

Structure and optical properties of ZnO nanowires coated with silica

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It is essential to passivate one-dimensional nanostructures with insulating materials to protect them from contamination and oxidation as well as to avoid cross-talking between the building blocks of complex nanoscale circuits. The ZnO nanowires synthesised by the thermal evaporation of ZnO powders were coated with SiO₂ by the sputtering technique. Transmission electron microscopy and X-ray diffraction analyses revealed that the cores and shells of the ZnO core–SiO₂ shell nanowires were single crystal wurtzite type ZnO and amorphous SiO₂ respectively. Photoluminescence measurements at room temperature showed that the passivation of the ZnO nanowires was successfully achieved with SiO₂ without nearly degrading the near band edge emission from the wires. However, subsequent thermal annealing treatment was found to be undesirable owing to the degradation of the near band edge emission in intensity.

Keywords: Nanowires, ZnO, SiO₂, Core–shell structure, Photoluminescence, TEM

Introduction

ZnO has been an important industrial material in a variety of applications for many years. ZnO has found applications in surface acoustic wave filters, varistors, ultrasonic oscillators, transducers and photoprotective coatings, as well as a white pigment in fluorescent light bulbs and a filler for rubber products. In recent years, it also has been applied in the field of transparent conducting oxides, gas sensors, optical wave guides and solar cells.¹ Since the late 1990s, ZnO has rapidly emerged as a promising oxide semiconductor owing to its potential applications in optoelectronic devices emitting UV/blue light such as light emitting diodes, laser diodes and photodetectors due to its direct wide bandgap of 3.37 eV at room temperature and low power threshold for optical pumping. ZnO has many advantages over GaN which is currently used for fabricating short wavelength optoelectronic devices in the industry: a large exciton binding energy (60 MeV), the availability of ZnO substrates, amenability to chemical wet etching, the possibility of low temperature epitaxial growth, and excellent radiation resistance. Moreover, ZnO is thermally and chemically stable in ambient air.²

For the past two decades one-dimensional (1D) nanostructures have attracted considerable attention due to their wide variety of applications in electronics, optoelectronics and chemical sensing devices.^{3,4} It is essential to passivate

1D nanostructures with insulating materials to protect them from contamination and oxidation as well as to avoid cross-talking between the building blocks of complex nanoscale circuits.^{5,6} Passivation also offers many advantages such as substantial reduction of surface states, prevention of the surface from adsorption of unwanted species, prevention of unnecessary charge injection, and partial screening of the external fields.^{7,8} In particular, passivation of nanowires is required in the fabrication of field effect transistors and sensor devices based on nanowires. Silicon dioxide (SiO₂) is known as one of the most suitable insulating material for nanowire passivation owing to its excellent insulating property, low dielectric constant, and high mechanical strength as well as compatibility with other materials widely used in integrated circuit fabrication.⁹ SiO₂ is also optically transparent for light absorption or emission of semiconductor nanowires, resulting in minimal destruction of their intrinsic optical properties such as photoluminescence (PL).^{10,11} On the other hand, various techniques have been reported to be used to form SiO₂ passivation layers on the nanowire cores. These techniques include sol–gel processes, thermal heating, solution based methods, chemical vapour deposition, atomic layer deposition and sputtering.^{12–19} Of these techniques, the sol–gel process and solution based wet processes are prone to contamination. SiO₂ cannot be grown on the ZnO nanowires by thermal heating because no silicon source is contained in the ZnO nanowires. It is difficult to optimise the ALD process condition for SiO₂ coating using a silicon precursor such as SiH₄, Si₂Cl₂ or SiCl₄, and an oxygen precursor such as O₂ or N₂O, because of a narrow process window. Therefore, among the above mentioned techniques for the formation of SiO₂ passivation layers, sputtering is the simplest clean technique which can be used for coating SiO₂ onto ZnO nanowires. In this paper, the authors report fabrication of ZnO core–SiO₂ shell nanowires by using a two step process: thermal evaporation of ZnO powders and sputter deposition of SiO₂. The

