Argon and nitrogen plasma modification on spin coated ZnO thin films for gas sensing applications

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Abstract:Herein, we report improved NO_2 and O_2gas sensitivity of spin coated ZnO thin film treated with Ar and N_2 plasma for different time intervals (15, 30 and 45minutes). X-ray diffraction study suggested no change in the structure while the SEM investigation showed major change in topography of plasma irradiated films. The I-V curves are indicative of increase in conductivity and NO_2 and O_2 gas sensitivity. The oxygen sensitivity for 45 min Argon and oxygen plasma treated ZnO thin films showed highest sensitivity compared to pristine ZnO films. The improved sensitivity is attributed to the modified surface morphology of plasma treated ZnO thin films.

Keywords:Plasma treatment, Surface modification, Gas sensing.

1. INTRODUCTION

ZnO is a one of the highly studied material among metal oxide family. It boasts with the richest family of nanostructures and wide variety of application in various areas [1]. Gas sensing application is one such application area in which the potential of ZnO thin film is being explored from past several decades due to its high sensitivity and low response time for various gases and gas compositions [1].

Spin coated ZnO thin films represent a cost effective solution for realizing low cost high performing sensing device [2]. There are several reports in the literature which advocate use of spin coated ZnO thin films for gas sensing applications [3, 4]. Spin coated ZnO thin films usually exhibit high resistance which is due to highly porous morphology. These high resistance films require high operating temperatures which poses relatively higher power consumption for it to be realized as a device compared to Rf/ DC magnetron sputter deposited films. Rf/DC magnetron sputter deposited ZnO thin films generally represent thin films with high density, preferential growth and low resistance. Therefore, in order to effectively use spin coating as a cost effective solution to synthesize good quality thin films for gas sensing device applications, one need to device a method and/or suitable surface treatment which may reduce the resistance and at the same time contribute to the betterment of sensing parameters.

The present work targets both of the aspects for betterment of sensing layer i.e. increasing the density of the films and suitable surface treatment for improvement in conductivity. The density of ZnO spin coated thin films may be improved by increasing the temperature of heat treatment during the coating of consecutive layers of ZnO. Moreover, plasma modification/treatment is one of the methods to increase the conductivity of ZnO thin films [5-8]. Hydrogen plasma treatment has been used by many researchers aiming for modification in electrical and optical properties of ZnO especially for TFT display and solar cell applications [9,10]. It has been reported that in the hydrogen plasma ambient, oxygen desorption from the grain boundaries leads to a large increase in the Hall mobility and the conductivity [5-8, 11].Apart from H_2 plasma treatment [12],there are other reports on use of N_2O [13, 14], NH_3 [15], O_2 [16, 17], O_2+N_2 [18] plasma, which study the modification of electrical and/or optical properties on ZnO thin films. Moreover, surface smoothening effects due to plasma treatment is also reported [19, 20] for reduction of surface porosity.

Therefore, these two method may prove useful for producing better ZnO thin films with better sensing properties. In this study, ZnO thin films were prepared from spin coating of ZnO nanoparticles suspended in a solution and then these films were treated with N_2 and Ar plasma to explore the possibility of high quality ZnO films for gas sensing applications.

2. EXPERIMENTAL DETAILS

2.1 Synthesis of ZnO thin films

The nanostructured ZnO powder was prepared by a wet chemical reported earlier [21] using Zinc acetate dihydrate ($Zn(CH_3COO)_2.2H_2O$) in dimethylsulpoxide (DMSO) and potassium hydroxide (KOH) in ethanol. This ZnO powder was mixed in methanol and ultrasonicated for 30 mins and then spin coated using a programmable spin coater (Make: Apex Instruments Co., model: SCU-2008C) on corning glass substrate at 3000 rpm. Eight coating processes each with 250 µl of solution were done on the substrate to obtain uniform ZnO films. After each coating the specimen was heated at 200˚C for 5 min. These films were then annealed at 300°C in an open air tubular furnace for 4 hr in order to obtain a uniform grain size distribution [22].

