Zinc-indium-oxide: A high conductivity transparent conducting oxide

Julia M. Phillips, R. J. Cava, G. A. Thomas, S. A. Carter, J. Kwo, T. Siegrist,
J. J. Krajewski, J. H. Marshall, W. F. Peck, Jr., and D. H. Rapkine
AT&T Bell Laboratories, Murray Hill, New Jersey 07974

(Received 7 November 1994; accepted for publication 6 August 1995)

We report the fabrication and characterization of zinc-indium-oxide films with similar electrical conductivity and better transparency in both the visible and infrared compared with indium–tin–oxide, a widely used transparent conductor in many technological applications. Dramatically superior transmission properties in the 1–1.5 μm range in particular make zinc–indium–oxide attractive for use in infrared devices, where transparent electrodes are required. Resisitivities as low as 400 $\mu\Omega$ cm result from doping with small quantities of Sn; Al, Ga, and Ge are also effective dopants. Deposition on glass and quartz substrates as amorphous films by pulsed laser deposition and dc reactive sputtering is described. © *1995 American Institute of Physics.*

Several transparent conducting oxides (TCOs), such as indium-tin-oxide (In_2O_3:Sn, ITO), ZnO:Al, and SnO_2:F have been investigated extensively.[1–5] Of these, indium–tin–oxide (ITO) has become the preferred TCO for a wide variety of applications. Typical ITO films have a sheet resistance of 10 Ω/square [i.e., a conductivity of about $2.5–5\times10^3$ $(\Omega\ \mathrm{cm})^{-1}$], which is inadequate for future technologies such as flat panel displays. Increasing the thickness of the ITO to lower the sheet resistance leads to unacceptable light absorption. Even given currently attainable sheet resistances, there is a need for a conductor with better transparency across the visible spectrum, especially in the green-blue region. Other applications such as contacts for surface emitting lasers require materials that are transparent in the infrared, especially in the 1.0–1.5 μm region, where ITO is strongly absorbing. Meeting these challenging goals requires a major improvement in the properties of materials used as transparent conductors.

$GaInO_3$ is a recently identified transparent conductive material.[6,7] While its optical properties are considerably better than those of ITO, it suffers from a resistivity that is approximately ten times higher than that of state-of-the-art material. This has motivated the search for a new material with transparency similar to that of $GaInO_3$, but with enhanced conductivity, approaching that of ITO. Our studies of zinc-indium-oxide show it to satisfy these criteria.

Polycrystalline pellets suitable for pulsed laser deposition (PLD) or sputtering targets are synthesized from ZnO, In_2O_3, and SnO_2 weighed out in the appropriate mole ratios to yield $Zn_xIn_{2-y}Sn_yO_{3+x-\delta}$ for $1.4\leqslant x\leqslant4.0$ and $0\leqslant y\leqslant0.4$. The powders are mixed together and ground in a mechanical mortar and pestle for 15 min. They are then fired in high density Al_2O_3 crucibles in air for 15 h at 1100 °C, reground, and fired at 1200 °C for 15 h in air. After a third grinding, pellets are pressed in a standard steel dye (3000 lb on a 0.5 in. pellet) and heated at 1300 °C in air for up to 16 h. Pellets are typically buried in powder of their own composition inside the covered Al_2O_3 crucibles for the pellet firing step. The pellets are then cooled at the natural cooling rate of the furnace, reaching 300 °C in approximately 2 h, at which point they are removed. PLD and sputtering targets of $Zn_{2.5-x}Al_xIn_2O_{5.5+0.5x-\delta}$, $Zn_{2.5-x}Ga_xIn_2O_{5.5+0.5x-\delta}$, and $Zn_{2.5-x}Ge_xIn_2O_{5.5+x-\delta}$ are prepared by the same method with the use of Al_2O_3, Ga_2O_3, or GeO_2 in place of SnO_2 as a starting material. The bulk material after air firing is not optimal, requiring a reduction treatment to improve the conductivity. In this treatment, pellets are heated for 10–12 h in flowing N_2 (approximately 100 cc/min, N_2 containing approximately 50–100 ppm O_2) in a ceramic tube furnace at 1200 °C, and again allowed to cool at the natural furnace cooling rate. Alternatively, the pellets are reduced in flowing forming gas (85% N_2, 15% H_2) by heating at 400 °C for 1 h.