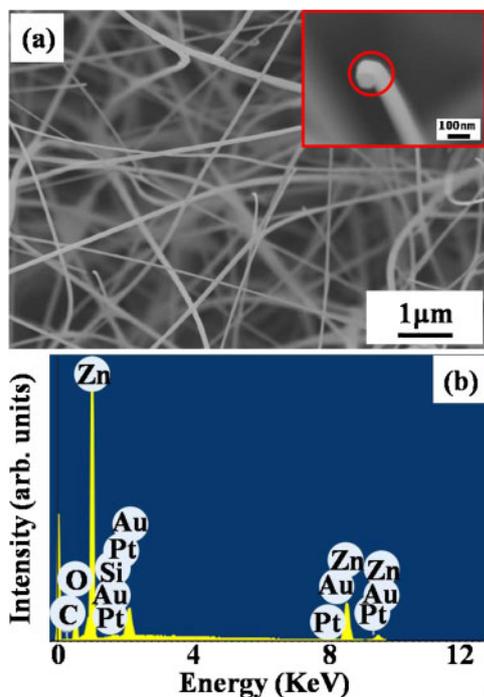
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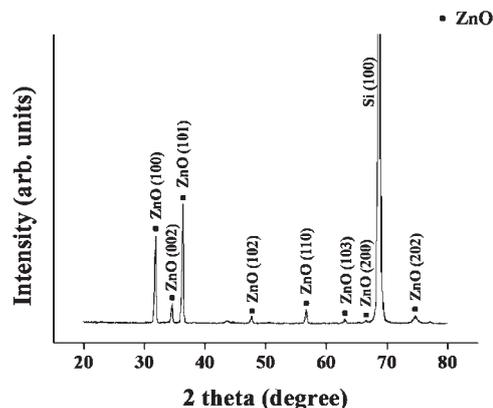
1 a SEM image of SiO₂-coated ZnO nanowires: inset is enlarged image of the nanowires. b EDX spectrum of SiO₂-coated ZnO nanowires. Au and Pt are the metal used as a catalyst for the nanowire synthesis and the metal used as a conductor for SEM sample preparation, respectively

authors also investigated the influence of SiO₂ coating on the PL properties of ZnO nanowires and thermal annealing on the PL properties of core-shell nanowires and the origin of the degradation of the PL emission by annealing.

Experimental

The preparation of ZnO core-SiO₂ shell 1D nanostructures consists of two steps: the thermal evaporation of a mixture of ZnO and graphite powders (ZnO/C=1:1) in an oxidative atmosphere and the sputter deposition of O₂. First, the Au coated p-type Si (100) substrate was put on top of an alumina boat containing a mixture of ZnO and graphite positioned at the centre of a quartz tube furnace. The furnace was heated up to 900°C and maintained at the temperature under a constant total pressure of 10 torr with a mixture of N₂ and O₂ gas. The flowrates of N₂ and O₂ gas were 1000 and 10 standard cubic centimetres per minute (sccm) respectively. The thermal evaporation process was conducted for 1 h and then the furnace was cooled down to room temperature.

Next, coating of the ZnO nanowires with SiO₂ was carried out by sputtering. The sputter deposition was done at room temperature using a 99.999% SiO₂ target in a radio frequency magnetron sputtering system. After the vacuum chamber was evacuated to 1×10^{-6} torr using a turbomolecular pump backed by a rotary pump, Ar was provided at a flowrate of 30 sccm. Depositions were carried out at room temperature for 25 min. The system pressure and the radio frequency sputtering power were 2.2×10^{-2} torr and 100 W respectively. Some of the as prepared ZnO core-SiO₂ shell coaxial nanowire samples were subsequently annealed in an O₂ or N₂/3 mol.-%H₂ atmosphere at 600°C for 30 min to



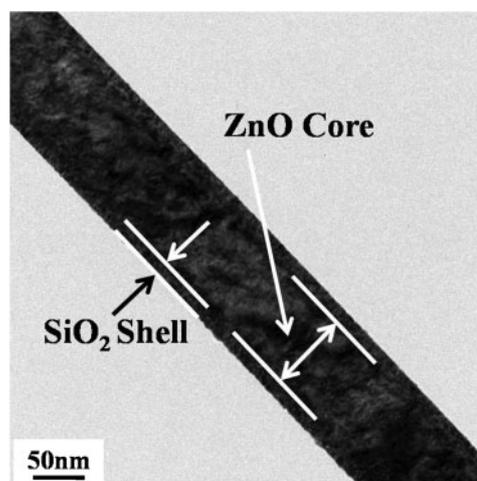
2 Glancing angle XRD patterns of as synthesised SiO₂ coated ZnO nanowires

see the influence of annealing on the PL properties of the coaxial nanowire structures.

