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Suppression of phase separation in InGaN due to elastic strain

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The effect of elastic strain in epitaxial InGaN layers coherently grown on GaN wafers on spinodal decomposition of the ternary compound is examined. The effect results in considerable suppression of phase separation in the strained InGaN layers. To predict correctly the position of the miscibility gap in the T-x diagram it is important to take into account the compositional dependence of the elastic constants of the ternary compound. The contribution of the elastic strain to the Gibbs free energy of InGaN is calculated assuming uniform compression of the epitaxial layer with respect to the underlying GaN wafer. The interaction of binary constituents in the solid phase is accounted for on the base of regular solution model. The enthalpy of mixing is estimated using the Valence Force Field approximation. The strain effect becomes stronger with increasing In content in the InGaN. As a result the miscibility gap shifts remarkably into the area of higher InN concentration and becomes of asymmetrical shape. Various growth surface orientations and the type of crystalline structure (wurtzite or sphalerite) provide different effects of the elastic strain on phase separation in ternary compounds.

1 Introduction

One of the specific features of group-III nitrides is that various binary compounds have crystalline lattice constants differing significantly from each other. For example, the lattice constant mismatch between GaN and AlN is 2.5% and 4.1% for a and c constants respectively; the mismatch between GaN and InN is much greater – 10.7% and 15.0% ; for the pair InN and AlN the lattice constant mismatch approaches 13.6% and 19.7% for a and c constants [1]. The latter values are even comparable to the mismatch between the lattice constants of GaN and sapphire commonly used as the substrate for growth of group-III nitride epilayers. Such a large difference in the lattice constants results in two main effects. First, due to very different bond lengths, a considerable internal strain arises in ternary nitrides due to a crystalline lattice distortion. This is exhibited in the evident tendency of ternary compounds (first of all, InGaN and AlInN) to phase separation. Second, even small additions of some group-III elements into a ternary compound changes its lattice constant remarkably. As a result, a layer of ternary compound grown on an underlying binary wafer becomes highly strained. This not only influences the properties of grown material but also can affect just the growth process.

Evidence of phase separation in InGaN ternary compounds has been found in material grown by a number of techniques — molecular beam epitaxy (MBE) [2], metal-organic chemical vapor phase deposition (MOCVD) [3] and hydride vapor phase epitaxy (HVPE) [4]. This effect resulted, first of all, in compositional non-uniformity clearly observed by photoluminescence. Apparently, defects of various kinds can be formed in the crystal during the phase separation. In particular, it was recognized that phase separation was the effect responsible for the appearance of deep localized states (with an activation energy of >100 meV) in the InGaN quantum well serving as the active region of a laser heterostructure [5].

All these experimental observation are in qualitative agreement with the results of theoretical predictions of the miscibility gap carried out for ternary nitrides [6], [7], [8]. According to [7], [8] the critical temperature corresponding to InGaN spinodal decomposition is ≈1200°C, and the stable ternary compound with In content higher than 10% can not be obtained up to the growth temperature of 800°C. These results have been obtained using the Valence Force Field (VFF) approach for the analysis of lattice distortion. The authors of [6] gave all the more hard estimates for critical temperature:

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≈2460°C. Subsequently, much lower maximum InN concentration is predicted to be reached in thermodynamically stable InGaN ternary compounds. In [9] an intermediate value of critical temperature ≈1950°C is suggested based on *ab initio* calculations of the properties of special solid clusters approximating the ternary compounds. Since normally, the application of VFF model to other III-V compounds gives results close to experimental ones, the latter two values of critical temperature seem to be overestimated (see Section 3). Such uncertainty in determination of the critical temperature shows that proper choice of interaction energy of binary constituents in the ternary compound is important for correct analysis of phase separation. In particular the well-known semi-empirical Delta-Lattice-Parameter model [10] successfully applied to other III-V compounds fails in evaluation of the interaction energy of ternary nitrides [8], [11]. In this paper, the Valence Force Field approach [12] is used for the determination of the interaction energy of GaN and InN in InGaN ternary compounds. This approach is found to give the results very close to those obtained by the elaborated model [8] accounting for relaxation of the crystalline lattice of ternary compound in several coordination shells.

