Paper based ZnO thin film UV light detector using graphite pencil based electrodes

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Received: 03 April 2016, Revised: 26 September 2016 and Accepted: 20 April 2017

DOI: 10.5185/amp.2017/705
www.vbripress.com/amp

Abstract

Ultraviolet (UV) light detection characteristics with sputtered ZnO films deposited on paper with graphite pencil drawn conducting inter-digital electrodes on normal paper have been investigated. Structural, electrical and microstructural properties of ZnO films grown by magnetron sputtering technique at under different sputtering pressures have been evaluated for ultraviolet (UV) light detection. Different types of paper used as substrate material, and the influence of their surface microstructure on the growth of ZnO film quality is examined. Films deposited on the fibrous paper are found to be polycrystalline, whereas the same films on dense glass substrates promote a c-axis oriented growth. The nucleation of sputtered ZnO films on paper is found to occur along the fine fibers of the paper and vary with sputtering pressure. Films grown at higher sputtering pressures (30 to 40 mTorr) in Ar/O_2 =50:50 are found to yield dense deposits. Pencil drawn inter-digital electrode structures on paper overlaid with 0.25 µm thick ZnO films exhibit reproducible photo response to ultraviolet (UV) light (λ = 365 nm), with low dark current. It's important for low prize and easy fabrication of optoelectronic foldable devices. Copyright © 2017 VBRI Press.

Keywords: ZnO, thin films, UV light, graphite, papers, detector.

Introduction

Normal paper used in daily life is attracting attention as an alternate substrate material for laying out electronic circuitry with inter-connecting graphite based pencil/ink conducting tracks and electrode structures for integrating active and passive planar devices and sensors [**1**]. The simple paper substrate consisting of a three dimensional cellulosic fibrous structure with varying porosity, and its interesting mechanical properties, biocompatibility, biodegradability, and low price are being seen as the unique advantages available on the newly discovered paper based substrate as an alternate platform. These advantages are becoming extremely attractive for developing foldable, disposal , and inexpensive portable electronic circuits. A new trend towards developing an environmental friendly technology is slowly emerging with green materials such as graphite ink/pencil drawn electrodes, and active organic layers for developing various electronic devices [**2**]. The possible use of paper as a substrate for future electronics is very intriguing and equally challenging, when compared to the already established substrate materials such as semiconductor silicon (wafers/membranes), glass, and flexible plastic/polymer sheets. However the recent trends in research and development demonstrating conformable sensors, flexible/foldable circuits and displays are quite promising, and besides the experiments on normal paper [**3**]. unusual and unfamiliar substrates such as transparent paper are also being envisaged for develop optical sensors and displays [**4**]. Paper is electrically insulating, heat resistant, light weight and can be easily shaped, and conveniently disposed. Its surface is amenable for easy exfoliation of conducting graphite particles through mechanical abrasion, or graphitic deposition by normal evaporation/sputtering. However surface smoothness, resistance to humidity, and optimum device performance need careful optimization, and there is still room for improvement Interesting developments have been reported and potential use of conducting graphite tracks/resistors, UV sensors, piezo-resistive, thin film batteries, super capacitors, nano generators and bio-sensors have been demonstrated [**5-8**].

Some recent developments on paper based electronic devices have focused on the integration of zinc oxide (ZnO) films with paper for developing ultraviolet light sensing devices. The continuing interest in ZnO is due to its multifunctional properties based on its semiconducting, insulating, transparent conducting and piezoelectric properties. In addition, ZnO is bio-compatible and can be easily grown in the form of textured/polycrystalline layers using simple chemical and physical methods.

