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Effect of oxygen flow rate on the ultraviolet sensing properties of zinc oxide nanocolumn arrays grown by radio frequency magnetron sputtering

M.H. Mamat[a,b,*], M.F. Malek[a,b], N.N. Hafizah[b], M.N. Asiah[b], A.B. Suriani[c], A. Mohamed[c], N. Nafarizal[d], M.K. Ahmad[d], M. Rusop[a,b]

[a] *NANO-ElecTronic Centre (NET), Faculty of Electrical Engineering, Universiti Teknologi MARA (UiTM), 40450 Shah Alam, Selangor, Malaysia*
[b] *NANO-SciTech Centre (NST), Institute of Science (IOS), Universiti Teknologi MARA (UiTM), 40450 Shah Alam, Selangor, Malaysia*
[c] *Nanotechnology Research Centre, Faculty of Science and Mathematics, Universiti Pendidikan Sultan Idris (UPSI), 35900 Tanjung Malim, Perak, Malaysia*
[d] *Microelectronic and Nanotechnology–Shamsuddin Research Centre (MiNT-SRC), Faculty of Electrical and Electronic Engineering, Universiti Tun Hussein Onn Malaysia (UTHM), 86400 Batu Pahat, Johor, Malaysia*

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Abstract

Highly transparent metal–semiconductor–metal ultraviolet (UV) photoconductive sensors were fabricated using thin (less than 100 nm in thickness), dense, small-diameter ZnO nanocolumn arrays prepared via low-power, catalyst-free radio frequency (RF) magnetron sputtering at different oxygen flow rates ranging from 0 to 25 sccm. The FESEM images revealed the average nanocolumn diameter decreased with increasing oxygen flow rate. The transmittance spectra show that with the introduction of oxygen, the transmittance of the nanocolumn arrays in the visible region improves relative to that of a film prepared in the absence of oxygen with values greater than 95%. The UV responsivity and sensitivity were significantly improved for sputtered ZnO nanocolumn arrays prepared at oxygen flow rates up to 10 sccm, with the highest values of 9.70 mA/W and 2.20×10^4. Furthermore, the responsivity and sensitivity decreased at oxygen flow rates greater than 10 sccm, which can be attributed to the increased electrical resistance of the nanocolumn arrays. Our findings indicate that a high-performance UV photoconductive sensor can be realised using very thin sputtered ZnO nanocolumn arrays and that such a sensor would exhibit high sensitivity.

Keywords: D. ZnO; Nanocolumn arrays; RF magnetron sputtering; UV photoconductive sensor; Oxygen flow rate

1. Introduction

Nanostructured zinc oxide (ZnO) has emerged as a promising material for applications in UV photoconductive sensors because of its unique physical and chemical characteristics, wide bandgap energy of 3.3 eV, and high exciton binding energy of 60 meV. Nanostructured ZnO-based UV photoconductive sensors have been widely studied because of their numerous applications, which include gas sensors, surface acoustic wave (SAW) devices, flame sensors, and ozone monitoring. Various ZnO nanostructures have been studied for UV photoconductive sensor applications, including nanofibers [1], nanoflakes [2], nanosheets [3], and nanorods [4–7]. The performance of UV photoconductive sensors has been significantly improved through the use of ZnO one-dimensional (1D) nanostructured arrays, in particular, because of the characteristics of the 1D nanostructured arrays, which have a high surface-to-volume ratio and high electron mobility. Numerous synthesis methods have been reported for the preparation ZnO 1D nanostructured arrays, including vapour solid deposition [8], electrodeposition [9,10], metal–organic chemical vapour deposition (MOCVD) [11], pulsed laser deposition (PLD) [12], and solution-based processes [13–17]. The preparation of ZnO 1D nanostructured arrays using a sputtering process is important in the fabrication of devices because of this method's advantages, which include a low deposition temperature, the possibility of large-scale synthesis, and the relatively low cost compared with that of other vacuum-

*Corresponding author. Tel.: +60 3 55211883; fax: +60 3 55443870.
E-mail address: mhmamat@salam.uitm.edu.my (M.H. Mamat).

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based techniques, such as MOCVD and PLD. Furthermore, due to the stability of the sputtering process, the growth of films can be well controlled and is reproducible [18].

