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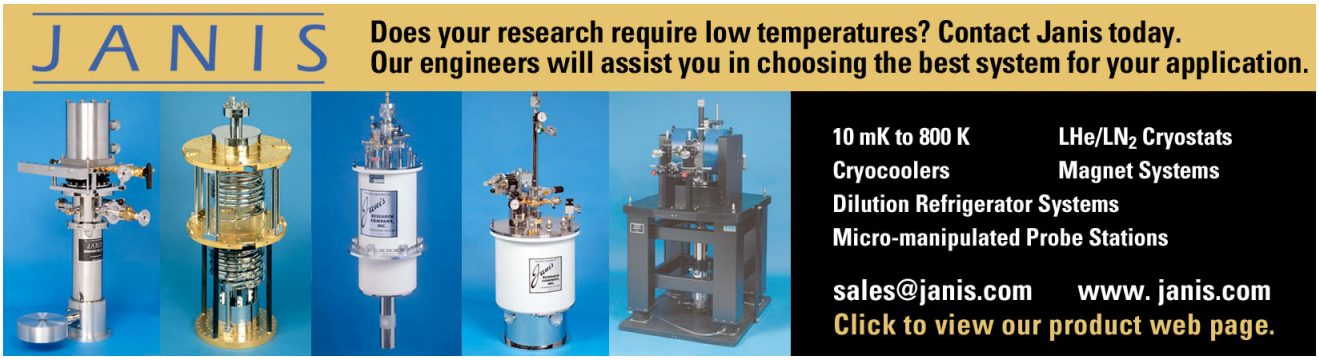

Stable highly conductive ZnO via reduction of Zn vacancies

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Growth of Ga-doped ZnO by pulsed laser deposition at 200 °C in an ambient of Ar and H_2 produces a resistivity of 1.5×10^{-4} Ω-cm, stable to 500 °C. The resistivity can be further reduced to 1.2×10^{-4} Ω-cm by annealing on Zn foil, which reduces the compensating Zn-vacancy acceptor concentration N_A to 5×10^{19} cm^{-3}, only 3% of the Ga-donor concentration N_D of 1.6×10^{21} cm^{-3}, with N_D and N_A determined from a degenerate mobility theory. The plasmon-resonance wavelength is only 1060 nm, further bridging the gap between metals and semiconductors. © *2012 American Institute of Physics*. [http://dx.doi.org/10.1063/1.4748869]

Highly conducting thin films of ZnO are useful in applications such as transparent electrodes (TEs) for flat-panel displays, solar cells, and light-emitting diodes.[1–5] For such electrodes, Al- and Ga-doped ZnO are the prime candidates to replace the present workhouse material, Sn-doped In_2O_3, called ITO.[1] The key figures of merit for TEs are the resistivity ρ and the optical transmission OT in the visible and near-IR (NIR) regions. In the visible region, OT will be mainly limited by the reflectance $R(\varepsilon_\infty)$, which is about 0.1 for ZnO ($\varepsilon_\infty \approx 3.8\varepsilon_{vac}$). In the NIR region, R increases due to the excitation of plasmons, characterized by a resonance frequency $\omega_{p,res} = (e^2 n/m^* \varepsilon_\infty)^{1/2}$, or resonance wavelength, $\lambda_{p,res} = 2\pi c/\omega_{p,res}$, where all symbols have their usual meanings. For concentration $n = 1.46 \times 10^{21}$ cm^{-3} (this study), $\lambda_{p,res} = 1058$ nm, so R will begin to increase (and OT decrease) rapidly near this wavelength. The decreased OT is detrimental to solar cells, since a greater part of the solar spectrum is lost, but it may be useful for IR filter designs. In any case, the *control* of n, up to 1.5×10^{21} cm^{-3} in our case, is an extremely valuable asset for plasmonic applications, one that metals do not possess.

