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Origin of conductive surface layer in annealed ZnO

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The highly conductive surface layers found in nearly all as-grown or annealed bulk ZnO wafers are studied by temperature-dependent Hall-effect and secondary-ion mass spectroscopy (SIMS) measurements. In this work, we have used annealing in N₂ at 900 °C, and forming gas (5% H₂ in N₂) at 600 °C, to cause a large enough surface conduction that SIMS measurements can be reliably employed. The increased near-surface donor density, as determined from two-layer Hall-effect modeling, is consistent with an increased near-surface concentration of Al, Ga, and In atoms, resulting from diffusion. There is no evidence for participation of any donors involving H. © 2008 American Institute of Physics. [DOI: 10.1063/1.2903505]

In recent years, the wide-bandgap semiconductor ZnO has been extensively studied because of potential photonic and electronic applications, including UV emitters and detectors, transparent transistors, and gas sensors.¹⁻³ In many of these applications, the surface properties are important and, in particular, the conductivity of the near-surface region. For example, surface conductivity may affect the properties of gas sensors,⁴ and also devices that incorporate Schottky barriers.⁵ Recently, we have shown that nearly all commercially available ZnO wafers (that we have examined) have a conductive surface layer (CSL) that totally dominates the sample conductance at low temperatures and sometimes strongly influences the conductance even at room temperature.⁶ Thus, to accurately characterize the total electrical properties of a wafer, it is necessary to separate the bulk and surface contributions.

Since the existence of two or more conductive layers is a rather common problem in studies of semiconductor materials, several methods have been devised to accurately obtain the electrical properties. The most powerful of these methods involves analysis of the magnetic-field dependences of the conductivity σ and Hall coefficient R_H . If only two conductive layers are involved in a particular sample and if the magnetic-field dependences of σ and R_H in each separate layer are negligible, then the problem can be exactly solved.⁷ However, if more than two layers are important, or potentially important, then complicated algorithms are necessary to effect a solution.⁸⁻¹⁰ In practice, if the surface and bulk mobilities are high enough, say ≥ 1000 cm²/V s, then the magnetic-field-based methods can be implemented with common laboratory magnets, of magnetic-field strength (B) on the order of 1 T. However, for ZnO at room temperature, or very low temperatures, mobilities are typically low enough that much higher fields ($B \geq 10$ T) are necessary to ensure accurate results. Even with $B = 10$ T, it would be difficult or impossible to characterize surface layers with mobility ≤ 1 cm²/V s and indeed we find such low mobilities under certain annealing conditions, including those of the present work.

The technique employed here takes advantage of the fact that the CSL is dominant at temperatures that are low enough that the bulk carriers are frozen out.¹¹ In this temperature region, the CSL carrier concentration n_{surf} is usually degenerate (temperature independent), and the mobility μ_{surf} can be adequately modeled solely with Brooks–Herring ionized-impurity scattering,^{6,11} in either nondegenerate or degenerate form. Furthermore, the data can usually be fitted well enough by assuming that n_{surf} and μ_{surf} have flat depth profiles within a surface region of thickness d_{surf} so that the total sample can be modeled as two, uniform conductive layers: (1) the bulk layer with parameters n_{bulk} , μ_{bulk} , and d_{bulk} and (2) the surface layer, with n_{surf} , μ_{surf} , and d_{surf} . In principle, since Hall-effect measurements are sensitive only to sheet concentrations (cm⁻²), not volume concentrations (cm⁻³), it is impossible to precisely determine d_{bulk} and d_{surf} . However, in all commercial wafers that we have studied, it is clear that $d_{\text{surf}} \ll d_{\text{bulk}}$, and since $d_{\text{total}} = d_{\text{surf}} + d_{\text{bulk}}$, we can approximate $d_{\text{bulk}} \approx d_{\text{total}}$, usually about 0.5 mm. Thus, we can accurately determine the *bulk* donor and acceptor volume concentrations, $N_{D,\text{bulk}}$ and $N_{A,\text{bulk}}$, and the donor energy, $E_{D,\text{bulk}}$, but we cannot determine the *surface* donor and acceptor volume concentrations $N_{D,\text{surf}}$ and $N_{A,\text{surf}}$, without an independent measurement of d_{surf} . However, as we have recently shown,⁶ the value of $N_{D,\text{surf}}$ calculated in our analysis is not very sensitive to d_{surf} , and is accurate to within a factor two or three even without an independent measurement of d_{surf} . Unfortunately, an accurate value for $N_{A,\text{surf}}$ does indeed require a measurement of d_{surf} .

