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NANOCRYSTALLINE ZnO THIN FILM FOR GAS SENSOR APPLICATION

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Nano-crystalline (NC) materials exhibiting small particle size and large surface area may be applied for gas sensors, for which an excellent surface effect is required. Thin films of zinc oxide (ZnO) have been deposited onto glass substrates using a simple and inexpensive ultrasonically spray pyrolysis technique. Aqueous methanolic solution of zinc acetate was used as a spraying solution. The concentration of the solution was 0.1 M. The films prepared at different substrate temperature were uniform and well adherent to the substrates. X-ray diffraction (XRD) studies showed that all the films were polycrystalline in nanosize scale. The SEM photographs reveal the nano-size of the constituents. The electrical resistivity of the films was found to be dependent on the deposition temperature. The room temperature electrical resistivity was found to be varying in the range 10^{-5} to 10^{-6} Ω cm^{-2}. The sample resistance is measured with the presence of CH_4 in Ar carrier gas. The obtained responses of the samples were studied where our data were analyezed on the basis Yamoze SnO_2 sensor.

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1. Introduction

There exists a worldwide strong interest in realizing inexpensive oxide thin films to be used, for example, in solar cells, as gas sensor devices or as coating to heat glass windows. It has some advantages over other possible materials such as ZnO, In_2O_3, Cd_2SnO_4 or SnO_2 due to its unique combination of interesting properties: non-toxicity, good electrical, optical and piezoelectric behavior, stability in a hydrogen plasma atmosphere and its low price. Zinc oxide is a versatile material having applications in the areas like SAWdevices [1], varistors [2], transparent electrodes [3], gas sensors [4],

Methane gas is highly volatile when mixed with air and can cause explosion due to ready inflammability. Methane may also oxygen to cause asphyxiation in cramped or inadequately ventilated areas. In addition, it has recently been reported that methane is about 20 times more effective green house warming gas than carbon monoxide [5]. Thus, the development of a reliable and cost effective methane gas sensor remains a promising problem for timely detection of its conspicuous presence in the environment around us and in coalmine atmosphere to save human life.

Spray pyrolysis is a useful alternative to the traditional methods for obtaining thin films of pure ZnO. It is of particular interest because of its simplicity, low cost and minimal waste production. The spray pyrolysis process allows the coating of large surfaces and it is easy to include in an industrial production line. Many researchers have prepared the ZnO films by spray pyrolysis techniques in aqueous medium with and without addition of alcohol [6-8]. However, very few researchers have paid attention to deposit the ZnO films through aqueous, nonaqueous medium and their characterization.

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In our study, it is found that, by a simple CVD method, i.e. the ultrasonic spray pyrolysis (USP) technique at atmosphere, the chemical and thermal pyrolysis reactions, occurring in its low-temperature nonequilibrium process at atmosphere, is favorable to enhance some properties of ZnO film. In this paper, we report ZnO films synthesized by the USP technique. The as-grown ZnO films were characterized by X-ray diffraction (XRD), the field emission scanning electron microscopy (FESEM). The prepared films were examined for methane sensor application. The sensor study in resistive mode was performed and the response was studied as a function of methane concentration.

2. Experimental

ZnO films were deposited by ultrasonic spray pyrolysis technique onto corning glass 1737 substrates using zinc acetate as precursor. The solution of zinc acetate was prepared in methanol+ water. Films were prepared by varying the deposition temperature from 350 to 400 ^{o}C in order to study the effect of substrate temperature on the properties of the films. The films were deposited by spraying solution of zinc acetate, sprayed through a commercial designed ultrasonic humidifier with 1.63 MHz fixed frequency to get fume with fine droplets with size ranged from 0.5-6 μ. A compressed N_2 was used as a carrier gas, and spray time was maintained at 40 min. The structural characterization of the films was carried out using Rigaku Cu-Ka X-ray diffractometer by varying the diffraction angle 2θ from 10^o to 90^o with the step width 0.02 ^{o}. The film morphology and microstructure was studied by field emission electron microscope. The electric resistance study was carried out by using two-probe method in and without CH_4+Ar gas environment.