Much of the reported work on ultraviolet light sensing has been focused on ZnO films prepared by chemical methods. Hasan *et al.* [**9**]. observed UV photo response with screen printed ZnO nanocrystal (NC) paste paper which was derived chemically from zinc nitrate hexahydrate [$Zn(NO_3)_2.6H_2O$] and hexamethylenetetramine ($C_6H_{12}N_4$), and used simple 4B pencil drawn electrodes on paper. Gimenez et al [**10-12**]. used regular bond paper embedded with fine ZnO powder suspension and observed reproducible sensitivity to UV light. Recently growth of aligned ZnO nanorod arrays on paper substrates with an ultrathin gold (50 nm) buffer film on paper has shown promising features towards the growth of one dimensional (1D) ZnO nanostructures directly on paper substrates for potential fabrication of ultraviolet light detectors [**13**]. A high performance photo conductive UV detector has been fabricated with 9B graphite pencil drawn electrodes on paper using ZnO nano-dot structures developed by a green solvo-thermal method. Although the reported UV light sensing properties of ZnO films on paper substrates are quite promising, the commonly observed photo response characteristics are found to be slow (in seconds) in comparison to developments on other flexible substrates. Moreover a persistent photoconductivity continues upon switching off the incident UV light, and the recovery time is slow. Therefore in view of the developments reported so far, it is noted that further improvements are needed to achieve ultra-fast, response and recovery characteristics, combined with lower dark currents and realize high sensitivity at low levels of UV illumination. These ultimate requirements emphasize further improvements in the quality of ZnO films grown on paper substrates. Key issues relating to nucleation of the deposited ZnO films on the fibrous microstructure of paper, the origin for efficient light absorption need further understanding. On the technological side development of closely spaced inter-digital electrodes with graphite pencil/ink need to be developed on paper substrates.

Motivated by the above described developments with ZnO films, in the present work we have focused on the following: (i) Growth of ZnO films on paper using a cold magnetron sputtering technique which has not been reported so far, (ii) Deposition of sputtered ZnO on different types of paper to understand the film nucleation and crystallization, (iii) study the influence of ZnO film sputtering conditions on the resulting microstructure, and (iii) investigate the ultraviolet (UV) photo response using electrodes graphite pencil drawn electrodes on paper.

Experimental

Materials

Different types of papers including (normal A4 paper, paper used for currency notes, Whatman paper, and thick bond paper normally used for making visiting cards) were used as substrate materials. Graphite pencil (10B) was used to draw inter-digital electrode (IDE) lines on the paper as shown in **Fig. 1(a)**. Three electrode pairs were drawn to form the IDE structure, and the line width is ~ 1mm, the line gap is ~1.5mm, and the length of the line is ~ 6mm. A magnified view of the IDE line on paper in **Fig. 1(b)** shows that repeated strokes of the pencil line compress the paper and smoothen its surface, and the fine graphite particles fill up the porosity in the paper.

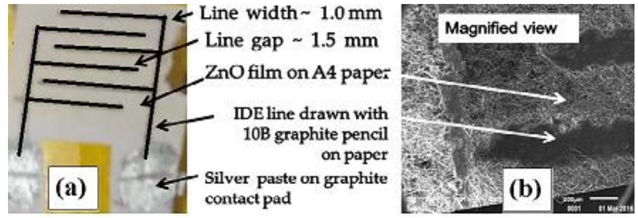

Fig. 1. (a) Inter digital electrodes (IDE) drawn on paper with 10B graphite pencil, (b) magnified view by the JEOL JSM 6610 Scanning elecrtron microscope.

Sputtered ZnO films

ZnO films were deposited by a reactive sputtering process using a high purity (99.99%) zinc (Zn) metallic sputtering target, 6 inches in diameter and of 4 mm thickness. The paper substrates with or without inter digital electrodes (IDE), alongwith standard glass substrates were fixed with adhesive Kapton tape on a metal plate, and mounted in front of the sputtering target. The typical sputtering conditions used for the deposition of ZnO films on the paper substrates are mentioned in **Table. 1**.

Table 1. Typical sputtering conditions for ZnO film deposition.