In this work, we compare our Hall-effect values of $N_{D,\text{surf}}$ with secondary-ion mass spectroscopy (SIMS) concentrations of known donor-type impurities in ZnO, such as H, Al, Ga, and In. One motivation for this study is that we and others have found that high-temperature annealings of hydrothermally-grown ZnO often produce a strong increase of surface conductance,^{12,13} and it is important for some types of device processing to determine the cause of this problem.

The four ZnO samples used in the present study were $5 \times 5 \times 0.5$ mm³, hydrothermally grown, [0001]-oriented plates cut from the same 10×10 mm³ plate supplied by Tokyo Denpa.¹⁴ One sample, R59-2b, was used as a control

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TABLE I. RT (294 K) and 20 K electrical properties of ZnO samples subjected to various annealing treatments. "FG" designates forming gas.

Sample	Annealing	Resistivity (Ω cm)	Mobility ($\text{cm}^2/\text{V s}$)	Concentration (cm^{-3})
		294 K (20 K)	294 K	294 K
R59-2b	None	1.5×10^3 (9×10^5)	1.8×10^2	2.3×10^{13}
R59-2a	600 °C, FG, 30 min	6.2 (1×10^8)	2.2×10^2	4.6×10^{15}
R59-2c	600 °C, N ₂ , 30 min	3.6×10^6 (no data)	4.4	3.9×10^{11}
R59-2d	(1) 930 °C, N ₂ , 30 min	3.7×10^3 (1×10^5)	3.3	5.0×10^{14}
R59-2d	(2) 600 °C, FG, 30 min	6.8 (4×10^3)	2.0×10^2	4.7×10^{15}

and the other three samples were annealed in flowing N₂, or forming gas (5% H₂ in N₂), or both, as outlined in Table I. The annealings were carried out in a horizontal tube furnace, with the samples sitting on a glass plate with the Zn face up. Sample R59-2d was annealed at 930 °C in N₂ for a period of 30 min, and then at 600 °C in forming gas for a period of 30 min. The original idea of this combination of annealings was to get rid of most of the H in the sample, as is known to occur during a >800 °C annealing in N₂ and then introduce new H from the surface, during the 600 °C/forming-gas annealing. It was anticipated that any increase in surface conductance would be due to H donors coming from the forming gas, but this turned out to not be the case, as shown below.

Room-temperature (RT=294 K) Hall-effect measurements were performed with an Accent HL5500PC system, and temperature-dependent (20–320 K) measurements, with a LakeShore 7507 system. Ohmic contacts were formed by soldering In dots on the corners of each sample. The RT resistivity ρ , mobility μ , and carrier concentration n data are presented in Table I. At 20 K, it was not possible to get reliable μ and n data for all four samples, so only the ρ data are presented. As we have shown previously, the 20 K data are nearly always representative of the surface electrons, because of bulk carrier freezeout, while the RT properties are mainly determined by the bulk electrons because of their much higher mobilities.^{6,11,12}

SIMS measurements were performed with a Cameca 4FE7 instrument. Calibration factors for the donor-type impurities H, Al, Ga, and In, were obtained by using ion-implanted standards. A 5.5 keV beam of Cs⁺, 42° from the

normal, was used as the primary ion species, and positively charged secondary ions were detected. The profiles of ¹H and ²H were quite flat and not systematically different in any of the experimental ZnO samples, whether annealed or unannealed; thus, it is likely that the H profiles simply represent background levels of H in the SIMS instrument. However, a comparison in Table I of the RT and 20 K resistivity data for sample R59-2a, which was annealed only in forming gas, shows that while the H in the forming-gas greatly lowers the RT resistivity, i.e., increases the *bulk* conductance, it actually raises the 20 K resistivity, i.e., lowers the *surface* conductance. Thus, the evidence from this annealing is that H increases bulk conductance (directly or indirectly) but not surface conductance.

We next consider the group III atoms, Al, Ga, and In, which are known to be shallow donors in ZnO, soluble to very high concentrations 10^{20} – 10^{21} cm⁻³. We compare the SIMS profiles of these elements in the unannealed sample, R-59-2b, with those in the annealed sample, R59-2d, and define the difference as $\Delta[\text{Al}] = [\text{Al}]_{\text{R59-2d}} - [\text{Al}]_{\text{R59-2b}}$, with similar relationships for Ga and In. In Fig. 1, we show the combined *excess* concentrations of these three elements $\Delta\{[\text{Al}] + [\text{Ga}] + [\text{In}]\}$ as a function of depth in sample R59-2d. Clearly there has been diffusion of these elements into a region ≤ 80 nm below the surface. The broad hump is due to In, whereas the rest of the profile, the major part, is about 70% Al and 30% Ga. If we ignore the broad hump, which may not be representative of the whole CSL, we can then integrate this curve to get an excess sheet group III concen-

