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David C. Look
Wright State University - Main Campus, david.look@wright.edu

G. M. Renlund

R. H. Burgener

J. R. Sizelove

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As-doped *p*-type ZnO produced by an evaporation/sputtering process

D. C. Look[a)]
Materials and Manufacturing Directorate, Air Force Research Laboratory, Wright-Patterson Air Force Base, Ohio 45433 and Semiconductor Research Center, Wright State University, Dayton, Ohio 45435

G. M. Renlund and R. H. Burgener II
ON International, Inc., 418 West Winchester Street, Salt Lake City, Utah 84107

J. R. Sizelove
Materials and Manufacturing Directorate, Air Force Research Laboratory, Wright-Patterson Air Force Base, Ohio 45433

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Strongly *p*-type ZnO is produced by the following sequence of steps: (1) evaporation of Zn_3As_2 on a fused-quartz substrate at 350 °C; and (2) sputtering of ZnO with substrate held at 450 °C. The electrical characteristics include: resistivity of 0.4 Ω cm, a mobility of 4 $cm^2/V\,s$, and a hole concentration of about 4×10^{18} cm^{-3}. This resistivity is among the best (lowest) ever reported for *p*-type ZnO. Secondary-ion mass spectroscopic analysis gives an average As concentration about 5×10^{19} cm^{-3}, and a simple one-band fit of the temperature-dependent mobility curve yields an acceptor concentration of about 9×10^{19} cm^{-3}. This is strong evidence that the *p*-type dopant involves As, although it is not clear whether the acceptor is simply As_O or the recently suggested $As_{Zn}-2V_{Zn}$. © *2004 American Institute of Physics*. [DOI: 10.1063/1.1825615]

Crystalline ZnO has been studied for more than 50 years,[1–3] and bulk or epitaxial samples ranging from highly conducting to semi-insulating are now commercially available.[4,5] However, the conduction properties are not easily controlled, and virtually all "undoped" ZnO materials are *n*-type, evidently due to background donor impurities such as Al and H, and native defects such as the Zn interstitial.[1,6–9] Indeed, the production of *p*-type ZnO has proven to be very difficult, and has hindered the development of ZnO-based blue/UV $p-n$ junction light-emitting diodes (LEDs) and laser diodes (LDs). In the last few years, research on *p*-type ZnO has proceeded at a more rapid pace,[10–30] in spite of the fact that GaN-based blue LEDs and LDs have already been developed and have found many applications. The reason is that ZnO has some fundamental advantages over GaN as a room-temperature emitter, including a more stable exciton, the availability of large-area substrates, the amenability to wet chemical etching, a high radiation resistance, and relatively low materials costs.[3]

A perusal of the periodic table suggests that possible acceptor candidates for ZnO include Group I elements Li, Na, K, Cu, Ag, and Au, substituting for Zn, and Group V elements N, P, As, and Sb, substituting for O. Although most of these elements have been tested as dopants, only N, P, and As, have produced low-resistivity (<100 Ω cm), *p*-type material, to our knowledge. Several groups have found success with N doping,[10,11,13,14,16,18–20,22–25,28,29] which is not surprising since the ionic radius of N is about that of O, so that N should be quite soluble as N_O. On the other hand, there are only a few reports of *p*-type ZnO from P[21,27,30] or As[12,26] doping, and almost no reports involving any of the other possible dopants. In this letter, we discuss an evaporation/sputtering method of creating As-doped, *p*-type ZnO. This technique has produced *p*-type samples with resistivities as low as 0.1 Ω cm, lower than any others reported so far.

[a)]Electronic mail: david.look@wpafb.af.mil

Growth was accomplished by first evaporating a layer of Zn_3As_2 on a glass substrate at 350 °C, then sputtering ZnO on top of the Zn_3As_2 at 450 °C. Secondary-ion mass spectroscopic (SIMS) data[31] for layer 12 503 are presented in Fig. 1. The As concentration is accurately determined by comparison with an ion-implanted standard, while the Zn and O concentrations are simply normalized at the surface to their atomic values of about 4×10^{22} cm^{-3}. An important observation from the Zn and O profiles is that they are quite flat over most of the sample, which strongly suggests that the layer is basically ZnO. Further evidence comes from x-ray rocking curves (not shown), which show a dominant (0002) ZnO reflection.

