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Preparation of nanocrystalline nickel oxide thin films by sol–gel process for hydrogen sensor applications

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ABSTRACT

Preparation of nanocrystalline NiO thin films by sol–gel method and their hydrogen (H_2) sensing properties were investigated. The thin films of NiO were successfully deposited on the glass and SiO_2/Si substrate by a sol–gel coating method. The films were characterized for crystallinity, electrical properties, surface topography and optical properties as a function of calcination temperature and substrate material. It was found that the films produced by this method were polycrystalline and phase pure NiO. The H_2 gas sensitivity of these films was studied as a function of H_2 concentration and calcination temperature. The results indicated that the sol–gel derived NiO films could be used for the fabrication of H_2 gas sensors to monitor low concentration of H_2 in air quantitatively at low temperature range (<200 °C).

1. Introduction

Recently, metal oxide thin films have been investigated for gas sensor applications at low temperature. In particular, monitoring of hydrogen (H_2) in air is very important because of rapid increase in H_2 usage in industries, laboratories, and energy technologies. Also, sensors that operate with low power consumption and at low temperature are important for continuous monitoring of H_2 concentrations in ambient conditions in a safe manner. However, the current commercial gas sensors suffer from severe limitations due to their high power consumption, high measurement temperature and low sensitivity [1–4]. Therefore, there is an urgent need for new sensor materials that can be used to design sensors with low power consumption. In order to further improve the gas sensor performance, nanocrystalline metal–oxide semiconductor materials have been widely studied for the fabrication of gas sensors [4–6].

Nickel oxide (NiO) thin films are p-type and transparent semiconductor with a band gap energy in the range of 3.6–4.0 eV [7]. NiO thin films have been investigated for electrochromic devices, gas sensors, organic light emitting diodes (OLED), and display devices [8–11]. Thin films of NiO have been fabricated by different methods such as reactive sputtering [12], chemical vapor deposition [13], reactive pulsed laser deposition [14] and sol–gel method [15]. Nickel is a transition metal which can have multiple oxidation states such as Ni^{2+} and Ni^{3+}. Also, NiO exhibits a p-type semiconducting behavior due non-stoichiometry of metal oxides [2]. In recent years, metal oxide thin films have been fabricated by sol–gel process because of its cost effectiveness, scalability and reproducibility. The sol–gel process produces high quality thin films on different substrates. The sol–gel derived metal oxide films have several important properties such as high porosity, uniformity, and nanocrystallinity, which are key factors related to gas sensing properties such as sensitivity and response and recovery times [16].

In the present study, p-type and transparent NiO films were prepared by a sol–gel process on the glass and SiO_2/Si substrates. The film properties were investigated as a function of calcination temperature and substrate material. The effectiveness of substrate and calcination temperature was investigated by measuring the gas sensing properties of NiO. It was found that the H_2 sensors fabricated using these NiO can be operated at a temperature as low as 175 °C with high sensitivity, fast response and recovery times. The results were highly reproducible and repeatable with high material stability in a wide temperature range. In this paper, these experimental results are presented.

2. Experimental procedure

NiO thin films were synthesized by a sol–gel coating method on the alkali free glass substrate and oxidized silicon wafer (SiO_2/Si), where the thickness of SiO_2 was around 1 μm. The nickel nitrate hexahydrate was used as the starting material and it was dissolved in equal amount of isopropanol alcohol and polyethylene glycol 200 to get a 0.1 M solution. The prepared solution was stirred at a temperature of 40 °C for 60 min to yield a transparent and homogenous solution. A dilute ammonium hydroxide solution was introduced to the

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solution to produce nano nickel hydroxide particles. In order to eliminate particle agglomeration, Triton X-100 (Alfa Aesar) was added to the solution prior to the addition of ammonium hydroxide solution. The prepared solution was used to coat on alkali-free glass and SiO_2 (1 μm)/Si substrates by a spin coater. The spin coater was set to a rotation speed of 3000 min^{-1} for 30 s. In order to remove extra solvent and the organic residuals, the coated samples were heated up to 350 °C for 5 min after each coating step. This step was repeated for ten times for each sample to produce a uniform multilayer thin film. Finally, the coated samples were calcinated at different temperatures for 3 h in a tube furnace in air. Table 1 lists sample numbering and their calcination temperatures and substrate materials.

The crystal structure of the samples was studied with X-ray diffraction (XRD) measurements using a Cu K_α radiation (45 kV, 40 mA, Panalytical X-ray). The surface topography and particle size were studied using scanning electron microscope (SEM, JEOL 6100). The optical transmittance measurements of NiO thin films were extracted using a double beam UV/Visible spectrometer (UV-1650 PC Shimadzu) as a function of wavelength in the range of 250–1050 nm. The electrical resistivity of the samples was measured in the temperature range of 25–300 °C under vacuum condition (30 mTorr). The Fresnel approach was used to theoretically estimate the optical properties and the thickness of the films [17]. A program developed using Matlab software to theoretically estimate the refractive indices and the thickness of NiO film based on the experimental values of the reflectance data from bi-layer of NiO/glass or NiO/SiO_2/Si substrates. The value of the thickness was estimated around 94 ± 5 nm.

