

## Gallium/aluminum interdiffusion between *n*-GaN and sapphire

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The distribution profiles of Ga and Al near the interface of the *n*-GaN/sapphire system were measured by x-ray energy dispersive spectroscopy (XEDS). The results are obtained by the corrected XED spectra. First, the gallium diffusing into the sapphire substrate obeys the law of remainder probability function. The gallium diffusion coefficient  $D_{\text{Ga}} = 2.30 \times 10^{-13} \text{ cm}^2 \text{ s}^{-1}$  was calculated by theoretical fitting. Second, the diffusion is associated with the GaN growth process at high temperature. Compared to the diffusion of Ga into the sapphire substrate, much less Al antidiffusion from the substrate to the GaN film, with diffusion coefficient  $D_{\text{Al}}$  approximately equal to  $4.8 \times 10^{-15} \text{ cm}^2 \text{ s}^{-1}$ , was observed in the film. © 1998 American Institute of Physics.

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III-V nitride semiconductors, such as GaN, have great physical hardness, extremely large heterojunction offsets, high thermal conductivity, and high melting temperature.<sup>1</sup> In the late 1980's there was only modest interest in III-V materials, but since then the field has been revolutionized by successes in fabricating blue light-emitting diodes from GaN/InGaN.<sup>2,3</sup> In this area, there has recently been great progress in the crystal quality, *p*-type control, and growth method of GaN films.<sup>4-6</sup>

GaN films grown on sapphire substrates by metalorganic chemical vapor deposition (MOCVD) have been widely used in industrial processes. Two-flow MOCVD is one of the most successful methods used in production.<sup>7,8</sup> Up to now, a vast number of reports on the studies of film's electrical, chemical, and growth thermodynamical characteristics have been made<sup>9</sup> but very little attention has been paid to diffusion properties near the interface of the GaN film and the sapphire substrate except only one surface diffusion study of GaN hexagonal pyramids on a dot-patterned GaN/sapphire system.<sup>10</sup> The aim of this communication is to report the study of bulk diffusion characteristics, such as interdiffusion near the interface and to hopefully stimulate further interest in this kind of study, which will be beneficial to the improvement of both growth technology and crystal film quality.

Undoped *n*-GaN films were grown by the two-flow MOCVD method. The growth was conducted at atmospheric pressure. Sapphire with (0001) orientation,  $10 \times 10 \text{ mm}^2$ , were used as substrates. Trimethylgallium (TMG) and ammonia ( $\text{NH}_3$ ) were used as Ga and N sources, respectively. First the substrates were heated to  $1050 \text{ }^\circ\text{C}$  in a stream of hydrogen. The substrate temperature was then lowered to  $510 \text{ }^\circ\text{C}$  for growing the GaN buffer layer. The thickness of

the buffer layer was approximately  $300 \text{ \AA}$ . The substrate temperature was elevated to  $1020 \text{ }^\circ\text{C}$  for growing the GaN films. During the deposition, the flow rates of  $\text{NH}_3$  and TMG in the main flow were maintained at 4 l/min and  $30 \text{ } \mu\text{mol}/\text{min}$ , respectively. The flow rates of  $\text{H}_2$  and  $\text{N}_2$  in the subflow were both maintained at 10 l/min. The GaN films were grown for 1 h. The thickness of the films were  $2 \text{ } \mu\text{m}$ . The electron concentrations of the undoped *n*-GaN films were about  $8 \times 10^{17} \text{ cm}^{-3}$ , the electron mobilities around  $150 \text{ cm}^2 (\text{V s})^{-1}$ , and the resistivity about  $5 \times 10^{-2} \text{ } \Omega \text{ cm}$ , at room temperature.