Note in Fig. 1 that the As signal is very strong in the bottom 0.1 μm of the layer, and then quickly reduces to the mid-10^{19} cm^{-3} range. We interpret the lower part of the SIMS As profile as possibly representing some remaining Zn_3As_2, or some As metal, if all of the Zn has reacted to form ZnO. Experiments were performed to test the possible electrical activity of this As-dominated layer, especially since

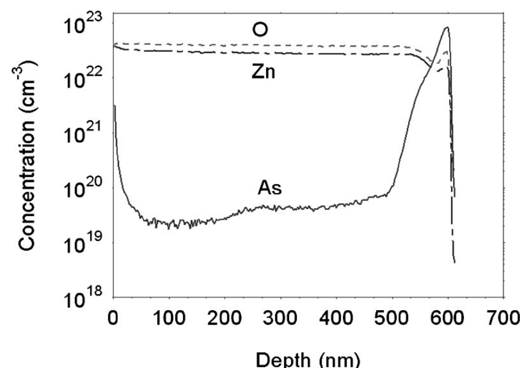

FIG. 1. SIMS measurements of O, Zn, and As in As-doped *p*-type ZnO. The As concentration is determined from an ion-implanted standard, while the O and Zn concentrations are normalized at the surface to roughly their atomic concentrations of 4×10^{22} cm^{-3}.

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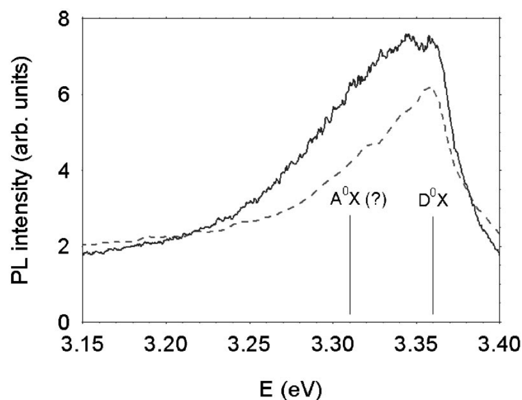

FIG. 2. PL (at 4 K) in two As-doped *p*-type ZnO samples. The dashed line is from a clear region while the solid line represents a darker region, evidently more heavily doped.

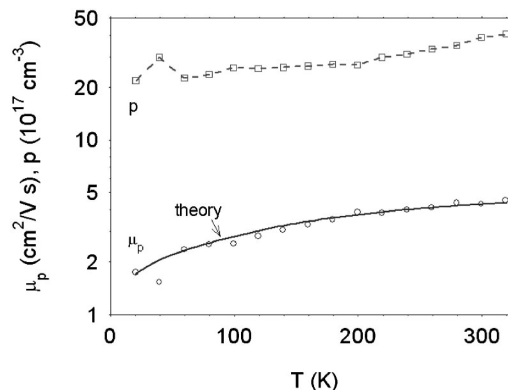

FIG. 3. Hole mobility and concentration in As-doped *p*-type ZnO. The solid curve is a theoretical fit of the mobility assuming a single hole band represented by effective mass $m^*=0.64\, m_0$, and a fitting parameter $N_D=8 \times 10^{19}$ cm^{-3}.

both pure Zn_3As_2 and As metal are known to be *p*-type, in single-crystalline form. In one such test, the sputtered ZnO was constrained to only partially overlap the evaporated Zn_3As_2, so that three different regions (ZnO, Zn_3As_2, and ZnO/Zn_3As_2) could be examined separately, after the annealing step was completed. The pure ZnO region turned out to be *n*-type, as expected, while the ZnO/Zn_3As_2 was *p*-type, and the Zn_3As_2, semi-insulating. Thus, it is doubtful that the Zn_3As_2 could account for the *p*-type conductivity, in this case. Another possibility is that the layer under the ZnO, after all of the processing, is As metal. However, the resistivity of a metal is known to *increase* with temperature, and that of our sample decreases. Thus, we believe that the lower As-rich layer, whether Zn_3As_2 or metallic As, is not responsible for the *p*-type activity in our material. The rest of the As profile is reasonably flat at the mid-10^{19} cm^3 level, which suggests that the main part of the ZnO layer is doped with As by a gas-phase reaction, rather than a diffusion process. However, these issues require further study.