The best conductive properties of conventional polycrystalline ceramic samples are associated with the chemical compound $Zn_3In_2O_6$. Single phase well crystallized material of composition $Zn_3In_{2-x}Sn_xO_6$ for $0.0\leqslant x\leqslant0.15$ can be synthesized from ZnO, In_2O_3, and SnO_2 mixed and mechanically ground for 1 h, then pressed into 0.5 in. pellets and fired in air, in a covered crucible, and buried in powder of its own composition. The firing schedule involves successive 8 h soaks at 1200, 1300, 1400, and 1500 °C. After the reduction treatment described above, optimal conductivity was obtained for $Zn_3In_{1.975}Sn_{0.025}O_6$. A metallic $\rho(T)$ results with resistivity of approximately 1.8 mΩ cm at room temperature and $\rho_{300\ \mathrm{K}}/\rho_{4.2\ \mathrm{K}}=1.17$.

PLD films are grown using a target of either pure or doped zinc–indium–oxide prepared as described above. $Zn_xIn_{2-y}Sn_yO_{3+x+0.5y-\delta}$ targets in the range $1.4\leqslant x\leqslant4$; $0\leqslant y\leqslant0.4$ have been used for most of the experiments using the conditions described previously.[7] Films with the highest conductivity and only slightly suboptimum transparency can be grown at a substrate temperature of 250 °C in an oxygen pressure of 1 mTorr. Film quality is independent of growth rate, which has been varied between ~3 and 8 nm/min. Optical microscopy shows the films to be featureless. Zinc–indium–oxide films can also be deposited by dc reactive sputtering in both on-axis and off-axis sputtering configurations as described in our previous work on $GaInO_3$.[7,8] The optimal O_2 pressure is about 0.5–1.0 mTorr; the growth rate is about 3 nm/min. As-grown films with the lowest resistivity (380 $\mu\Omega$ cm) can be prepared from a $Zn_{2.5}In_{1.7}Sn_{0.3}O_{5.65-\delta}$ target at a substrate temperature of 450 °C and have a composition of $Zn_{1.0}In_{1.7}Sn_{0.3}O_{4.15-\delta}$, measured by Rutherford backscattering spectrometry (RBS) as described below.

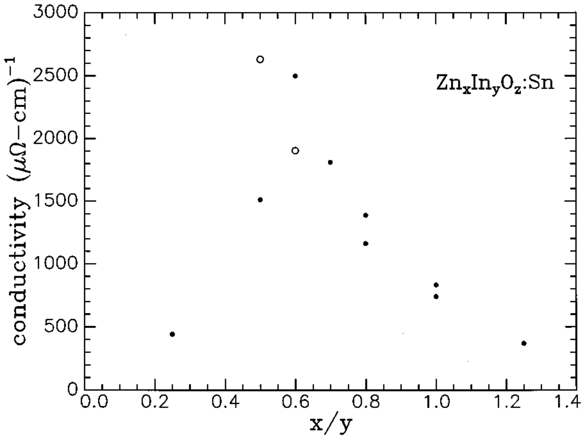

FIG. 1. The variation of conductivity with Zn/In ratio in $Zn_xIn_yO_z$:Sn films deposited by PLD (closed circles) and sputtering (open circles). The Sn/In ratio is in the range 0.05–0.18 for all films shown.

