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Spray Coated Nanostructured Nickel Oxide Thin Films for Ethanol Sensing

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Abstract: Nanostructured nickel oxide (NiO) thin films were prepared using spray pyrolysis technique over cleaned glass substrate with nickel (II)-acetate tetrahydrate and nickel chloride as precursor. The substrate temperature during deposition is varied between 473 and 523 K to study the influence of temperature over the structural and electrical properties of NiO thin films. The structural analysis of NiO thin films were carried out using X-ray Diffraction (XRD) technique and it is observed that the films are highly crystalline with face centered cubic structure. The surface morphology of NiO thin film samples was analyzed using Field Emission-Scanning Electron Microscope (FE-SEM). The sensing behavior of nanostructured NiO thin films towards various concentrations of ethanol was studied and reported.

Key words: Nanostructured NiO thin film, spray pyrolysis, XRD, FE-SEM, sensing

INTRODUCTION

NiO is a p-type semiconductor having wide band gap from 3.5 to 4.0 eV (Boschloo and Hagfeldt, 2001) and it has excellent chemical stability. Because of its better optical, electrical and magnetic properties, NiO is suitable for electrochromic display devices (Yoshimura *et al*., 1995).

In the recent past NiO has been used for gas sensing applications by employing chemi-resistive principle (Hotovy *et al*., 2006). Resistivity of NiO thin film depends on the concentration of cation (Ni) vacancies (Wittenauer and van Zandt, 1982). Recently, a thick-film type of thermoelectric (TE) hydrogen gas sensor has been developed using NiO as TE oxide thick film (Shin *et al*., 2001). The sensing properties of NiO towards various gases such as NO_2 (Hotovy *et al*., 2002), CO (Hotovy *et al*., 2001), NH_3 (Hotovy *et al*., 2000), H_2 (Imawan *et al*., 2000; Brilis *et al*., 2007) and HCHO (Lee *et al*., 2007) were reported.

Among various deposition techniques like, NiO magnetron sputtering (Sato *et al*., 1993; Hotovy *et al*., 2004) sol-gel (Li *et al*., 2012), advanced reactive gas deposition (Luyo *et al*., 2009), electron beam evaporation (Seika and Negai, 1991), vacuum evaporation (Tsu *et al*., 1969), anodic oxidation (Lampert *et al*.,1986), atomic layer epitaxy (Utriainen *et al*., 1998), etc. spray pyrolysis (Patil and Kadam, 2002; Boschloo and Hagfeldt, 2001) is found to be an efficient and cost effective technique.

Investigated the structural, morphological and sensing properties of the samples towards various concentration of ethanol, which is a good marker for quality of assessment of highly perishable food products like milk and fish (Marsili, 1999; Ampuero and Bosset, 2003).

Hence, in the present study, an attempt were made to deposit nanostructured NiO thin film samples using two different precursor solution at an optimized concentration and deposition condition.

MATERIALS AND METHODS

The nanostructured NiO thin films were deposited on ultrasonically cleaned glass substrates using spray pyrolysis technique at an optimized substrate temperature of 493 K. Nickel (II)-acetate tetra hydrate (98% purity, Merck, India) and Nickel (II)-chloride (99.9% purity, Fisher, India) were used as precursor. The experiments were carry out with an optimized precursor solution concentration of nickel acetate tetrahydrate in bi-distilled solvent as 0.05 M and with nickel chloride 0.05 M separately. Nanostructured NiO thin films with two different precursors were deposited under optimized deposition conditions reported in our earlier works (Sivalingam *et al*., 2012).

Structural properties of the as-deposited thin film samples were studied using X-ray powder diffractometer (XRD) (D8 Focus, Bruker, Germany) with Cu K_α radiation of wavelength 1.5418 Å. The microstructure of films were observed using field emission scanning electron microscope (FE-SEM, 6701F, JEOL, Japan), Further, the

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sensing characteristics of the as-deposited nanostructured NiO thin film samples were studied, using electrometer (6517A, Keithley, USA) connected to Volatile Organic Compound (VOC) testing chamber of 5 L capacity with a septum provision to inject desired concentration of VOCs using a micro-syringe. The chamber has a digital thermostat coupled compact heater.