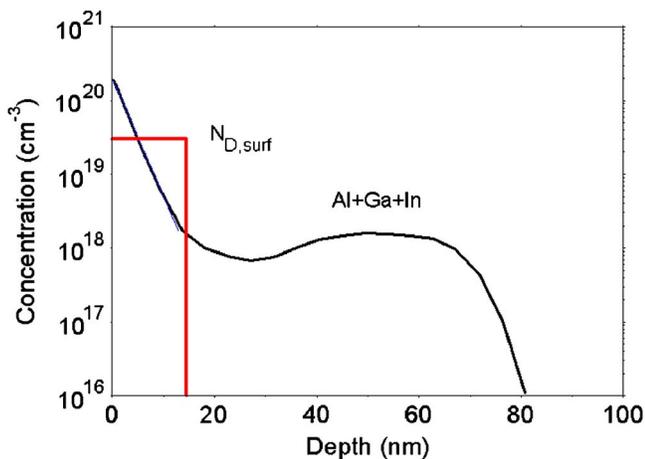


FIG. 1. (Color online) Hall-effect square approximation of the $N_{D,\text{surf}}$ profile, and SIMS profile of the *excess* $[\text{Al}] + [\text{Ga}] + [\text{In}]$ that has diffused into the surface region of sample R59-2d (annealed at 930 °C, N₂, 30 min, and then at 600 °C, forming gas, 30 min). The SIMS profile from 0–14 nm can be fitted with a relationship: $\text{conc} \propto \exp(-d/13)$.

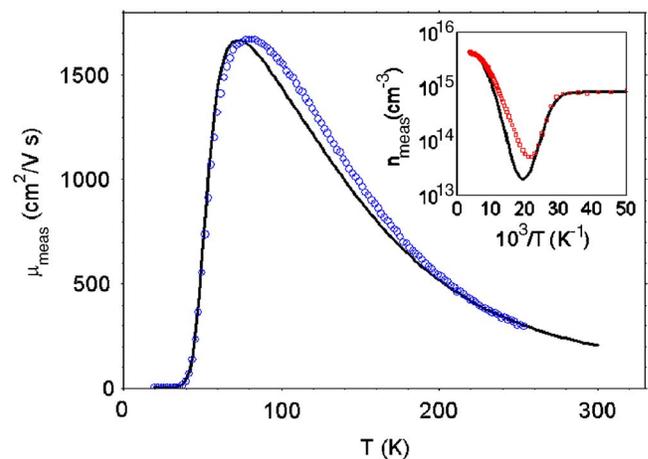


FIG. 2. (Color online) Temperature-dependent mobility μ_{meas} (main figure) and carrier concentration n_{meas} (inset) of annealed ZnO sample R59-2d. Here, both bulk and surface contributions to n_{meas} are normalized to the *total* sample thickness, $d_{\text{total}} \approx 0.5$ mm. The solid lines fitting μ_{meas} and n_{meas} derive from only one set of parameters.

tration of about $5.4 \times 10^{13} \text{ cm}^{-2}$. (Actually, the broad hump adds only about $0.4 \times 10^{13} \text{ cm}^{-2}$.)

The temperature-dependent Hall-effect data for sample R59-2d are shown in Fig. 2. The surface conduction is dominant from about 20–30 K, and $N_{D,\text{surf}}$ and $N_{A,\text{surf}}$ can be approximately determined from the following equations:⁶

$$N_{D,\text{surf}} = \frac{1}{2} \left(\frac{7.647 \times 10^{17} T^{3/2}}{\mu_{H,\text{meas}}(T) \left\{ \ln[1 + y(d_{\text{surf}})] - \frac{y(d_{\text{surf}})}{1 + y(d_{\text{surf}})} \right\}} + n_{\text{meas}} \frac{d_{\text{total}}}{d_{\text{surf}}} \right), \quad (1)$$

$$N_{A,\text{surf}} = \frac{1}{2} \left(\frac{7.647 \times 10^{17} T^{3/2}}{\mu_{H,\text{meas}}(T) \left\{ \ln[1 + y(d_{\text{surf}})] - \frac{y(d_{\text{surf}})}{1 + y(d_{\text{surf}})} \right\}} - n_{\text{meas}} \frac{d_{\text{total}}}{d_{\text{surf}}} \right), \quad (2)$$

where

$$y(d_{\text{surf}}) = 1.392 \times 10^{-6} \left(n_{\text{meas}} \frac{d_{\text{total}}}{d_{\text{surf}}} \right)^{1/3}. \quad (3)$$