The films contain less zinc than do the targets, except for films deposited at room temperature. The ratio of Zn to (In +Sn), measured by RBS for all films, varies from as little as 0.25 for a target of composition $Zn_{1.4}In_{1.7}Sn_{0.3}O_{4.55-\delta}$ to 1.6 for target of composition $Zn_4In_{1.8}Sn_{0.2}O_{7.1-\delta}$. X-ray diffraction studies of the films deposited at room temperature or 250 °C reveal only a single diffuse feature, indicating that the films are amorphous with no long range order greater than ~2 nm. The only exception is the film with a Zn:(In +Sn) ratio of 0.25, in which the peaks can be indexed as In_2O_3. This film has considerably worse electrical properties than the best films. The best results are obtained for a target of composition $Zn_{2.5}In_{1.9}Sn_{0.1}O_{5.55-\delta}$ for PLD films deposited at 250 °C in 1 mTorr O_2, which yields a Zn:(In+Sn) ratio of 0.6. A target of composition $Zn_{2.5}In_{1.7}Sn_{0.3}O_{5.65-\delta}$ for off-axis sputtered films deposited at 450 °C in 0.5 mTorr O_2, yields a Zn:(In+Sn) ratio of 0.5. In both cases the film resistivity is $\leqslant 400$ $\mu\Omega$ cm.

The conductivity has been measured by a four-probe dc technique using silver paint to make contacts to the films. Hall measurements, in a 2 T field, yield an effective carrier density of 3.4×10^{20} cm^{-3} and a mobility of 46 cm^2/V s for a film of composition $Zn_{1.2}In_{1.9}Sn_{0.1}O_{4.25-\delta}$. These values are within the ranges typically reported for ITO films.[1–4] We have measured a sheet resistance of 3.5 Ω/square for a 1.4 μm thick film of this composition with transmission $\geqslant$80% over much of the visible region. Film conductivity σ depends strongly on the ratio of the number of Zn atoms to the number of (In+Sn) atoms as shown in Fig. 1. The conductivity is sharply maximized around a value of 0.5–0.6. Though the films are amorphous, this suggests the existence of a distinct chemical compound in the film near stoichiometry $Zn(In,Sn)_2O_4$ or $Zn_3(In,Sn)_5O_{10.5}$. $ZnIn_2O_4$ is a known stable spinel structure material, but $Zn_3In_5O_{10.5}$ is not known as a stable bulk phase. The chemical makeup of our zinc–indium–oxide films suggests that they may have significantly different etching, chemical compatibility, and aging characteristics than does ITO. This is worth consideration for technologies where processing or aging characteristics of ITO make it unsuitable for use.

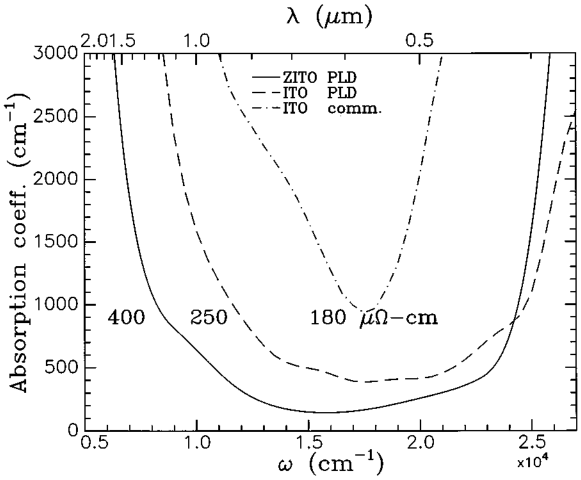

FIG. 2. Absorptoin coefficient α as a function of frequency ω (lower scale) and wavelength λ (upper scale) for a film deposited by PLD with a measured composition of $Zn_{1.2}In_{1.9}Sn_{0.1}O_{4.25-\delta}$ and a resistivity of 400 $\mu\Omega$ cm (solid line), an ITO film deposited under the same conditions with a resistivity of 250 $\mu\Omega$ cm (dashed line), and a commercial ITO film (supplied by Leybold) with a resistivity of 180 $\alpha\Omega$ cm (dot-dashed line).