RESULTS AND DISCUSSION

NiO thin film formation during pyrolytic reaction mechanism: NiO thin films were deposited using nickel acetate as well as nickel chloride as precursors. The possible reaction mechanisms during the deposition of NiO thin film samples N1 and N2, using nickel acetate (1 and 2) (Desai *et al*., 2006) and nickel chloride (3) (Patil and Kadam, 2002) precursor, respectively, are as follows:

$$Ni\ (C_2H_3O_2)_2.4H_2O \rightarrow Ni\ (C_2H_3O_2)_2 \quad (1)$$

$$Ni\ (C_2H_3O_2)_2 \rightarrow NiO+3H_2O\uparrow+4CO_2\uparrow \quad (2)$$

$$NiCl.6H_2O \rightarrow NiO+2HCl\uparrow+5H_2O\uparrow \quad (3)$$

During spray pyrolysis process, when aerosol droplets arrive close to the preheated substrate at 493 K, undergoes pyrolytic reaction and deposit as NiO.

Structural and morphological characterization: The as-deposited NiO thin film samples N1 and N2 were analyzed using x-ray diffraction (XRD) technique shown in Fig. 1, to identify the structure and change in the crystallinity. From the XRD pattern, it was found that all the samples were polycrystalline in nature with face centered cubic structure, comprising a strong diffraction along (111) plane.

The grain size of the crystallites (mean crystallite diameter) was calculated for major reflex (111) using the well-known Scherrer's formula (4) (Mikrajuddin and Khairurrijal, 2008), by assuming the factors, viz. instrumental broadening, distortion of lattice, etc. are common among all the samples:

$$g = K\lambda / \beta \cos\theta \quad (4)$$

where, g is the mean crystallite dimension, K is the shape factor (0.89), λ is the X-Ray wave length typically 1.54 Å, β is the line broadening at half the maximum intensity (FWHM) in radians, θ is the Bragg's angle of the XRD peak in degrees. The grain size was calculated as 14.5 nm for N1 sample and 17.2 nm for N2 sample.

The morphology of the prepared films was investigated by FESEM, which shows inhomogeneous nanostructured grains with spherical morphology. The grain size of the NiO thin film observed from the micrographs was found to be same as from XRD data.

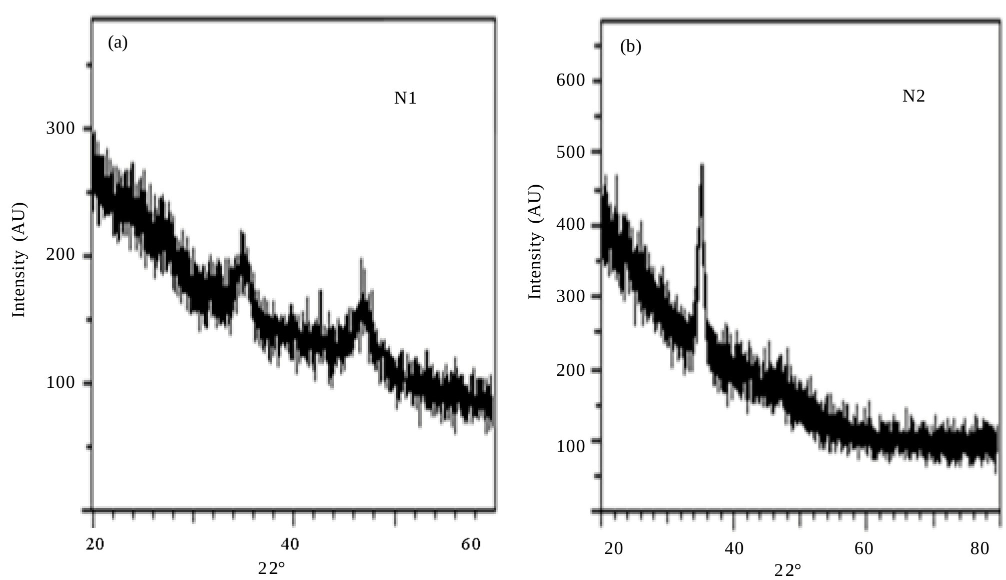

Fig. 1(a-b): XRD pattern of NiO thin film samples deposited with, (a) Nickel acetate tetra hydrate (N1) and (b) Nickel chloride precursor (N2)

