ZnO: From Transparent Conducting Oxide to Transparent Electronics

1. *Wurtzite ZnO as a Transparent Conducting Oxide*

Wurtzite zinc oxide (ZnO) is a remarkable multifunctional material with a distinctive property set and a huge range of existing and emerging applications (Look 2006). In particular, it is a direct wide bandgap semiconductor ($E_g \sim 3.4\,eV$) with intrinsically high transparency over the whole visible range (Fig. 1) and a resistivity that can be tuned from semi-insulating right through to semimetallic by doping. In the latter case, it can be considered as belonging to a class of materials termed transparent conducting oxides (TCOs), which are degenerate n-type semiconductors with resistivities under about $10^{-3}\,\Omega\,cm^{-1}$, free-electron concentrations of the order of $10^{20}\,cm^{-3}$, an $E_g > 3.1\,eV$, and average transmittance $>80\%$ for the whole visible range.

Although many new TCO materials have been developed in recent years, most practical TCO applications employ doped oxides of indium (In), tin (Sn), and Zn. These are passive applications including window defrosting, filtering of ultraviolet and/or infrared light, electromagnetic shielding, transparent wiring, touch-sensitive panels, and transparent contacts for use in flat panel displays, solar cells, and light-emitting diodes (LEDs) (Gordon 2000). Most of these applications need as conductive and transparent a TCO as possible. There is, however, no single TCO material which has optimal properties for all applications because other considerations must be taken into account (see Table 1).

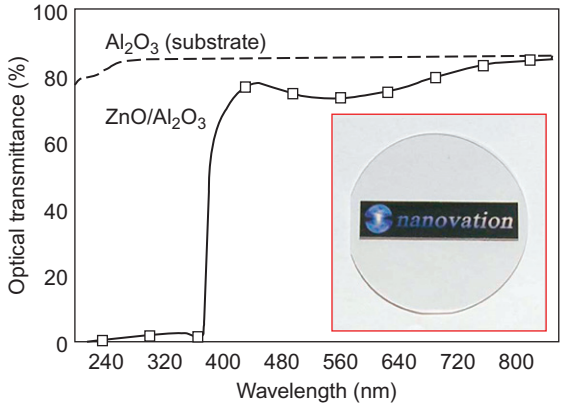

Figure 1
Optical transmittance spectra illustrating the high intrinsic transparency in the visible range of a nominally undoped ZnO film grown on c-sapphire by pulsed laser deposition. Courtesy Z. Djebbour, LGEP.

Up till now, the most widely used TCO has been Sn-doped In_2O_3 (ITO). Recently, there has been a trend toward the substitution of wurtzite ZnO for ITO (particularly aluminum (Al)-doped ZnO (AZO)). There are several reasons for this. (i) In is toxic, rare, and costly, whereas there is no shortage of Zn, and ZnO offers the lowest toxicity and materials cost of all common TCOs. (ii) ZnO can be readily fabricated in crystalline form at relatively low temperatures compared with ITO (Gordon 2000). (iii) ZnO is easier to process due to a greater amenability to chemical etching and a superior resistance to hydrogen (H) plasmas than ITO. (iv) The properties of ZnO can be readily tuned by doping. For instance, doping with fluorine (F) gives ZnO the highest optical transparency and the lowest plasma frequency of all TCOs. Moreover, both the mobility and conductance attainable with ZnO have considerably improved over recent years and AZO can now give resistivities comparable with ITO (Fig. 2).

2. *ZnO-based Amorphous Oxide Semiconductors*

Recently, a new type of ZnO-based TCO has emerged: amorphous oxide semiconductors (AOSs) (Hosono 1996). Compared to wurtzite ZnO, amorphous ZnO-based alloys have lower processing temperatures, are cheaper to fabricate, are lighter, and have better uniformity of properties (due, in part, to a lack of grain-boundary-related issues).

Table 1
Best of class crystalline materials for transparent conducting applications.

Property	Material
Highest transparency	ZnO:F, Cd_2SnO_4
Highest conductivity	In_2O_3:Sn
Lowest plasma frequency	SnO_2:F, ZnO:F
Highest plasma frequency	Ag, TiN, In_2O_3:Sn
Highest work function, best contact to *p*-Si	SnO_2:F, $ZnSnO_3$
Lowest work function, best contact to *n*-Si	ZnO:F
Best thermal stability	SnO_2:F, TiN, Cd_2SnO_4
Best mechanical durability	TiN, SnO_2:F
Best chemical durability	SnO_2:F
Easiest to each	ZnO:F, TiN
Best resistance to H plasmas	ZnO:F
Lowest deposition temperature	In_2O_3:Sn, ZnO:B, Ag
Least toxic	ZnO:F, SnO_2:F
Lowest cost	SnO_2:F

From Gordon R G 2000 Criteria for choosing transparent conductors. *MRS Bull* **25**, 52–7, with permission.

