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Ga-doped ZnO grown by pulsed laser deposition in H₂: The roles of Ga and H

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Highly conductive thin films of ZnO doped with Ga were grown by pulsed laser deposition with 10 mTorr of H₂ in the growth chamber. Compared with a more conventional method of producing conductive films of ZnO, i.e., growth in O₂ followed by annealing in forming gas (5% H₂ in Ar), the H₂ method requires no postgrowth anneal and also produces higher carrier concentrations and lower resistivities with better depth uniformity. As an example, a 65-nm-thick sample had a room-temperature mobility of 32 cm²/V s, a concentration of 6.8×10^{20} cm⁻³, and a resistivity of 2.9×10^{-4} Ω cm. From a scattering model, the donor and acceptor concentrations were calculated as 8.9×10^{20} and 2.1×10^{20} cm⁻³, respectively, as compared to the Ga and H concentrations of 11×10^{20} and 1×10^{20} cm⁻³. The authors conclude that growth in H₂ produces higher Ga-donor concentrations but that H-donors themselves do not play a significant role. © 2011 American Vacuum Society. [DOI: 10.1116/1.3523296]

I. INTRODUCTION

Transparent conductive oxides (TCOs) are being considered for many applications, including (1) electrodes for flat-panel displays and photovoltaic cells, (2) low-emissivity windows, (3) window defrosters, and (4) *n*-type layers in light-emitting and laser diodes.¹⁻⁴ At present, the workhorse TCO is indium tin oxide (ITO) because ITO can reach resistivities as low as 1×10^{-4} Ω cm. However, ITO suffers from several deficiencies: (1) In has become very expensive, (2) In is somewhat toxic, (3) the thermal stability of ITO is rather poor, and (4) the transparency is only moderately good. Thus, there is a surge of interest in developing ZnO as a replacement for ITO because ZnO is cheap, nontoxic, stable, and highly transparent. Several groups have achieved room-temperature ZnO resistivities below 3×10^{-4} Ω cm, but only a very few have approached 1×10^{-4} Ω cm. To do better at this stage of development, it will be necessary to understand the fundamental components of resistivity ρ . Indeed, ρ involves the inverse product of mobility μ and carrier concentration n , but even more fundamentally, ρ is determined by donor N_D and acceptor N_A concentrations,⁵ and these quantities must be determined if the material is to be developed to its fullest potential. In this work, we employ a simple, analytical method to determine N_D and N_A from μ and n in degenerate semiconductor materials. This method is based on the fact that mobility in TCOs that are not too thin (say, >50 nm) is mainly determined by scattering from ionized donors and acceptors and can be described by the degenerate form of the Brooks–Herring formula: $\mu_{ii}(n, K)$

$= \mu_{ii, \max}(n)(1-K)/(1+K)$, where $K = N_A/N_D$. According to this equation, the goal is clearly to minimize K , i.e., maximize N_D and minimize N_A .

In the case of ZnO, most efforts to maximize N_D have centered on doping with Al, Ga, or In because it is relatively easy to obtain concentrations of these elements in the mid- 10^{20} cm⁻³ range and even higher. Often, Ga is chosen because Al tends to form its own oxides and In is large and causes more lattice distortion. In our initial studies at the Air Force Research Laboratory (AFRL), we employed pulsed laser deposition (PLD) with a target composed of ZnO with 3 wt % Ga₂O₃, an atmosphere of 10 mTorr O₂, a substrate of SiO₂/Si, and a substrate temperature of 400 °C.⁵ (The SiO₂ in this case was 1-μm-thick in order to fully isolate the ZnO layers from the Si substrate.) The as-grown layers had typical room-temperature electrical properties of $\mu = 5$ cm²/V s, $n = 5 \times 10^{19}$ cm⁻³, and $\rho = 2 \times 10^{-2}$ Ω cm, insufficiently conductive for practical TCOs. However, annealing in forming gas (FG: 5% H₂ in Ar) greatly improved the electrical properties, typically giving $\mu = 32$ cm²/V s, $n = 3 \times 10^{20}$ cm⁻³, and $\rho = 6 \times 10^{-4}$ Ω cm. While these results were much better, they were not uniform with thickness.^{5,6} Following previous conjectures in the literature, we surmised that the H in the FG served two functions: (1) directly adding H_O donors and (2) passivating acceptors such as Zn vacancies [$2\text{H}^+ + \text{V}_{\text{Zn}}^{--} \rightarrow (\text{V}_{\text{Zn}} - 2\text{H})^0$]. Because both n and μ increased after the FG had annealed, it was immediately obvious that acceptor passivation, not donor addition, had to be the dominant effect; however, whatever the cause is, H had a desirable effect on the resistivity, except for the uniformity issue. To attack this problem, we decided to do PLD growth in a H₂, rather than O₂, atmosphere. Indeed, growth in pure H₂ had already been pioneered by Li *et al.*^{7,8} at the Pacific Northwest National Laboratory (PNNL); however, their studies at that time involved only undoped ZnO.