3. Results and discussion

During spray pyrolysis process, when aerosol droplets arrive close to the preheated substrates, the droplets undergo thermal decomposition, which results into the highly adherent zinc oxide film formation. During the pyrolytic process, following reaction takes place

$$Zn(CH_3COO)_2 + 2CH_3OH \rightarrow CH_3COCH_3 + H_2\uparrow + O_2\uparrow$$

The as-deposited films were transparent and well adherent to the glass substrates. Film thickness was determined by using Stylus technique. Table.1 shows the variation of the film with substrate temperature. It is observed that the growth rate (film thickness) increase with decreases in deposition temperature. However, this decrease in growth rate may be due to the variation in deposition efficiency, which may have resulted from diminished mass transport to the substrate, and due to gas convection pushing the droplets of precursors away at lower temperature.

Table 1. Variation of film thickness with deposition temperature

Temperature (^{o}C)	Thickness (nm)
350	320
375	250
400	235

X-ray diffraction was carried out on all the samples to determine the structure of the films. Fig. 1 shows the XRD patterns for samples deposited at 350 ^{o}C, 375 ^{o}C and 400 ^{o}C. All the samples were polycrystalline in nature having nanosize scale. Sample deposited 350 ^{o}C was found to be less crystalline. Upon increasing the substrate (deposition) temperature, crystallinity of the samples increased due to the effect of energy got from the substrate temperature for enhance the crystallinity of the film. The analogous results were reported for spray-deposited ZnO films, deposited through aqueous medium [9]. This was explained based on higher chemical purity of the

ZnO films, which resulted from thermal decomposition. All the peaks in the diffraction pattern were indexed on the basis of a JCPDS data card ((36-1451). A slow scan of XRD was used to calculate the grain size (d) of the crystallites with the help of Scherrer's relation [10], $D = \lambda/\beta\cos\theta$ where λ is the wavelength (1.5406 A^o) and β is full width in radian at half maximum of the peak and is the Bragg's angle of the XRD peak.

Values of grain size are given in Table 2. The Crystallite size was found to be varying between 15-18 nm. With higher substrate temperature of the initial ingredient, exhibits maximum grain size as compared with other samples. This can be understood from XRD results.

Table 2. Values of crystallite size.

Temperature (^{o}C)	Crystallite size (Å)
350	150
375	162
400	186

Morphology studies (Fig. 2.) reveal randomly oriented grains are in the range of nanometer size, which is very useful for gas sensing application.

The undoped ZnO consists of non-stoichiometric ZnO, which contains bulk oxygen vacancies and interstitial oxygen ions that act as donor states. These states permit the adsorption of oxygen. When oxygen molecule gets adsorbed at the ZnO film surface or at the grain boundaries, it extract electrons from the conduction band, thus, reducing the concentration of the electrons which allowing an increase in the film resistivity. As adsorbed oxygen concentration increases, the number of conduction band electrons decreases further and the ZnO film become more resistive [11].

As the deposition temperature raised, the sprayed film resistance decreased. The ZnO films deposited at 350, 375 and 400^{o}C at constant deposition time (40 min.), show almost the same trend of decreasing the resistance with increasing the test temperature(table 3). The samples prepared at 350^{o}C shows high resistivity all over the covered temperature range compared with the samples prepared at temperatures higher than 400^{o}C. This may be due to the structure of the ZnO films as revealed by their XRD.