Target	Metallic Zinc target 6 inch dia, 4 mm thickness
Substrate	Paper, and glass
Target to substrate distance	10 cm
RF power on target	300 W on CX-12505 rf generator
Sputtering gas	Ar + O_2 (40:60)
Sputtering pressure	20 to 40 mTorr
Substrate temperature	No heating

Films were deposited at different sputtering pressures (20, 30 and 40 mTorr), and the sputtering gas composition ($Ar:O_2$=50:50) was maintained constantly throughout the experiments. Films of ~ 0.2 μm thickness were grown on different types of papers, and specifically on A4 paper, ZnO films of two different thickness (0.25 and 1.0 μm) thickness were grown for the samke of comparison. The crystallographic properties of ZnO films on paper was evaluated by X-ray diffraction (XRD) using Cu-Kα radiation with a Bruker D-8 Advance X-ray diffractometer. The microstructure and grain growth were examined by scanning electron microscopy using a JEOL (JSM 6610 LV) electron microscope.

Results and Discussion

X-ray diffraction

Fig. 2 (a and **b)** compare the X-ray diffractograms of ZnO films grown on glass and paper substrates. It is noted that the same ZnO film when deposited on a glass substrate **(Fig. 1(a))** exhibits a show a sharp (002)

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reflection at 2θ ~ 34.32° identified for ZnO phase, and indicates preferentially growth along the (002) c-axis of ZnO. The estimated value of the crystallite size from the sharpness of the peak is ~ 50 nm. However, on the paper substrate **(Fig. 1(b))**, a prominent peak corresponding to $CaCO_3$ which is present in the paper composition alongwith cellulose, and the other reflections could be indexed as those correspond to (100), (002), and (101) planes of ZnO phase, which indicated the polycrystalline nature of ZnO film developed on the paper substrate. The reason for the evolution of the polycrystalline nature of ZnO film on paper is attributed to the rough fibrous microstructure present on the paper substrate surface. On the different types of paper used in the present study, we observe the similar polycrystalline growth of ZnO.

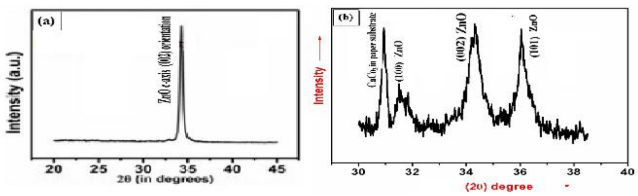

Fig. 2. Typical X-ray diffractograms of sputtered ZnO films deposited on (a) glass substrate, and (b) paper substrates (A4 paper). Thickness of ZnO film = 0.2 μm. using Bruker D-8 Advance X- Diffractometer.

Microstructure

Fig. 3. shows the microstructure of ZnO films sputtered at different sputtering pressures on currency paper. It is noted that films sputtered at lower sputtering pressure of 20 mTorr **(Fig. 3(a))** show crystallization of fine ZnO crystallites on the cellulose fibers of the paper, and with sputtering pressure increasing from 30 to 40 mTorr the density of the crystallites begins to increase as shown in **Fig. 3(b) and (c)** respectively. For films deposited at higher pressures (40mTorr) large areas covered ZnO deposit are seen **(Fig. 3(c))** along with embedded porosity underneath.

The surface microstructure of different types of paper used in the present study was examined to understand the crystallization of the deposited ZnO films.

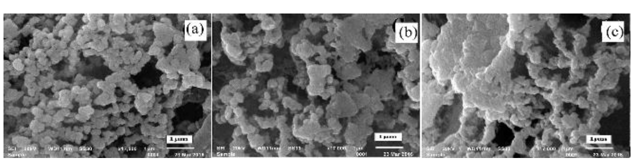

Fig. 3. Microstructure of ZnO films on currency paper when sputtered at different pressures (a) 20 mTorr, (b) 30 mTorr, (c) 40 mTorr.