The conductivity of as-grown PLD films with Sn doping increases with decreasing temperature, as expected for metallic behavior, with a slight downturn in σ occurring below 100 K due to disorder effects. The optimum conductivity occurs for a Sn doping of 0.1–0.3; however, we also observe high conductivities in samples containing no Sn. These results suggest that oxygen vacancies are donors of conduction electrons, as they are in ITO and $GaInO_3$.[2] Postannealing in a reducing environment, such as 15% H_2/N_2 or 100% N_2, at temperatures between 300 and 450 °C yields less than a 10% increase in the conductivities of the as-grown films. Annealing in an O_2 atmosphere results in a decrease in the conductivity, density of carriers, and optical band gap, with exposure at 450 °C for 2 h resulting in a transition to insulating behavior with a critical conductivity of 100 $(\Omega\ \mathrm{cm})^{-1}$.[9] The optical transparency of the films is destroyed on heating in the H_2/N_2 mixture of temperatures above 500 °C.

Figure 2 shows the absorption coefficient α as a function of frequency ω (and wavelength λ) for a PLD-deposited film with composition $Zn_{1.2}In_{1.9}Sn_{0.1}O_{4.25-\delta}$ with resistivity $\rho=400$ $\mu\Omega$ cm. The absorption coefficient is measured using a conventional Fourier-transform spectrometer. The transmitted light through the sample on its substrate (usually quartz) I_{sam} is normalized to the light through a segment of uncoated substrate I_{ref}. The relative transmitted intensity $I_{\mathrm{sam}}/I_{\mathrm{ref}}$ is then corrected for the Fabry–Pe´rot inteference fringes in the film to give a corrected transmission coefficient T. We use the interference pattern and the measured film thickness d (in this case 225 nm), to calculate the optical index of refraction in the spectral region where the transparency is high, giving $n=1.85\pm0.10$. This slightly lower n than ITO ($n=2$) is expected to decrease reflective losses at TCO-glass interfaces slightly. Values of α are calculated using $\alpha=\ln(1/T)/d$. We have also calculated the absorption coefficient from the transmitted intensity and the reflectivity using the full formulae (including the Fabry–Pe´rot interference) for selected films and have demonstrated that the use of the corrected transmission coefficient gives equivalent results within 1% over the region of frequency shown in Fig. 2. The results shown in Fig. 2 for this PLD-deposited film indicate that the zinc-indium-oxide has an energy gap 2Δ in the blue end of the visible spectrum near $\lambda=420$ nm (or $\omega=24\,000$ cm^{-1} or 3 eV) and a tail of absorption in the blue part of the spectrum. Toward the red end of the spectrum (ω of 15 000 to 20 000 cm^{-1}), the absorption is very low, of order 200 cm^{-1}. The absorption remains low (below 10^3 cm^{-1}) well into the near infrared (8000 cm^{-1}, or 1250 nm, or 1 eV).

For comparison, Fig. 2 also shows the absorption coefficient of two films of ITO. The commercial sample of ITO (supplied by Leybold) has much higher absorption over the whole spectrum and is typical of a number of ITO films we have measured. Using a similar rough criterion to that used above for the zinc–indium–oxide, we would estimate its energy gap as $2\Delta\sim18\,000$ cm^{-1} (or 560 nm, or 2.2 eV). The resistivity of this film is $\rho=180$ $\mu\Omega$ cm, which is typical of the most highly conductive ITO films.[1–4] However, we have made films of ITO under specially controlled conditions, and have obtained substantially lower α than the commercial one shown but similar to state-of-the-art films reported in Ref. 2, and also similar to zinc-indium-oxide in the blue part of the visible range of wavelengths, as also shown in Fig. 2.[10] In the infrared, near $\lambda\sim1\mu$m, however, we find that the zinc–indium–oxide has much lower α than even our best ITO, with $\rho=250$ $\mu\Omega$ cm.