The distribution profile of Ga and Al near the interface of the *n*-GaN/sapphire system was measured by x-ray energy dispersive spectroscopy (XEDS). This was achieved by scanning the cleaved cross section perpendicular to the plane of the interface. The electron beam of the apparatus of diameter around  $100 \text{ \AA}$  was incident normally on this cross section. The desired interface profile scanning was carried out by varying the position of this electron beam in the direction normal to the interface. The actual position of the measurement was located by a scanning electron micrometer (SEM). The XEDS and the SEM are fitted together with an electron microprobe analysis system (produced by Cambridge Co.). XEDS is a well-known method which has been widely used in element analysis.<sup>11</sup> The reason that the characteristic x-ray intensities are, to a first approximation, proportional to mass concentration (whereas atomic concentration might appear more reasonable) is related to the fact that incident electrons penetrate an approximately constant mass in materials of different composition. This is because these electrons lose their kinetic energy mainly through interactions with orbital electrons of the target atoms, the number of which is approximately proportional to atomic mass. The depth distribution XED spectra of Ga and Al near the interface are shown in Fig. 1.

The relationship between the intensity of an x-ray line

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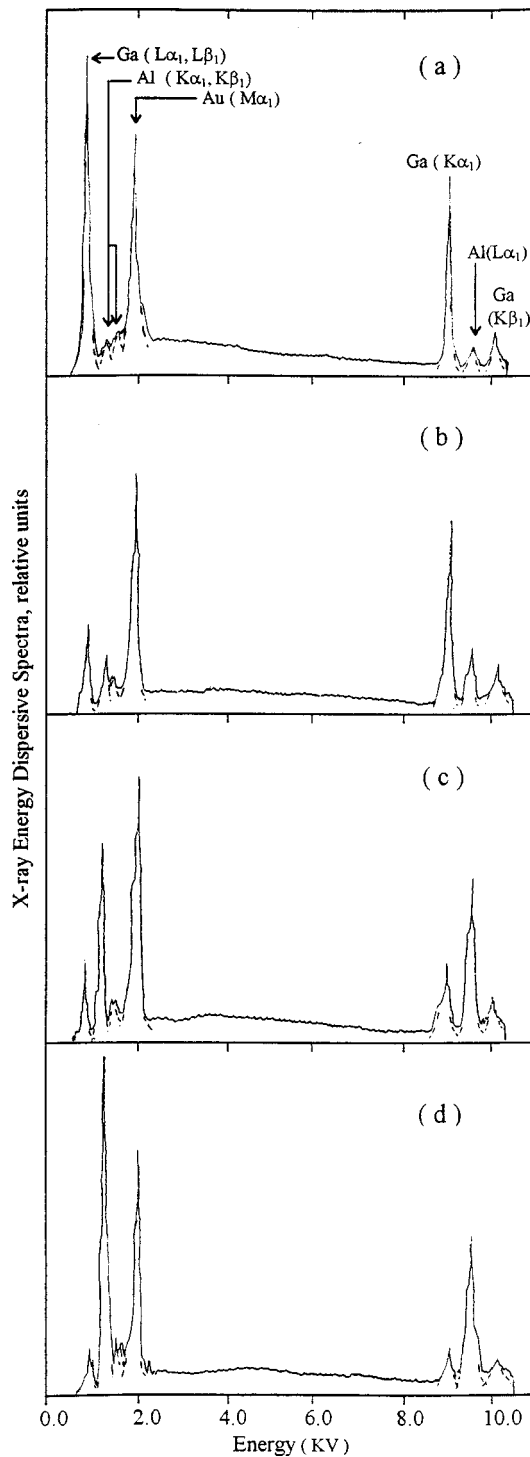


FIG. 1. XED spectra of Ga and Al at different depths near the interface of the GaN/sapphire system. The sample lateral faces were deposited with a 20 Å gold film to prevent charge buildup. The actual position of measurement was located by SEM. (a) is in the GaN film at a distance of 0.05  $\mu$  from the interface. (b), (c), and (d) are spectra for the sapphire substrate at distances of 0.15, 0.70, and 1.40  $\mu$  from the interface, respectively. Dotted lines indicate the real peaks.

and the concentration of the element concerned depends on the composition of the sample. "Matrix corrections"<sup>11</sup> are used to convert sample/standard intensity ratios into concentrations. This is obtained by multiplying the specimen intensity by a factor  $F$  and the standard intensity by  $F_0$ .

