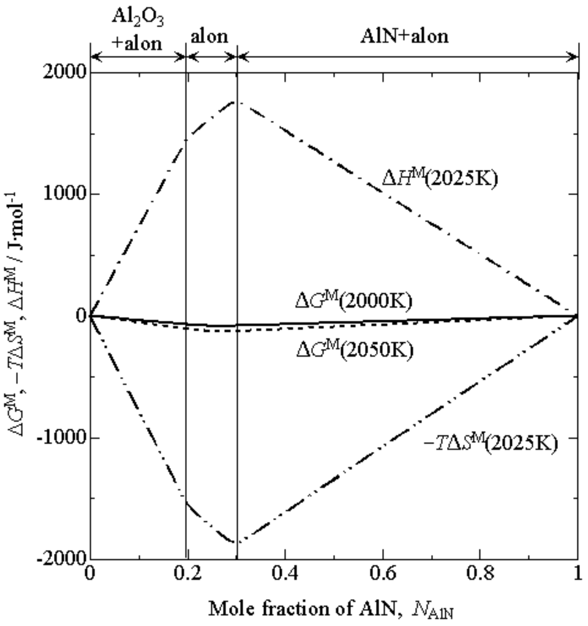

Figure 1 Gibbs energies of mixing for the Al_2O_3-AlN system, ΔG^M, at 2000 K and 2050 K as a function of mole fraction of AlN, with $-T\Delta S^M$ and ΔH^M at a mean temperature of 2025 K.

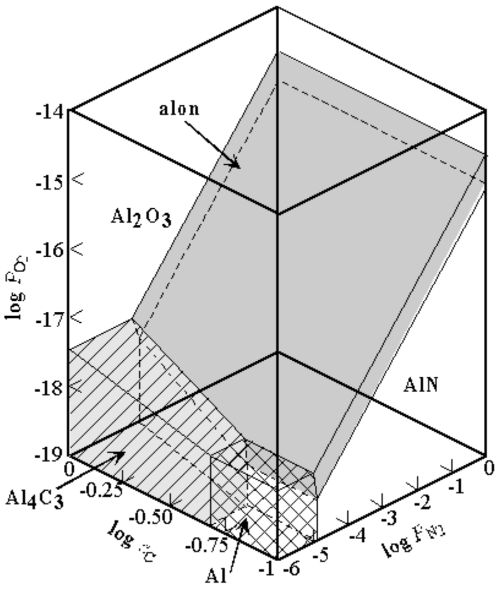

Figure 2 Three-dimensional chemical potential diagram of the Al-O-N-C system at 2000 K.

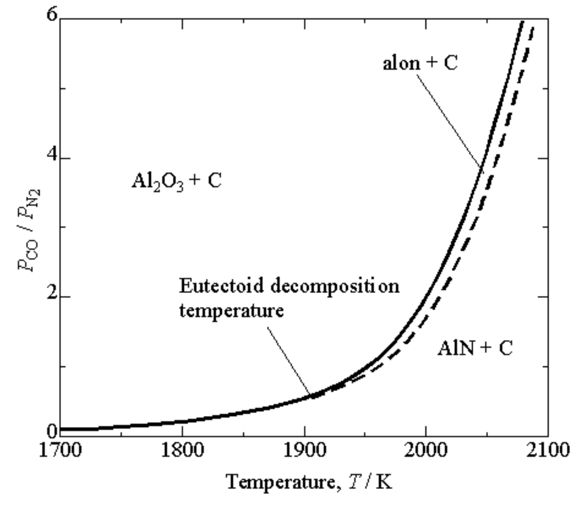

Figure 3 Phase stability diagram of the Al-O-N-C system under the condition of $a_C = 1$ and $P_{CO} / P_{N2} = 1$.