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Diffusion of gallium in sapphire

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Abstract

In this paper, the characteristics of the diffusion of gallium into sapphire are investigated by SIMS analysis, as a step towards the fabrication of optimized Ga:sapphire optical waveguides. The diffusion coefficient was obtained for temperatures between 1400 °C and 1600 °C, and the results confirm that sapphire substrates can be readily doped with gallium, to depths in the order of microns, at a temperature of 1600 °C. The procedure yields samples with low surface roughness and no apparent unwanted surface features, and the dopant concentration can be selected over a wide range, as gallium has a high solid solubility in sapphire.
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1. Introduction

Sapphire is a common ceramic material with a wide variety of applications, and the characterization of cation diffusion into sapphire is well documented.[1–4] Sapphire is used for many optical applications, and particularly as a host for dopants to realize laser gain media. Chromium-doped sapphire is ruby, with which the first laser was demonstrated. Titanium-doped sapphire is a well-known laser medium exhibiting a broad emission spectrum, rendering it ideal for short pulse and tunable operation.[5] In earlier work, titanium was diffused into sapphire to realize optical channel waveguides and waveguide lasers.[6,7] To design efficient waveguide lasers, it is important to have independent control of the waveguide properties and the concentration of the lasing dopant, so that a second dopant must be sought to provide elevation of the refractive index, without compromising the efficiency of the Ti:Al_2O_3 laser emission. It has been shown that passive optical waveguides can be fabricated by thermal diffusion of gallium into sapphire,[8] and it is expected that the combination of the two ions will lead to the fabrication of novel active integrated optical circuits. The purpose of this work is to investigate the diffusion of gallium in sapphire substrates and determine the diffusion coefficient of gallium into sapphire in the range of 1400–1600 °C, with the aim of optimizing future optical waveguide fabrication. Fung et al.[4] have previously reported gallium diffusion into sapphire to small depths (~300 nm) at a temperature near 1000 °C, studied using scanning electron microscopy. In the present work, the characterization is performed using secondary ion mass spectrometry (SIMS), which offers good resolution for the characterization of concentration profiles with penetration depth less than 1 μm.

2. Fabrication and experimental procedure

Samples of dimensions 1 cm × 1 cm and thickness ~330 μm were cut from commercial z-cut sapphire wafers. A 50 ± 5 nm film of gallium oxide was then thermally evaporated onto the surface of the samples from gallium sesquioxide powder, and the thickness was confirmed using a stylus profilometer (Tencor Alphastep 200). The deposited film is expected to consist mainly of Ga_2O_3 potentially with traces of

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gallium metal.[9] Gallium oxide was selected as the diffusion source because it has a high melting point of approximately 1800 °C, appropriate for solid state diffusion experiments up to this temperature, and because thin films created by thermal evaporation are of good quality. The coated samples were annealed according to each of the following conditions: (i) 1400 °C for 4 h, (ii) 1500 °C for 4 h and (iii) 1600 °C for 1 h. The annealing was performed in an open-ended tube furnace in an argon atmosphere, and the argon flow was approximately 0.5 l/min. The samples were introduced into and removed from the furnace when it was at diffusion temperature, so that all the experiments were performed with fast heating and cooling (∼100 °C/s). During the annealing Ga_2O may be produced and at this temperature it will evaporate leaving a gallium sequioxide film diffusion source.

SIMS analysis of the diffusion profiles was carried out using a Cameca IMS 4f apparatus. A 50 nm thick coating of silver was deposited on the samples in order to minimize sample-charging effects. The primary ion species were O^- and O_2^+ with ion energies of 10 keV and 12.5 keV and primary ion current of 0.1 μA. The analysis of the samples was performed with positive secondary ion detection. O^- and O_2^+ primary ions were used, as this combination gives reasonable sensitivity to electropositive species whilst minimizing sample charging effects that otherwise occur with bulk insulators. During the sputtering process the Al and Ga counts were recorded. The depth origin, corresponding to the sapphire surface, was considered to be the point at which the Al signal reached a constant value. Assuming a constant sputtering rate, the depths corresponding to the SIMS intensities were calculated from the sputtering time and the depth of the craters. The depth of the craters was determined using interference microscopy and stylus profilometry. The SIMS signals in this work could not be calibrated to give absolute gallium concentrations because a reference sample with a known quantity of Ga in sapphire was not available. A typical depth analysis, showing gallium 69 counts and gallium 71 counts together with Al counts is given in Fig. 1.

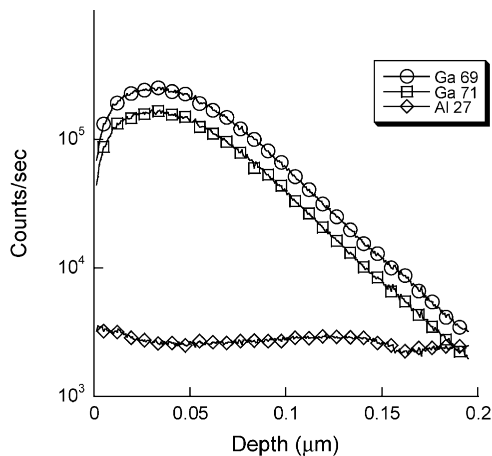

Fig. 1. SIMS counts vs. depth, comparing gallium and aluminium counts.