2.2 Plasma treatment of ZnO thin films

The plasma treatment was carried out in a custom build plasma etching facility. A pumping stage consisting of rotary and diffusion pump is used to maintain vacuum in a stainless steel chamber of 28 liter volume. The chamber houses electrodes which are separated by Pyrex cylinder. These electrodes are connected to a DC generator for high voltage supply. The chamber has many inlet, outlets, and needle valves to control gas flow and chamber pressure. Four circles each of 1cm diameter were cut from two 2"x 2" Aluminum sheets of 1 mm thickness. ZnO coated substrates of 1 mm x 1 mm were sandwiched between these plates to act as mask, substrate holder and electrode as shown in figure 1. A magnet is placed on the top of this arrangement of 2.5"diameter for better confinement of the glow discharge plasma leading to efficient etching. The glow discharge plasma was maintained by supply of 5 kV voltage at 0.01 mbar pressure with continuous flow of Ar/N_2 for a given time.

2.3Characterization of ZnO thin films

The structure and morphology of the ZnO thin films were studied using X-ray diffraction (XRD) (Bruker-D8 Advance) and scanning electron microscopy (SEM) (Zeiss EVD 18), respectively.Current-voltage (I-V) and oxygen sensing measurements were taken on a custom built combustible gas sensing facility (CGSF) [23]. This unit consisting of a 1 lit volume stainless steel chamber housing a PID controlled heater which also acts as a substrate holder. Cold water is circulated in the walls of the chamber to prevent it from excess heating. Cu pressure contacts were used to make contact with sensing layer. A constant gas flow of total 100 sccm is maintained used mass flow controllers (Aalborg DFC) and the chamber is evacuated with a rotary vacuum pump to maintain a constant pressure of 0.28 mbar throughout sensing measurement. The system is configured in two-point measurement and is driven with voltage sourcing and current measurement by a Keithley 2400 SMU interfaced to computer using National Instrument's LabVIEW software.A real-time temperature monitroing is done using Measurement computins's USB-TC temperature logger for measurement of temperature fluctuation with gas injection to avoid false senisng signals.

3. RESULTS AND DISCUSSION

3.1 XRD study

XRD pattern corresponding to pure ZnO thin film is shown in figure 2 indexed to pure wurtzite phase of ZnO with a=b=3.248Å, c=5.215Å and c/a~1.60. Particle size was calculated using Scherrer's formula and found in the range 8-10 nm. XRD patterns corresponding to plasma treated ZnO thin did not exhibit any change (data not shown here) in phase, particle size, position and intensity of the X-ray diffraction peaks confirming that the surface modification did not result in to the modification of the structural properties of ZnO thin films. This is expected due to higher density of spin coated ZnO films in comparison to the modification reported (decrease in grain size with treatment time) in our earlier work [18]. The plasma penetration depth would have been smaller in this case resulting in etching of lesser depths and thereby producing less effect along the entire thickness of the ZnO film.

