Growth of bulk GaN single crystals by flux method

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Abstract

The progresses on the growth of bulk GaN crystals by the flux method in our research group are reported in this review. The research work is mainly focused on the ternary system Li–Ga–N. The phase relations are constructed by the calculation of phase diagram (CALPHAD) technique based on the optimized thermodynamic data of the corresponding binary systems Li–N, Li–Ga and Ga–N. There exists a two-phase region of liquid + GaN at above 750 °C. The well-crystallized, transparent GaN plate-like crystals up to a size of 4 mm can be grown from the Li–Ga–N system under pressures of 1–2 N2 atmospheres. The yield and quality of the GaN crystals depend on the composition of the starting materials, the growth temperature, the cooling rate, and the position of Li3N in the crucible. Efforts are still needed to further enlarge the size of crystals.

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1. Introduction

GaN, a wide direct bandgap semiconductor, is an important material for fabrication of short wave light emitting diodes, laser diodes and power electronic devices as well [1–3]. Up to now, the GaN-based thin films are fabricated mainly on foreign crystal substrates including sapphire, Si, 6H–SiC, MgAl2O4, LiAlO2, LiGaO2, etc. Among these, sapphire is the most commonly used due to its cheapness and stable physical and chemical properties despite a lattice mismatch of 13.5%. The lattice and the thermal expansion mismatch can result in a significant dislocation density as high as 1010/cm2 in the grown GaN-based films [4]. The high dislocation density in the epitaxy film will undoubtedly deteriorate the performance of the GaN-based light emitting and power device. The factors such as stability at high temperatures (~1000 °C), lattice and thermal mismatch limit the wide applications of other crystals as substrates for growth of GaN films. Therefore, quality GaN single crystals are highly desired to be used as substrates for homoepitaxial growth.

Bulk GaN crystals, however, are difficult to grow from its stoichiometric melt either by Czochralski or Bridgman method due to its extremely high decomposition pressures [5] and high theoretical melting temperature [6]. Attempts have been tried to grow the bulk crystals by the sublimation method [7], the hydride vapor-phase epitaxy (HVPE) method [8], the high-pressure solution growth method [9] and the flux method using sodium [10]. Only needle-like crystals can be obtained by the sublimation method. The crystals grown by HVPE are virtually thick films. The two latter methods require high pressures.

We tried to develop a new route based on the flux method to grow bulk GaN single crystals under more moderate temperatures and pressures. The key to the flux method is to find a suitable flux that has certain solubility to GaN. Yonco and coworkers [11] measured the solubility of nitrogen in metal Li from 468 to 714 K. They found that the solubility increases with temperature and attains about 2 mol% at 714 K. They also revealed that from a view of thermodynamic point, transition metal nitrides are more stable at elevated temperatures. In this paper, we report our progresses on growing bulk GaN crystals by using flux method based on the Li–Ga–N ternary system during
the recent years. Transparent, quality GaN crystals with sizes up to 4 mm can be obtained.

2. Thermodynamics [12]

To get the necessary phase relations in the ternary system Li–Ga–N for growing crystals, we first start with the corresponding binary system. The approach of the combination of thermodynamic calculation with the experimental data was adopted to construct the binary phase diagrams and extract the useful thermodynamic data such as excess Gibbs free energy, activity, etc. for liquid phases. Then the phase relations for the Li–Ga–N ternary system can be obtained by the calculation of phase diagram (CALPHAD) from the assessed thermodynamic data.

Phase relations in the ternary system Li–Ga–N are completely unknown in the literatures. We first assessed the thermodynamic data for Ga–N sub-system were taken from [15–17]. Only one ternary nitride Li$_3$GaN$_2$ was reported [18]. Li$_3$GaN$_2$ was found to be cubic, space group $Ia-3$. It decomposes and transfers into GaN and Li$_3$N at 900 °C.

