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**Abstract.** X-ray photoelectron spectroscopy (XPS) is used to compare the composition as a function of depth of as-grown zinc oxide (ZnO) films heavily doped with Ga and similar samples annealed in air for 10 min at 600°C, with particular attention given to the near-surface region. Films are grown by pulsed laser deposition (PLD) using a ZnO target containing 3 wt% Ga<sub>2</sub>O<sub>3</sub>. Electrical properties of these samples are determined from temperature-dependent Hall-effect measurements. The as-grown film has the following characteristics: (1) ~1:1 Zn:O ratio with a Ga concentration of ~3.3 at %; (2) no excess Ga in the near-surface region; and (3) excellent electrical characteristics:  $\rho = 2.42 \times 10^{-4} \Omega\text{-cm}$ ,  $n = 8.05 \times 10^{20} \text{ cm}^{-3}$ , and  $\mu = 32.1 \text{ cm}^2/\text{V-s}$  at 300 K. For the annealed sample: (1) the Zn:O ratio remains ~1:1, but the Ga concentration is ~3 at %, which is ~10% lower than in the as-grown film; (2) ~7 at % Ga is measured in the near-surface region; and (3) a significant increase in resistivity to  $\rho = 0.99 \Omega\text{-cm}$ ,  $n = 1.97 \times 10^{18} \text{ cm}^{-3}$ , and  $\mu = 3.2 \text{ cm}^2/\text{V-s}$  at 300 K. Analysis of the O chemical shift suggests formation of a mixed ZnO/Ga<sub>2</sub>O<sub>3</sub> surface layer  $\leq 5\text{-nm}$ -thick accounts for the observed changes in the Ga profile after annealing. © The Authors. Published by SPIE under a Creative Commons Attribution 3.0 Unported License. Distribution or reproduction of this work in whole or in part requires full attribution of the original publication, including its DOI. [DOI: [10.1117/1.OE.52.5.053801](https://doi.org/10.1117/1.OE.52.5.053801)]

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## 1 Introduction

Transparent conductive oxides (TCOs) have been used for more than 60 years as transparent electrodes for a wide range of applications such as photodetectors, displays, solar cells, and light-emitting diodes.<sup>1-7</sup> Indium tin oxide (ITO) is the most common commercially available TCO material, but limited world supplies of In have increased costs significantly over the past decade.<sup>8</sup> One promising candidate to replace ITO is zinc oxide (ZnO) heavily doped with one or more of the group III metals, Al, Ga, or In, since material costs are lower, and high-quality ZnO films can be easily deposited on many different substrates, using a variety of growth techniques.

Several groups have successfully grown thin film and bulk samples of ZnO heavily doped with group III metals.<sup>9-13</sup> For TCO applications, it is desirable to maximize the activated dopant concentration to realize the lowest resistivity film possible. This dopant activation commonly involves some form of high-temperature annealing treatment. However, it has been shown that high-temperature annealing causes group III metals to accumulate at the surface.<sup>14</sup> There have been several experimental estimates of group III metals' solubility limits in ZnO,<sup>11,15-18</sup> which suggest that in thin films it is possible to greatly exceed the thermodynamic doping limit found in bulk crystal growth; however, we are not aware of any quantitative theoretical values for these solubility limits.<sup>19</sup>

In the present work, we use x-ray photoelectron spectroscopy (XPS) to compare the dopant profiles for as-grown ZnO films heavily doped with Ga versus those of similar samples annealed in air. Hall-effect measurements of the electrical characteristics of these films are used in conjunction with

this composition information to help understand changes in bonding chemistry that result from this anneal.

## 2 Experiment

A 540-nm-thick Ga-doped ZnO film was deposited on a 3-in. sapphire wafer by pulsed-laser-deposition (PLD) at 200°C in a pure Ar atmosphere, using a ZnO target containing 3 wt% Ga<sub>2</sub>O<sub>3</sub>. This unconventional growth process, in the absence of an O<sub>2</sub> ambient, has been previously described in detail<sup>13</sup> and shown to produce highly conductive ZnO films. Two adjacent 1 × 1 cm<sup>2</sup> pieces were cut from the center region of this wafer for the present study; one was used to characterize the as-grown film, while the second sample was annealed at 600°C in air for 10 min prior to analysis.

