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Structural and optical studies on nickel oxide thin film prepared by nebulizer spray technique

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ABSTRACT

In the present work, nickel oxide thin film has been deposited on glass substrates at temperature 400 °C by simple and inexpensive nebulizer spray technique. The effect of the volume of sprayed solution on structural and optical properties of the films were investigated using X-ray diffractometer, UV–Vis–NIR spectrometer, photoluminescence, Raman spectrum and linear four probe resistivity measurement, respectively. It is found that increase in the sprayed volume of solution with 0.3 M leads to increase in the film thickness. XRD studies indicated cubic structure and the crystallites are preferentially oriented along the [1 1 1] direction. It is also found that as the sprayed volume of the solution increases the transmittance decreases, consequently the band edge shifted from lower wavelength to higher wavelength and the band-gap energy wanes from 3.64 eV to 3.13 eV. From PL spectra, the sample shows sharp and strong UV emission around 376 nm corresponding to the near bandedge emission of NiO under excitation of 275 nm.

1. Introduction

Nowadays thin film science and technology plays an important role in microelectronics, communications, optoelectronics, integrated optics and photovoltaic devices. Many transition metal oxide films exhibit an electrochromic (EC) effect as they change their optical transmittance upon charge insertion or extraction. These materials may be integrated into multilayer devices [1]. Electrochromic (EC) effect occurs in many transition metal oxide materials as well as in some organic molecules and polymers. The main advantage of an electrochromic device is that, it can regulate the throughput of solar energy. All of the interesting materials are oxides that are employed into thin films. Nickel oxide (NiO) is an attractive material for use as an antiferromagnetic layer [2], p-type transparent conducting film [3], electrochromic layer [4,5], and functional sensor layer for chemical sensors [6].

It has an excellent chemical stability and shows p-type conductivity due to Ni vacancies and/or O interstitials [7]. It is a semitransparent material of pale green colour and has a wide band gap in the range of 3.5 eV to 4.3 eV [8,9]. Nickel oxide thin films are very interesting for a variety of applications, for instance, as active material in chemical gas sensors [10,11], as anode in oxygen fuel cells [12], as counter electrode in smart windows due to its p-type electrochromic property [13], and in other optoelectronic devices such as elements for information display, light shutter and variable reflectance mirrors [14–16].

Among the electrochromic materials, nickel oxide thin film has been mostly produced by several techniques like spray pyrolysis, sputtering, vacuum evaporation, chemical deposition, sol–gel and pulse laser deposition [17]. The advantage of chemical spray pyrolysis is manifold: nanostructure of the film (compact or porous) can be altered depending on the spray condition, repeatability, adherent of deposits and cost effective [18]. Spraying is performed in an ambient atmosphere using air as driving gas and in most cases aqueous precursor solutions were used. The present work focuses on the effect of various sprayed volume of solution for the preparation of NiO film using simple nebulizer spray technique and its effect on structural and optical properties.

2. Experimental

2.1. Mechanism of simple nebulizer

The most commonly used nebulizers are jet nebulizers, which are also called “atomizers” Jet nebulizers are connected by tubing

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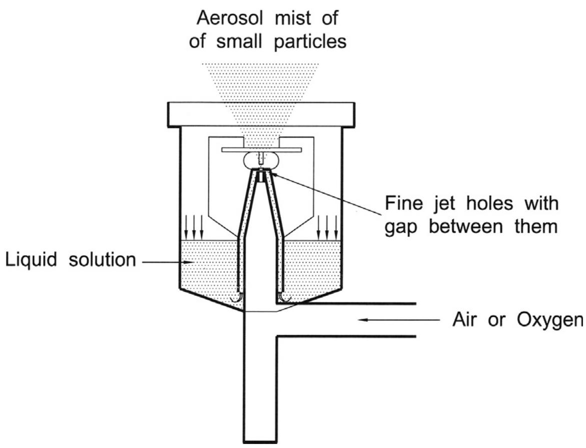

Fig. 1. Schematic diagram of the simple nebulizer.

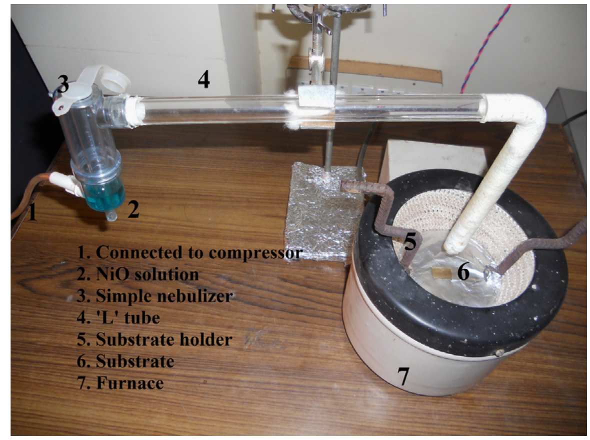

Fig. 2. Experimental set up of nebulizer technique.

to a compressor, that causes compressed air or oxygen to flow at high velocity through a liquid chemical to turn it into an aerosol, which is then sprayed on the substrate through the optimized 'U' type glass tube which has small tapering at the substrate side to transmit the fine droplets. Fig. 1 represents the schematic diagram of the simple nebulizer.