The surface microstructure of papers including (a) A4 paper, (b) currency paper, (c) Whatman filter paper exhibit a typical rough surface and the cellulose fibers of similar size as shown in **Fig. 4 (a, b, and c)**. However the thicker bond paper (1mm) normally used for visiting cards exhibited a relatively smooth surface microstructure as seen in **Fig. 4(d)**. The growth of a constant thickness of ZnO film (0.2 μm) sputtered under similar conditions (30 mTorr) is compared on the different pieces of paper. On the A4 paper **(Fig.4e))** the porosity is still retained after depositing ZnO as seen in **Fig. 4(e)**, and the ZnO crystallites appear to be sticking to the fine fibers. In the case of the currency paper **(Fig. 4(b))** the porosity appears to be less, but accordingly we see clusters of ZnO crystallites sticking to the fibers **(Fig. 4(f))**. However, on the Whatman filter paper **(Fig. 4(c))** the sticking coefficient of the ZnO crystallites and their nucleation appears to be intense centered around the fibers, and the ZnO deposit along the fibers is more dense **(Fig. 4(g))**. Lastly on the thicker bond paper used for normal visiting cards **(Fig. 4(d**)), reduced porosity is seen, and granular deposit of ZnO films are seen **(Fig. 4(h))**.

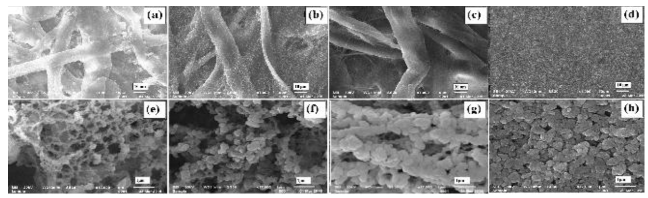

Fig. 4. Scanning electron microscope images of different types of papers used in the present study (a) A4 paper, (b) currency paper, (c) Whatmann filter paper, (d) visiting card bond paper, and images (e, f, g and h) show the microstructure of 0.2 μm thick ZnO films grown on the corresponding papers.

A comparison of thick and thin ZnO films on A4 paper is shown in **Fig. 5**. It is noted that the deposition of very thick ZnO films of about 1.0 μm in thickness complete cover the porosity seen in the A4 paper shown earlier in the image (**Fig. 4**(**a**), but the surface remains rough. In comparison, a thinner film of about 0.25 μm systematically sticks along the fibers and the porosity remains significantly.

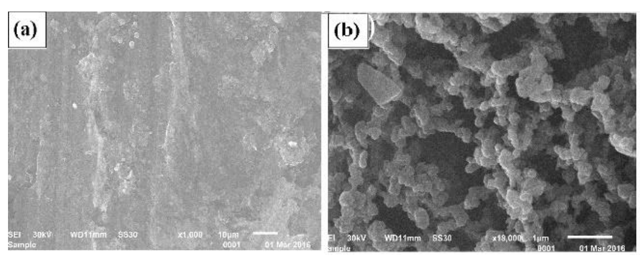

Fig. 5. Comparison of surface coverage and microstructure on A4 paper with (a) 1.0 μm thick, and (b) 0.25 μm ZnO films grown under similar conditions (30 mTorr).

Photoconductivity measurements

For the measurement of photo detector characteristics of the ZnO coated IDE electrode structures on paper as shown in **Fig. 1(a)**, the measurements were made under UV illumination (λ=365nm) using a pulsed InGaN –UV LED source, and the measured intensity of UV light falling on the device structure was fixed at (220 $\mu W/cm^2$). The photocurrent was measured using a Keithley microvolt ammeter (150B) and a Tektronix digital storage oscilloscope (TDS 2024B). To measure the transient characteristics shown in **Fig. 6**, the following method was