Temperature-dependent Hall-effect measurements were performed over the range 6 to 320 K using a LakeShore 7507 apparatus. Ohmic contacts were made using indium dots at the four corners of each sample to allow for measurements using the Van der Pauw geometry. The composition of each sample was determined by XPS using a Perkin-Elmer (PHI) 5500 spectrometer equipped with a hemispherical analyzer and a monochromatic Al K  $\alpha$  x-ray source operated at 400 W. High-resolution spectra of Zn 2p<sup>3/2</sup>, O 1s, Ga 2p<sup>3/2</sup>, and Al 2p photoelectron peaks were acquired at a pass energy of 11.75 eV with a 400  $\mu\text{m}$  aperture. Depth profiles were acquired using an Ar ion sputtering source operated at 4 keV. Sputtering rates of 23 and 21 nm/min were determined for the as-grown and annealed samples, respectively. A series of very short duration sputtering steps were used to probe the near-surface region of each sample, followed by longer duration sputter steps through the "bulk" of these films until the substrate was reached. Elemental

**Table 1** Room temperature electrical characteristics of as-grown and annealed ZnO:Ga samples derived from Hall-effect measurements.

| Operation | $\rho$ ( $\Omega$ -cm) | $\mu$ ( $\text{cm}^2/\text{V-s}$ ) | $n$ ( $\text{cm}^{-3}$ ) | $N_D$ ( $\text{cm}^{-3}$ ) | $N_A$ ( $\text{cm}^{-3}$ ) | $K = N_A/N_D$ |
|-----------|------------------------|------------------------------------|--------------------------|----------------------------|----------------------------|---------------|
| As-grown  | $2.42 \times 10^{-4}$  | 32.1                               | $8.05 \times 10^{20}$    | $1.05 \times 10^{21}$      | $1.76 \times 10^{20}$      | 0.168         |
| 600C-air  | 0.992                  | 3.2                                | $1.97 \times 10^{18}$    | $0.94 \times 10^{21}$      | $4.1 \times 10^{20}$       | 0.436         |

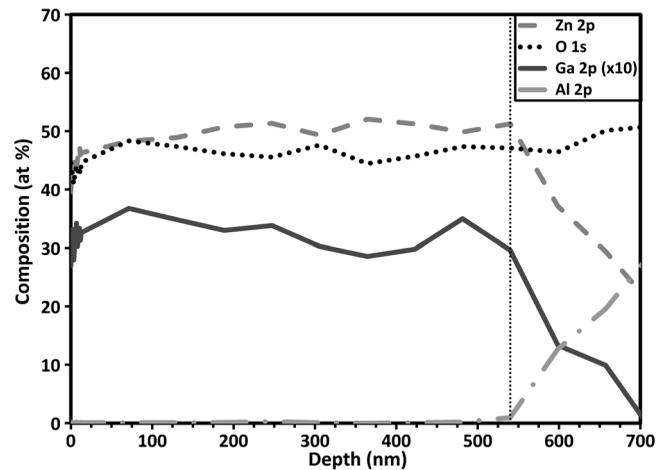
compositions were determined following each sputter step from integrated core-level XPS peaks using known sensitivity factors.<sup>20</sup>

### 3 Experimental Results and Analysis

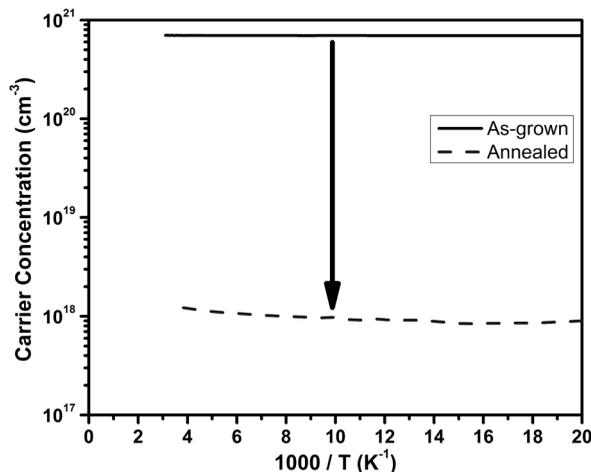
Room temperature electrical characteristics of as-grown and annealed ZnO:Ga samples were derived from Hall-effect measurements and are listed in Table 1. The values of  $N_D$  and  $N_A$  were calculated by assuming doubly charged acceptors, probably Zn vacancies ( $V_{\text{Zn}}$ ). Analysis details and fitting processes have been described elsewhere<sup>21</sup> and are not reproduced here. For both samples, the carrier density is nearly independent of temperature, as shown in Fig. 1, which confirms that the electrons in these layers are degenerate. The electron concentration decreases by a factor of  $\sim 400\times$  and the mobility decreases by a factor of  $\sim 10\times$  following the 600°C anneal resulting in a corresponding  $\sim 4000\times$  increase in resistivity. It is interesting to note, however, that the donor concentration in the annealed sample is only reduced by about 10%. A significant increase in compensating acceptors (see Table 1) has a much larger impact on the electron density, possibly because H, which passivates acceptors in ZnO,<sup>22</sup> diffuses out above 475°C.<sup>23</sup>