Despite the strict limitation caused by spinodal decomposition, the InGaN ternary compounds with high In content have been repeatedly grown inside the miscibility gap (for example, InGaN epilayers with In content up to 30% were grown at temperature of 780-800°C in [2] and [3] without any evidence of phase separation). This means that either metastable compounds are easily formed during epitaxial growth or some mechanisms providing suppression of phase separation exist. One of such possible mechanisms refers to additional elastic energy accumulated in a uniformly strained epitaxial layer coherently grown on the underlying wafer. This mechanism has been initially considered in respect to cubic III-V compounds (see [13] and the references cited therein) and after then to group-III nitrides [14]. In the latter case an average value of the effective elastic constant independent on composition of the ternary compound was taken for calculations. However, following examination revealed that compositional dependence of the elastic constants was important for quantitative predictions of the location and shape of the miscibility gap.

In this paper the results of a refined analysis of the influence of strain on phase separation in ternary InGaN compounds are presented with accounting for compositional dependence of the elastic constant of the material. We study epitaxial layers with interface orientation either parallel or perpendicular to the hexagonal axis of the nitride crystal. Different effects of the strain on the phase separation in hexagonal and cubic crystals are considered as well.

2 Theory

Assume that an epitaxial layer of ternary compound $A_x^{III}B_{1-x}^{III}C^V$ (hereafter AC and BC denote the binary constituents of the ternary compound) with lattice constants a and c is coherently grown on underlying wafer which has the lattice constants a_s and c_s. Normally the thickness of the wafer is much greater than the thickness of epitaxial layer. In this case the epilayer is uniformly strained while the wafer remains free of strain. Elastic energy accumulated in the epitaxial layer due to the strain has been derived in [15]. According to this work the elastic energy depends on the orientation of the interface between the wafer and epilayer. If the interface plain is perpendicular to the hexagonal axis of wurtzite crystal, then the elastic energy per mole is given by the expression

$$H_{str} = BN_A\Omega\cdot\left(\frac{\Delta a}{a}\right)^2 \quad , \quad B = C_{11} + C_{12} - 2\frac{C_{13}^2}{C_{33}} \tag{1}$$

where $\Delta a = a - a_s$, C_{ij} (i,j = 1 ... 6) are the elastic stiffnesses of the material and $\Omega = \frac{\sqrt{3}}{4}a^2c$ is the molecular volume of ternary compound. The lattice constants of the ternary compound as well as the effective elastic constant B are assumed to obey the Vegard law

$$a = a_{AC}x + a_{BC}(1-x) \quad , \quad c = c_{AC}x + c_{BC}(1-x)$$
$$B = B_{AC}x + B_{BC}(1-x) \tag{2}$$

If the interface is parallel to the hexagonal axis of the crystal, then the elastic energy per mole can be calculated as

$$H_{str} = N_A\Omega\cdot\left[B_{aa}\left(\frac{\Delta a}{a}\right)^2 + B_{ac}\frac{\Delta a\cdot\Delta c}{ac} + B_{cc}\left(\frac{\Delta c}{c}\right)^2\right] ,$$
$$B_{aa} = \frac{1}{2}\left(C_{11} - \frac{C_{12}^2}{C_{11}}\right) \quad , \quad B_{ac} = C_{13} - \frac{C_{13}C_{12}}{C_{11}} \quad , \tag{3}$$
$$B_{cc} = \frac{1}{2}\left(C_{33} - \frac{C_{13}^2}{C_{11}}\right) \quad , \quad \Delta c = c - c_s$$

Using the regular solution approximation for Gibbs free energy of ternary compound and adding to the Gibbs potential the elastic energy of the strained epitax-

