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Highly conductive ZnO grown by pulsed laser deposition in pure Ar

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Ga-doped ZnO was deposited by pulsed laser deposition at 200 °C on SiO_2/Si, Al_2O_3, or quartz in 10 mTorr of *pure* Ar. The as-grown, bulk resistivity at 300 K is 1.8×10^{-4} Ω cm, three-times lower than that of films deposited at 200 °C in 10 mTorr of O_2 followed by an anneal at 400 °C in forming gas. Furthermore, depth uniformity of the electrical properties is much improved. Mobility analysis shows that this excellent resistivity is mostly due to an increase in donor concentration, rather than a decrease in acceptor concentration. Optical transmittance is approximately 90% in the visible and near-IR spectral regions. © *2010 American Institute of Physics*. [doi:10.1063/1.3481372]

Forming-gas (FG) (5% H_2 in Ar) annealing of ZnO films doped with donor impurities such as Al, Ga, or In, has been shown to increase conductivity[1,2] and is often used in preparing transparent conductive oxides (TCOs). The improved conductivity has often been attributed to the ability of H to directly provide donors and also to passivate negatively charged acceptors, including those causing potential barriers in grain boundaries.[3,4] However, as shown recently, the bulk electrical properties after FG anneals are not uniform with depth, as evidenced by the thickness dependences of resistivity ρ, mobility μ, and carrier concentration n.[5,6] Furthermore, H is known to be quite mobile, potentially impacting the reliability of certain devices.[7] Thus, it is preferable to obtain the desired high film conductivity without the assistance of H.

Ga-doped ZnO films are often grown using pulsed laser deposition (PLD), and generally in an oxygen-rich environment, presumably to ensure stoichiometric films. However, as the partial pressure of oxygen is increased, the film resistivity increases and electron mobility decreases.[8,9] This high resistivity resulting from excess oxygen is likely related to (1) an increase in compensating point-defect-related acceptors, such as the Zn vacancy V_{Zn} and (2) diffusion of O_2 (forming O_2^-) into grain boundaries (GBs) and other macroscopic defects. The O_2 centers at GBs capture electrons that can induce high potential barriers; these barriers can further impede transport by reducing mobility.

In the present work, Ga-doped ZnO was deposited at 200 °C in Ar instead of O_2. There are reasons to believe that growth in Ar might enhance conductivity by inhibiting the formation of V_{Zn} acceptors in the bulk and O_2 acceptors at grain boundaries. The Ga-doped ZnO films were deposited using a Neocera Pulsed Energy deposition tool. The target, consisting a ZnO ceramic sintered with 3 wt % Ga_2O_3, was ablated with a 248 nm KrF pulsed laser operating at a frequency of 30 Hz. The energy density at the target surface was 2.6 J/cm^2. During deposition, the target was rotated at

40 deg/s and rastered by +/−2 deg to prevent preferential ablation at the center of the target, and the susceptor was rotated at 20 deg/s The target to wafer distance was fixed at 9.5 cm. The substrate was heated by means of a coiled resistive element located approximately 3 mm from the substrate wafer. The pressure was controlled for both O_2 and Ar processes by flowing the appropriate volume of gas and setting the turbo pump to 250 Hz. The number of laser pulses was chosen to achieve film thicknesses of 30 to 300 nm.