Many groups have achieved low resistivities in ZnO, and at least five have reported resistivity $\rho \leq 1.3 \times 10^{-4}$ Ω-cm.[1–5] In cases for which n and mobility μ are also reported, it is now possible to roughly calculate donor N_D and acceptor N_A values by employing a recently developed mobility model.[6] For the n and μ values in a few of these reports, our calculations of N_D and N_A give negative values of the latter, which is unphysical. These problems, of course, could result from typographical errors in the data or from a deficiency in our mobility model. In other reports, the relationship $\rho = 1/(en\mu)$ is not satisfied, which can result only from errors in one or more of the quantities ρ, μ, and n. But in spite of potential inconsistencies in some cases, it appears that resistivities at least as low as 1.1×10^{-4} Ω-cm are reasonable. In this work, we show that resistivities as low as 1.2×10^{-4} Ω-cm and concentrations as high as 1.5×10^{21} cm^{-3} may be consistently achieved in common pulsed-laser-deposition (PLD) systems, and that they are stable, increasing less than a factor-two during a 500 °C, 10-min anneal in air. Moreover, if lower concentrations are desired for longer-wavelength plasmonic applications, we can simply anneal the sample in air above 500 °C. For example, in one study, a 600 °C, 10-min anneal in air reduced n from 1.4×10^{21} cm^{-3} to 2.0×10^{18} cm^{-3}. At this concentration, $\lambda_{p,res} = 25$ μm, showing that a simple air anneal allows a very large range of plasmonic-resonance control.

Four, Ga-doped ZnO samples were grown sequentially by PLD using a ZnO target containing 3 wt. % Ga_2O_3. The substrates were 2-inch-diameter c-plane Al_2O_3 wafers, held at 200 °C during growth, and the ambients were 10 mTorr mixtures of H_2 and Ar having ratios H_2/Ar = 0/100, 33/67, 67/33, and 100/0, which we will also use as the four sample designations. We have previously shown that the growth of ZnO by PLD at 200 °C in pure Ar produces material of very high conductivity.[7] Although PLD growth of ZnO in high partial pressures of H_2 is not common, the group at Pacific Northwest National Laboratories has used it in the past.[8,9] Unfortunately, an equipment malfunction occurred during the 100/0 growth, so this sample could not be easily compared to the other three. Furthermore, it was found that the electrical and optical properties of the 67/33 wafer were similar to those of the 33/67 wafer. Thus, in this study, only the 0/100 and 33/67 wafers were analyzed and were sufficient to determine the effects of a high H_2 fraction in the ambient.

To begin with, it was necessary to establish accurate thicknesses, because this parameter is extremely important for the calculations of ρ and n, especially when excellent values are claimed. In this regard, wafer 33/67 was mapped by Rutherford backscattering spectrometry (RBS) measurements at several points, and a thickness of 620 ± 10 nm was obtained over a center portion of about 1-cm diameter. Several other optical and mechanical methods were also explored and a reliable process to determine thickness was developed: (1) cut out a 5-mm × 5-mm sample close to the sample being characterized; (2) pattern the sample and then etch off half of it down to the Al_2O_3 substrate; and (3) measure the resulting step height by scanning white-light interferometry (SWLI) at three positions. This procedure gave

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TABLE I. Improvements in room-temperature mobility and concentration from annealing on Zn or Zn/Ga foil at 550 °C for 10 min in forming gas. Donor and acceptor concentrations are determined from the theoretical fits.

Sample	Treatment	ρ_{RT} (Ωcm)	μ_{RT} (cm^2/Vs)	n_{RT} (cm^{-3})	N_D (cm^{-3})	N_A (cm^{-3})	N_A/N_D
0/100	as-grown	1.55×10^{-4}	29.0	1.39×10^{21}	1.61×10^{21}	1.30×10^{20}	0.081
0/100	Annealed: Zn	1.29×10^{-4}	33.7	1.44×10^{21}	1.57×10^{21}	0.64×10^{20}	0.041
33/67	as-grown	1.49×10^{-4}	30.6	1.36×10^{21}	1.55×10^{21}	1.02×10^{20}	0.066
33/67	Annealed: Zn/Ga	1.23×10^{-4}	34.8	1.46×10^{21}	1.52×10^{21}	0.48×10^{20}	0.031

values of 568 ± 10 nm for 0/100 and 574 ± 10 nm for 33/67. The conclusion from the RBS and SWLI measurements was that the centers of the two wafers were roughly the same thickness d, and that the absolute value of d was somewhere in the range 570–620 nm. We will use the higher (more conservative) value for the calculations in Table I.