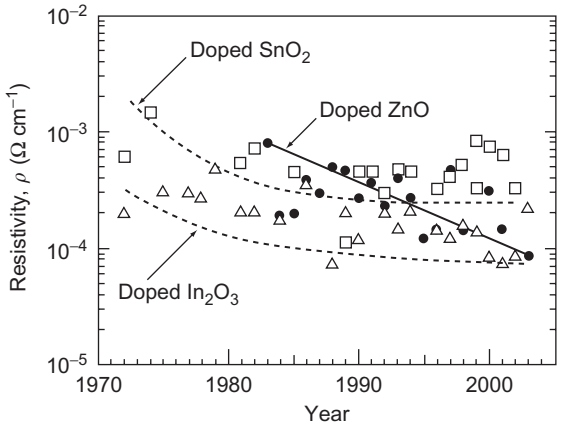

Figure 2
The evolution of the state-of-the-art resistivity for alloys of SnO_2, In_2O_3, and ZnO over time. Reproduced from Minami T 2005 Resistivity of impurity doped binary compound TCO firms 1972-present. *Semicon. Sci. Technol.* **20**, 35–44, with permission.

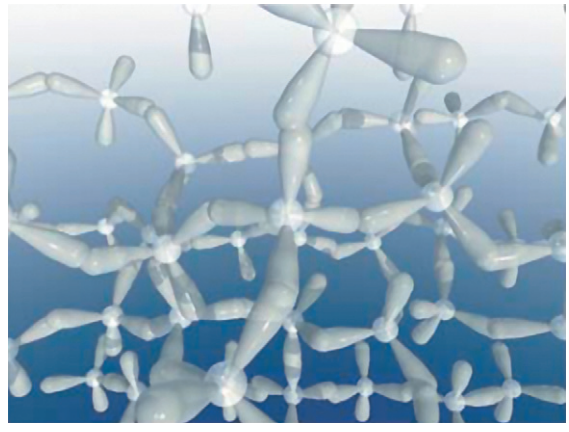

Figure 3
Schematic of the electron orbitals at the bottom of conduction band in CAS. Reproduced from Nomura K, Ohta H, Takagi A, Kamiya T, Hirano M, Hosono H 2004 Room-temperature fabrication of transparent flexible thin-film transistors using amorphous oxide semiconductors. *Nature* **432**, 488–92, with permission.

Moreover, their performance is stable and reproducible during and after repetitive bending, making them compatible with flexible substrates.

Although AOSs are not a new class of materials (Denton *et al.* 1954), the new generation of ZnO-based AOS exhibits enhanced electron mobility (μ), superior capacity for processability in air, and improved thermodynamic stability compared with conventional covalent amorphous semiconductors (CASs) and existing AOS (Nomura *et al.* 2004).

Nomura *et al.* (2004) proposed that the improved μ's are obtained because of differences in the intrinsic nature of the chemical bonding between AOS and CAS. Figures 3 and 4 illustrate the wave function at the bottom of the conduction band in CAS and AOS.

It can be seen that the hybridized sp^3 orbital overlap in CAS is highly directive. Therefore, any bond-angle fluctuations significantly alter the electronic levels, and carrier transport is controlled by hopping between localized tail states rather than band conduction. Thus, structural randomness can greatly degrade the carrier mobility. AOSs, in contrast, have higher ionicity and the bottom of the conduction band has extended spherical *s* orbitals associated with the metal ion. These electronic levels have an overlap, which is relatively insensitive to distortion of the metal–oxygen–metal chemical bonds. Thus, strain and disorder within the material do not strongly impact the conduction. Hence, AOS materials can show degenerate band conduction and superior electron μ compared with CAS, even though they are formed at room temperature. Indeed, amorphous $InGaZnO_4$ (a-IGZO) (Orita *et al.* 2001) can have a Hall mobility, $\mu > 12\,\mathrm{cm^2\,V^{-1}\,s^{-1}}$

