

Chemical aspects of the A^{III} nitride epitaxial growth by MOVPE

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1. Introduction

A^{III} nitrides and their solid solutions are important materials with many applications in electronics and optoelectronics. Various methods are utilized for deposition of epitaxial layers and structures of these materials. MOVPE has some advantages over other techniques and it became the leading epitaxial technology in the last decade. Three topics related to the MOVPE growth of A^{III} nitride are discussed in this contribution, namely thermodynamic stability of A^{III}N, limited miscibility of A^{III}N and possibility of chemical interactions at the A^{III}N – substrate interface.

2. Thermodynamic calculations

2.1 Stability of A^{III} nitrides

Thermodynamic stability of the A^{III}N is connected with nitrogen decomposition pressure through the Gibbs energy change of the reaction



$$\Delta G^0_r = RT \ln p(N_2) \quad (1)$$

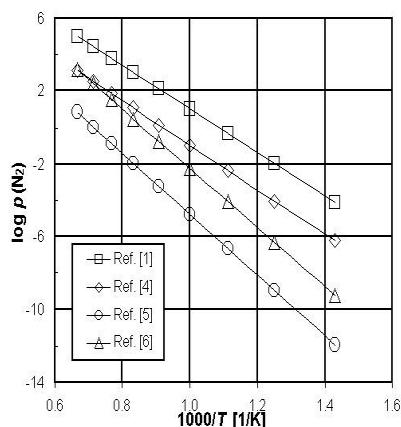


Fig.1 Temperature dependence of equilibrium nitrogen pressure in the system GaN(s) – Ga(l) – N₂(g)

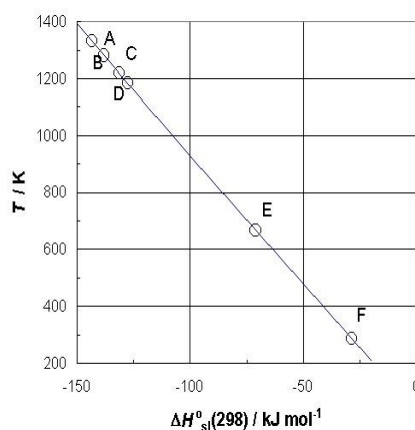


Fig.2 Calculated decomposition temperature in the system InN(s)–In(s,l)–N₂(g,p/p⁰=1) in dependence on the standard heat of formation of solid InN
A–Ref.[10],B–Ref.[11],C–Ref.[12],D–Ref.[14]
E–Ref.[3],F–Ref.[7]

Thermodynamic data of solid A^{III}N are necessary for the calculation of ΔG^0_r as a function of temperature. As for the aluminum nitride, data from various sources are in general agreement and relevant calculations reveal high thermal stability (low N₂ decomposition pressure) of AlN [1–3]. On the other hand, data for GaN and particularly for InN presented in various sources differ significantly. Fig. 1 shows the temperature dependencies of nitrogen

equilibrium pressure in the system GaN(s)–Ga(l)–N₂(g) calculated using various sets of thermodynamic functions ($\Delta H_f^\circ(298)$, $S_m^\circ(298)$ and $C_{pm}^\circ = f(T)$) from literature. The calculated dependencies are compared with an experimental one [6].

There are large discrepancies between the values of $\Delta H_f^\circ(298)$ for solid InN experimentally obtained or recommended by various authors [7]. Quite fundamental impact of the $\Delta H_f^\circ(298)$ value used in the calculation of decomposition temperature ($p(N_2)/p^\circ = 1$ at this temperature) shows Fig. 2. Molar entropy derived from low temperature heat capacity measurements [8] and the temperature dependence of C_{pm} above the room temperature based on our own measurements [9] were utilized in the calculation. The value of $-70 \text{ kJ}\cdot\text{mol}^{-1}$ seems to us as reliable.