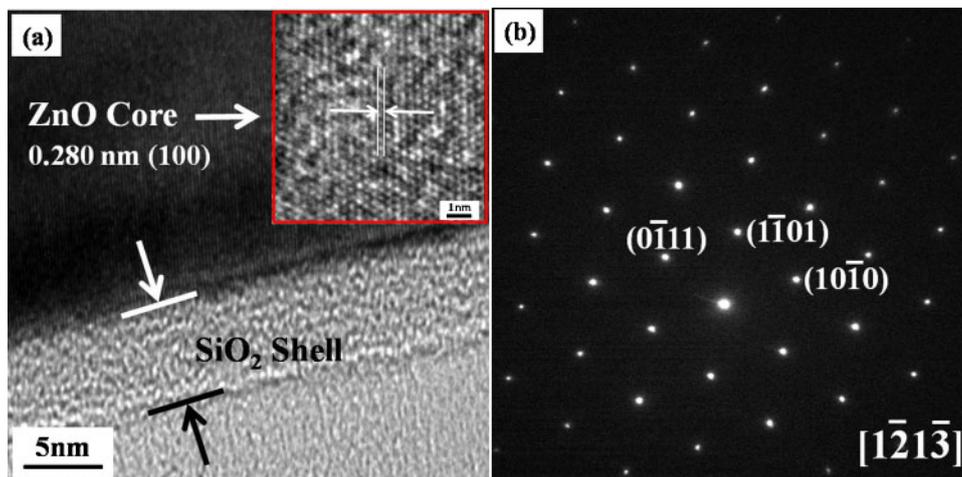
The morphology and size of the final products were examined by using scanning electron microscopy (SEM, Hitachi S-4200). High resolution transmission electron microscopy (HRTEM) and selected area electron diffraction (SAED) were carried out on a Philips CM-200 electron microscope at an acceleration voltage of 200 kV. The samples used for characterisation were dispersed in absolute ethanol and ultrasonicated before SEM and TEM observations. Glancing angle (0.5°) X-ray diffraction (XRD) analysis was performed using a Rigaku DMAX 2500 X-ray diffractometer with Cu K_α radiation with an incident angle of 0.5° to investigate the phases of the obtained products. The compositional analysis was done by using an energy dispersive X-ray spectroscope installed in the TEM. The PL measurement was carried out at room temperature by using a He-Cd laser (Kimon, 1 K, Japan) line (325 nm, 55 mW) as the excitation source.

Results and discussion

Figure 1a shows the SEM image of the as synthesised SiO₂ coated ZnO nanostructures. The spherical droplets or particles are observed at the tip of a typical nanowire in the inset in Fig. 1a and the energy dispersive X-ray spectroscopy spectrum for the particle (Fig. 1b) indicates that the particle comprises Au as well as Zn, O and Si.



3 Low magnification TEM images of a typical SiO₂ coated ZnO nanowire



4 *a* image (HRTEM) of region near interface of core and shell in typical SiO₂ coated ZnO nanowire and *b* corresponding SAED pattern, inset is the enlarged TEM image showing the fringes of the ZnO core clearly

The Pt detected in the spectrum was not used as a catalyst but as a conductor for SEM sample preparation. In addition, each nanowire is very uniform in diameter along its axis as shown in the SEM image (Fig. 1*a*). These results suggest that the ZnO nanowires were grown through the conventional vapour–liquid–solid mechanism in which a liquid Au catalyst droplet was located at the growth front of each wire.^{20–22}

The XRD pattern of the as synthesised SiO₂ coated ZnO nanowires is shown in Fig. 2. Besides the peak from the Si substrate, eight peak characteristics of wurtzite type ZnO (P6₃mc, $a=0.3241$ nm, $c=0.5187$ nm) are identified, which are indexed as the (100), (002), (101), (102), (110), (103), (200), (202) reflections from ZnO. On the other hand, no reflection peaks of SiO₂ are observable, suggesting that the SiO₂ shells are amorphous.

