Effect of Microstructure on Gas Sensing

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Abstract: Zinc oxide compact pellets and thin films by two different growth techniques, sol-gel spin coating and MOCVD are synthesized. Structural and micro structural characteristics of the synthesized samples are studied using X-ray diffraction and FESEM analyses respectively. Gas sensing characteristics of the samples are investigated on exposure of hydrogen gas at various operating temperatures. It is found that samples grown using MOCVD shows higher response% and lower response and recovery time. The under lying mechanisms for the above observations are analyzed. It is said that micro structure of the samples plays crucial role in enhancing the sensing characteristics.

Keywords: *Pellets; Thin film; Sol-gel; MOCVD; Gas sensor*

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I. INTRODUCTION

Gas sensor is a device which can detect the presence of various toxic and combustible gases present in its surroundings. There are numerous uses of these gas sensors in various sectors, such as in industry, domestic applications, in automobiles, and so on [1-2]. SMO based sensors are one of the most widely studied gas sensors [3]. In these SMO based sensing elements, the effect of microstructure which includes different parameters like grain size, pore size, surface to volume ratio and thickness is important in yielding superior gas sensing characteristics [4]. Thin film type sensing elements may be of two types, compact and porous [5]. In compact structure the gas may not enter into the film, thus the gas-solid interaction mainly takes place on the surface only [6]. However, if the film is very thin and porous then gas molecules can enter up to the bottom of the film. In this case the gas-solid interaction takes place on the surface of individual grains, on grain boundaries and also on the film substrate interface. Hence in this case the active surface area is much larger and hence yields better sensing performance.

In view of the above in this work we have synthesized compact circular pellets and thin films of different thickness (both thin and thick) grown by sol-gel and MOCVD to ensure different micro structures. Structural and micro structural characteristics of the synthesized samples are studied. Gas sensing characteristics of all the samples are studied in presence of hydrogen gas and the sensing principle is explored in light of the micro structure of the samples.

II. EXPERIMENTAL

Zinc oxide powders were prepared from zinc acetate using a wet chemical synthesis route. Zinc acetate was dissolved in 2-methoxyethanol through continuous stirring. MEA was added into the solution. The solution was heated at 80 °C and cooled to form a gel. The gel was dried at 80 °C for 12 hours to form powder [7]. The powders are mixed with PVA solution (binder) and pressed in the form of thin circular discs using a hydraulic press. The pellets are heated at 600 ^{o}C for 2 h in air. For synthesis of ZnO thin films by sol gel technique ZnO precursor sol was prepared by dissolving zinc acetate in 2-methoxyethanol. MEA was added to the mixture and the solution was stirred at 60 ^{o}C for 2h. The precursor sol was spin coated on quartz substrate using a spin coating unit. Just after deposition, the film was kept at 300 ^{o}C for 5 min and then cooled to room temperature. Repeating this process the film thickness was increased. After final coating the film was annealed at 600 ^{o}C for 1 h in air [8]. For synthesis of ZnO thin films by MOCVD technique DEZn and t-BuOH were used as zinc and oxygen precursors, respectively. The flow rates of the DEZn and t-BuOH were maintained at 20 and 60 sccm, respectively. The growth was carried out in atmospheric pressure at 450 ^{o}C for 1 hour [3]. The crystalline structure of the samples was determined by X-ray diffraction using Cu Kα radiation. The microstructure was characterized by field emission scanning electron microscopy. The gas sensing performance was evaluated using an automated dynamic volume measurement set-up, the detail of which is described elsewhere [9].

III. RESULTS AND DISCUSSION

a. Structural characterization

Fig. 1 (a), (b), and (c) show the X-ray diffraction pattern of ZnO powder, sol-gel grown and MOCVD ZnO thin films respectively. As observed from Fig. 1 (a) particles show polycrystalline hexagonal ZnO structures with peaks at 31.72°, 34.28 °, 36.20 °, 47.50 °, 56.46 °, 62.85 °, 67.76 °, 68.94 °, 72.45 ° and 76.71 ° corresponding to (100), (002), (101), (102), (110), (103), (112), (201), (004) and (202) planes respectively.