Table 3.Variation of resistance with deposition temperature

Deposition temperature ^{o}C	R_{sh} (Ω/square)
350	1.129×10^6
375	8.039×10^5
400	1.389×10^5

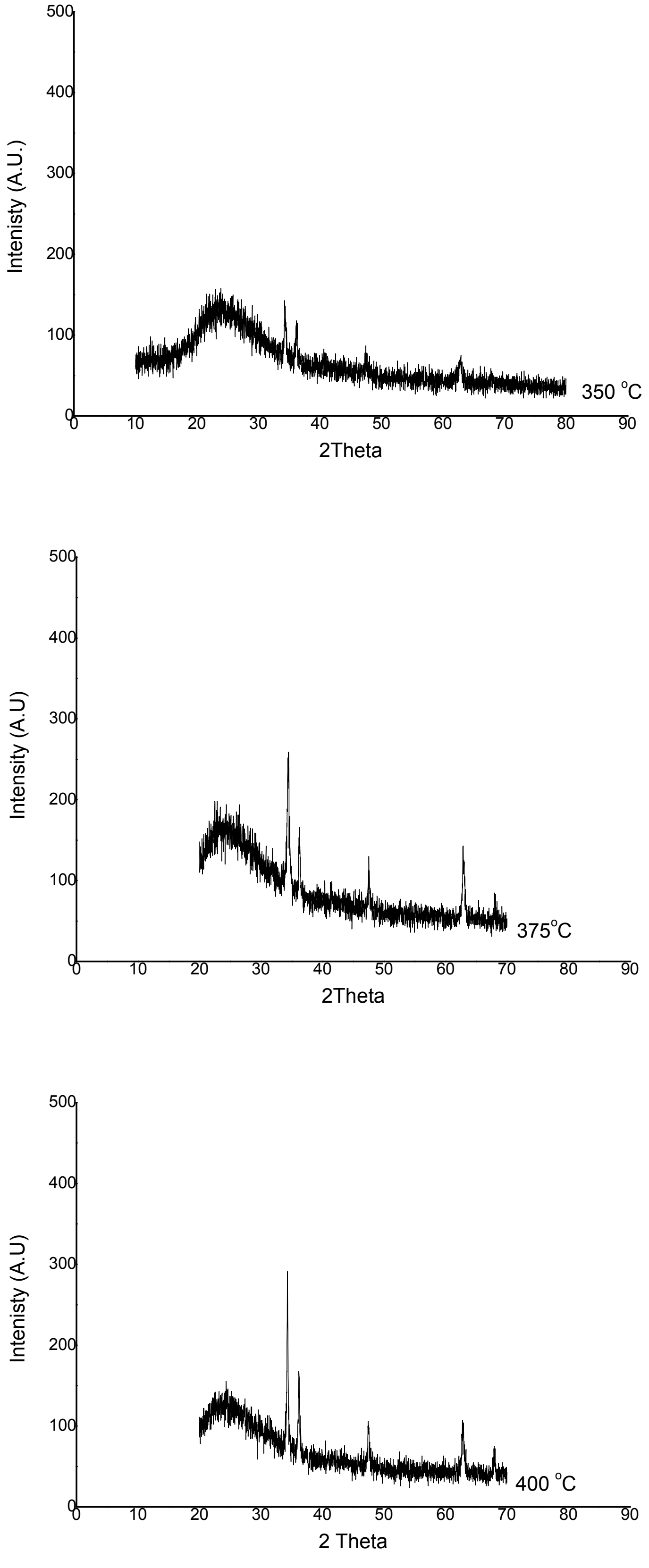

Fig.1. XRD patterns of the films deposited different substrate temperatures

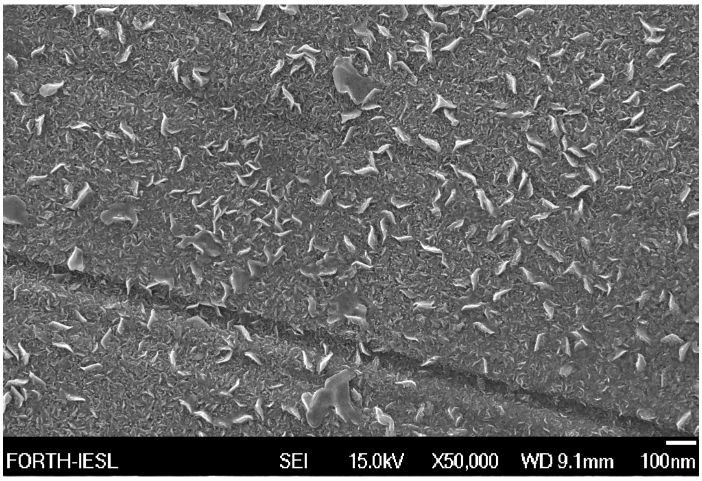

Fig.2. FESEM micrographs for the ZnO film prepared at 400 °C

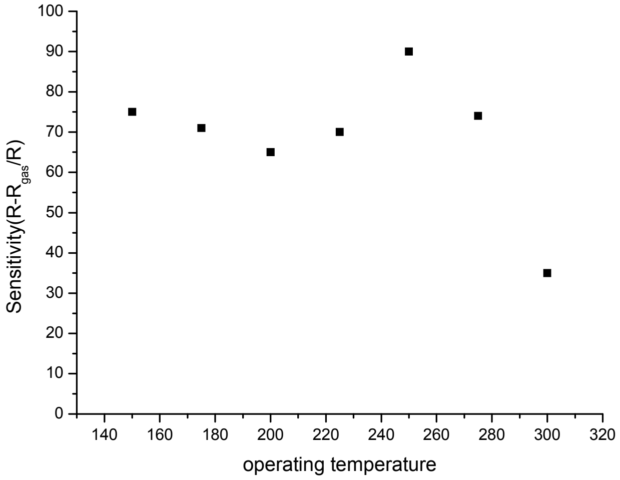

Fig.3. ZnO(prepared at 400 °C) sensitivity for CH_4 at different operating temperature

The higher resistivity for the investigated ZnO films regardless the preparation conditions could be explained as: during film deposition, it is quite likely that large numbers of oxygen molecules are adsorbed in the film both at grains boundaries and on the surface. The adsorbed oxygen will produce potential barriers which hinder the electron transport. Also, the adsorbed oxygen withdraws the electron from the conduction band allowing high resistivity.

The sensitivity S for gases is defined by the form:

$$S = (R_o – R_{gs})/R_o$$

where R_o is the resistance of the sensor before passing the gas and R_{gs} that after passing it. Systematic gas sensing studies were made on ZnO thin films, prepared at 400 °C, using Ag contacts. Crystallite size and the gas concentration are constant while the operating temperature is varied. The sensitivity of the sample is calculated and traced as a function of operating temperature as shown in Fig.(3). The samples show high sensitivity to CH_4 gas at operating temperature 250 °C.

A possible mechanism for methane sensing in the present study is depicted as follows. It is known that addition of a small amount of noble metal (from the contact), e.g. Ag, to the metal oxide can promote the gas sensitivity to a great extent due to the catalytic activities of these metals for oxidation of inflammable gases like methane. According to Yamazoe [12], Ag, diffused on the top of the films from the contact electrodes, acts as an electronic sensitizer as they affect the work function of metal oxide thin film during gas sensing. As reported by Kohl [13], methane dissociates to a methyl group and hydrogen, followed by combining the adsorbed hydrogen atoms producing hydrogen molecule, as shown below:

$$CH_{4gas} \leftrightarrow CH_{3ads} + H_{ads}$$
$$H_{ads} + H_{ads} \leftrightarrow H_2$$

The hydrogen molecule then reacts with the adsorbed oxygen on the Ag surface and produces H_2O. The adsorbed organic radicals undergo a chain of reactions and finally produce CO_2 as another product.

4. Conclusion

In this work, nanocrystalline zinc oxide thin films produced by well-known ultrasonic spray pyrolysis method were found to produce an efficient resistive gas sensor for CH_4.

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