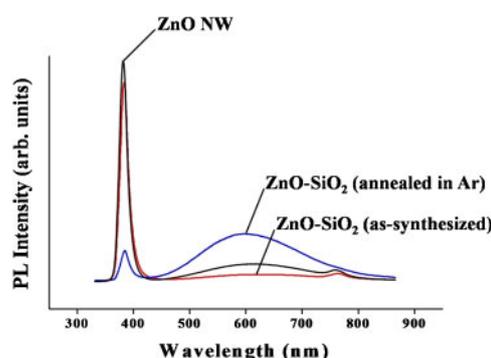
Figure 3 is the low magnification TEM image of a typical SiO₂ coated ZnO nanowire clearly showing two segments: a thicker core ~ 80 nm thick and two thinner coating layers with an average thickness of ~ 15 nm on both sides of the core. It is worthy of noting that the shell layers are quite uniform along the length of the nanowires despite their being deposited by the sputtering technique which is known as a typical physical vapour deposition technique. The HRTEM image of the interfacial area of the core and shell of a typical SiO₂ coated ZnO nanowire and the associated SAED pattern taken along the $[1\bar{2}1\bar{3}]$ zone axis are shown in Fig. 4. The resolved spacing between the parallel fringes is ~ 0.28 nm, corresponding to the (100) lattice plane of wurtzite ZnO. Both the HRTEM image and the SAED pattern indicate that the ZnO core is monocrystalline. In contrast, neither a fringe pattern in the shell layer of the HRTEM image nor the spotty or ring pattern for crystalline SiO₂ in the SAED pattern is observed, suggesting that the SiO₂ shell is amorphous.

Room temperature PL measurements were carried out. Figure 5 displays the PL spectra of the as synthesised ZnO nanowires and SiO₂ coated ZnO nanowires, i.e. ZnO core–SiO₂ shell nanowires. The ZnO nanowire sample exhibits a relatively strong UV emission at ~ 385 nm corresponding to the NBE emission and very weak broad emission band centred at ~ 770 nm. The NBE emission of ZnO is known to be associated with excitons bound to shallow donors, whereas the deep level (DL) emission of

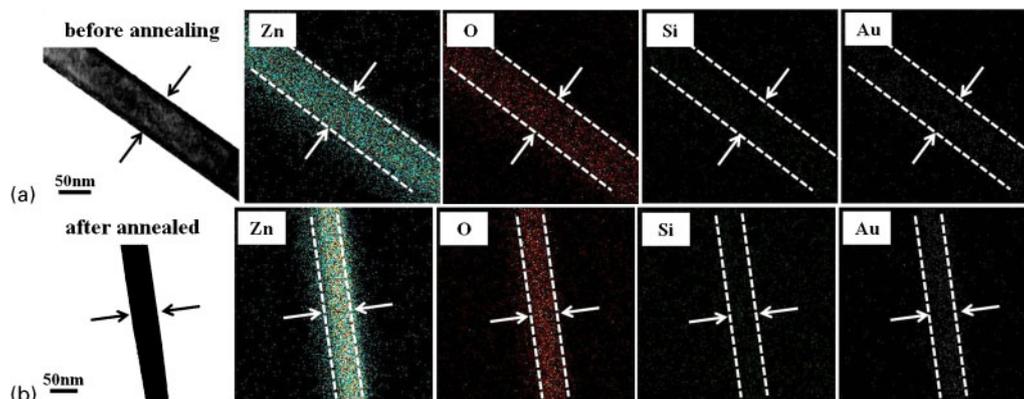
ZnO was reported to be associated with oxygen vacancy related defects such as singly ionised oxygen vacancies which can easily form recombination centres.²³

In contrast to the ZnO nanowires, the ZnO core–SiO₂ shell nanowires exhibit a stronger NBE emission and a very weak broad DL emission band centred at ~ 620 nm with a shoulder at ~ 770 nm. In other words, both the NBE and DL emissions were slightly decreased by coating the ZnO nanowires with SiO₂. This decrease in the PL emission intensity may be attributed to the light absorption by the SiO₂ shell layer. Incident light to the nanorods and the light emitted by the nanorods must pass the SiO₂ shell layer. Therefore, the final intensities of the PL emissions must be influenced by the transmittance of the shell layer. It is assumed that the intensity of the light passing through the SiO₂ shell layer is somewhat lower than that of the light before entering the shell layer because the transparency of the thin SiO₂ layer is not perfect. It is desirable that the UV emission is not significantly degraded by coating the ZnO nanowires with a passivation layer since a strong UV emission is essential in realising high quality UV optoelectronic devices such as UV light emitting diodes and laser diodes.