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employed. The circuit consists of a monostable multivibrator 74121 connected with the light emitting diode (InGaN UV-LED) operating at 365nm. A monostable multivibrator was designed to produce a one-shot pulse of UV illumination which could be triggered manually. The pulse width of the UV output pulse could be varied, and in the present study an exposure time of 2.5 seconds was set to illuminate the sample with the UV light. The steady state photoconductivity measurements and the transient photo response profiles were recorded directly using a digital storage oscilloscope (TDS 3032B). The electrical equivalent of the sample can be considered as a resistance corresponding to the ZnO film conductance which changes in the presence of UV light, and the measured photocurrent is measured when the contact pads of the IDE electrodes are connected in series with a battery of 1.5 volts which provides the electrical field between the IDE lines.

Reproducible photo response under UV illumination observed with 0.25 µm thick ZnO films deposited on the A4 paper is shown in **Fig. 6**. The photo response switching behavior is seen clearly under the 'ON' and 'Off' conditions of the at a low bias voltage of 1.5 V applied between the IDE electrode lines. Initially the dark current is quite low (0.05 nA),and upon UV illumination the photo-generated current increases slowly to a high value (3 nA) for ZnO film deposited with 40% oxygen contentment in the sputtering gas. A persistent photoconductivity is observed even after switching off the UV illumination, and the recovery to the initial state of the device is seen to take a long time.

The slow rise and recovery characteristics could be understood by the photoconduction process in occurring ZnO primarily by a surface related process. A surface related process is normally slow. In the absence of UV light, oxygen is absorbed by taking a free electron from the surface of the n-type ZnO to form a chemically adsorbed surface state, leaving behind a depletion region near the surface of the films **[16, 17]**. In the case of thin ZnO films the depletion region can sometimes extend through the entire thickness of the film.

$$O_2 + e^- \longrightarrow O_2^- \quad (1)$$

When photons of energies higher than the fundamental absorption band of ZnO are incident, holes produced due to the absorption of light near the surface, discharge the negatively charged oxygen ions.

$$h\upsilon \longrightarrow h^+ + e^- \quad (2)$$

$$h^+ + O_2^- \longrightarrow O_{2(g)} \quad (3)$$

Electrons produced at the same time increase the conductivity of the film. The decay in the photoconductivity is therefore strongly dependent on the ambient gas conditions, and the characteristics features in the photo response profile show the slow rise time, a non-saturating photo-current, and a slow recovery time as shown in **Fig. 6**.

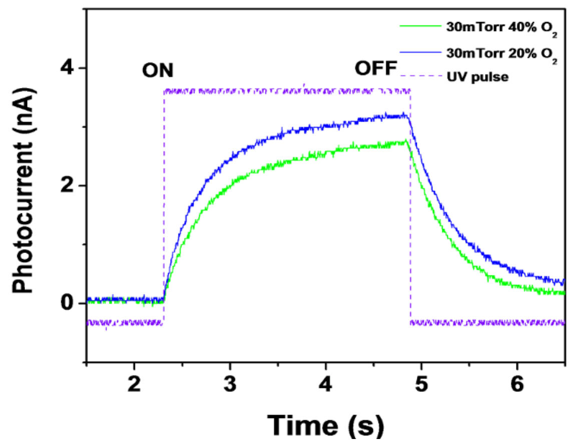

Fig. 6. Photoresponse of 0.25 µm thick ZnO films on A4 paper under UV illumination with 10 B graphite pencil drawn IDE electrode structure shown in **Fig. 1(a).**

Conclusion

Magnetron sputtered ZnO films have been grown on different types of paper. One micron thick ZnO films smoothen the rough surface of the paper substrate and fill up the porosity. However thinner films (0.25 µm) are seen to stick to the cellulose fibers in the paper. A high sputtering pressure of 40 mTorr, and deposition on Whatman filter paper shows dense and clustered ZnO deposits centered around the fibers. Reproducible UV photo response under an UV illumination intensity of (220 µW/cm^2) is observed with sputtered ZnO films deposited on normal A4 paper with graphite pencil drawn electrodes. However the photo response characteristics is slow, and suggests for further improvement in the ZnO thin film quality to achieve fast photo-response characteristics. Now replace the glass substrate by the paper page which is low prize and easy fabrication of all the optoelectronic devices

Acknowledgements

The authors wish to thank University of Delhi for R&D grant (2015-2016), One of the author (Mohd. Azaj Ansari) is thankful to University Grant Commission, India for providing financial assistance through Junior Research Fellowship (Ref No. Ref: FOS-1/114/PhD/4805).