2.2. Venturi effect

The venture effect is the reduction in fluid pressure that results when a fluid flows through a constricted section of the tube. It is a jet effect; as with a funnel velocity of the fluid increases as the cross sectional area decreases, with the static pressure correspondingly decreasing. When a fluid flows through a tube that narrows to a smaller diameter, the partial restriction causes a higher pressure at the inlet than that at the narrow end. According to the laws governing fluid dynamics, a fluid's velocity must increase as it passes through a constriction to satisfy the principle of continuity, while its pressure must decrease to satisfy the principle of conservation of mechanical energy. Thus any gain in kinetic energy of a fluid may accrue due to its increased velocity through a constriction is negated by a drop in pressure. The schematic diagram of the nebulization is given in Fig. 1.

2.3. Materials and methods

Nickel oxide thin films have been deposited using 0.3 M aqueous solution of nickel chloride $NiCl_2 \cdot 6H_2O$ by nebulizer technique onto pre cleaned microscopic glass substrates, which were chemically and ultrasonically cleaned before coating. Fig. 2 shows the experimental setup of the nebuliser technique with a photograph of the simple nebulizer. This technique has some advantages such as an atomization based on hydraulic pressure without using any carrier gas, intermittent spraying and fine atomization. The films are having more uniform thickness and there is no pinhole. During the film deposition, the sprayed volume was kept at 1 ml, 2 ml, 5 ml, 10 ml and 20 ml for the preparation of uniform NiO thin film. The substrate temperature for each deposition was kept at 400 °C in the air atmosphere. Only the small amount was consumed in this nebulisation and 10 min taken for spraying 5 ml of precursor solution i.e the nebulisation rate is 0.5 ml per min. The nozzle to substrate distance was fixed at 7 cm and the optimized compressed carrier gas as air flow rate was optimised as 1.2 kg/cm^2. After deposition, the films were allowed to cool slowly to room temperature. The rate of cooling was 100 °C/h.

2.4. Formation of nickel oxide thin films

Nickel chloride solution was sprayed onto the pre-heated glass substrates, which undergoes evaporation, solute precipitation and pyrolytic decomposition. The overall reaction process can be expressed as heat decomposition of nickel chloride to clusters of nickel oxide in the presence of water and air. The following chemical reaction took place on the substrate at elevated temperature.

$$NiCl_2 \cdot 6H_2O \rightarrow NiO + 2HCl\uparrow + 5H_2O\uparrow$$

Uniform and specular reflected NiO thin films were prepared by the process corresponding to a heat decomposition of nickel chloride to nickel oxide in the presence of water and air. The deposited films may be disorder $Ni(OH)_2$ structure or crystalline NiO structure according to the following reactions [19].

$$NiCl_2 + 2H_2O \xrightarrow{Ts} 2HCl + Ni(OH)_2$$

$$NiCl_2 + 2H_2O \xrightarrow{Ts} 2HCl + NiO + H_2O$$

Kamal et al. [19] had shown that the formation of $Ni(OH)_2$ is more probable at higher temperature (420 °C) than the one used in the present work (400 °C). In this process, the growth rate of the films increases with the sprayed volume. Hence, the efficiency of rearrangement of the arriving material is small and the thickness of the films increases with sprayed volume i.e., after microparticles land on the film surface, decomposition of chlorides and desorption of chlorine and material rearrangement should take place.

The NiO thin film properties were studied for various sprayed volumes such as 1 ml, 2 ml, 5 ml, 10 ml and 20 ml keeping the substrate temperature at 400 °C. The film thickness was measured by stylus profilemeter (Mitutiyo SJ-30). The crystallinity of film was determined using X'pert PRO PANalytical powder X-ray diffractometer. The optical transmittance and band gap were demonstrated by Ocean Optics HR-2000 UV–Vis–NIR spectrophotometer. A photoluminescence spectrum was analyzed by Cary Ellipse Fluorescence Spectrophotometer (VARIAN). Raman spectra were measured at room temperature using a 100 × microscope objective using micro-Raman spectrometer (M/s Seki, Japan) equipped with an argon laser (514.5 nm). The spectral signal was dispersed by the 2400 grooves/mm grating onto a cooled (−70 °C) CCD detector. The Raman spectra were acquired with a laser excitation power of 100 mW.