Figure 5 also compares the room temperature PL spectra before and after thermal annealing. The NBE emission of the ZnO core–SiO₂ shell nanowires was decreased while the deep level emission was increased in



5 Photoluminescence spectra of as synthesised ZnO nanowires, as synthesised SiO₂ coated ZnO nanowires, and annealed SiO₂ coated ZnO nanowires



6 Energy dispersive X-ray spectroscopy elemental maps of typical SiO₂ coated ZnO nanowire samples along the diameter of nanowire: *a* as synthesised (unannealed) and *b* annealed in an Ar atmosphere

intensity by thermal annealing, which may be attributed to the following two factors:

(i) the increase in the concentration of deep levels such as O interstitials and Zn vacancies in the ZnO cores due to the inflow of O atoms from the Ar atmosphere into the cores during the annealing process. Comparison of Fig. 6*b* with Fig. 6*a* indicates that the concentration of O element in the ZnO core in Fig. 6*b* is distinctly higher than that in Fig. 6*a*, suggesting that the former has a higher concentration of deep levels such as O interstitials and Zn vacancies in the cores than the latter

(ii) the increase in the transmittance of the SiO₂ shells due to the increase in the O concentration of the shells by annealing in an O atmosphere. It is well known that increase in the O concentration in an oxide material generally enhances the transmittance of the material.²⁴ Besides these two factors, the increase in the deep level emission in intensity may be attributed to the enhancement of the ZnO crystallinity by thermal annealing. It is widely accepted that the crystallinity of a thin crystalline film is enhanced by thermal annealing. The enhancement of the crystallinity of the ZnO cores may, in turn, lead to the increase in the PL enhancement due to the suppression of non-radiative recombination centres in the ZnO cores and removal of excessive O atoms trapped in the cores. Consequently, the PL emission intensity of the core-shell nanowires is enhanced. The electrical resistivities of the SiO₂ passivated and unpassivated (as synthesised) ZnO nanowires measured using a four point probe technique were 3.0 and 3.491×10^{-4} Ω cm respectively. This result verifies that ZnO nanowires can be passivated by SiO₂ coating in terms of electrical insulation.

Conclusion

ZnO core-SiO₂ shell nanowires were synthesised by a two step process: the thermal evaporation of ZnO powders and the sputter deposition of SiO₂. The ZnO cores and the SiO₂ shells are single crystal wurtzite type ZnO and amorphous SiO₂ respectively. The as synthesised ZnO nanowires have a strong NBE emission band centred at ~385 nm and a very weak broad DL emission band centred at ~620 nm with a shoulder at ~770 nm. Passivation of the ZnO nanowires can be achieved with SiO₂ without nearly degrading the NBE emission from the wires. Thermal annealing treatment is, however, not desirable owing to the degradation of the NBE emission in intensity.