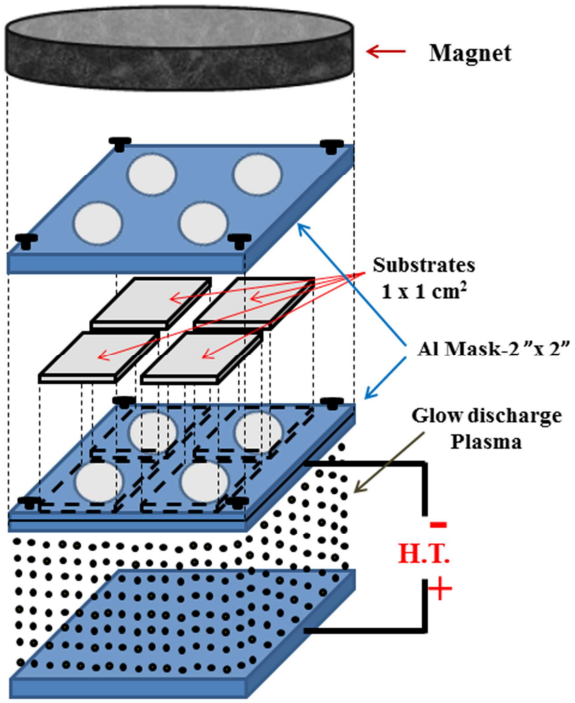

Figure 1: Schematic of plasma treatment facility

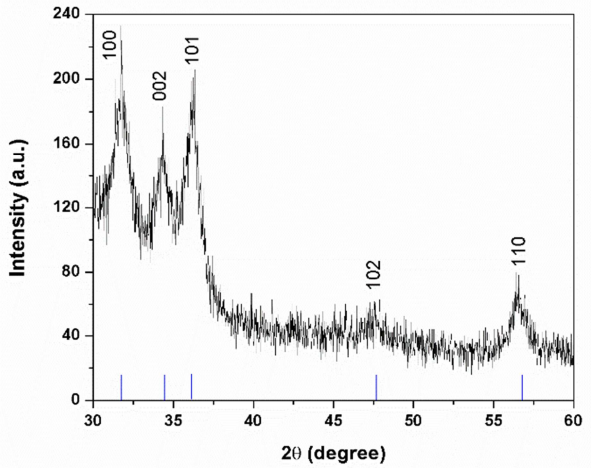

Figure 2 : XRD diffraction pattern for ZnO thin film indexed to pure wurtzite phase of ZnO. Vertical marker on X-axis show the peak position of standard spectra

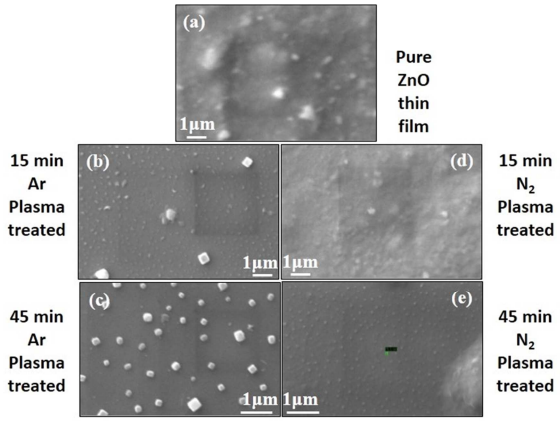

Figure 3 : SEM images of pristine (a) and plasma treated (b-e) ZnO thin films

3.2SEM study

The SEM micrographs of pristins ZnO thin film is shown in figure 3 (a) which is indicative of formation of a relatively denser thin film compared to the reported spin coated thin films. There are also some visible cluster formations on the rough surface of these films which are relatively denser ZnO verified by elemental maping of energy dispersive X-ray spectroscopy (image not shown here). Figure 3(b) and 3(c) represent SEM micrographs for Argon plasma treated films for 15 and 45 minutes, respectively which show relative smooth surface in contrast to the pristine film. However, there are island like structures on the surface of both of these films, which become more pronounced in the 45 min Argon plasma treated specimen. Figure 3(d) and 3(e) show SEM micrographs for the Nitrogen plasma treated ZnO thin films indicating the smoothening effects which is due to surface etching [24, 25] mediated by plasma treatment. The surface smoothening is increasing with the increase in plasma processing time. The relative difference between the Argon and Nitrogen plasma treated specimen is due to relative sizes of plasma species and effective impact/charge transfer inducing heating effects leading to the growth of unique structures on the thin film surface. A pictorial representation of the process is shown as figure 4 which details the conversion of denser portions of the film in islands.