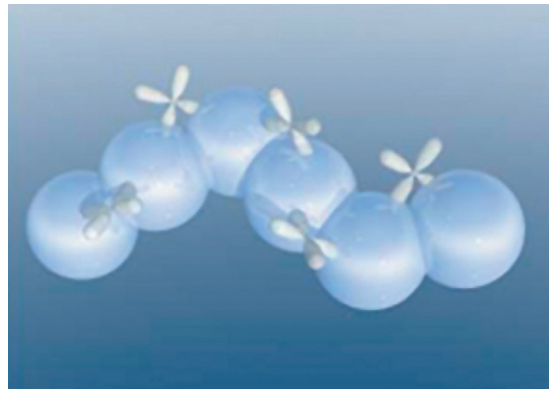

Figure 4
Schematic of the electron orbitals at the bottom of the conduction band in ZnO-based AOS. Spheres denote metal *s* orbitals. The contribution of oxygen 2*p* orbitals is small. Overlap of neighboring *s* orbitals is rather large, and is not significantly affected even in an amorphous structure. Reproduced from Nomura K, Ohta H, Takagi A, Kamiya T, Hirano M, Hosono H 2004 Room-temperature fabrication of transparent flexible thin-film transistors using amorphous oxide semiconductors. *Nature* **432**, 488–92, with permission.

(Hosono 2006) compared with a typical μ of $< 1\,\mathrm{cm^2\,V^{-1}\,s^{-1}}$ for hydrogenated amorphous silicon (a-Si) and it is reported to be stable up to 500 °C in air (Nomura *et al.* 2004). Amorphous InZnO (a-IZO) can have even higher μ ($> 100\,\mathrm{cm^2\,V^{-1}\,s^{-1}}$)

as reported by Fortunato *et al.* (2007) in addition to a transparency and conductivity which are comparable with ITO (Sashabayashi *et al.* 2003). As such, it is an alternative material for electrode applications. However, it shows inferior control of carrier concentrations compared with a-IGZO (Nomura *et al.* 2006).

3. ZnO-based Thin Film Transistors

Recently, a new generation of ZnO-based n-channel metal–insulator–semiconductor field-effect transistors (MISFETs), namely transparent thin film transistors (TTFTs), has been developed. Although ZnO-based TTFTs are not a new concept (Boesen and Jacobs 1968, Ohya *et al.* 2001), the new generation exhibits a high on–off ratio ($>10^6$) and a higher channel μ than the Si-based devices, which are currently used for state-of-the-art microelectronics applications such as select transistor drivers in commercial liquid crystal displays (LCDs) and systems on glass. Two main ZnO TTFT variants, employing either wurtzite or AOS ZnO alloys as channels, have emerged (Carcia *et al.* 2003, Hoffmann *et al.* 2003, Masuda *et al.* 2003, Nomura *et al.* 2003, 2004, Wager 2003).

These ZnO-based TTFTs offer several advantages over the incumbent Si-based devices. First of all, they are transparent so that generally more light can be transmitted through each pixel, yielding a brighter, more efficient display. This also means that the aperture ratio can be increased, so as to give smaller pixels. Next, state-of-the-art wurtzite ZnO and a-IGZO TTFTs can now exhibit channel μ as good as $250\,cm^2\,V^{-1}\,s^{-1}$ and $12\,cm^2\,V^{-1}\,s^{-1}$, respectively, as compared with typical values of $100\,cm^2\,V^{-1}\,s^{-1}$ and $1\,cm^2\,V^{-1}\,s^{-1}$ for poly-Si and a-Si (Nozawa 2007). This gives faster device operation, which leads to a quicker response and an increased refresh rate. In addition, because of their wide bandgap, the ZnO-based TTFTs have reduced sensitivity to light (exposure to ambient light has no significant effect on the current–voltage characteristics) and less degradation on exposure to light compared with their a-Si counterparts. TTFTs made with a-IGZO are of particular significance because they give excellent performance when fabricated at room temperature and can be fabricated in large-area format. This resolves the existing trade-off between processing temperature and device performance and allows fabrication on inexpensive heat-sensitive substrates such as transparent polymers or paper (poly-Si deposition temperature is too high for many flexible polymer substrates). Finally, ZnO-based TFTs can support higher device currents. This offers possibilities for higher power operation. Figure 5 illustrates a staggered, bottom-gate TTFT based on ZnO.