The gas sensing devices were fabricated by vacuum deposition of a thin layer of gold (~75 nm) on the surface of NiO films followed by photolithography and etching in a KI + I_2 solution with a comb like structure with 200 μm length and 20 μm width and spacing. The sensors were installed in a custom-build closed chamber (200 cm^3) with Au connecting electrodes. The sensors were placed on a resistive heater coupled with a DC regulated power supply while the temperature was fixed at 175 °C using a Ni–Cr thermocouple in contact with NiO films. Total air flow rate through the chamber was kept constant at 100 standard cubic centimeters per minute (sccm) for all measurements. The samples were installed inside the chamber and maintained in air for 60 min at 175 °C before introducing H_2 gas for the first time. This step was necessary for the chamber to reach to stable temperature before starting each test. High purity H_2 was introduced to the air flow through the closed chamber and the air flow rates were manipulated by needle valves and mass flow controllers. After introducing the gas into the chamber, the resistance of the sensor was measured using a high mega ohm multimeter (Keithly, Model-1200) and LabVIEW software.

3. Results and discussion

3.1. Characterization of microstructure

Fig. 1 shows the XRD spectra of NiO thin films deposited on alkali free glass and SiO_2/Si substrates. The calcinations were carried out at different temperatures to investigate the effect of temperature on the crystallinity. In the XRD patterns, peak appeared corresponding to (200) and (111) crystal planes of NiO. The XRD patterns indicate that the films have a polycrystalline structure and that the degree of crystallinity depends on the substrate materials as well as the calcination temperatures. When the temperature increased, the full width at half maximum (FWHM) of XRD peaks decreased indicating that the crystallinity was enhanced and the grain size was increased by increase of the calcination temperature. The average grain size of NiO films was calculated using Scherer formula as 45, 62 and 68 nm for G-550, S-550 and S-700, respectively. These results indicate that the average crystal size depends on the calcination temperature and substrate materials.

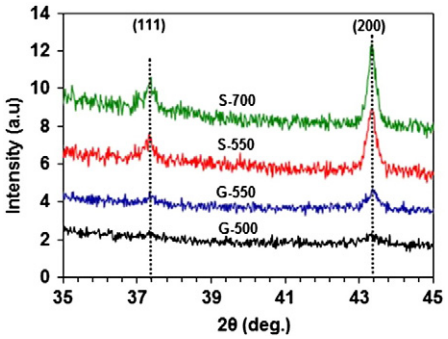

Fig. 1. XRD patterns of NiO films described in Table 1 (measured intensity data were shifted 200 for clarity).

Fig. 2 shows the SEM images of sol–gel coated NiO thin films on glass and SiO_2/Si substrates. The surface morphology was studied with SEM as a function of calcination temperature and substrate material. It can be seen that the G-500 film had a uniform distribution of small size particles on the surface. The grain size was increased as the increase of the calcination temperature. For the film fabricated on SiO_2/Si substrate, the grain size increased by increasing the calcination temperature to 700 °C (see sample S-700). Although calcination temperature was same, the grain size NiO film changed when different substrates were used (G-550 and S-550). In this case, the same sol-mixture was coated on glass and SiO_2/Si substrates under identical conditions and calcination was done by keeping both samples together in the same temperature zone of the furnace. The effect clearly indicated that the substrate has a significant influence in the grain size. The result can be interpreted as due to the fast thermal expansion of SiO_2/Si compared with the glass substrate. A cubic-like structure was observed on the surface of NiO films deposited SiO_2/Si substrates. The shape of grains was changed and the size was increased rapidly at high temperature and the film calcinated at 700 °C exhibited a largest grain size among this set of samples. Here, both XRD patterns and SEM images of NiO films indicated that the crystal size increased and the film porosity decreased when calcination temperature was increased. The crystal size, crystallinity and porosity are three most important factors that affect the gas sensitivity of metal oxide thin film devices. The distribution of the grain size was inserted for each film.

Table 1
Description of nickel oxide films investigated in this study.

Sample	Substrate	Calcination temperature (°C)
G-500	Glass	500
G-550	Glass	550
S-550	SiO_2/Si	550
S-700	SiO_2/Si	700

3.2. Electrical and optical properties

Fig. 3 shows the change of resistance as a function of temperature for NiO films in the range of 25–300 °C. The results indicate that the change of resistance with temperature has a typical Arrhenius behavior. When the calcination temperature was increased the electrical resistivity of NiO films increased. Generally, the resistivity of the film can be affected by isotropic background scattering due to external surface and grain boundaries [18]. The fitted line using the Arrhenius equation can be used to estimate the activation energy [10]. It is clear that the slope of the fitted line increases with increasing the calcination temperature. The activation energy of S-550 and S-700 were calculated as 0.23 eV and 0.30 eV, respectively. The activation energies of G-500 and G-550 were close to 0.22 eV. Phase pure stoichiometric NiO