



Promoted nitrogen dissolution due to the addition of Li or Ca to Ga–Na melt; some effects of additives on the growth of GaN single crystals using the sodium flux method

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Abstract

The effect of the addition of Li or Ca to Ga–Na melt on the promotion of nitrogen dissolution was examined quantitatively in the growth of GaN single crystals using the sodium flux method. The addition of Li or Ca to Ga–Na melt increased both the solubility of solid GaN and that of gaseous nitrogen against the solution. The increase in the solubility of gaseous nitrogen seems to be caused by additives having a high binding energy with nitrogen. We measured the solubility of GaN and that of gaseous nitrogen against Ga–Na, Ga–Na–Li and Ga–Na–Ca melt in this study. On the basis of these data, we clarified the relationship between the N/Ga ratio in the solution and the coloration of GaN crystals grown in each system, and between changes in the yield of GaN and the absolute value of supersaturation.

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1. Introduction

Many researchers have made great efforts to realize the short wavelength-light-emitting devices and high-power/high-speed electronic devices using GaN-based semiconductors in recent years. Progress in the fabrication techniques of GaN thin

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film on another substrate, such as sapphire, GaAs, SiC, etc. [1–3] has made possible the practical use of blue and white light-emitting diodes (LEDs) [4–6]. However, many dislocations are generated due to lattice mismatch between GaN and the substrate, and these prevent further development. Large GaN single crystals with a low dislocation density for homoepitaxial growth are extremely desirable in order to fabricate devices with low dislocation density.

The sodium flux method has been reported to be a growth method for GaN single crystals with low dislocation density [7–9]. Using this method, GaN can be grown by the dissolution of pressurized nitrogen gas into Ga–Na melt under conditions of approximately 1100 K and 5.0 MPa. On the other hand, the growth of GaN by applying gaseous nitrogen pressure to Ga melt without Na (High-Pressure Solution Growth (HPSG) method [10,11]) is reported to require the severe conditions of about 1800 K and more than 1200 MPa. The decrease in the required pressure and temperature to grow GaN by the addition of Na to Ga results from promoted nitrogen dissolution into the solution. In a previous study, we measured the solubility of nitrogen in Ga–Na melt and found that nitrogen dissolution was drastically promoted by the addition of Na to Ga at temperatures above 900 K [12]. We concluded that the high reduction power of Na ionizes the nitrogen molecules at these temperatures, and that the ionized nitrogen can then be sufficiently dissolved into Ga–Na melt to grow GaN crystals at a low pressure of approximately 5 MPa.

Although GaN can be grown at relatively low temperatures and pressures using the sodium flux method, several problems remain in this method, such as a low growth rate and the coloration of crystals due to nitrogen vacancies [7,13,14]. We previously reported that the addition of Li or Ca to Ga–Na melt in the growth of GaN using the sodium flux method increases the growth rate and makes it possible to grow transparent crystals [15,16]. The origin of these phenomena may be due to the increase in the solubility of gaseous nitrogen in the solution brought about by the addition of Li or Ca. In the present study, the solubility of solid GaN and that of gaseous nitrogen in Ga–Na–Li

and Ga–Na–Ca melt were measured in order to clarify the functions of the addition of Li or Ca to Ga–Na melt. The absolute value of supersaturation and the N/Ga ratio in the solution can be calculated using data on the solubility of GaN and nitrogen. On the basis of these data, we investigated the growth conditions under which transparent GaN crystals can be grown and changes in the yield of GaN due to the absolute value of supersaturation.

2. Experimental procedures

2.1. Measurement of solubility of GaN

The solubility of GaN against Ga–Na, Ga–Na–Li and Ga–Na–Ca melt was measured by the weight loss method. Fig. 1a shows a schematic illustration of the experimental apparatus for measuring the solubility of GaN.

Each component (Ga, Na, Li and Ca) was weighed as follows: (1) Ga:Na = 27:73 mol, Ga = 25.8 g; (2) Ga:Na:Li = 27:69.4:3.6 mol, Ga = 26.3 g; (3) Ga:Na:Ca = 27:69.4:3.6 mol, Ga = 25.7 g. The ratio of Ga against flux (Na, Li and Ca) in each solution was constant at 27 mol% and the additive (Li or Ca) against Na was constant at 5 mol%. GaN single crystals with a size of more than 100 μm were used for dissolution; these crystals were prepared in advance using the sodium flux method. The reagents and GaN single crystals were placed into a stainless steel tube with an inner diameter of 21.2 mm. In this process, materials other than GaN and Ca were charged as a melt in the stainless steel tube on the hot plate in order to avoid free space. The tube containing the reagents was heated to a set temperature in an electric furnace, and the temperature was then maintained for 36 h. The solution including the solid GaN was stirred by shaking the tube continuously throughout the experiment using an electric motor. When the experiment was completed, the stainless steel tube was immediately removed from the electric furnace and was quenched. Once the tube had cooled to room temperature, it was cut with a tube cutter. Na, Li, and Ca were removed using a reaction with

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