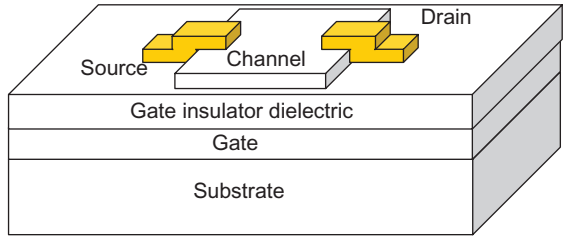

Figure 5
Schematic of a generic staggered, bottom-gate TTFT.

In these devices, the channel would typically be in either wurtzite ZnO or a-IGZO. In contrast to TCO applications, the channel needs as low a carrier concentration as possible (Kwon *et al.* 2004)—ideally $< \sim 10^{14}\,cm^{-3}$, according to Nomura *et al.* (2004). In the case of ZnO, this can be accomplished by minimizing the incorporation of n-type dopants, growing the ZnO as intrinsic as possible, alloying with Mg to increase the bandgap, and/or intentionally adding acceptor impurity dopants (such as N or P) to compensate the donors. In the case of a-IGZO, sufficient Ga content is essential for suppressing excessive carrier generation through oxygen vacancies.

Another key point about such TTFTs is that they are enhancement-mode devices, which is preferable to the depletion-mode alternative, since circuit design is simpler and because the power dissipation is lower as the off-state is the power-down state. Fully functional active matrix LCD (AM-LCD) (Hirano *et al.* 2006), active-matrix organic LED (AM-OLED) (Gorn *et al.* 2006), and electronic paper (e-paper) (Ito *et al.* 2007) have already been demonstrated.

Recently, some novel ZnO-based TFTs have been developed. Figure 6 shows a metal–oxide–semiconductor field-effect transistor (MOSFET) in which the paper acts as both the dielectric and the support, or interstrate (Martins *et al.* 2008, Fortunato *et al.* 2008).

Another recent development is ZnO-based metal–semiconductor field-effect transistors (MESFETs) (Frenzel *et al.* 2008). These devices can operate in a lower-voltage regime (± 1 V) compared with MISFETs. Thus, they should be better suited to driving display pixels. A method to obtain fully transparent MESFET devices (including all contacts) has also been developed. This methodology can be adapted to crystalline and amorphous substrates and films.

4. ZnO-based Transparent Electronics

In addition to TFTs, ZnO has been proposed for use as the active layer in a whole range of future transparent electronics devices. Some of the main

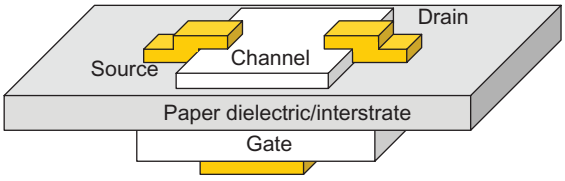

Figure 6
Schematic of a paper interstrate TTFT.

driving forces for this are the stability of the ZnO free exciton (which has a binding energy of ~60 meV, as compared with a value of ~21 meV for gallium nitride (GaN); Klingshirn 2007), the high drift mobility (Albrecht *et al*. 1999), and the fact that ZnO has one of the highest piezoelectric responses of all semiconductors (Triboulet 2000).

A key outstanding issue for ZnO, however, is the development of a reliable method for p-type doping. Indeed, nominally undoped ZnO is n-type. This is because native defects (O vacancies and Zn intersitials) along with common background impurities (such as H, Al, and Ga) act as donors in ZnO (Look 2005).

High levels of p-type doping, on the other hand, are relatively hard to achieve. This is because it has proven difficult to incorporate and activate sufficient acceptor concentrations. Recently, many groups have reported significant progress in the development of p-type ZnO (Look 2006) with hole concentrations allowing the demonstration of light-emitting p–n junctions (Tsukazaki *et al*. 2005, Ryu *et al*. 2006, Lim *et al*. 2006, Look 2006). The main acceptor dopants adopted are the group V elements N, P, As, and Sb. Key developments in this respect are the recent development of high-quality native substrates (Maeda *et al*. 2005) and the adoption of higher-purity sources, which allow reduced defect densities and impurity concentrations, respectively, and thus reduce donor compensation.