3. Results and discussion

The diffusion profiles for annealing at temperatures of 1400 °C, 1500 °C and 1600 °C are shown in Figs. 2–4, respectively, together with fitted Gaussian functions. Diffusion theory indicates that during the diffusion of impurities into solids, two extreme cases can be identified. When the solid solubility of the impurity is high a thin source film may be approximated as an instantaneous source. Conversely, when the solid solubility is low even a very thin source film may not be completely exhausted during the diffusion and in this case it may be approximated as a constant source. In the case

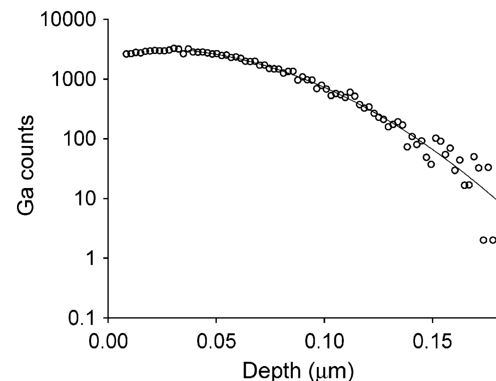

Fig. 2. Gallium concentration profile after diffusion at 1400 °C for 4 h.

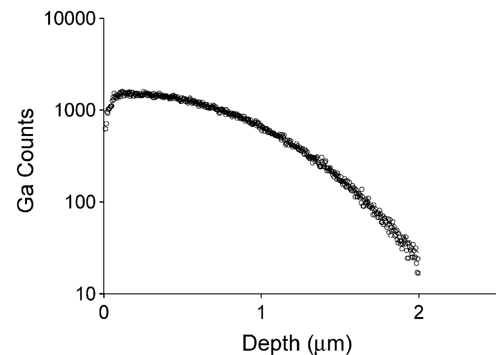

Fig. 3. Gallium concentration profile after diffusion at 1500 °C for 4 h.

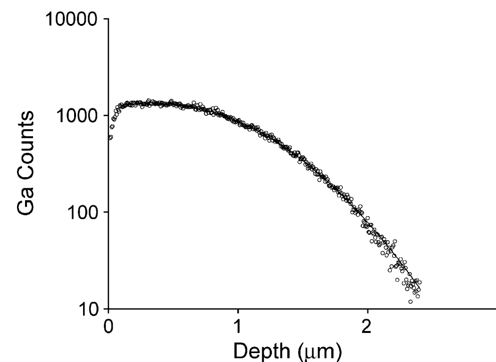

Fig. 4. Gallium concentration profile after diffusion at 1600 °C for 1 h.

of the sample diffused at 1400 °C, there is a very thin (<5 nm) layer of elevated gallium concentration at the surface, indicating that the source has not fully diffused into the sapphire. This top few nanometers is not shown in Fig. 2, nor is it used in the calculation of the Gaussian fit, as the Al counts have not reached a stable value in this region and the data are unreliable. Nonetheless, the qualitative observation that there is a concentrated gallium residue on the surface for this annealing temperature is of use in interpreting the diffusion profiles. In the cases of the samples diffused at 1500 °C and 1600 °C, the Ga depth profile did not show a similar narrow pronounced peak near the surface, showing that there was no residue of the source film on the surface of these samples. The gallium oxide source can therefore be assumed to be an instantaneous source for these higher temperature diffusions. Simple theory predicts that the depth profile of an instantaneous source can be fitted with the following Gaussian function:

$$C(x,t) = \frac{Q}{\sqrt{\pi D t}} \exp\left(-\frac{x^2}{4Dt}\right)$$

where Q is the total number of atoms supplied per unit area, in this case approximately $2 \times 10^{21}\ \mathrm{m}^{-2}$. According to this simple theory, the peak concentration is always at the surface and decreases with time. The diffusion profile is also characterized by an effective diffusion depth, $d_{\mathrm{eff}} = \sqrt{Dt}$, at which the dopant concentration is reduced to 1/e of its surface value.

Although the maximum gallium concentration is expected to be at the sapphire surface, it can be seen from Figs. 1–4 that the diffusion profiles have maxima below the surface of the sapphire, significantly deeper than the point at which the aluminum counts have reached their maximum (steady-state) value. According to the phase diagram of the two solids, shown in Fig. 5, it is apparent that an alpha-solid solution (sapphire) will be in contact with a beta-solid solution (diffusion source).[10] The diffusion source loses gallium ions due to diffusion towards sapphire, and when the gallium concentration falls to 27% at the interface the beta solid solution will be transformed into a mixture of alpha and beta solid solutions.[10] It is expected that this interface then travels up through the 50 nm thick source film until the concentration throughout is below 13% and the entire sample is in the alpha phase, from which diffusion progresses as normal. It is further suggested that part of this mixture sublimes from the surface, leaving a maximum in the gallium concentration inside the bulk of sapphire. The Gaussian functions fitted to the diffusion profiles have been given a depth offset from the sapphire surface to allow for the intermediate surface film, complicating the comparison between profiles. The diffusion coefficients estimated from the Gaussian fitting, the parameters of the Gaussian fits and the corresponding fabrication conditions for the samples are given in Table 1.