To determine donor N_D and acceptor N_A concentrations, temperature-dependent Hall-effect measurements were carried out over a range of 15–320 K using a Lakeshore 7507 apparatus. The values of n were independent of temperature, and those of μ and ρ, only slightly dependent. It is instructive to compare n for a sample grown in Ar (called the "Ar layer") with that of one grown in O_2 (the "O_2 layer"). Since the O_2 layer had earlier been grown on SiO_2/Si, the Ar layer was also grown on this material; however, up to this point we have noticed no great dependence of n on choice of substrate. The Ar-layer thickness was 82 nm, as measured by spectroscopic ellipsometry (SE), and the O_2-layer, 99 nm. In the as-grown O_2 layer, n was low, about 6×10^{19} cm^{-3}. As mentioned earlier, such a low value of n is probably due to high concentrations of V_{Zn}–related acceptors in the bulk and O_2-related acceptors at the GBs. However, when the O_2 layer was annealed in FG at 400 °C for 10 min, n increased greatly, up to about 4.3×10^{20} cm^{-3}. This increase is likely due to the H-induced reduction of O_2 from the GBs and the H passivation of V_{Zn}, i.e., $V_{Zn}+2H \rightarrow V_{Zn}-2H$. On the other hand, the Ar layer has a high value of n, *as deposited*, about 8.1×10^{20} cm^{-3}. Upon annealing in FG, n actually decreases slightly, while the mobility μ increases slightly, a scenario that can be explained only by a *decrease* in the donor concentration N_D. This observation is not in line with conventional wisdom which would have predicted an increase in N_D, due to the addition of H donors, and a decrease in N_A, due to the passivation of acceptors. Thus, the role of H is unclear in this case.
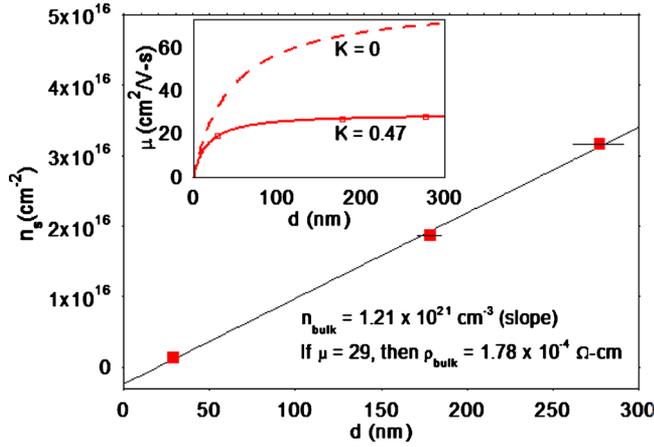
FIG. 1. (Color online) Plots of sheet carrier concentration as a function of layer thickness for samples grown on Al_2O_3. Inset: mobility as a function of thickness. The squares are measured data and the solid line is a fit to these data, with n=1.2×10^{21} cm^{-3} and K=0.47. The dashed line is the hypothetical mobility for n=1.2×10^{21} cm^{-3} and K=0, or equivalently, $N_A \ll N_D$.

Thicknesses of Ga-doped $ZnO/SiO_2/Si$ films deposited in oxygen are routinely measured using SE with a well-established model for the layer stack. However, as the optical constants of Ga-doped ZnO films deposited in Ar have not been fully characterized, the films were deposited on Al_2O_3 to assure correct thicknesses for ρ and n calculations. An abrupt step was obtained for profilometer (Tencor P-10) measurements by partially masking the Ga-doped ZnO film, then immersing the wafer into an acid solution known to have a high selectivity for ZnO/sapphire, (1:1000 HCL:deionized water). In Fig. 1, sheet carrier concentration n_s versus thickness d is plotted with error bars indicated for the two thickest samples. The data were taken at room temperature but there is very little change in n from 15–320 K. Within error, the points fall on a straight line, and the slope of this line is just the volume carrier concentration n=1.2×10^{21} cm^{-3}. (More points will be needed to determine if there is a slight nonlinearity in the data.) The y-axis intercept, -2×10^{15} cm^{-2}, can perhaps be interpreted as a depletion charge due to acceptors in the ZnO/Al_2O_3 interface region; however, again more points will be necessary to provide a definite conclusion in this matter.

The room-temperature mobilities of the three points are plotted as a function of thickness in the inset of Fig. 1. For samples such as these, the low-temperature mobilities are only slightly higher than those at room temperature. This is because most of the scattering is due to the ionized donors and acceptors, rather than phonons, even at room temperature. To fit the mobility data we apply a recently developed model that includes degenerate Brooks–Herring theory along with an empirical formula for boundary scattering, as follows:[5]

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

where

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

and

$$\mu_{ii}(n,K) = \frac{24\pi^3\varepsilon_0^2\hbar^3}{Z^2 e^3 m^{*2}}\frac{n}{N_{ii}}\frac{1}{\ln[1+y(n)] - \dfrac{y(n)}{1+y(n)}}$$

$$= \frac{146.9}{\ln(1+6.46n_{20}^{1/3}) - \dfrac{6.46n_{20}^{1/3}}{1+6.46n_{20}^{1/3}}}\frac{1-K}{1+K}\left(\frac{cm^2}{V\,s}\right). \quad (3)$$