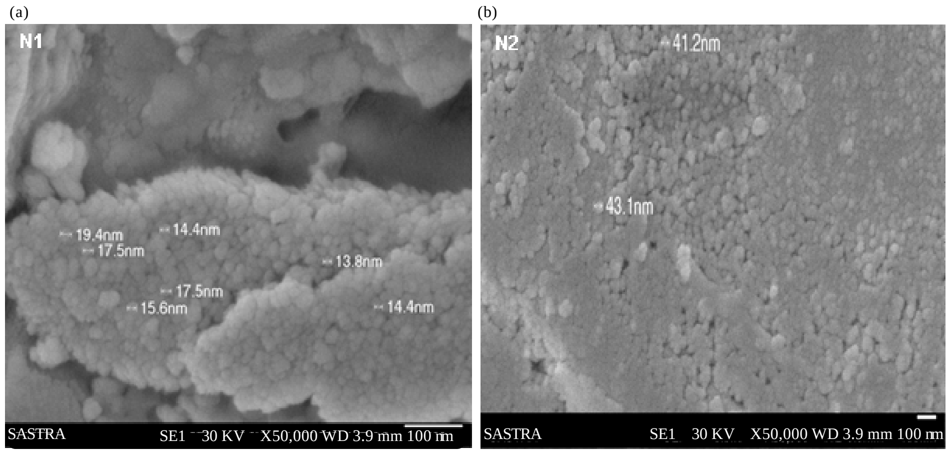

Fig. 2(a-b): SEM micrograph of as-deposited NiO thin film samples, (a) Nickel acetate tetra hydrate (N1) and (b) Nickel chloride precursor (N2)

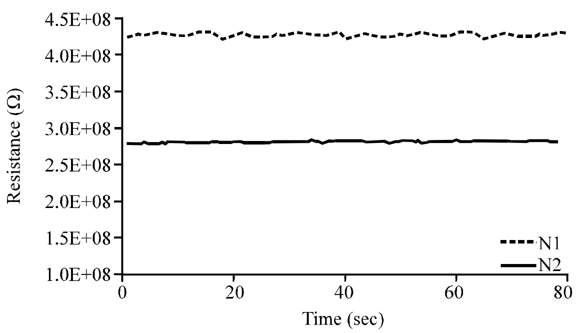

Fig. 3: Baseline resistance of samples N1 and N2

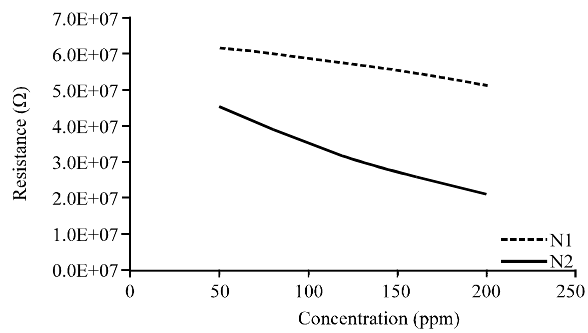

Fig. 4: Change in resistance vs. ethanol concentration for samples N1 and N2

Figure 2 shows the SEM micrographs of NiO thin film deposited at different concentration and precursor solution at 473 K. It is observed that as the concentration of spray solution increases grain size also increases. This is due to that the fact that highly concentrated solution yields larger sized particles.

The majority carrier type of NiO thin film samples were checked using hot probe technique and found to be of p-type.