3.3I-V and Gas sensing study

The electrical contacts were imprinted by spraying silver pasted through a laser cut mask on the pristine and inert gas plasma treated thin films and annealed at 300°C for stability. The current-voltage (I-V) characteristic curves were collected on the room-temperature in continuous flow of 200 sccm Nitrogen flow using CGSF at normal atmospheric pressure. The I-V curves for both pristine and plasma treated specimen indicate formation of ohmic contacts. The resistance can be deduced from these curves which suggest the increased conductivity in plasma treated thin films regardless of type of inert gas. However, Argon plasma treated thin films showed better conductivity over other counterparts. The conductivity is also found to be increasing with duration of plasma treatment. Table 1 summarizes the surface resistance of these films. The table is indicative of improvement in conductivity with plasma treatment time. Similar results have already been reported by other investigator with H_2 plasma [26, 27] advocating the role of hydrogen as shallow donor in ZnO lattice. However, in this case the decrement can be connected with appearance of denser structure on the surface (with better inter-grain connection) leading to higher charge transport. The results obtained from Ar and N_2 plasma treatment are comparable and in line with other reports [28, 29].

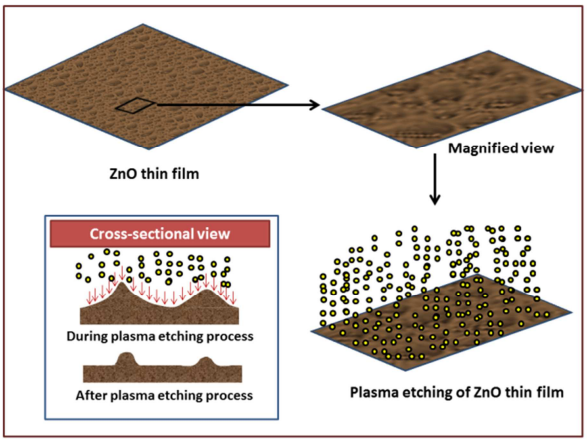

Figure 4 : Schematic showing process of formation of unique morphology of plasma treated ZnO thin films

Table 1: Surface Resistance of pristine and plasma treated specimen

Specimen	Surface resistance (in kΩ)
Pristine ZnO thin film	856
15 min Ar Plasma treated	605
30 min Ar Plasma treated	524
45 min Ar Plasma treated	468
15 min N_2 Plasma treated	715
30 min N_2 Plasma treated	589
45 min N_2 Plasma treated	485

The gas sensing taken over different operating temperatures (150°C-315°C) for 100 ppm NO_2 gas are shown in the figure 5 which indicate higher sensitivity in Ar plasma treated specimen as compared to the N_2 plasma treated specimen. The higher sensitivity could be explained on the basis of spill over effect due to formation of island over the surface and better contacts between grains. The N_2 plasma treatment has smoothened the surface which have resulted in to the lesser surface area as compared to pristine ZnO thin film which is expected to be a major cause of decrement in gas sensitivity.

4. CONCLUSION

The paper demonstrates synthesis of high density spin coated ZnO thin films and advocate plasma treatment to improve surface morphology and conductivity of ZnO thin films. The Ar plasma treatment is also demonstrated to produce unique morphology on the surface of films and therefore could be more useful in various other applications.

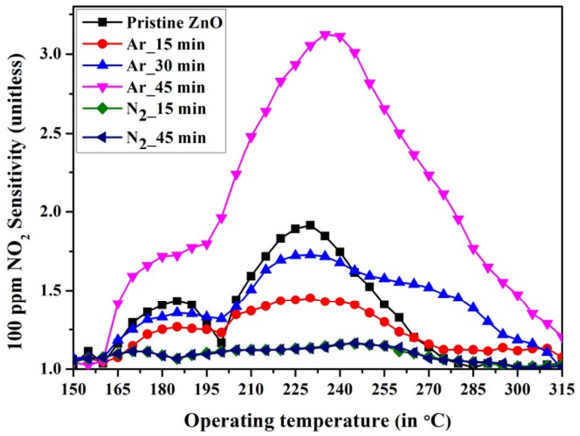

Figure 5 : 100 ppm NO_2 gas sensitivity of pristine and plasma treated specimen at different operating temperatures

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