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ial layer, one can obtain analogously to [16] the expressions for chemical potentials of binary constituents AC and BC. In the case of interface oriented perpendicular to the hexagonal axis of the crystal

$$\mu_{AC} = \mu^0_{AC} + \tfrac{\sqrt{3}}{4} N_A \varepsilon_s \left[B\Delta^2_{AC} + \Delta B (\Delta a)^2 (1-x) \right] + RT \ln x + \left[W - \tfrac{\sqrt{3}}{4} N_A \varepsilon_s B \Delta^2 \right] (1-x)^2 \quad ,$$

$$\mu_{BC} = \mu^0_{BC} + \tfrac{\sqrt{3}}{4} N_A \varepsilon_s \left[B\Delta^2_{BC} - \Delta B (\Delta a)^2 x \right] + RT \ln (1-x) + \left[W - \tfrac{\sqrt{3}}{4} N_A \varepsilon_s B \Delta^2 \right] x^2 \quad ,$$

$$\Delta_{AC} = a_{AC} - a_s \quad , \quad \Delta_{BC} = a_{BC} - a_s \quad ,$$
$$\Delta = a_{AC} - a_{BC} \quad , \quad \Delta B = B_{AC} - B_{BC} \tag{4}$$

where μ^0_{AC} and μ^0_{BC} are chemical potentials of binary constituents (they can be calculated using standard thermodynamic properties of binary compounds), N_A is the Avogadro number and W is the interaction energy of binary constituents in the ternary solid phase. It is easy to prove that Equation (4) is consistent with the Gibbs-Dugem relationship

$$x \frac{\partial \mu_{AC}}{\partial x} + (1-x) \frac{\partial \mu_{BC}}{\partial x} = 0 . \tag{5}$$

If the interface is oriented parallel to the hexagonal axis of the crystal the respective expressions for chemical potentials are

$$\mu_{AC} = \mu^0_{AC} + \tfrac{\sqrt{3}}{4} N_A \varepsilon_s \left\{ \left(B_{\omega\omega} \Delta^2_{AC} + B_{xx} \zeta \Delta_{AC} \tilde{\Delta}_{AC} + B_{xx} \zeta^2 \tilde{\Delta}^2_{AC} \right) + \left[\Delta B_{\omega\omega} (\Delta a)^2 + \Delta B_{xx} \zeta \Delta a \Delta c + \Delta B_{xx} \zeta^2 (\Delta c)^2 \right] (1-x) \right\} + RT \ln x + \left[W - \tfrac{\sqrt{3}}{4} N_A \varepsilon_s \left(B_{\omega\omega} \Delta^2 + B_{xx} \zeta \Delta \tilde{\Delta} + B_{xx} \zeta^2 \tilde{\Delta}^2 \right) \right] (1-x)^2$$

$$\mu_{BC} = \mu^0_{BC} + \tfrac{\sqrt{3}}{4} N_A \varepsilon_s \left\{ \left(B_{\omega\omega} \Delta^2_{BC} + B_{xx} \zeta \Delta_{BC} \tilde{\Delta}_{BC} + B_{xx} \zeta^2 \tilde{\Delta}^2_{BC} \right) - \left[\Delta B_{\omega\omega} (\Delta a)^2 + \Delta B_{xx} \zeta \Delta a \Delta c + \Delta B_{xx} \zeta^2 (\Delta c)^2 \right] x \right\} + RT \ln (1-x) + \left[W - \tfrac{\sqrt{3}}{4} N_A \varepsilon_s \left(B_{\omega\omega} \Delta^2 + B_{xx} \zeta \Delta \tilde{\Delta} + B_{xx} \zeta^2 \tilde{\Delta}^2 \right) \right] x^2 \quad ,$$

$$\tilde{\Delta}_{AC} = c_{AC} - c_s \quad , \quad \tilde{\Delta}_{BC} = c_{BC} - c_s \quad ,$$
$$\tilde{\Delta} = c_{AC} - c_{BC} \quad , \quad \zeta = a_s / c_s \tag{6}$$

Here $\Delta B_{\alpha\beta}$ ($\alpha,\beta = x,z$) denote the difference between the respective effective elastic constants of binary compounds AC and BC. Similar expressions valid for cubic modification of group-III nitrides are given in [16].