The Gibbs energy function $G_i^m(T)=^0G_i^m(T)-H_i^{SER}$ (298.15 K) for the element $i$ ($i=\text{Ga, Li, N}$) in the phase is described by the following equation

$$G_i^m(T) = a + bT + cT \ln T + dT^2 + eT^3 + f/T$$

$$+ gT^7 + hT^{-9}$$

(1)

where different sets of coefficients ($a$–$h$) may be used in different temperature ranges, and $H_i^{SER}$ (298.15 K), the molar enthalpy of pure solid element $i$ at 298.15 K, is taken as Standard Element Reference (SER) state; bcc for elemental Li and orth for elemental Ga. In the present work, the Gibbs energy functions of Ga, Li and N are taken from the SGTE data for pure elements compiled by Dinsdale [19].

For substitutional solutions, like the liquid, the molar Gibbs energy is equal to

$$^0G_i^m - H_i^{SER} = ^{\text{ref}}G_i^m + ^{\text{id}}G_i^m + ^{\text{ex}}G_i^m$$

(2)

where

$$H_i^{SER} = x_LH_i^{Li}^{SER} (298.15 K) + x_GaH_i^{Ga}^{SER} (298.15 K)$$

$$+ x_NH_i^{N}^{SER} (298.15 K),$$

$$^{\text{ref}}G_i^m = x_Ga[G_{Ga}^\phi(T) - H_{Ga}^{SER} (298.15 K)] + x_L[G_{Li}^\phi(T) - H_{Li}^{SER} (298.15 K)] + x_N[G_{N}^{SER} (T)] - H_i^{SER} (298.15 K)] + x_GaH_i^{SER} (298.15 K),$$

$$^{\text{id}}G_i^m = RT(x_Ga \ln x_Ga + x_L \ln x_L + x_N \ln x_N)$$

$G_i^m$ is the excess Gibbs energy, expressed by the Redlich–Kister polynomial: $G_i^m = $ binary contributions + ternary contributions, with

$$G_i^m = x_i^a x_j^b x_k^c$$

binary := $x_i^a x_j^b x_k^c$ and ternary :

$$= x_i x_j (L_0 x_i + L_j x_j + L_k x_k)$$

where $aL_i^\phi$ are the interaction parameters between $i$ and $j$ elements, whose general form is:

$$aL_i^\phi = a + bT + cT \ln T + dT^2 + eT^3 + fT^{-1}$$

(3)

The calculation is carried out by means of the ChemSage software [16]. The principle is to minimize the Gibbs energy of phases in equilibrium. For each of the selected data, a certain weight is given based on personal experience and is changed by ‘trial and error’ method during the program run, until most of the selected experimental information is reproduced within the expected uncertainty limits.

For the ternary calculations, the binary data sets were combined and extrapolated into the ternaries. Calculations were performed including the gas phase at 1 bar total gas pressure. The calculated isothermal section of the Li–Ga–N system at 800 °C is shown in Fig. 1. From Fig. 1, there is a liquid phase L, a two-phase region with liquid phase and GaN and a three-phase region with liquid phase, GaN and Li$_3$GaN$_2$. On the tie line between Li$_3$N and GaN, there exists a ternary compound Li$_3$GaN$_2$. According to the Li–Ga–N phase diagram, GaN single crystal can be grown from the liquid phase, justifying that the diagram is reasonable.

Fig. 1. Phase relations constructed by using the CALPHAD technique for the ternary system Li–Ga–N at 800 °C [12].
3. Experimental

The starting materials for the growth of GaN single crystals are pure Ga metal (99.999%) and Li3N (synthesized using Li metal (99.9%) and N2 (99.999%) in our lab). These starting materials were weighed as predetermined molar ratio and put into a tungsten crucible (50 mm inner diameter, 60 mm depth), then the crucible was placed inside an induction heating furnace. The schematic for the furnace is shown in Fig. 2. After removing the air by a vacuum pump, the apparatus was filled with nitrogen and the pressure was increased up to 1–2 atm. The sample was heated to 800 °C and maintained at this temperature for certain time, then was slowly cooled at a rate of 2–3 °C per day. The growth process lasted for 24–180 h. Some of the products were taken and analyzed by X-ray diffraction. Most of the products were soaked in HCl solution. The GaN crystals were separated from the other substances by dissolving these substances in HCl solution.