Here, μ_{meas} and n_{meas} are the values of μ and n plotted in Fig. 2, and n_{meas} (inset) is normalized to the thickness of the whole sample, $d_{\text{total}} = d_{\text{bulk}} + d_{\text{surf}}$. That is, to be able to plot both the bulk and surface contributions to n on the same graph, it is necessary to assume a common layer thickness, and the total-layer thickness $d_{\text{total}} \sim 540 \mu\text{m}$ is the obvious one, since it is the only one we can measure. Because $d_{\text{surf}} \ll d_{\text{bulk}}$ in most cases, we have $d_{\text{bulk}} \approx d_{\text{total}}$, so that the bulk-electron contribution to n_{meas} (i.e., n_{bulk} , roughly the part of the curve to the left of the minimum) is accurate. However, the surface-electron contribution to n_{meas} (i.e., n_{surf} , roughly the flat part of the curve) does not accurately portray the true volume concentration in the surface region, and must be explicitly renormalized in Eqs. (1)–(3) as $n_{\text{meas}}(d_{\text{total}}/d_{\text{surf}})$. As discussed earlier, we do not know d_{surf} but at least we can get its minimum value, $d_{\text{surf,min}}$, by setting $N_{A,\text{surf}} = 0$ (obviously the lower limit of $N_{A,\text{surf}}$), as described in Ref. 6. Then we can calculate $N_{D,\text{surf}}(d_{\text{surf,min}})$ and as argued elsewhere, $N_{D,\text{surf}}$ is fortunately not a strong function of d_{surf} .⁶ For sample R59-2d, at 21.2 K, we have $n_{\text{meas}} = 8.1 \times 10^{14} \text{ cm}^{-3}$ and $\mu_{H,\text{meas}} = 2.9 \text{ cm}^2/\text{V s}$. Inserting these values into Eq. (1) and setting $N_{A,\text{surf}} = 0$, we calculate $d_{\text{surf}} = 14.5 \text{ nm}$ and this value is then the minimum possible value of d_{surf} , i.e., $d_{\text{surf,min}}$. At $d_{\text{surf}} = 14.5 \text{ nm}$, Eq. (1) gives $N_{D,\text{surf}} = 3.0 \times 10^{19} \text{ cm}^{-3}$, and these values of d_{surf} and $N_{D,\text{surf}}$ constitute a simulated “square” profile, as shown in Fig. 1. The sheet concentration of this profile is $(3.0 \times 10^{19})(14.5 \times 10^{-7}) = 4.4 \times 10^{13} \text{ cm}^{-2}$.

The solid lines in Fig. 2 are theoretical fits to the μ_{meas} and n_{meas} curves using a single-donor model, with the following fitting parameters: $d_{\text{surf}} = 14.5 \text{ nm}$; $N_{D,\text{surf}} = 3.0 \times 10^{19} \text{ cm}^{-3}$; $N_{A,\text{surf}} = 0$; $N_{D,\text{bulk}} = 6.0 \times 10^{15} \text{ cm}^{-3}$; $N_{A,\text{bulk}} = 2.0 \times 10^{15} \text{ cm}^{-3}$; and $E_{D,\text{bulk}} = 50 \text{ meV}$. The low value of $N_{A,\text{bulk}}$ is likely due to the passivation of Li_{Ga} and other ac-

ceptors by the H in the forming gas. Note that the peak mobility, about $1700 \text{ cm}^2/\text{V s}$, is one of the highest ever reported for hydrothermally grown ZnO. The rather poor fit of n in the region of 50–100 K (Fig. 2, inset) is likely the result of using only a single-donor model for the bulk electrons. However, the surface-conduction region, $T < 50 \text{ K}$, is well fitted, and that is the main focus of this paper.

Clearly, the SIMS and Hall-effect profiles are quite compatible, especially considering the approximations inherent in each method. For example, the sheet donor concentration measured by the Hall-effect ($4.4 \times 10^{13} \text{ cm}^{-2}$) is close to the excess sheet group-III element concentration that has diffused into the near-surface region ($5.4 \times 10^{13} \text{ cm}^{-2}$). Also, the value of $d_{\text{surf,min}}$ (14.5 nm) is comparable to the $1/e$ depth of the SIMS profile (13 nm). These correlations give a strong indication that the surface conductance in this case is mainly due to group III ions, not H or any native-defect related donors, such as $\text{Zn}_I\text{-N}$ or V_O . Of course, the present work does not prove that the conductive surfaces in typical *as-grown* ZnO wafers (e.g., R59-2b) are due to near-surface group-III elements, but that possibility must be considered in light of the present findings.

In summary, we have found a quantitative correlation between the near-surface donor concentration, and the combined concentrations of Al, Ga, and In, in hydrothermally grown ZnO annealed in N_2 and forming gas. Surprisingly, there is no evidence that H-related donors are active in the surface region, in spite of the forming-gas annealing. However, this annealing does strongly increase the *bulk* conductance, due largely to the passivation of acceptors by H.

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