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Li *et al.* found that PLD growth of pure ZnO (no Ga) in a H₂ atmosphere caused resistivities to decrease by about three orders of magnitude, to about $10^{-1} \Omega \text{ cm}$, with n in the mid- 10^{18} cm^{-3} range. They also grew samples in D₂, rather than H₂, in order to get more accurate impurity concentration measurements by secondary-ion mass spectroscopy (SIMS). They found that the SIMS concentrations of H and D were within about a factor 2 of n and thus deduced that H_O was responsible for the increase in n . Furthermore, there was evidence that H also passivates acceptors. Thus, we decided to grow ZnO with a Ga-doped target (3 wt % Ga₂O₃) in a H₂ atmosphere so we could see if the presence of H would increase the conductivity over that produced by using the same target in an O₂ atmosphere. Somewhat surprisingly, as shown below, a H₂ ambient increases both the concentration of Ga and also the percentage of Ga participating as donor states. On the other hand, H itself contributes only about 10% of the donor states or less.

Before discussing our results, we should note that other workers, besides Li *et al.*, have found that the addition of H increases the conductivity of ZnO. For example, Duenow *et al.*⁹ grew Al-doped ZnO layers by rf magnetron sputtering in an Ar ambient augmented by small amounts of H, from 0% to 2% H₂. They found that a very small amount of H ($\sim 0.3\%$ H₂/Ar) increased the mobility, especially in layers only lightly doped with Al, and that excellent resistivities of $3\text{--}4 \times 10^{-4} \Omega \text{ cm}$ could be obtained with 2 wt % Al₂O₃ in the target (reading from a graph, their Fig. 1). These results are important because sputtering is one of the dominant methods of producing ZnO for TCO applications. However, one drawback of sputtering in this context is that the growth rate (and thus thickness) depends strongly on the amount of H in the ambient.

Duenow *et al.*⁹ speculated that at least one of the roles of H in their material was to passivate defects. This conclusion is likely true; however, neither in this nor in any other former work, to our knowledge, has the role of H been discussed quantitatively. In this work, we compare the values of N_D and N_A , found from a unique mobility analysis, with Ga and H concentrations, found from SIMS measurements, to show that the major role of H, at least for our samples, is *not* to passivate acceptors or directly provide H-donors, but to allow more Ga to enter the growing crystal. This was a surprise to us and will likely be a surprise to many readers; indeed, it is a critical finding since H is an omnipresent background element in most ZnO growth environments and, in the past decade, has been often blamed for the pervasive propensity of ZnO to be n -type.

II. EXPERIMENT AND ANALYSIS

Two ZnO samples of different thicknesses were grown in a 10 mTorr H₂ atmosphere at the PNNL, and, for comparative purposes, two samples were also grown in O₂. Thicknesses were determined by measuring the depths of the respective SIMS craters with a profilometer. The two different thicknesses in each case allowed a rough check of depth uniformity though additional points would be needed to fully

FIG. 1. (Color online) Changes in carrier concentration due to 600 °C and 10 min anneals in Ar.

determine that characteristic. The substrate temperature was chosen to be 400 °C and the O₂ pressure was set at 10 mTorr in an attempt to match the previous work at the AFRL; however, one difference is that Al₂O₃ substrates were used for the PNNL growths, whereas SiO₂/Si substrates were used for those grown at the AFRL. In that regard, we should note that the electrical properties do not seem to depend strongly on the choice of substrate. Other details of growth in H₂ can be found in Refs. 7 and 8.