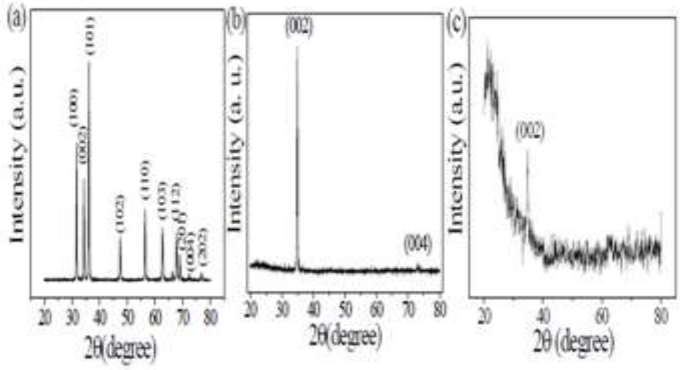

Fig. 1: XRD pattern of (a) ZnO powder [7], (b) ZnO thin film deposited by sol-gel spin coating technique, and (C) ZnO thin film deposited by MOCVD technique [3].

Fig. 1(b) and (c) show the X-ray diffraction pattern of the ZnO thin films grown by sol-gel and MOCVD techniques respectively. As observed from the figure there is only one prominent peak corresponding to (002) planes. This indicates the grown ZnO films are oriented along c-axis and is perpendicular to the substrate. This could be due to the maximum packing density along these planes [10]. However, the sharper peak obtained from sol-gel grown thin film may be due to the higher growth temperature (600 °C in case of sol-gel and 450 °C in case of MOCVD grown films). From the XRD pattern the average crystallite size (D) is found to be 46.5 nm and 22.8 nm respectively (in Fig. 1(b) and (c)), using the Debye-Scherer formula [3]:

$$D = \frac{0.9\lambda}{\beta cos\theta} \qquad (1)$$

where λ (= 0.154 nm) is the wavelength of the X-ray radiation used, θ is the Bragg diffraction angle of the XRD peak and β is the measured broadening of the diffraction line at half maxima measured in radian.

b. Micro- structural Characterization

Fig. 2 (a) shows the FESEM image of the ZnO powders. As shown in the image individual grains grow much larger with average grain size of ~300 nm. The microstructure is denser with small grain boundary density and large and well defined grains.

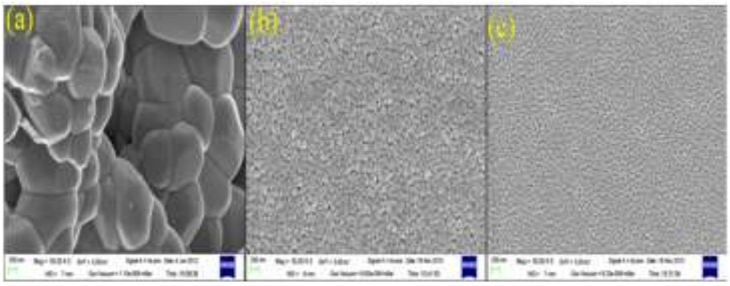

Fig.2: FESEM image of (a) ZnO powder, (b) ZnO thin film deposited by sol-gel spin coating technique, and (C) ZnO thin film deposited by MOCVD technique [11].

Fig. 2 shows the FESEM images of ZnO thin films deposited by (a) sol–gel and (b) MOCVD technique. As observed from the image both the films are continuous and have uniform grain distribution. Since the sol–gel grown films are thicker (having thickness ~353 nm) as compared to MOCVD grown films (having thickness ~110 nm), the average grain size of the sol–gel grown films (Fig. 2(b)) are larger and also it is more porous as compared to MOCVD grown ZnO films (Fig. 2(c)).

c. Gas sensing characteristics

The principle of operation of n-type semiconducting materials such as ZnO is a two step process [3]. In the first step the ambient oxygen is chemi adsorbed on the surface of ZnO grains, thus picking up of electrons from the conduction band of ZnO and thus increasing the resistance. Now in the second step when the reducing gases such as H_2 reacts with the adsorbed oxygen all the trapped electrons are returned back to the conduction band and hence the resistance decreases. The resistance transients thus recorded by the three types of samples in presence of 1660 ppm of H_2 gas at 350 °C surface temperature are shown in Fig. 3 (a).