As seen in Fig. 2, 4 K photoluminescence (PL) data show a broad peak in the 3.36 eV region, which is well known as the region of donor-bound exciton (D^0X) lines in ZnO. This is further strong evidence that the layer is basically ZnO, and not some undefined mixture of Zn, O, and As. The two PL lines in Fig. 2 are from adjacent areas near the edge of the overlapping ZnO and Zn_3As_2 regions, mentioned earlier. The dotted line represents a clear (but still *p*-type) area close to the pure (nonoverlapping) ZnO region, and the solid line, a darker area just inside the overlapping ZnO/Zn_3As_2 region. The darker area is presumably more heavily doped with As, and indeed has a stronger *p*-type conductivity. Previous PL studies in N-doped and P-doped *p*-type ZnO have shown that the D^0X spectrum moves to lower energies in these materials, enhancing the region of the well-known 3.357 eV feature, and that a new line appears in the 3.31 eV region.[19,27,32] Although the identities of these lines are still controversial, there is some evidence that each results from acceptor-bound excitons.[19,33] Whatever its identity, the 3.31 eV line has been found to be associated particularly with *p*-type ZnO, which strengthens the conclusions of the present work.

The temperature-dependent carrier concentration p and mobility μ_p are displayed in Fig. 3. Since the holes are neither fully degenerate nor fully nondegenerate, the curves are not easily amenable to quantitative fitting. However, we have attempted to fit the mobility with a single-band scattering model based on a hole mass of 0.64. (This mass is derived from the assumption that N_O is a hydrogenic acceptor with a transition energy $E_{A0}=133$ meV at low acceptor concentrations. The latter value is estimated from: (1) Hall data,[34] which give $E_A \sim 90$ meV at $N_A \sim [N] \sim 10^{19}$ cm^{-3}; and (2) the screening formula, $E_A=E_{A0}-\beta N_A^{1/3}$, with $\beta \sim 2 \times 10^{-5}$ meV cm. The mobility fit is surprisingly good, with a fitting parameter 8×10^{19} cm^{-3} for the donor concentration N_D. The acceptor concentration N_A would then have to be about 9×10^{19} cm^{-3}, since the hole concentration at high temperature is in the 10^{19} cm^{-3} range. In view of the rather severe approximations involved in the scattering model, it is seen that N_A is quite consistent with the As concentration of about 5×10^{19}. It is doubtful that the agreement would be this good if the measured layer did not basically consist of As-doped ZnO, as claimed in this work.

Thus, the SIMS, x-ray diffraction, PL, and *T*-dependent Hall-effect measurements all indicate that the evaporation/sputtering method discussed here produces low-resistivity, As-doped, *p*-type ZnO. However, the microscopic structure of the As-related acceptor is not clear at this point. The simplest structure would be As_O, but density-functional theory suggests that the large ionic radius of As would preclude a high solubility for As_O, and also that the consequent strain relaxation would lead to a deep, not shallow, acceptor.[35] Another possibility, recently presented, is that the structure is much more complex, namely, As_{Zn}-$2V_{Zn}$, in which the As substitutes on the Zn site, forming a donor, but that it then induces two Zn-vacancy acceptors.[36] The total defect is then acceptor-like, with a (0/−) transition at 0.15 eV above the valence band. This energy is consistent with our results, but more rigorous confirmation would require analysis of Hall-effect measurements in a nondegenerate sample. The As_{Zn}-$2V_{Zn}$ defect also presumably has a significantly lower formation energy than that of As_O, thus predicting a much higher solubility. At this stage, we cannot positively identify either of these structures in our material.

In summary, we have used an evaporation/sputtering method to produce As-doped, *p*-type ZnO. Structural, optical, and electrical properties are all consistent with this conclusion, and the resistivity, an important figure of merit, is among the lowest ever reported for *p*-type ZnO. The dominant acceptor is related to As, but its microscopic structure is not yet established.

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