The effect of an aliovalent dopant on the Zn site has been studied by growing films from pellets of $Zn_{2.3}M_{0.2}In_2$ oxide, where M is Al, Ga, or Ge. All films are transparent with resistivities in the range of 800–1000 $\mu\Omega$ cm. These preliminary results suggest that Sn is a more effective dopant. Further research would be necessary to explore Al, Ga, or Ge doped materials further to see whether their characteristics might ultimately equal those of Sn-doped materials.

The low absorption can be reconciled with the high dc conductivity in terms of the current theories of transport in heavily doped, wide band-gap semiconductors.[11] The wide band gap allows high transmission provided that the crystal structure is not drastically modified. Our material is heavily doped with a combination of both Sn and oxygen-vacancy donors. At our doping levels, these donors overlap to an extent that substantial hopping is possible, producing a Drude-like conductivity spectrum[11] with a high dc conductivity and a rolloff of the conductivity as a function of frequency with a characteristic frequency equal to the scattering rate which is, in turn, determined by the combined scattering of lattice vibrations, crystalline defects, and the ionized donor centers.[11] In comparison to ITO, our films of ZITO have a slightly larger energy gap and comparable scattering, rate, phonon scattering and defect density, and a lower carrier density.

Zinc-indium-oxide is a promising TCO. It can be grown in thin film form by PLD and by dc reactive sputtering. Doping can be accomplished by the introduction of oxygen vacancies and/or substitution of aliovalent elements such as Sn for In or Al, Ga or Ge for Zn. The optical transmission characteristics are significantly better than those of state-of-the-art TCOs, while the conductivity approaches that of the best TCOs in current use including indium-tin-oxide. This combination of properties makes possible the use of thicker films to achieve lower sheet resistance, while still preserving equivalent or even superior optical transmission characteristics compared with established materials. In particular, its superior transmission properties in the 1–1.5 μm range make it a preferred material for use in infrared devices where transparent electrodes are required.

We acknowledge the contributions of J. S. Winn to the studies of the optical properties of our films.

[1] G. Haacke, Annu. Rev. Mater. Sci. **7**, 73 (1977).
[2] J. M. Jarzebski, Phys. Status Solidi A **71,** 13 (1982).
[3] C. G. Granqvist, Appl. Phys. A **52**, 83 (1991).
[4] H. Sato, T. Minami, S. Takata, T. Miyata, and M. Ishii, Thin Solid Films **236**, 14 (1993).
[5] K. L. Chopra, S. Major, and D. K. Pandya, Thin Solid Films **102**, 1 (1983).
[6] R. J. Cava, J. M. Phillips, J. Kwo, G. A. Thomas, R. B. van Dover, S. A. Carter, J. J. Krajewski, W. F. Peck, Jr., J. H. Marshall, and D. H. Rapkine, Appl. Phys. Lett. **64**, 2071 (1994).
[7] J. M. Phillips, J. Kwo, G. A. Thomas, S. A. Carter, R. J. Cava, S. Y. Hou, J. J. Krajewski, J. H. Marshall, W. F. Peck, D. H. Rapkine, and R. B. van Dover, Appl. Phys. Lett. **65**, 115 (1994).
[8] J. Kwo, S. A. Carter, R. J. Cava, S. Y. Hou, J. M. Phillips, D. H. Rapkine, G. A. Thomas, and R. B. van Dover, Mater. Res. Soc. Symp. Proc. **345**, 241 (1994).
[9] S. A. Carter, G. A. Thomas, J. M. Phillips, R. J. Cava, J. Kwo, J. J. Krajewski, J. H. Marshall, W. F. Peck, Jr., and D. H. Rapkine (unpublished).
[10] J. M. Phillips, R. J. Cava, S. Y. Hou, J. J. Krajewski, J. Kwo, J. H. Marshall, W. F. Peck, Jr., D. H. Rapkine, G. A. Thomas, and R. B. van Dover, Mater. Res. Soc. Symp. Proc. **345**, 255 (1994).
[11] N. F. Mott, *The Metal-Insulator Transition* (Taylor and Francis, London, 1990).