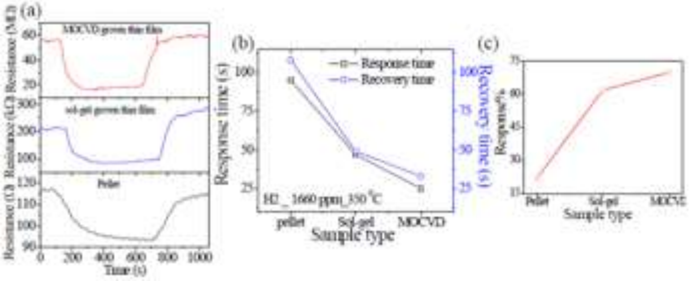

Fig. 3: (a) Resistance transients recorded by ZnO pellet, sol-gel grown and MOCVD grown ZnO thin films in presence of 1660 ppm of H_2 gas at 350 °C, (b) response and recovery time, and (c) value of response%, as estimated from the resistance transients of these three different samples.

From the resistance transients the response and recovery time is estimated following the definition that the response time (τ_{res}) is the time at which the sensor attains 63% of stabilized (final) value of electrical resistance after gas exposure and recovery time (τ_{rec}) is the time at which the sensor attains 63% of initial value of electrical resistance after recovering to air [9]. The response and recovery time thus estimated is plotted in Fig. 3 (b). As observed from the figure both τ_{res} and τ_{rec} is maximum for pellet and minimum for MOCVD grown films. From the measured value of resistance in air (R_a) and test gas (R_g), the response (S) % is calculated using the following relation [11]:

$$S = (R_a-R_g)/R_a \times 100 \qquad (2)$$

and is plotted in Fig. 3(c). As envisaged from the figure MOCVD grown film exhibits maximum response towards H_2 gas whereas pellet shows minimum.

The above observations may be explained as follows. When the sensing materials are in the form of compact circular pellet the sensor surface has a complex structure [12]. The surface consists of secondary particles known as grains. These secondary particles consist of number of primary particles known as crystallites. Generally, the pores between the secondary particles are macro-pores (>50 nm), whereas those in between the primary particles are mesopores (<50 nm). When the sensor is heated to higher temperature, oxygen gas diffuses through both the macro and meso-porous regions and is charge depleted due to chemisorption of oxygen. During gas sensing the reducing gases diffuse through macro and meso porous regions and react with chemi-adsorbed oxygen. However, the diffusion of gases through the meso porous regions is known to have important role during the gas sensing of semiconducting metal oxides [9]. On the other hand, in thin film based gas sensors, for thicker films (sol-gel grown film in the present case having thickness ~353 nm), gas molecules may not enter up to the bottom of the film. So due to the reduction of the utility factor response% reduces to a great extent. However, due to the smaller thickness (in MOCVD grown film in the present case having thickness ~110 nm), the gas molecules can easily enter and react with the whole volume of the material, thus increasing the response of the sensor. This improved performance of these gas sensors are attributed to the higher surface to volume ratio of the thin film sensing elements.

IV. CONCLUSION

In the present work, we have prepared ZnO compact pellets and thin films. Thin films are grown using two different growth techniques, sol-gel spin coating technique and MOCVD technique. Film grown using sol-gel route is thicker having thickness 353 nm whereas MOCVD grown film is 110 nm in thickness. Structural, micro structural characteristics of the samples are studied from XRD and FESEM analysis. Gas sensing characteristics of all the samples are investigated on exposure of hydrogen gas. It is found that thinner film (MOCVD grown film in the present case) yields superior sensing characteristics, being maximum response% and minimum response and recovery time. This superior sensing property is attributed to the micro structure of the sample which is conducive for gas sensing application.

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