Here, d_{nm} is the layer thickness in units of nm, n_{20} is the carrier concentration in units of 10^{20} cm^{-3}, and C is an empirical constant which depends on the details of surface and interface scattering. For the samples discussed in Ref. 5, a value of C=4 best fits the data, while for the three points presented in Fig. 1, C=2.5 gives a good fit. The other fitting parameter is K=0.47, and since $K=N_A/N_D$ and $n=N_D-N_A$, we get finally, N_D=2.3×10^{21} cm^{-3} and N_A=1.1×10^{21} cm^{-3}. These numbers must be considered tentative but clearly the layer has a very high donor concentration, composed mostly of Ga. Unfortunately, the layer also has a high acceptor concentration, and a key goal of TCO development is to get rid of the acceptors. Note that if n were the same but $N_A \ll N_D$ (i.e., $K\sim0$), then μ versus d would follow the dashed line in the inset of Fig. 1, and the resistivity for thick samples would drop by about a factor three at room temperature. For very thin samples, of course, surface/interface scattering, and ultimately quantum effects, will always limit the mobility.

Unalloyed Ohmic contacts were fabricated using e-beam evaporated Ti/Pt/Au:20/30/350nm at room temperature. Excellent specific contact resistance values of $2-4\times10^{-8}$ Ω cm^2 were measured using the transmission line method (TLM). Temperature stress tests were applied to samples in air at temperatures up to 350 °C by keeping samples at each temperature step for 1 h. No significant change in contact resistivity was observed in this temperature range. At higher temperatures, alloyed contacts were formed and the contact resistance dropped sharply. The bulk resistivity also was not strongly affected by the stress tests, increasing from 5×10^{-4} to 7×10^{-4} Ω cm, indicating that both the conductivity of the films and the unalloyed Ohmic contacts are stable with temperature.

For transparent electrode applications, the most important parameters are the sheet resistance ρ_s and the optical transmittance OT. For the 277 nm sample in Fig. 1, ρ_s=7.1 Ω/sq, a very impressive value. Unfortunately, the backsides of our Al_2O_3 wafers were not polished, so it was necessary to measure OT on other layers, grown on polished quartz. In Fig. 2, the wavelength dependence of the transmittance, measured with a Varian Cary 5000 spectrophotometer, is shown for Ar and O_2 layers grown on quartz under conditions nearly identical to those pertaining to the samples of Fig. 1. We note that the OT for as-deposited O_2 layers (not shown) is nearly 90% from the band edge all the way to 2500 nm but unfortunately the conductivity of such layers is too low for TCO applications. For the highly conductive layers, i.e., the O_2 layers annealed in FG, and the as-grown Ar layers, the transmission above 1000 nm decreases due to free-carrier absorption, as expected. The decrease in this region is higher for the Ar layer because its carrier concentration is higher; however, in the visible region, the Ar layer has a slightly better transmittance.
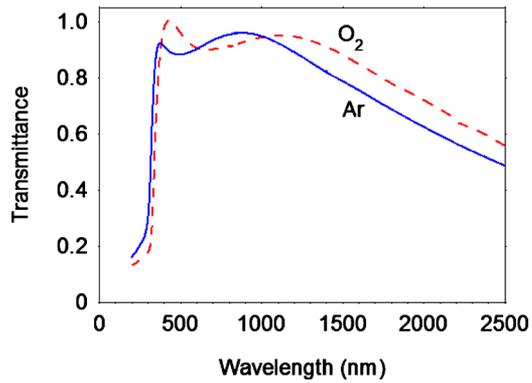
FIG. 2. (Color online) Optical transmittance as a function of wavelength for Ga-doped ZnO deposited at 200 °C and 10 mTorr in Ar (solid line) and O_2 (dashed line).

In conclusion, highly conductive Ga-doped ZnO with excellent optical transparency has been achieved at low deposition temperatures using PLD in a pure Ar environment without the need for postdeposition anneals. The significant increase in conductivity is attributed mainly to improved Ga incorporation on donor sites, although a detailed model of growth dynamics has yet to be worked out. Sheet resistance versus thickness data suggest that the bulk carrier uniformity in thick films grown in Ar is much better than that for thick films grown in O_2 and then annealed in FG.

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