The results show that the diffusion coefficient of gallium ions in sapphire is approximately 3 orders of magnitude greater than the self-diffusion coefficient of Al^{3+} ions.[1] Ga^{3+} ions in sapphire diffuse at a rate more similar to Cr^{3+} and Y^{3+} ions, albeit still approximately a factor of 10 faster at 1500 °C.[2,3] Cr^{3+} and other transition metal ions are reported to diffuse through aluminum vacancies, whose concentration is related to the quality and the impurity content of the crystal, so that the diffusion coefficients obtained may differ from study to study.[2,11] All these ions have equal charge and different ionic radii. Although the size of the ion is expected to influence the rate of diffusion, it is generally accepted that the ionic size by itself cannot predict diffusion coefficients.[3] Conversely, the similarity of the diffusion coefficient of Ga^{3+} ions to those of Cr^{3+} and Y^{3+} ions may indicate that these ions diffuse through the same mechanism, although this may only be verified by further diffusion studies.

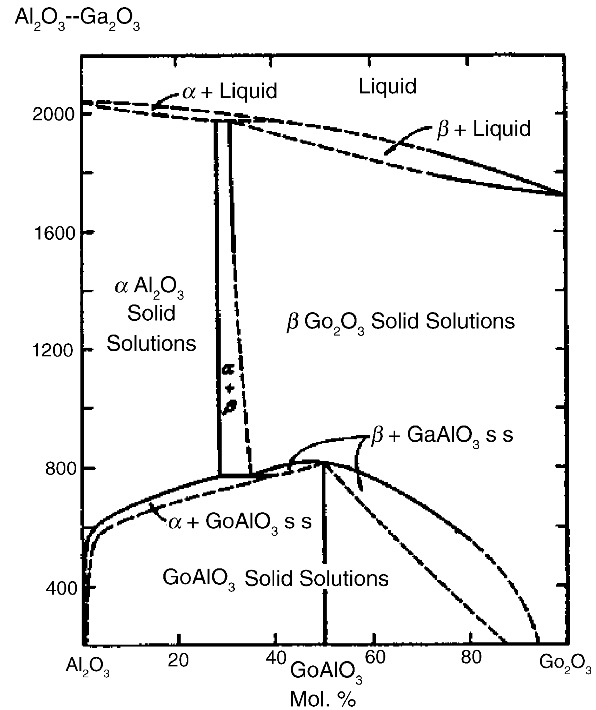

Fig. 5. Phase diagram of the system of Al_2O_3–Ga_2O_3 from.[10]

In the cases of the samples diffused at 1500 °C and 1600 °C, the concentration of Ga^{3+} ions in the sapphire after diffusion may be calculated normalizing the SIMS counts of the depth profile data to the gallium ions supplied by the thin film. It is assumed that the fraction of gallium atoms which do not diffuse into the sapphire is insignificant. The

Table 1
Fabrication parameters and calculated diffusion characteristics for Ga in sapphire

Temperature (°C)	Duration (h)	Gaussian centre (μm)	Diffusion depth (μm)	Diffusion coefficient (m^2/s)
1400	4	0.018	0.047	3.89×10^{-20}
1500	4	0.16	0.65	7.37×10^{-18}
1600	1	0.37	0.68	3.25×10^{-17}

peak gallium ion concentrations are then estimated, in terms of their ratio to the Al ion density in pure sapphire, to be approximately 4.8% and 3.7%, for the 1500 °C and 1600 °C diffusions, respectively. This calculation is complicated in the case of the sample diffused at 1400 °C, because there is a thin source residue at the surface, so it cannot be assumed that all the gallium ions have entered the sapphire, and because the diffusion depth is very similar to the original source film thickness, so that the material in the gallium-doped region has a composition very different to sapphire, which may change the SIMS etch rates. Omitting the region containing the residue of the thin source film, the maximum Ga:Al ion ratio for the sample diffused at 1400 °C may be crudely estimated to be 50%.

4. Conclusions

The diffusion coefficients obtained for the diffusion of gallium into sapphire show that sapphire substrates can be readily doped with gallium in the order of microns at 1600 °C in a few hours, yielding a rate suitable for optical waveguide fabrication. The procedure gives good quality samples with no apparent increase in surface roughness and no unwanted surface features. Gallium has high solid solubility in sapphire, and this combination allows selection of dopant depths and concentrations over a wide range. Gallium diffusion into sapphire is an excellent fabrication procedure for optical waveguides, as shown previously,[8] and detailed knowledge of the diffusion characteristics will allow further optimization of fabrication procedures. Research is now concentrated on investigating the combination of gallium and titanium diffusion into sapphire for the implementation of novel active integrated optical circuits. The mechanism of gallium diffusion in sapphire and the hypothesis of loss of source due to evaporation during annealing will be investigated further.

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