



Properties of NiO Thin Films Prepared by Chemical Spray Pyrolysis using NiSO₄ Precursor Solution

S. MORKOÇ KARADENİZ^{1*}, A.E. EKINCI¹, F.N. TUZLUCA¹ and M. ERTÜBRUL²

¹Department of Physics, Faculty of Art and Sciences, Erzincan University, 24100 Erzincan, Turkey

²Department of Electric & Electronics, Faculty of Engineering, Atatürk University, 25240 Erzurum, Turkey

*Corresponding author: E-mail: smorkoc@erzincan.edu.tr

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Nickel oxide thin films were deposited by chemical spray pyrolysis. The influence of the nickel sulfate hexahydrate (NiSO₄·6H₂O) precursor on the thin film properties was studied. Present experimental conditions such as the substrate temperature and precursor concentration which are 350 °C and 0.3 M, respectively, were investigated. It is found that pure NiO thin films crystallized in the cubic phase. Nickel oxide thin films have been annealed at 425 °C for 3 h under vacuum. It is found that annealing under vacuum is more efficient for the NiO films under the present experimental conditions. After the annealing process NiO thin film was evaluated by XRD, SEM and optical microscopy.

Key Words: Nickel oxide, Chemical spray pyrolysis, XRD, SEM, Optical microscopy.

INTRODUCTION

Transparent conductive oxide films, such as indium tin oxide (ITO), zinc oxide, *etc.* are widely used for transparent electrodes, window coating, *etc.* which are n-type films, however p-type transparent conducting thin films are also required in applications such as transparent electrodes for optoelectronic devices, smart windows, transparent electronic devices, *etc.*¹

Relatively few metal oxides tend to be p-type. Usually the p-type conductivity is due to metal deficit or oxygen excess¹. Nickel oxide is a good example of a p-type semiconductor². It is a stable wide band gap compound and in the case of p-type organic material, after light absorption by the dye, there is hole transfer from the dye to the NiO thin film and electron transfer from the dye to the electrolyte².

Nickel oxide films show anodic electrochromism and are well suitable for device operations in conjunction with tungsten oxide films¹. Nickel oxide exhibits a higher work function than indium tin oxide is more favourable for the hole injection into the organic, in organic light emitting diodes¹.

There are many fundamental issues related to electronic structure and magnetism of 2D oxide over layers grown on different substrates, which still remain to be explored. Nickel oxide has been the model system to study many important properties like antiferromagnetism, electron correlations in narrow band systems³, electrochromic device solar thermal absorber, Tandem dye-sensitized solar cells, battery cathode

and gas sensors⁴, high coloration efficiency, large dynamic range, good cyclic reversibility and low material cost⁵ and is still, interestingly, a model system to study the growth and properties of low dimensional oxide layers³. The most attractive features of NiO are excellent durability, chemical stability and a large span optical density⁴.

A number of nickel oxides with various oxidation states such as nickelous oxide (NiO), nickel dioxide (NiO₂), nickel sesquioxide (Ni₂O₃), nickelosic oxide (Ni₃O₄) and nickel peroxide (NiO₄) have been reported, among these, NiO has rhombohedral or cubic structure and possesses a pale green color⁶. The stoichiometry of NiO is roughly indicated by the color of the sample and the color of NiO is highly sensitive to the presence of higher valence states of nickel, even in traces⁶. It exhibits widely varying magnetic, optical, electronic and electrochemical properties depending on the synthesis process and resulting defect structures⁶.

Under anodic potentials NiO films change color from transparent to deep brown and for chemically prepared NiO thin films the magnitude of the optical modulation during potential switching is crucially influenced by their heat-treatment, which is always performed after the deposition process⁷.

Monoxides such as NiO and CoO are also prototype compounds to study the strongly correlated electron systems⁸.

Because of low-cost and high coloration efficiency electrochromic films, electrochemical applications have been fabricated by several physical and chemical methods and

current limitations in electrochromic technologies are low cost manufacturing and large-area deposition with well-specified nano-porosities⁹.