References

1. Kurra, N.; Kulkarni. G.U.; *Lab Chip.*, **2013**,*13*, 2866.
DOI: 10.1039/C3LC50406A
2. Ren, T.L.; Tian, H.; Xie, D.; Yang, Y.; *Sensors.*, **2012**, *12*, 6685.
DOI: 10.3390/s120506685
3. Lin,C.W.; Zhao, Z.; Jaemyung,K; Huang,J.; *Scientific Reports.*, 2014, *22*, 3812.
DOI: 10.1038/srep03812
4. Huang, J.; Zhu,H.; Chen,Y.; Preston,C.; Rohrbach,K.; Cumings, J.; Hu,L.; *J. Am. Chem. Soc.*, **2013**, *7*, 2106.
DOI: 10.1021/nn304407r
5. Emilia.; Nery, W.; Kubota, L.T.; *Anal Bioanal Chem.*, **2013,** *23*, 7573.
DOI: 10.1007/s002 16-013-6911-4
6. Liana, D. D.; Raguse ,B.;Gooding ,J.J.; Chow, E.; *Sensors.*, **2012**,*12* , 11505.
DOI: 10.3390/s120911505

7. Kim, K. Ho.; Lee, K.Y.; Seo, J.S.; Kumar, B.; Kim ,S.W.; *Small.*, **2011**, *18*, 2577.
DOI: 10.1002/smll.201100819
8. Shafiee, H.; Asghar, W.; Inci, F.; Yuksekkaya, M.; Jahangir, M.; Zhang, M.H.; Durmus, N.G.; Gurkan, U.A.; Kuritzkes, D.R.; Demirici, U.; *Scientific Reports*, **2015**, *6*, 8719.
DOI: 10.1038/srep08719
9. Hasan, K.U.; Nur, O.; Willander, M.; *Appl. Phys. Lett.*, **2012**, *100*, 211104.
DOI: 003-6951/2012/Joo(21)/211104/3/
10. Gimenez, A.J.; Limn, J.M Ya n ez.; Seminario, J.M.; *J. Phys. Chem. C.*, **2011**, *115*, 282.
DOI: 10.1021/jp107812w
11. Gimenez, A.J.; Limn, J.M .Y.; Seminario, J.M.; *J. Intell. Mat. Sys. Struc.*, **2012** O(*0*)1.
DOI: 10.1177/1045389X124557836
12. Gimenez, A.J.; Luna-Bárcenas, G.; Sanchez, I.S.; Yáñez, J.M.; *Sensors.*, **2014,** 10604.
DOI: 10.1109/JSEN.2014.2361780
13. Manekkathodi, A.; Lu, M.Y.; Wang, C.W.; Che, L.J.; *J. Adv. Material*., **2010**, *22*, 4059.
DOI: 10.1002/adma.201001289
14. Li,H.; Jiao,S.; Li,H.; Li,L.; Zhang, X.; *J. Mater. Chem.*, **2015**, *3*, 3702.
DOI: 10.1039/c4tc02787f
15. Sharma P.; Mansingh A.; Sreenivas, K.; *Appl. Phys. Lett.*, **2002,** 80 553.
DOI: 10.1063/1.1445480
16. Sharma, P.; Sreenivas K.; Rao, K.V.; *J. Appl. Phys*., **2003**, 93, 3963.
DOI: 10.1063/1.1558994