The T-x diagram of phase separation contains two important lines — binodal and spinodal. The binodal is the line corresponding to the two ternary compounds of different composition x_1 and x_2 being in equilibrium with each other. Actually these compounds are the final products of phase separation. At a given temperature the compositions x_1 and x_2 can be obtained as solution of the following equations

$$\mu_{AC}(x_1) = \mu_{AC}(x_2) \quad , \quad \mu_{BC}(x_1) = \mu_{BC}(x_2) \tag{7}$$

The spinodal is the curve bordering the area where uniform ternary compound becomes unstable. It is determined by equation

$$\frac{\partial \mu_{AC}}{\partial x} = \frac{\partial \mu_{BC}}{\partial x} = 0 \tag{8}$$

Using Equation (4) we obtain analytical solution of Equation (8) for the case of the epilayer interface oriented perpendicular to the hexagonal axis of the crystal

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$$T = \frac{2}{R}\left\{W - \frac{\sqrt{3}}{4} N_A \varepsilon_s \left[B(x)\cdot\Delta^2 + 2\Delta B\cdot\Delta\cdot\Delta a(x)\right]\right\} x(1-x). \quad (9)$$

An analogous expression can be derived for the orientation of the epilayer interface parallel to the hexagonal axis of the crystal.

3 Results

To calculate the T-x diagram one should know the interaction energy W and the elastic constants of the binary nitrides. The interaction energy of InN and GaN in $In_xGa_{1-x}N$ compounds has been estimated in [14] using the Valence Force Field model [12] [a] .

As a result, the value W = 25700 J/mol was obtained, which is close to that reported in [8]. There is limited experimental information on the elastic constants of binary group-III nitrides, especially for InN. That is why the data obtained by first-principle calculations [17] are accepted for the elastic constants C_{ij} . On the one hand they are in a reasonable agreement with the experimental data reported for AlN and GaN. On the other hand, Ref. [17] provides self-consistent results for all nitrides of both wurtzite and sphalerite modifications. The values of the lattice constants are taken from [1]. All calculations are carried out for the epitaxial layers coherently grown on a GaN wafer.

Figure 1 compares the T-x diagrams calculated for the relaxed $In_xGa_{1-x}N$ layers and the strained ones corresponding to the interface oriented perpendicular to hexagonal axis of the crystal (the interface lies in the (0001) plane). In contrast to the results reported in [14], the miscibility gap in the case of the strained ternary compound is found to have an asymmetric shape shifted toward the In-rich corner. It is interesting that in the case of strained epilayers, the solubility of InN in GaN is predicted to reach ≈35% at room temperature. The critical temperature of phase separation lowers due to the strain effect from 1135°C (at x = 0.5) for the relaxed layers down to 735°C (at x = 0.79) for the strained one.

Figure 2 shows the T-x diagrams calculated for the strained $In_xGa_{1-x}N$ layers of wurtzite crystalline structure having the interface oriented parallel to hexagonal axis of the crystal. Such layers are found to be even more strained as compared to those with the interface lying in (0001) plane. As a result, the phase separation in these layers is further suppressed – the critical temperature is ≈395°C (at x = 0.83).

The most pronounced effect of elastic strain is in the case of cubic semiconductors (see Figure 2). One can see from the figure that the strain almost completely suppresses the tendency of $In_xGa_{1-x}N$ ternary compounds to phase separation.