The performance of UV photoconductive sensors based on ZnO film can be improved via several methods. For example, surface treatments (i.e., plasma and heat treatments) have been shown to increase the UV-sensing capability of ZnO film by improving the surface conditions, which allow for more efficient interactions with the surrounding environment [19–21]. In addition, coating the film with certain materials also results in an improved photoresponse of the UV-sensing device [22,23]. Furthermore, the surface area of the sensing material has been increased through the utilisation of 1D nanostructured with a small diameter and a dense array in the UV sensor, resulting in a UV sensor with improved performance [24]. Among these strategies for improving UV sensing, the preparation of small-diameter and dense 1D nanostructured arrays is the most fundamental aspect in the production of high-performance UV sensors. The preparation of a small-diameter and dense 1D nanostructured array via surface treatments and coating processes may further improve the performance of UV sensors and represents an approach that is challenging but nonetheless attractive, particularly if high quality ZnO 1D nanostructured arrays can be produced using a sputtering technique. Although grain boundary that exists in sputtered ZnO 1D nanostructured arrays is generally regarded to be worse for devices, the enhancement of surface area due to grain boundary can effectively improves the UV sensor performance. Therefore, the UV photoconductive sensor fabricated using sputtered ZnO nanocolumn arrays is expected to give higher performance than that of thin film-based UV sensor. Various sputtering parameters, including radio frequency (RF) power, deposition pressure, and the insertion of oxygen, may influence the deposition process and the quality of the resulting ZnO film. Sputtered ZnO films produced with oxygen introduced during the deposition have shown different optical, structural, and electrical characteristics when prepared under different oxygen flow rates [25–27]. Therefore, variations in the oxygen flow rate are expected to result in sputtered-ZnO-based UV photoconductive sensors with different performance characteristics. Generally, the growth of ZnO 1D nanostructured arrays is most likely determined by surface energy. According to Shet et al., substrate temperature played important role to the growth of nanostructured arrays [28]. Insertion of oxygen gas during sputtering process is also essential for 1D nanostructured growth. According to Chou et al., higher oxygen content or oxygen partial pressure during sputtering process results in higher area density of 1D ZnO nanostructures [29]. They explained that at higher oxygen partial pressure, there will be more collision between the oxygen and substrate, creating more energetic or active sites on the substrate in the process, which enhance the growth of the ZnO nanostructures. Besides, the addition of oxygen also enhances the (002) orientation or the *c*-axis preferred growth and forms single crystalline ZnO.

Herein, we report the fabrication of UV photoconductive sensors using highly transparent, dense, and small-diameter ZnO 1D nanostructured in form of nanocolumn arrays, which were prepared via catalyst-free RF magnetron sputtering at different oxygen flow rates. In addition, the prepared ZnO nanocolumn arrays have thicknesses of less than 100 nm, which is rare among ZnO films used in highly responsive UV photoconductive sensors. These fabricated sensors exhibit high sensitivity on the order of 10^4, which indicates that sputtered ZnO nanocolumn arrays are a promising sensing material for UV photoconductive sensors. Our study also reveals that the performance of the UV photoconductive sensors differs when the sensors are fabricated with ZnO nanocolumn arrays prepared at different oxygen flow rates.

2. Experimental procedure

ZnO nanocolumn arrays were deposited on a glass substrate without a catalyst using an RF magnetron sputtering (SNTEK, Korea) technique at a low power of 50 W. The nanocolumn arrays were deposited using a pure ZnO target (4 in., Process Materials, USA, 99.99%) at a deposition pressure of 0.67 Pa and a substrate temperature of 100 °C for 30 min. After a base pressure of 1×10^{-4} Pa was achieved in the chamber, pure argon and oxygen gases were fed into the chamber for the deposition process. During this process, the flow rate of argon was fixed at 45 sccm, whereas the flow rate of oxygen was varied from 0 to 25 sccm. The sample was subsequently removed from the deposition chamber and annealed in air for 1 h at 500 °C. To complete the metal–semiconductor–metal (MSM)-type ultraviolet photoconductive sensor structure, 60-nm-thick Al-metal contacts were deposited onto the samples with inter-electrode distances of 2 mm using a thermal evaporator at a deposition pressure of 4×10^{-4} Pa. A schematic diagram of sputtered ZnO nanocolumn array-based UV photoconductive sensor is shown in Fig. 1.

The surface morphology and cross-sections of the ZnO nanocolumn arrays were characterised by field-emission scanning electron microscopy (FESEM, JEOL JSM-7600F). The crystallinity of the samples was characterised using X-ray diffraction (XRD, Panalytical X'pert Pro). The optical properties of the nanocolumn arrays were characterised using ultraviolet–visible–near-infrared (UV–vis–NIR) spectrophotometry (Perkin Elmer Lambda 750). The current–voltage (*I*–*V*) characteristics of the samples were investigated using a two-probe *I*–*V* measurement system (Keithley 2400). UV photoresponse measurements of the fabricated sensors were

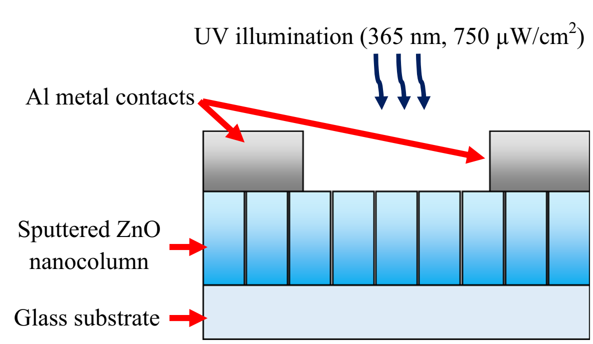

Fig. 1. A schematic diagram of sputtered ZnO nanocolumn array-based UV photoconductive sensor.