4. Results and discussion [12,20–23]

A series of experiments were conducted to investigate the possibility of growing bulk GaN crystals in the Li–Ga–N ternary system under different growth conditions. The main results are summarized in Table 1. It is found that the crystallization of GaN in this ternary system is possible under a wide range of temperatures, molar ratios of starting materials, growth duration and N2 pressures. In particular, the crystallization can occur at 1 atm pressure of N2, without needing high pressures. Fig. 3 shows the typical GaN platelet crystals grown at 800 °C in N2 pressure of 1–2 atm for 180 h. The maximum size is up to 4 mm but only with a thickness of 0.5–1.0 mm. The yield and the size of GaN crystals strongly depend on the growing conditions. The yield increases with increasing molar ratio of Ga and Li3N but the size of GaN crystals does not increase. The GaN crystals of largest size were grown under the following conditions: the molar ratio 1:3 for Li3N and Ga, the starting temperature 800 °C, the cooling rate 2 °C per day, the N2 pressure 2 atm, and with Li3N raw material placed on the top of the crucible. In the Na–Ga–N system, it has been reported that the morphology of GaN single crystals changed from prismatic to platelet and fine grains with the increase of the molar ratio of Na and Ga [24]. In the Li–Ga–N system, the grown GaN crystals are always plate-like and no change of morphology is observed with alteration of the molar ratio of Li3N and Ga.

In addition, the size of the GaN crystals is also dependent on the position of Li3N in the W crucible. When Li3N floated on the surface of the liquid Ga, a lot of crystalline GaN of high quality could be obtained. When Li3N was completely immersed in liquid Ga, only poor crystalline GaN could be obtained. It is likely due to the fact that for the latter case, Ga may rapidly infiltrate into Li3N with the whole growth process swiftly completed. As a result, the quality of the GaN crystals deteriorated.

The crystallization mechanism is speculated as follows. Liquid Ga will react with bulk Li3N when the system is heated to a certain temperature, say 780 °C, through the reaction equation: Ga + Li3N = Li3GaN2 + Li. The existence of Li3GaN2 is evidenced by our experiments. Then Li3GaN2 dissolves in Li–Ga melt to form a liquid phase in

| Experimental conditions | Main products |
|-------------------------|---------------|
| Molar ratios of Li3N and Ga | Li3GaN2 |
| 2:1 | GaN |
| 1:1 | GaN |
| 1:2 | GaN |
| 1:3 | GaN |
| 1:4 | GaN |
| 1:10 | GaN |
| 1:14 | GaN |
| 1:20 | GaN |
| Growth temperature (°C) | Li3N, Ga |
| 700 | GaN |
| 760 | GaN |
| 800 | GaN |
| 850 | WLi6N4 |
| Growth duration (h) | Li3GaN2, LiGa alloy |
| 24 | GaN, Li3GaN2, LiGa alloy |
| 72 | GaN, Li3GaN2, LiGa alloy |
| 180 | GaN, LiGa alloy |
| N2 pressure (atm) | 0.5 Li+Ga |
| 0.9 GaN |
| 1.5 GaN |
| 2.0 GaN |
| Position of Li3N in crucible | Top GaN |
| Bottom GaN |

Fig. 2. Schematic of experimental set-up for the growth of GaN bulk crystals [21].
the Li–Ga–N ternary system. The composition of this liquid phase will enter into the two-phase region $L + \text{GaN}$ as the temperature decreases, see Fig. 1. GaN will nucleate and grow from the melt. There, however, exists another possible mechanism for the crystallization in this ternary system, i.e. the GaN crystals result from the direct reaction through the route $\text{Li}_3\text{GaN}_2 + \text{Ga} = 2\text{GaN} + 3\text{Li}$. To elucidate which of the processes mentioned above has actually happened, a mixture of $\text{Li}_3\text{GaN}_2$ and Ga (molar ratio 1:1 and 1:2) was heated to 800 °C under a N$_2$ pressure of 1–2 atm, and kept 3–4 days at this temperature. It was found that no reaction occurred, even if the temperature was increased to 820 °C.