$$C = C'(F/F_0), \quad (1)$$

where  $C$  is the true mass concentration in the specimen and  $C'$  is the uncorrected concentration of each element. The phenomena upon which matrix corrections depend are: (1) absorption of characteristic x-rays emerging from the specimen; (2) enhancement of the characteristic x-ray intensity due to fluorescence by other lines and continuum; (3) loss of x-ray intensity owing to incident electrons being backscattered out of the specimen; and (4) variation in the efficiency of x-ray production, as governed by the stopping power of the specimen (a function of atomic number). The effects may be represented by different factors, namely,  $F_a$  (absorption),  $F_b$  (backscattering),  $F_f$  (fluorescence), and  $F_s$  (stopping power). The overall correction  $F$  is given by the product of these individual factors:

$$F = F_a F_f F_b F_s. \quad (2)$$

The combined backscattering and stopping power corrections [both of which are dependent on atomic number ( $Z$ )], together with the absorption ( $A$ ) and fluorescence ( $F$ ) factors, comprise the ZAF correction.<sup>12</sup> There are five elements with high concentration, such as Ga, Al, Au, N, and O, in our system. The relative ZAF corrections and intensities are shown in Table I.

The aim of our study is to find a diffusion law based on the experimental results. Rice<sup>13</sup> studied in detail the impurities from the growing semiconductor film diffusing into a semi-infinite substrate, from which the growing velocity is considered as an item in the diffusion equation based on Fick's second law.<sup>14</sup> However, our case is somewhat different: (1) Our samples are undoped. (2) There is a very large Ga concentration, which is close to the mole concentration of GaN, in the substrate near the interface. (3) Our MOCVD growing velocity is 400 Å/min and is likely to be much greater than that of the diffusion velocity. Therefore, some information can be obtained from the above reasons: (1) the diffusion source seems to be GaN itself rather than an impurity; and (2) the growing velocity is large enough, so that the concentration of the diffusion source maintains a constant value. Thus, our case becomes one of diffusion from a source with a constant concentration into a semi-infinite substrate. The diffusion equation is then given by Fick's second law:

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2}, \quad (3)$$

where  $D$  is the diffusion coefficient and  $c$  is concentration.

The boundary condition is that of Ga (or GaN) diffusion into a semi-infinite solid  $\text{Al}_2\text{O}_3$ . We can consider that the composition is initially uniform; at time zero, the interface concentration is  $C_s$  and remains constant during the whole process. If  $c$  equals zero at  $t=0$  and  $c$  equals  $C_s$  at  $x=0$ , the distribution of material at some later time is given by

$$\frac{C - C_0}{C_s - C_0} = 1 - \frac{2}{\sqrt{\pi}} \int_0^{x/2\sqrt{Dt}} e^{-\lambda^2} d\lambda, \quad (4)$$

where  $t$  is the diffusion time. In our case,  $C_0=0$ , so Eq. (4) can be written as

TABLE I. Relative and corrected intensities of Ga and Al in different depths of the GaN/sapphire system.

Elements ZAF	Ga 0.87				Al 6.97			
Relative intensity <sup>a,b</sup> ( <i>K</i> - <i>X</i> )	-0.05	0.15	0.70	1.40	-0.05	0.15	0.70	1.40
	1.10	0.77	0.44	0.25	0.06	0.15	0.64	1.35
Corrected intensity <sup>c</sup> ( <i>K</i> - <i>X</i> )	0.93	0.65	0.085	0.023	0.40	1.00	1.00	1.00

<sup>a</sup>Upper row indicates the values of different depths *x* which takes the interface as *x*=0, the point in the film is negative value, and ones in the substrate are positive value; where the unit is micrometer, and *x* bars are ±0.025 at all points.

<sup>b</sup>Lower row indicates relative intensities at different depths.