Sensing characteristics: The NiO thin film samples deposited using various precursors were placed inside the testing chamber and the resistance was measured at room temperature. It is observed from the response that NiO thin films were stable at an optimized operating temperature of 373 K as shown in Fig. 3.

The response of the sensor elements towards various concentration of ethanol is shown in Fig.4. When oxygen ion adsorbs on the surface of NiO film, the adsorbed ion removes the conduction electrons and enhances the resistance of NiO thin film samples. The whole of the oxygen adsorption can be described by the following formulae:

$$O_{2\,(gas)} \leftrightarrow O_{2\,(adsorbed)} \quad (5)$$

$$O_{2\,(adsorbed)} + e^- \leftrightarrow O_{2\,(adsorbed)}^- \quad (6)$$

$$O_{2\,(adsorbed)}^{2-} + e^- \leftrightarrow 2O_{(lattice)}^{2-} \quad (7)$$

At an optimized operating temperature of 373 K, in the presence of ethanol, the resistance of NiO thin film decreased due to the intrinsic characteristics of the semiconductor. With a further increase in concentration of ethanol, further decrease in resistance of the film was observed.

The ethanol sensing mechanism of this NiO gas sensor can be described as follows: (Galvitaa *et al*., 2002; Sivalingam *et al*., 2011).

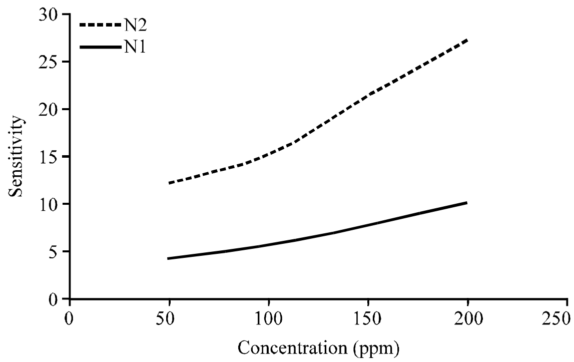

Fig. 5: Response vs. ethanol concentration for samples N1 and N2

$$CH_3CH_2OH \rightarrow CH_4+CO+H_2 \quad (8)$$

$$CH_3CH_2OH_{ads}+O_{ads}^{-} \rightarrow CH_4+CO_2+H_2 \quad (9)$$

Thus, when ethanol is injected into the testing chamber, it was subsequently adsorbed on the surface of NiO thin film and in turn the resistance decreased. This may be due to a decrease in the oxidative process and in turn lead to a decrease in resistance. The response of NiO thin film samples N1 and N2 were calculated using Eq. 10, (Varghese and Grimes, 2004). For p-type metal oxide in the presence of a reducing gas, response (S) is defined as:

$$S=\frac{(R_g-R_0)}{R_0}\approx\frac{R_g}{R_0} \text{ if } R_0 << R_g \quad (10)$$

where, R_0 and R_g are the electrical resistance of the film in the absence and presence of VOCs respectively. The, calculated response of N1 and N2 samples, shown in Fig. 5 were found to appreciable. The results clearly indicate that even at lower concentration of ethanol i.e., 50 ppm, the response is appreciable.

CONCLUSION

A highly adherent, nanostructured NiO thin films were successfully deposited on the glass substrates using spray pyrolysis technique. XRD confirmed the polycrystalline nature of the samples with face centered cubic structure and the FE-SEM results indicated that NiO thin film samples had spherical shaped morphology. From the sensing characteristics of NiO thin films towards various concentrations of ethanol it was observed that N2 sample exhibited appreciable response compared to N1 sample at an optimized operating temperature of 373 K. Hence it was concluded that the nanostructured NiO thin film, spray deposited using nickel chloride was found to show higher response in the order of 12 towards 50 ppm of ethanol. Therefore, as-deposited nanostructured NiO thin film can be used as a sensor element in the senor array of electronic nose for effective food quality assessment of milk, fish etc. where ethanol is a good marker.

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