4 Discussion

The results obtained in Section 3 show that elastic strain affects dramatically the phase separation in $In_xGa_{1-x}N$ ternary compounds. The effect is predicted to lower the critical temperature from 1135°C down to 735°C and 395°C and then down to complete disappearance of the miscibility gap depending on the interface orientation and crystalline structure of the material. One can expect that purposeful employment of the strain effect will allow one to improve quality of thin $In_xGa_{1-x}N$ epitaxial layers that serve as an active region in blue nitride-based semiconductor lasers.

However, this effect does work only if the relaxation of strain in the epitaxial layer is not yet started. The latter is valid for the layers with the thickness less than the critical one corresponding to the threshold of misfit dislocation formation. Normally the thickness of grown $In_xGa_{1-x}N$ layers exceeds the critical thickness. At the same time even after the relaxation starts some residual strain remains in the epitaxial layer to be build in. This strain can serve as an origin of elevated stability of ternary compounds observed experimentally [2], [3]. Therewith one would expect to observe phase separation prevailing at those points of the crystal where complete relaxation of the strain already takes place — dislocations, grain boundaries etc.

Another important effect coming from the developed model is the enhancement of nitrogen solubility in various III-V compounds caused by elastic strain (this effect will be reported in more detail elsewhere). This effect and the suppression of phase separation in ternary nitrides have a common nature. Enhancement of the nitrogen solubility in such compounds as GaN_xAs_{1-x} and GaN_xP_{1-x} is desirable for fabrication of new infrared light emitting devices.

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FIGURES

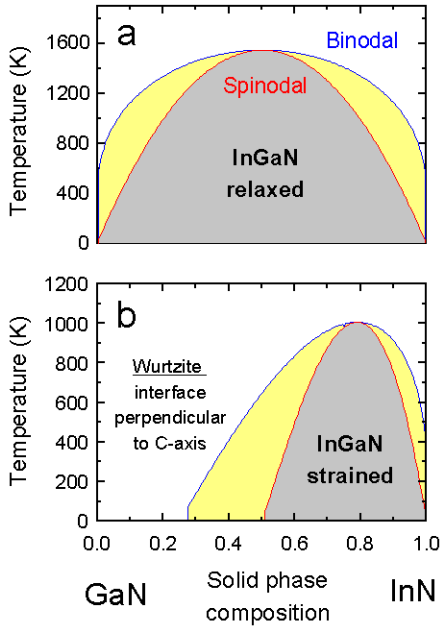

Figure 1. T-x phase diagram of ternary $In_xGa_{1-x}N$ compounds for: (a) relaxed layers, (b) strained layers with the interface orientation perpendicular to the hexagonal axis of the crystal.

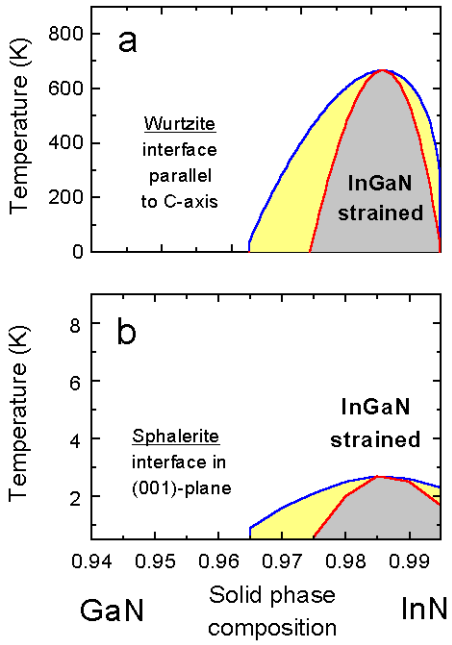

Figure 2. T-x phase diagram of ternary $In_xGa_{1-x}N$ compounds for: (a) strained layers of wurtzite modification with the interface orientation parallel to the hexagonal axis of the crystal, (b) strained layers of cubic modification with the interface lying in (001)-plane (notice the drastic change in the temperature and composition scales for the latter case).

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