<sup>c</sup>This row shows the corrected relative concentrations of Ga and Al at different depths, where the Al concentration in sapphire is normalized to 1.00. *Y* bars are ±0.03 at *x*=-0.05, 0.15, 0.70, and ±0.02 *x*=1.40.

$$C(x) = C_s \left( 1 - \frac{2}{\sqrt{\pi}} \int_0^{x/2\sqrt{Dt}} e^{-\lambda^2} d\lambda \right) = C_s \left[ 1 - \operatorname{erf} \left( \frac{x}{2\sqrt{Dt}} \right) \right], \quad (5)$$

where 1-erf(*z*) is called the remainder probability function.<sup>13,14</sup> If we take *C<sub>s</sub>*(Ga)=0.93 (Al concentration in the substrate=1.0, see Table 1), *C<sub>s</sub>*(Al)=1.0, and *t*=3600 s in the calculation, then the diffusion coefficient of Ga in sapphire *D<sub>Ga</sub>*=2.30×10<sup>-13</sup> cm<sup>2</sup> s<sup>-1</sup> and that of Al in GaN *D<sub>Al</sub>*≈4.8×10<sup>-15</sup> cm<sup>2</sup> s<sup>-1</sup> would give the best fitting for the experimental results (see Fig. 2).

In fact, the theoretical concentration ratio of Ga to Al is 0.937 assuming that there are not many vacancies in the GaN film and the sapphire substrate. This is based on the fact that the Al concentration in Al<sub>2</sub>O<sub>3</sub> is 4.7×10<sup>22</sup> cm<sup>-3</sup> and the Ga concentration in GaN is 4.4×10<sup>22</sup> cm<sup>-3</sup>. This theoretical

concentration ratio compares very well with the experimental result of 0.94. Therefore, the main diffusion source is probably GaN rather than Ga atoms. Recently, Shimizu *et al.*<sup>15</sup> reported their secondary-ion mass spectroscopy results of the InGaN/GaN/sapphire system, in which the curves of Ga and N diffusing into the sapphire are almost parallel to each other. This also confirms that at high growth temperature, the processes of diffusion and growth occur at the same time.

In conclusion, from the XEDS measurements of the distributions of Ga and Al near the interface of the *n*-GaN/sapphire system, several results have been obtained from the corrected XEDS data. First, the gallium diffusing into the sapphire substrate obeys the law of the remainder probability function. The gallium diffusion coefficient *D<sub>Ga</sub>*=2.30×10<sup>-13</sup> cm<sup>2</sup> s<sup>-1</sup> is calculated by theoretical fitting. Second, the diffusion source is GaN grown at high temperature. Compared to the diffusion of Ga into the substrate, much less aluminum antidiffusion was observed in the GaN film with a diffusion coefficient *D<sub>Al</sub>* approximately equal to 4.8×10<sup>-15</sup> cm<sup>2</sup> s<sup>-1</sup>.

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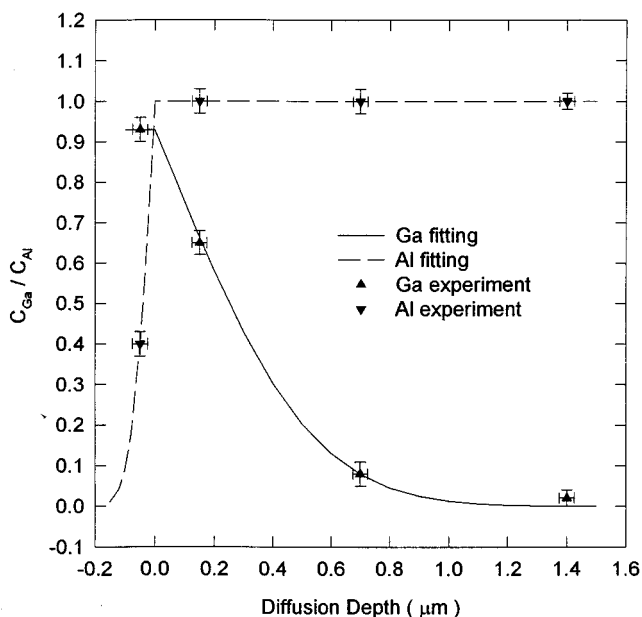


FIG. 2. Relative concentration distributions of Ga and Al as a function of depth. Ga diffusing into sapphire and Al into GaN are fitted by the remainder probability functions. The diffusion coefficients for Ga and Al are *D<sub>Ga</sub>*=2.30×10<sup>-13</sup> cm<sup>2</sup> s<sup>-1</sup> and *D<sub>Al</sub>*≈4.8×10<sup>-15</sup> cm<sup>2</sup> s<sup>-1</sup>, respectively.

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