Acknowledgements

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References

1. S. Nakamura and G. Fasol: 'The blue laser diode: GaN based light emitters and lasers'; 1997, Berlin, Springer.
2. D. C. Look: 'Recent advances in ZnO materials and devices', *Mater. Sci. Eng. B*, 2001, **B80**, 383-387.
3. H. W. Kim and N. H. Kim: 'Growth and structural properties of gallium oxide nanowires prepared by chemical vapour deposition', *Adv. Appl. Ceram.*, 2006, **105**, 84-87.
4. C. Chen, H. B. Guo, I. P. Shapiro, H. Peng, X. F. Zhao, P. Xiao and S. K. Gong: 'Residual stress trend in thermal barrier coatings in through thickness direction measured by photoluminescence piezospectroscopy', *Adv. Appl. Ceram.*, 2010, **109**, 95-100.
5. L. J. Lauhon, M. S. Gudiksen, D. Wang and C. M. Lieber: 'Epitaxial core-shell and core-multishell nanowire heterostructures', *Nature*, 2002, **420**, 57-61.
6. A. M. Morales and C. M. Lieber: 'A laser ablation method for the synthesis of crystalline semiconductor nanowire', *Science*, 1998, **279**, 208-211.
7. Y. B. Li, Y. Bando, D. Goldberg and Y. Uemura: 'SiO₂-sheathed InS nanowires and SiO₂ nanotubes', *Appl. Phys. Lett.*, 2003, **83**, 3999-4001.
8. X. Liang, S. Tan, Z. Tang and N. A. Kotov: 'Investigation of transverse conductance in semiconductor CdTe nanowires with and without a coaxial silica shell', *Langmuir*, 2004, **20**, 1016-1020.
9. H. Bartsch, D. Glöß, B. Böcher, P. Frach and K. Goedicke: 'Properties of SiO₂ and Al₂O₃ films for electrical insulation applications deposited by reactive pulse magnetron sputtering', *Surf. Coat. Technol.*, 2003, **174-175**, 774-778.
10. A. Pan, S. Wang, R. Liu, C. Li and B. Zou: 'Thermal stability and lasing of CdS nanowires coated by amorphous silica', *Small*, 2005, **1**, 1058-1062.
11. Y. Chang, M. Wang, X. Chen, S. Ni and W. Qiang: 'Field emission and photoluminescence characteristics of ZnS nanowires via vapor phase growth', *Solid State Commun.*, 2007, **142**, 295-298.
12. N. H. Kim, H. W. Kim, C. Seoul and C. Lee: 'Amorphous gallium oxide nanowires synthesized by metalorganic chemical vapor deposition', *Mater. Sci. Eng. B*, 2004, **B111**, 131-134.
13. S. Park, H. Kim, J. W. Lee, H. W. Kim and C. Lee: 'Influence of a ZnO coating on the photoluminescence properties of SnO₂ nanobelts', *J. Korean Phys. Soc.*, 2008, **53**, 657-661.
14. J. Jun, C. Jin, H. Kim, J. Kang and C. Lee: 'The structure and photoluminescence properties of TiO₂-coated ZnS nanowire', *Appl. Phys. A*, 2009, **96A**, 813-818.
15. S. Park, J. Jun, H. W. Kim and C. Lee: 'Preparation of one dimensional Bi₂O₃-core/ZnO-shell structures by thermal evaporation and atomic layer deposition', *Solid State Commun.*, 2009, **149**, 315-318.
16. J. Jun, C. Jin, H. Kim, S. Park and C. Lee: 'Fabrication and characterization of CuO-core/TiO₂-shell one-dimensional nanostructures', *Appl. Surf. Sci.*, 2009, **255**, 8544-8550.

17. C. Jin, H. Kim, H. W. Kim and C. Lee: 'Enhancement in the photoluminescence of ZnS nanowires by TiO₂ coating and thermal annealing', *J. Luminescence*, 2010, **130**, 516–519.
18. C. Jin, H. Kim, K. Baek, H. W. Kim and C. Lee: 'Preparation, structure, and photoluminescence properties of Ga₂O₃/SnO₂ coaxial nanowires', *Cryst. Res. Technol.*, 2010, **45**, 199–203.
19. Y. Wang, Z. Tang, X. Liang, L. M. Liz-Marzán and N. A. Kotov: 'SiO₂-coated CdTe nanowires: bristled nanocentipedes', *Nano Lett.*, 2004, **4**, 225–231.
20. R. S. Wagner and W. C. Ellis: 'Vapor–liquid–solid mechanism of single crystal growth', *Appl. Phys. Lett.*, 1964, **4**, 89–90.
21. R. S. Wagner: 'Whisker technology', (ed. A. P. Levitt); 1970, New York, Wiley.
22. S. N. Mohammad: 'Analysis of the vapor–liquid–solid mechanism for nanowire growth and a model for this mechanism', *Nano Lett.*, 2008, **8**, 1532–1538.
23. D. C. Reynolds, D. C. Look, B. Jogai, C. W. Litton, T. C. Collins, W. Harsch and G. Cantwell: 'Neutral-donor–bound-exciton complexes in ZnO crystals', *Phys. Rev. B*, 1998, **B57**, 12151–12155.
24. T. Tsuji and M. Hirohashi: 'Influence of oxygen partial pressure on transparency and conductivity of RF sputtered Al-doped ZnO thin film', *Appl. Surf. Sci.*, 2000, **157**, 47–51.