According to Ref. [14], Li$_3$N has a large solubility in Li metal at 700–800 °C, and we found that Li$_3$N can be also dissolved in Li–Ga melt as experimentally observed. Therefore, we deduced that the hexagonal platelet GaN crystallized from the Li–Ga–N liquid phase, not by the direct reaction of Li$_3$GaN$_2$ with Ga.

In the Na–GaN system, the growth of GaN single crystals with a size of 3–10 mm has been reported [4, 5], but in that system, a N$_2$ pressure of 50–100 atm was required for the growth of GaN crystals. In contrast, the growth of GaN single crystals was completed in the Li–Ga–N system under a N$_2$ pressure of only 1–2 atm. This is to be expected since the ability of Na to fix nitrogen is much less than that of Li at 700–800 °C. This is easy to understand since Na$_3$N decomposes above 400 °C under normal pressure, while Li$_3$N remains stable at 700–800 °C. But for the growth of GaN crystals by Li flux, pressure of N$_2$ should be higher than 0.5 atm as at lower pressures no GaN can be obtained. This may be caused by the decomposition of Li$_3$N at 800 °C. It has been reported that the melt of Li$_3$N may decompose under a N$_2$ pressure of lower than 400 Torr [25].

The facets of the GaN plate-like crystals are confirmed to be (001) or (010) as determined by X-ray diffraction patterns shown in Fig. 4. The typical full-width at half-maximum (FWHM) of the X-ray rocking curve of these crystals is 10–30 arcsec. They are colorless, transparent and of good crystalline contour. The crystals obtained by the sublimation method [7], as well as by the high temperature and high-pressure technique [9] are pale yellow or black in color probably because of nitrogen deficiency.

Fig. 5 shows the room temperature photoluminescence spectrum (PL) of an as-grown GaN single crystal. Only a strong unique and narrow peak centered at 3.43 eV can be observed. This band is due to the near band gap emission. Yellow luminescence band centered at 2.25 eV is not observed, which is often seen in n-type GaN materials.
and may originate from defect luminescence. The PL spectrum result demonstrates that these crystals are of good crystalline quality. Fig. 6 shows the Raman spectra recorded at room temperature using 5 mW of excitation at 514 nm line of an Ar⁺ laser, with a micro-Raman backscattering Z(Y,Y)Z configuration in a JYT 64000 system equipped with a charge coupled device detector and the resolution around 0.5 cm⁻¹. It can be seen that a very sharp and intense peak is at 569 cm⁻¹ of phonon frequency, corresponding to E₂ (high) phonon mode. This suggests that the crystals should be well crystallized. In addition, A₁ (TO) mode at 532 cm⁻¹ and A₁ (LO) mode at 735 cm⁻¹ are also observed. A₁ (TO) mode (weakly observed) is forbidden by the selection rules in this configuration, which may be attributed to the so-called leakage effect [26].

5. Conclusion

The phase relations of the ternary system Li–Ga–N were constructed by the CALPHAD technique based on the optimized thermodynamic data of the corresponding binary systems Li–N, Li–Ga and Ga–N. There exists a two-phase region of liquid + GaN at above 750 °C. The well-crystallized, transparent GaN plate-like crystals up to a size of 4 mm can be grown from the Li–Ga–N system under pressures of 1–2 N₂ atoms. The yield and quality of the GaN crystals depend on the composition of the starting materials, the growth temperature, the cooling rate, and the position of Li₃N in the crucible. The difficulty in further enlarging the crystal size lies in the prevention of homogeneous nucleation of GaN during the growth process. Efforts are needed to optimize the growth conditions in the future.

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