Samples of size 5-mm × 5-mm were investigated by temperature-dependent Hall-effect measurements over the range 15–320 K with a LakeShore 7507 apparatus. Ohmic contacts were achieved by soldering small dots of indium onto the corners. In all cases, n was constant as a function of temperature while mobility μ began to drop gradually at about 100 K and was typically about 15% lower at room temperature (RT). The temperature dependence of μ was reproduced accurately by a degenerate-semiconductor theory, and allowed good determinations of N_D and N_A from measurements of n and μ, a unique feature of this study.[6,10] The detailed theory with all equations is available in Ref. 6, and a convenient graphical determination of N_D and N_A is presented in Ref. 10.

The plots of μ(T) are presented in Fig. 1, along with their theoretical fits. Our orginal theory[6] is based completely on scattering formulas from the literature except that the formula for polar-optical mobility is multiplied by a slowly varying factor F(T). For most sample sets we have examined so far, the form $F(T) = 0.93\exp(T/T_{po})$ gives excellent fits to μ vs T, over the whole range of 10–320 K. However, for the present samples, grown in a different laboratory, we get better fits with $F(T) = 0.70\exp(T/T_{po})$. It is possible that this difference is due to the higher inhomogeneity of these samples, which were grown in a PLD apparatus with a smaller target

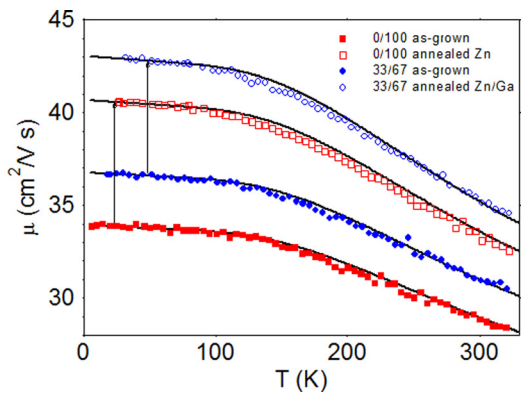

FIG. 1. Improvements in mobility from annealing on Zn or Zn/Ga foil at 550 °C for 10 min in forming gas. Closed (open) squares represent as-grown (annealed) sample 0/100; closed (open) circles represent as-grown (annealed) sample 33/67. The solid lines are theoretical fits. The arrows denote the transition from as-grown to annealed.

to substrate distance. In any case, the values of N_D and N_A are not affected by the different forms of F(T), since N_D and N_A are calculated from μ and n at low temperature, where polar-optical scattering is not important. The experimental values of ρ, μ, and n at RT, and the calculated values of N_D and N_A are given in Table I.

The first interesting observation is that the RT values of ρ, μ, and n for 0/100 are very close to those (not shown) of samples grown two years earlier in another PLD apparatus of different design.[7] This confirms the robust character and repeatability in the PLD growth of Ga-doped ZnO in Ar at 200 °C. Also, in the earlier studies,[6,10] we found from secondary-ion mass spectroscopy (SIMS) that $N_D \approx [Ga]$, showing that most of the Ga atoms reside on Zn sites, as donors, and that other impurity- or defect-related donors are not significant. More importantly, in Ref. 6 we showed that the dominant acceptor in our Ga-doped ZnO was the Zn vacancy V_{Zn}. This fact suggested a method of reducing the acceptor concentration, i.e., by filling the V_{Zn} with Zn. It was also evident that an even better improvement would result from filling the V_{Zn} with Ga, thus both destroying an acceptor and creating a donor. In the present study, we are testing both of these hypotheses.