To determine donor N_D and acceptor N_A concentrations, temperature-dependent Hall-effect (T-Hall) measurements were carried out over a range of 15–320 K using a Lakeshore 7507 apparatus. The temperature dependences of n for the two thinnest samples (65 nm for the “H₂ layer” and 123 nm for the “O₂ layer”) are shown in Fig. 1. Clearly, they are degenerate (independent of temperature). The resistivity (Fig. 2) and mobility (not shown) are only slightly temperature dependent because phonon scattering even at the higher temperatures is always much weaker than the ionized-impurity scattering. Figures 1 and 2 also include data for “annealed” samples, which will be discussed below.

We first compare the unannealed sample grown in H₂ with that grown in O₂. As seen in Fig. 1, $n(\text{O}_2, \text{unann}, 300 \text{ K}) = 0.84 \times 10^{20} \text{ cm}^{-3}$ and $n(\text{H}_2, \text{unann}, 300 \text{ K}) = 6.7 \times 10^{20} \text{ cm}^{-3}$, and in Fig. 2, $\rho(\text{O}_2, \text{unann}, 300 \text{ K}) = 2.2 \times 10^{-3} \Omega \text{ cm}$ and $\rho(\text{H}_2, \text{unann}, 300 \text{ K}) = 3.0 \times 10^{-4} \Omega \text{ cm}$. Thus, clearly, growth in H₂ results in a significantly higher n and lower ρ . At first glance, this would seem to be no surprise because H is a

FIG. 2. (Color online) Changes in resistivity due to 600 °C and 10 min anneals in Ar.

FIG. 3. (Color online) Sheet carrier concentration n_s as a function of the layer thickness d for samples grown in O₂ and H₂, respectively. The slope of n_s vs d is the volume concentration n . The arrows denote changes due to 600 °C and 10 min anneals in Ar.

known shallow donor in ZnO. However, to test this model, we annealed both the 65 nm H₂ film and the 123 nm O₂ film at 600 °C in Ar, a process known to eliminate H in any ZnO sample.^{9,10} Indeed, as shown in Fig. 3, the sheet concentration n_s slightly changed for the O₂ sample but greatly decreased for the H₂ sample, which is seemingly consistent with our hypothesis. However, the only true test is to measure [Ga] and [H] by SIMS and compare these quantities with N_D .

First, we must determine N_D and N_A from n and μ . Since the electrons are degenerate and n is independent of temperature, we can get one relationship immediately: $n = N_D - N_A$. The second relationship comes from the low-temperature mobility, which includes ionized-impurity and boundary scattering terms, combined by Matthiessen's rule, which is exactly valid for degenerate electrons,⁵

$$\mu(d, n, K, C) = [\mu_{ii}(n, K)^{-1} + \mu_{bdry}(d, n, C)^{-1}]^{-1}, \quad (1)$$

where

$$\mu_{bdry}(d, n, C) = \frac{e}{\hbar} \frac{d/C}{(3\pi^2 n)^{1/3}} = \frac{10.58}{C} \frac{d_{nm} \text{ cm}^2}{n_{20}^{1/3} \text{ V s}}, \quad (2)$$

and

$$\begin{aligned} \mu_{ii}(n, K) &= \frac{24\pi^3 \epsilon_0^2 \hbar^3}{Z^2 e^3 m^{*2}} \frac{n}{N_{ii}} \frac{1}{\ln(1 + y(n)) - \frac{y(n)}{1 + y(n)}} \\ &= \frac{146.9}{\ln(1 + 6.46n_{20}^{1/3}) - \frac{6.46n_{20}^{1/3}}{1 + 6.46n_{20}^{1/3}}} \frac{1 - K \text{ cm}^2}{1 + K \text{ V s}}. \end{aligned} \quad (3)$$