2.2 Limited miscibility of A^{III} nitrides

To predict miscibility behavior of the mixed A^{III} nitrides a number of theoretical calculations as well as

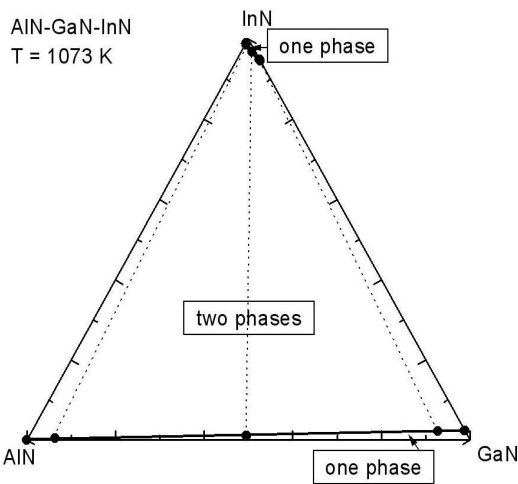


Fig.3 Phase diagram of the system AlN–GaN–InN

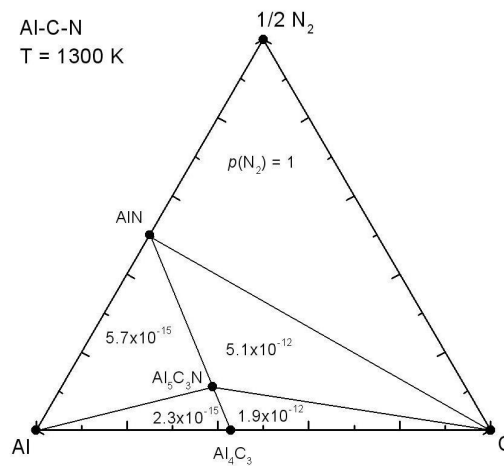


Fig.4 Phase diagram of the system Al–C–N

empirical estimations have been performed [14–17]. Based on the empirical correlation between the excess Gibbs energy and the differences between distances of the nearest neighbor atoms in the crystal lattice proposed recently [18], parameters of the Redlich–Kister equation for the pseudobinary (Al,Ga)N, (Al,In)N and (Ga,In)N solid solutions were estimated. Now the parameters are used for calculation of a miscibility gap in the pseudoternary (Al,Ga,In)N. Calculated phase diagram of the AlN–GaN–InN system at temperature of 1073 K is shown in Fig. 3. While the AlN–GaN binary behaves almost ideally and complete miscibility exists, InN additions leads to the formation of the large two–phase region due to the large differences between the lattice parameters of InN and the two other nitrides. If the homogeneous solid solutions within the miscibility gap are grown by the MOVPE, layers are unstable in from the thermodynamic point of view. It is a consequence of non–equilibrium course of the process although the strain energy at the substrate–layer interface could affect the layer's composition to some extent.

2.3 Interactions at $A^{III}N$ – substrate interface

The decomposition of trialkyl precursors can lead to the graphite formation especially if nitrogen is used as a carrier gas. Carbon contamination of the layers can be enhanced in the presence of aluminium due to the carbide Al_4C_3 or carbonitride Al_5C_3N formation. Equilibrium phase relations in the system Al–C–N at temperature of 1300 K are shown in Fig. 4. According to the nitrogen pressure solid AlN can co-exists with solid graphite, carbonitride or liquid Al. Thermodynamic data for solid Al_5C_3N has been assessed by Qiu and Metselaar [19] who estimated the low temperature limit of carbonitride stability as 1073 K.

Sapphire as well as silicon carbide substrates are used for A^{III} nitride epitaxial growth. In the case of Al-containing layers, solubility of AlN in SiC at higher temperatures as well as a number of compounds which can be formed in the Si–Al–C–N system can cause some serious difficulties in the course of the growth process. Phase relationships in the AlN–SiC and AlN– Al_4C_3 –SiC systems have been studied at high temperature region [20–22] well above the temperatures commonly used in AlN epitaxy. According to the tentative phase diagram [21], mutual solubility of AlN and SiC is limited below 2200 K but the boundaries of miscibility gap were not determined accurately. Composition of coexisting phases is 8 mol.% and 94 mol.% of AlN at 1973 K [20].