First of all, we placed sample 0/100 face-down on Zn foil and annealed it at 550 °C for 10 min. This action reduced N_A from 1.30×10^{20} cm^{-3} to 0.64×10^{20} cm^{-3} while leaving N_D roughly constant, and reduced ρ to 1.29×10^{-4} Ω-cm, an excellent value considering the simplicity of the growth and annealing. This decrease in N_A confirms our hypothesis about the possibility of filling the Zn vacancies with Zn.

Next, we consider sample 33/67. In this case, we annealed the sample face-down on Zn/Ga foil, hoping that Ga, rather than Zn, would fill at least some of the V_{Zn}. However, the main effect was again a reduction of N_A, not an increase of N_D. We could possibly increase N_D with a higher fraction of Ga in the Zn foil, and future effort will be directed along these lines. In any case, the final resistivity is a superb 1.23×10^{-4} Ω-cm, among the best ever reported.

It is important to point out that, although this study is concerned with *Ga-doped* ZnO, these ideas should be applicable to nearly *all* strongly n-type ZnO materials, whatever the donor dopant. The reason is that V_{Zn} defects will have a low formation energy in such material and will usually provide most of the compensating acceptors since it is unlikely that any impurity-related acceptors will be available in the $>10^{20}$-cm^{-3} range. A detailed discussion of this topic can be found in Ref. 6.

A comparison of as-grown samples 0/100 and 33/67 is instructive because the latter was grown in 33% H_2, and the

role of H in ZnO has been highly studied but is still ambiguous and controversial. From Table I, we see clearly that H does not increase the donor concentration, which is somewhat surprising in light of the donor nature of H in ZnO.[11] Indeed, the lower resistivity of 33/67 is totally due to a decrease in N_A, not an increase in N_D. To study this issue further, SIMS analysis was performed on 33/67, and showed that $[H] \approx 2 \times 10^{19}\,cm^{-3}$, only about 1% of N_D. It is possible that this H was active in passivating acceptors, but not in creating donors. With regard to the former, note that as-grown $N_A(0/100) - N_A(33/67) = 2.8 \times 10^{19}\,cm^{-3}$ and the concentration of H that would be necessary to explain this through the creation of neutral V_{Zn}-H_2 species[12] in 33/67 would presumably be $2(2.8 \times 10^{19}) = 5.6 \times 10^{19}\,cm^{-3}$, perhaps within error of the SIMS result. Thus, acceptor neutralization might be one of the advantages of PLD growth in H_2. However, basic PLD growth mechanisms may also be affected by H in the ambient and such possibilities should be investigated further. In any case, we can conclusively state that the principal role of H in our PLD growth of highly doped ZnO is not a supplement of the Ga donors, but may possibly involve a passivation of V_{Zn} acceptors.

In summary, we have produced very highly conductive ZnO layers by pulsed laser deposition on Al_2O_3, with resistivities as low as $1.2 \times 10^{-4}\,\Omega$-cm. This low value has been achieved by first determining that the dominant acceptor was the Zn vacancy V_{Zn}, rather than any impurity, and then promoting the reaction $Zn_I + V_{Zn} \rightarrow Zn_{Zn}$ by means of a simple anneal on Zn foil. We further attempted to replace the V_{Zn} with Ga ($Ga_I + V_{Zn} \rightarrow Ga_{Zn}$), thus replacing an acceptor with a donor, but the dominant process still seemed to be $Zn_I + V_{Zn} \rightarrow Zn_{Zn}$. However, a larger amount of Ga in the Zn foil may be effective in producing Ga_{Zn} and realizing even lower values of ρ. The highest carrier concentration achieved so far, $n = 1.46 \times 10^{21}\,cm^{-3}$, leads to a plasmon-resonance wavelength of 1058 nm, getting close to metal-based plasmonic resonances in the UV and visible regions. Moreover, the great advantage of semiconductors as plasmonic elements is that they are tunable and not as lossy as metals. Thus, they open up additional areas of application.[13]

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