Here, d_{nm} is the layer thickness in units of nanometers, n_{20} is the carrier concentration in units of 10^{20} cm^{-3} , $K = N_A/N_D$, and C is an empirical constant, which depends on the details of surface and interface scattering. For the samples discussed in Refs. 5 and 6, a value of $C=4$ best fits the data, and we will use that value here. At 20 K, the electrical parameters of the 65 nm H₂ sample are $\mu=34.1 \text{ cm}^2/\text{V s}$, $n=6.80 \times 10^{20} \text{ cm}^{-3}$, and $\rho=2.69 \times 10^{-4} \Omega \text{ cm}$, and those of the 123 nm O₂ sample are $\mu=33.7 \text{ cm}^2/\text{V s}$, $n=0.840 \times 10^{20} \text{ cm}^{-3}$, and $\rho=2.20 \times 10^{-3} \Omega \text{ cm}$. Thus, from Eq. (2), we can calculate $\mu_{bdry}(\text{H}_2)=90.7$ and $\mu_{bdry}(\text{O}_2)=344 \text{ cm}^2/\text{V s}$, each of which is much higher than the corresponding experimental value of mobility. In other words, the boundary scattering is much weaker than the ionized-impurity scattering, and thus a more accurate value of C is not too important in these cases. The only unknown now is K , and by using Eqs. (1)–(3), we get $K(\text{H}_2, \text{unann})=0.237$ and $K(\text{O}_2, \text{unann})=0.562 \text{ cm}^2/\text{V s}$. Finally, $N_D = n/(1-K)$ and $N_A = nK/(1-K)$, giving N_D and N_A values that are listed in Table I. Before discussing these results, we note that Fig. 3 also contains the sheet carrier concentrations of a 174-nm-thick layer grown in H₂ and a 344 nm sample grown in O₂. The purpose of these growths was to get a rough estimation of thickness uniformity, and the conclusion is that the uniformity appears to be much better than that of the samples grown in O₂ and annealed in forming gas (discussed in Refs. 5 and 6). However, more samples of different thicknesses would have to be examined to make this conclusion firm.

III. DISCUSSION

As stated earlier, to firmly establish the role of H, it is necessary to measure its concentration [H] and then compare it with N_D , determined by Eqs. (1)–(3). Since we know that N_D is in the mid- 10^{20} cm^{-3} range, the only potential impurity-related candidates for donors are Ga and H, and these were measured by SIMS (Refs. 7 and 8) at the PNNL.

TABLE I. Values of donor N_D and acceptor N_A concentrations compared with Ga and H concentrations.

Sample	d (nm)	Ambient	N_D (cm ⁻³)	N_A (cm ⁻³)	$N_D + N_A$	[Ga] (cm ⁻³)	[H] (cm ⁻³)
610B	123	O ₂	1.9×10^{20}	1.1×10^{20}	3.0×10^{20}	5.7×10^{20}	0.5×10^{20}
Ann'l'd		Ar, 600 °C	2.2×10^{20}	1.0×10^{20}	3.2×10^{20}	5.5×10^{20}	0.1×10^{20}
610C	65	H ₂	8.9×10^{20}	2.1×10^{20}	11.0×10^{20}	11.0×10^{20}	1.0×10^{20}
Ann'l'd		Ar, 600 °C	1.9×10^{20}	0.8×10^{20}	2.7×10^{20}	12.0×10^{20}	0.3×10^{20}

The SIMS-derived impurity concentrations were calibrated against ion-implanted Ga and H standards, with absolute uncertainties estimated at about 20% and with relative uncertainties at about 10%. The results for the 65 nm(H₂) and 123 nm(O₂) samples are given in Table I, and it should be noted that the results for the thicker samples are consistent with these. From Table I, we can draw at least four conclusions as follows:

- (1) Growth in H₂ produces donor concentrations significantly higher than those achieved by growth in O₂.
- (2) Surprisingly, however, $[H] \ll N_D$ in all cases, and thus H makes very little *direct* contribution to the donor concentration.
- (3) The overall concentration of Ga is about twice as high for growth in H₂ than for growth in O₂, and thus Ga can account for all of the donors and even the acceptors (i.e., the possibility of Ga_{Zn}V_{Zn} acceptors).
- (4) The 600 °C anneal in Ar has little effect on the O₂-grown layer but greatly decreases N_D in the H₂-grown layer. However, again surprisingly, it does not decrease [Ga].

Thus, we must conclude that the major role of H is to induce more Ga into the growing layer and to induce a higher percentage of the Ga into active donor states. Inactive donor states involving Ga would perhaps include Ga₂O₃ inclusions and Ga_{Zn}-O_I neutral complexes. These inactive species should be more prevalent in the layer grown in O₂ and, indeed, we note that $[Ga] > N_D + N_A$ in this sample. Also, the anneal in Ar would likely produce O vacancies V_O and interstitials O_I on the surface, and some of the O_I could diffuse into the bulk and passivate the Ga_{Zn} donors. Further studies will be necessary to validate some of these ideas.

IV. SUMMARY

Ga-doped ZnO samples grown in a H₂ atmosphere by pulsed laser deposition have greatly increased conductivity

with respect to samples grown in the usual atmosphere, O₂. However, the main role of H is not to add donors but to facilitate a higher incorporation of Ga and also to induce a higher percentage of the Ga into active donor states.

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