Composition profiles through the entire depth of the as-grown ZnO:Ga sample and focusing on the near-surface region are shown in Figs. 2 and 3, respectively. Note that the plotted Ga concentration has been multiplied by a factor of 10 for clarity. The concentration of Zn, O, and Ga remain uniform throughout the sample, with Zn and O nominally in a 1:1 ratio (as expected) and  $[\text{Ga}] \sim 3.3$  at %. Similar composition profiles for the annealed sample are shown in Figs. 4 and 5, respectively. In the “bulk” of the annealed sample, the

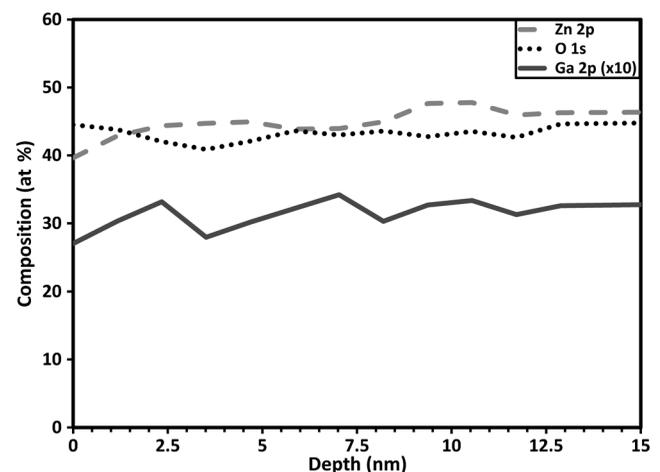
ratio of Zn and O is again  $\sim 1:1$ , which is similar to that of the as-grown film, but the Ga concentration has decreased slightly to  $\sim 3$  at %. However, at the surface, the annealed sample shows a layer  $\leq 5$  nm thick containing a significant accumulation of Ga (peak concentration more than  $2\times$  the measured concentration in the as-grown sample) and a corresponding Zn deficit. It is widely agreed<sup>18</sup> that the incorporation of group III metals in ZnO thin films deposited by physical vapor techniques such as PLD can exceed the thermodynamic solubility limits. The high Ga concentrations measured in the as-grown sample are much greater than the 0.001 at % thermodynamic solubility limit estimated for Ga in ZnO. Given this substantial imbalance, it is possible that



**Fig. 2** Composition profile in as-grown ZnO:Ga sample from x-ray photoelectron spectroscopy (XPS) sputter depth profile measurement. Note that the Ga concentration is multiplied  $10\times$  for clarity.



**Fig. 1** Temperature-dependent carrier concentration data for as-grown and annealed ZnO:Ga samples.



**Fig. 3** Composition profile in the near-surface region of the as-grown ZnO:Ga sample shows no Ga accumulation.

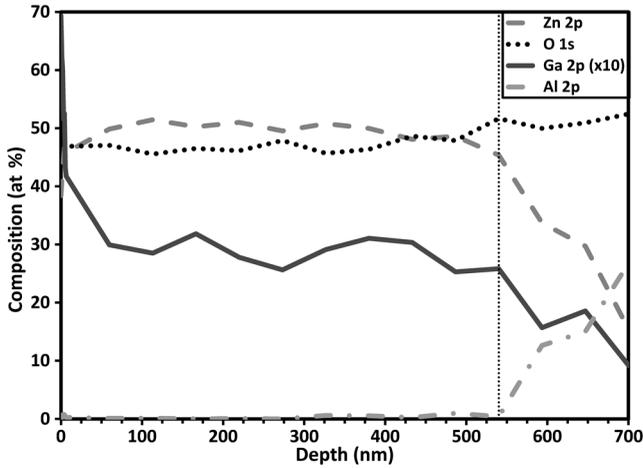


Fig. 4 Composition profile in annealed ZnO:Ga sample from XPS sputter depth profile measurement.

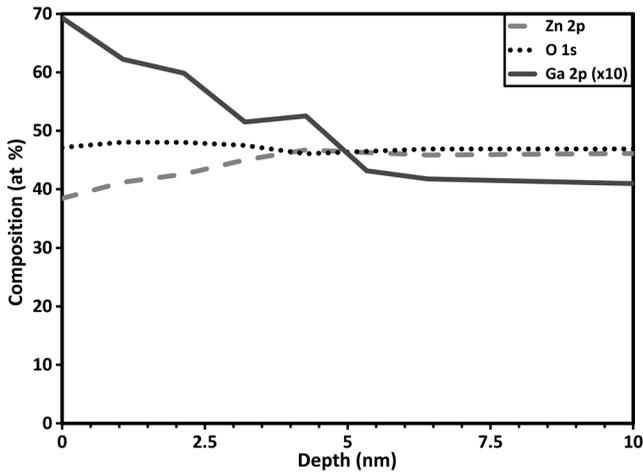


Fig. 5 Surface Ga accumulation layer,  $d \leq 5$  nm thick, observed in annealed ZnO:Ga sample. Peak Ga concentration is  $\sim 2\times$  value found in “bulk” of sample.

during the anneal at 600°C Ga rapidly diffuses to the surface because of the large thermodynamic driving force.