If these efforts to p-type ZnO continue to advance, we can expect to move on from discrete n-channel TTFTs to bipolar and complementary (n- and p-type) devices. These could form the building blocks of transparent integrated circuits and completely transparent electronic products with innovative new functionalities such as transparent displays or intelligent surfaces (Nozawa 2007). Furthermore, ZnO has shown itself to be a nanomaterial par excellence with probably the largest family of nanostructures of all materials (Wang 2004). This illustrates a remarkable propensity for miniaturization which has led to claims that self-assembling nanostructures of ZnO might have a key role to play in beyond-lithography electronics.

In summary, functional prototypes of TTFTs with n-type channels based on ZnO have already shown their potential for use in various display applications and e-paper. The trend to improved p-type doping capability presages the emergence of a new transparent electronics industry with completely novel applications and a remarkable set of potential performance advantages for existing products.

See also: Amorphous Semiconductor Solar Cells; Complementary Metal Oxide Semiconductor Field Effect Transistors; Fuel Cells: Materials; Photovoltaics: Advanced Inorganic Materials; Zinc Oxide, Bulk Growth of.

Bibliography

Albrecht J D, Ruden P P, Limpijumnong S, Lambrecht W R L, Brennan K F 1999 High field electron transport properties of bulk ZnO. *J. Appl. Phys.* **86**, 6864–7

Boesen G F, Jacobs J E 1968 ZnO field-effect transistor. *Proc. IEEE* **56** (11), 2094–5

Carcia P F, McLean R S, Reilly M H, Nunes G 2003 Transparent ZnO thin-film transistor fabricated by rf magnetron sputtering. *Appl. Phys. Lett.* **82**, 1117–9

Denton E P, Rawson H, Stanworth J E 1954 Vanadate glasses. *Nature* **173**, 1030–2

Fortunato E, Barquinha P, Pimentel A, Pereira L, Goncalves G, Martins R 2007 Amorphous IZO TTFTs with saturation mobilities exceeding 100 cm^2/Vs. *Phys. Stat. Sol. (RRL)* **1** (1), R34–6

Fortunato E, Barquinha P M C, Pimentel A C M B G, Gonçalves A M F, Marques A J S, Martins R F P, Pereira L M N 2004 Wide-bandgap high-mobility ZnO thin-film transistors produced at room temperature. *Appl. Phys. Lett.* **85** (13), 2541–3

Fortunato E, Correia N, Barquinha P, Pereira L, Gonçalves G, Martins M 2008 High-performance flexible hybrid field-effect transistors based on cellulose fiber paper. *IEEE Elec. Dev. Lett.* **29** (9), 988–90

Frenzel H, Lajn A, Brandt M, von Wenckstern H, Biehne G, Hochmuth H, Lorenz M, Grundmann M 2008 ZnO metal–semiconductor field-effect transistors with Ag-Schottky gates. *Appl. Phys. Lett.* **92**, 1921081–3

Gordon R G 2000 Criteria for choosing transparent conductors. *MRS Bull* **25**, 52–7

Gorn P, Sander M, Meyer J, Kroger M, Becker E, Johannes H, Kowalsky W, Riedl T 2006 Towards see-through displays: fully transparent thin-film transistors driving transparent organic light-emitting diodes. *Adv. Mater.* **18**, 738–41

Hirano T, Furuta M, Furuta H, Matsuda T, Hiramatsu T, Hokari H, Yoshida M 2006 High mobility top-gate zinc oxide thin-film transistors (ZnO-TFTs) for active-matrix liquid crystal displays. *SID 06 Digest*, 18–22

Hoffmann R L, Norris B J, Wager J F 2003 ZnO-based transparent thin-film transistors. *Appl. Phys. Lett.* **82**, 733–5

Hosono H 1996 Working hypothesis to explore novel wide band gap electrically conducting amorphous oxides and examples. *J. Non-Cryst. Solids* **198–200**, 165–9

Hosono H 2006 Ionic amorphous oxide semiconductors: material design, carrier transport, and device application. *J. Non-Cryst. Solids* **352**, 851–8