To extrapolate the solubility of AlN in hexagonal SiC at temperature of 1300 K, a simple version of the sublattice model [23] was used. It was assumed that Al and Si atoms can substitute each other on one sublattice and C and N atoms on the second. So the stoichiometric formula $(Si_{1-x}Al_x)(C_{1-y}N_y)$ expresses the composition of this solid solution. Gibbs energy per one mole of the solution is given by the general relation

$$G_m = G_{ref} + \Delta G_m^{M,id} + \Delta G_m^E \quad (2)$$

The first term on the right side of Eq.(1) represents Gibbs energy of pure components which are SiC, 'SiN', 'AlC' and AlN and it holds

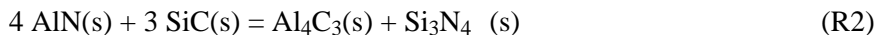
$$G_{ref} = (1-x)(1-y)G_m^0(SiC) + (1-x)yG_m^0('SiN') + x(1-y)G_m^0('AlC') + xyG_m^0(AlN) \quad (3)$$

Standard molar Gibbs energies G_m^0 of the hypothetical components 'SiN' and 'AlC' were calculated as follows: $G_m^0('SiN') = 1/4 (G_m^0(Si_3N_4) + G_m^0(Si))/w$ and $G_m^0('AlC') = 1/4 (G_m^0(Al_4C_3) + G_m^0(C))/w$. The value of parameter $w = 0.934$ was assessed from the condition which holds at critical temperature of 2173 K. Ideal mixing Gibbs energy is given by equation

$$\Delta G_m^{M,id} = RT[(1-x)\ln(1-x) + x\ln x + (1-y)\ln(1-y) + y\ln y] \quad (4)$$

excess Gibbs energy term which describes deviations from ideal mixing was not considered here. The calculated miscibility gap at 1973 K is within the composition of 19 mol.% and 81 mol.% of AlN. Extrapolating to 1300 K, one can calculate the solubility of SiC in AlN up to 1.9 mol.%.

According to equilibrium calculations the AlN–SiC interface is stable with respect to the exchange reaction



However, various ternary and quaternary compounds can be formed in the presence of aluminum carbide [22]. Fig. 5 shows a simplified version of phase diagram of the system Al_4C_3 –SiC–AlN at 1300 K in which all substances are considered as totally unmiscible. It follows that complex carbonitride $Al_4C_3*AlN*SiC$ can exist in equilibrium with AlN and SiC. Stability of this compound has been studied at temperatures above 2000 K [22], thus the phase relations which are extrapolated from the high temperature region should be considered as an approximation only.

To assess ability of substrate SiC to take part during an initial stage of deposition reactions complex calculations of equilibrium composition of the system Al–N–Si–C–H were performed.

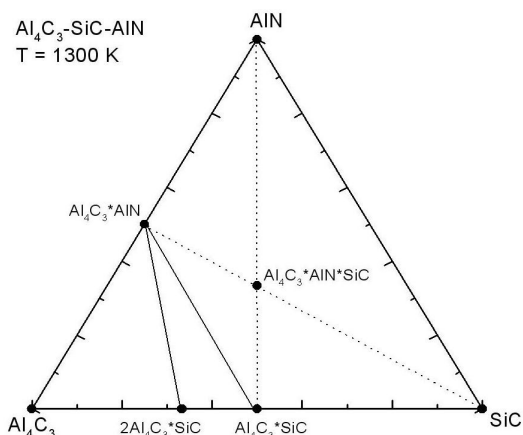


Fig.5 Phase diagram of the system $\text{Al}_4\text{C}_3\text{-SiC-AlN}$

The Gibbs energy minimization method was used [24] for the calculations in which ideal gaseous phase consist of 26 species, Al–Si liquid and eight stoichiometric solids, namely AlN, Al_4C_3 , $\text{Al}_5\text{C}_3\text{N}$, SiC, Si_3N_4 , Al_4SiC_4 , Al_8SiC_7 and C were included. Miscibility of AlN and SiC was neglected and $\text{Al}_4\text{C}_3*\text{AlN}*\text{SiC}$ was not considered as any thermodynamic data for this compound are not available at the present time. Equilibrium composition were calculated for temperature of 1300 K, relative pressure $p/p^o = 1$ and 0.01 for the input V/III ratio of 10^2 , 10^3 and 10^4 ($V/\text{III} = n^o(\text{NH}_3)/n^o(\text{TMAI})$). The obtained results reveal that during the initial stage of the growth SiC substrate can be attacked by the gas phase giving rise to silicon nitride Si_3N_4 and graphite. Solid AlN is creating simultaneously. Partial nitridation of SiC can carry out as the initial nitrogen pressure in the system is greater then equilibrium N_2 pressure $p(\text{N}_2)/p^o = 5.8 \times 10^{-4}$ corresponding to the reaction



This reaction is restricted later due to the slow diffusion of nitrogen through the growing AlN layer.

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