In addition to providing these quantitative measures of atomic concentration, XPS is a powerful technique for investigating the local bonding environment of atoms through small changes in their binding energies or chemical shifts. High-resolution photoelectron spectra of the O 1s peak in the surface and “bulk” regions of the annealed sample are shown in Fig. 6(a) and 6(b), respectively, along with least-squares fits to Voigt functions. In the surface region, the O 1s photoelectron spectrum is composed of two peaks separated by a  $\sim 1.0$  eV chemical shift, whereas in the bulk region, only one fitted peak is required. Comparing Fig. 6(a) and 6(b), it is clear that the lower binding energy peak corresponds with Zn-O bonding, which is the only spectral feature present in the “bulk” region of the sample. The higher binding energy peak observed in the surface region spectrum is consistent<sup>24,25</sup> with Ga-O bonding in Ga<sub>2</sub>O<sub>3</sub>. The relative proportion of these two components in the surface layer was estimated to be  $\sim 50\%$  ZnO and  $50\%$  Ga<sub>2</sub>O<sub>3</sub> by comparing the integrated intensities of these two peaks. A corresponding chemical shift in the Ga 2p<sup>3/2</sup> photoelectron peak was too small and the peak intensity too weak to be evaluated reliably.

#### 4 Summary

We investigated the electrical properties and composition profiles of heavily Ga-doped ZnO films grown by PLD. As-grown films exhibit excellent electrical characteristics with a room temperature resistivity value of  $\rho = 2.42 \times 10^{-4} \Omega\text{-cm}$  and uniform levels of Zn, O, and  $\sim 3.3$  at % Ga. No excess Ga is seen in the near-surface region. Heavily doped ZnO:Ga samples annealed at 600°C in air show an  $\sim 4000\times$  increase in room temperature resistivity resulting primarily from an increase in compensation by unpassivated acceptors. A surface Ga accumulation layer  $\leq 5$  nm thick with a peak concentration more than twice the level in the as-grown film is found in the annealed sample. Analysis of the O 1s chemical shift measured by XPS suggests that this surface layer is composed of a mixture of ZnO and Ga<sub>2</sub>O<sub>3</sub> in  $\sim 1:1$  ratio.

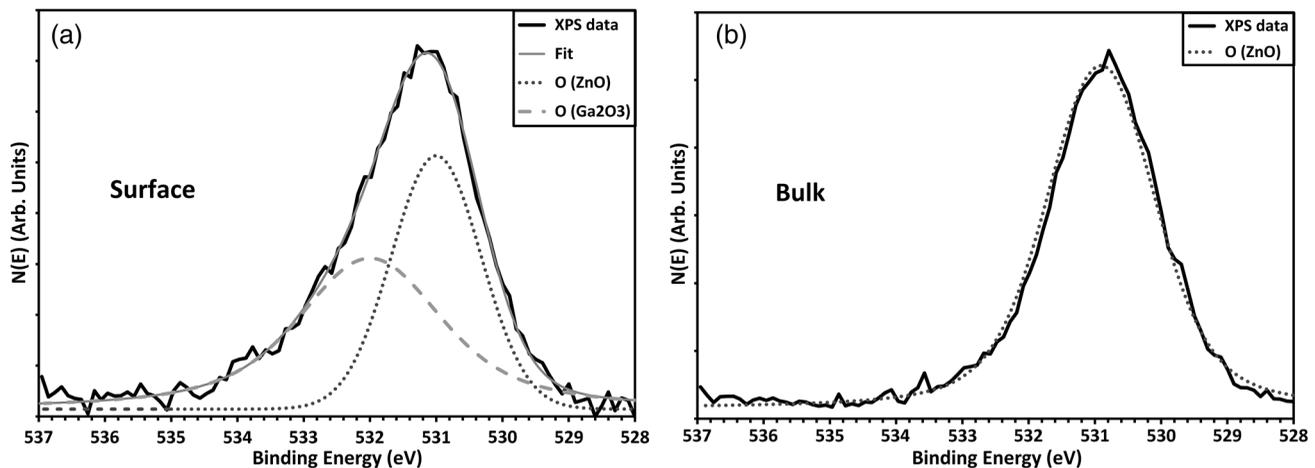


Fig. 6 Comparison of high resolution O 1s photoelectron spectra measured in (a) surface and (b) bulk regions of the annealed ZnO:Ga sample.

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Biographies and photographs of the authors are not available.