Ito M, Kon M, Miyazaki C, Ikeda N, Ishizaki M, Ugajin Y, Sekine N 2007 Front drive display structure for color

electronic paper using fully transparent amorphous oxide TFT array. *IEICE Trans. Electron.* **E90-C** (11), 2105–11
Klingshirn C 2007 ZnO: from basics towards applications. *Phys. Stat. Sol. (B)* **244** (9), 3027–73
Kwon Y, Li Y, Heo Y, Jones M, Holloway P, Norton D, Park Z, Li S 2004 Enhancement-mode thin-film field-effect transistor using phosphorus-doped (Zn,Mg)O channel. *Appl. Phys. Lett.* **84**, 2685–7
Lim J-H, Kang C-K, Kim K-K, Park I-K, Hwang D-K, Park S-J 2006 UV electroluminescence Emission from ZnO light-emitting diodes grown by high-temperature radiofrequency sputtering. *Adv. Mater.* **18**, 2720–4
Look D C 2005 Electrical and optical properties of p-type ZnO. *Semicond. Sci. Technol.* **20**, 55–61
Look D C 2006 Progress in ZnO materials and devices. *J. Elec. Mater.* **35** (6), 1299–305
Maeda S, Sato M, Niikura I, Fukuda T 2005 Growth of 2 inch ZnO bulk single crystal by the hydrothermal method. *Semicond. Sci. Technol.* **20**, 49–54
Martins R, Fortunato E, Barquinha P, Pereira L, Correia N, Gonçalves G, Ferreira I, Fortunato E 2008 Write–erase and read paper memory transistor. *Appl. Phys. Lett.* **93**, 2035011–3
Masuda M, Kitamura K, Okumura Y, Miyatake S, Tabata H, Kawai T 2003 Transparent thin film transistors using ZnO as an active channel layer and their electrical properties. *J. Appl. Phys.* **93**, 3
Minami T 2005 Transparent conducting oxide semiconductors for transparent electrodes. *Semicond. Sci. Technol.* **20**, 35–44
Nomura K, Ohta H, Takagi A, Kamiya T, Hirano M, Hosono H 2004 Room-temperature fabrication of transparent flexible thin-film transistors using amorphous oxide semiconductors. *Nature* **432**, 488–92
Nomura K, Ohta H, Ueda K, Kamiya T, Hirano M, Hosono H 2003 Thin film transistor fabricated in single-crystalline transparent oxide semiconductor. *Science* **300**, 1269–72
Nomura K, Takagi A, Kamiya T, Ohta H, Hirano M, Hosono H 2006 Amorphous oxide semiconductors for high-performance flexible thin-film transistors. *Jpn. J. Appl. Phys.* **45**, 4303–8
Nozawa T 2007 Transparent electronic products soon a reality. *Nikkei Electronics Asia* **November**, 1024–30
Ohya Y, Niwa T, Ban T, Takahashi Y 2001 Thin film transistor of ZnO fabricated by chemical solution deposition. *Jpn. J. Appl. Phys. Part 1* **40**, 297–8
Orita M, Ohta H, Hirano M, Narushima S, Hosono H 2001 Amorphous transparent conductive oxide $InGaO_3(ZnO)_m$ ($m<4$): a Zn 4s conductor. *Phil. Mag.* **B 1**, 501–15
Ozgur U, Alivov Y I, Liu C, Teke A, Reshchikov M A, Dogan S, Avrutin V, Cho S-J, Morkoc H 2005 A comprehensive review of ZnO materials and devices. *J. Appl. Phys.* **98**, 0413011–30
Ryu Y, Lee T-S, Lubguban J A, White H W, Kim B-J, Park Y-S 2006 Next generation of oxide photonic devices: ZnO-based ultraviolet light emitting diodes. *Appl. Phys. Lett.* **88**, 2411081–3
Sashabayashi T, Ito N, Nishimura E, Kon M, Song P K, Utsumi K, Kaijo A, Shigesato Y 2003 Comparative study on structure and internal stress in tin-doped indium oxide and indium–zinc oxide films deposited by r.f. magnetron sputtering. *Thin Solid Films* **445**, 219–23
Triboulet R 2000 The scope of the ZnO growth. *Proc. SPIE* **4412**, 1–8
Tsukazaki A, Ohtomo A, Onuma T, Ohtani M, Makino T, Sumiya M, Ohtani K, Chichibu S, Fuke S, Segawa Y, Ohno H, Koinuma H, Kawasaki M 2005 Repeated temperature modulation epitaxy for p-type doping and light-emitting diode based on ZnO. *Nat. Mater.* **4**, 42–6
Wager J F 2003 Transparent electronics. *Science* **300**, 1245–6
Wang Z L 2004 Nanostructures of zinc oxide. *Materials Today* **7**, 26–33

D. J. Rogers and F. Hosseini Teherani

Encyclopedia of Materials: Science and Technology
ISBN: 978-0-0804-3152-9
pp. 1–5