Nickel oxide thin films have been fabricated by several techniques such as dipping and spin coating, spray pyrolysis, reactive sputtering, chemical vapor deposition, sol-gel chemical bath deposition (CBD), vacuum evaporation, electron beam evaporation, pulse laser deposition, electro-deposition process^{1,4-6,9}.

Among these methods, the chemical bath deposition and spray pyrolysis have many advantages of low cost, low temperature and are easy to be large area prepared, moreover it is well known that the structural properties and surface morphology of materials in thin-film form depend on the deposition conditions and post-deposition annealing⁶.

EXPERIMENTAL

A spray pyrolysis deposition (SPD) technique is employed for a thin film preparation method. Because the film formation is carried out in air by a simple apparatus in spray pyrolysis deposition, the technique is one of the most attractive film preparation methods. Spray pyrolysis deposition is essentially the same film processing technique as the so-called pyrosol technique, in which a source solution is sprayed on the heated substrate to be deposited as a film. In other words, when a source solution is atomized, small droplets splash, vapourize on the substrate, and leave a dry precipitate in which thermal decomposition occurs. The schematic representation of an spray pyrolysis deposition apparatus is shown in Fig. 1.

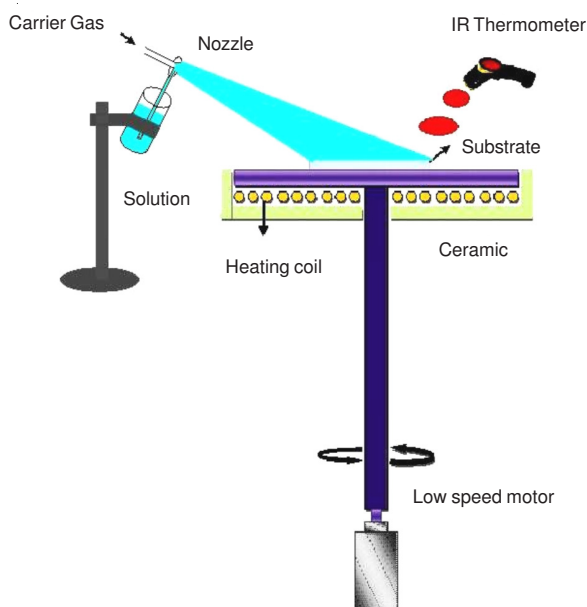


Fig. 1. Schematic representation of a spray pyrolysis deposition (SPD) apparatus

In the experiment, Nickel Sulphate Hexahydrate solution was used by a precursor for preparing NiO thin films.

Bare glass was used as a substrate. 350 °C substrate temperature and 0.3 M precursor concentration were used to deposit the NiO thin film in the experiment. Before the deposition of a NiO thin layer, the substrates were first cleaned by acetone and methanol to eliminate any greasy track in the ultrasonic cleaner.

The volume of the solution for each deposition was 60 mL and precursors were deposited at a 350 °C substrate temperature by using chemical spray pyrolysis. Compressed air was used as a carrier gas. The spray rate was fixed 6 mL min⁻¹ here to achieve the expected thickness. The low speed motor rotation speed was fixed at 0.6 cycles per second. After deposition, NiO thin films were annealed at 425 °C for 3 h under vacuum (10⁻² Pa) by using the PLD chamber system.

Structure and surface properties of the nickel oxide thin films have been characterized by XRD, SEM and optical microscopy.

RESULTS AND DISCUSSION

Fig. 2 shows the X-ray diffraction data of as-deposited and annealed NiO thin film. The crystal structure of NiO thin film was determined by the X-ray diffraction technique. Fig. 2 reveals a marked not only (200) preferred growth orientation but also (111) orientation. There are two major diffraction peaks which are identified to be the (111) and (200) reflection of a cubic NiO structure.

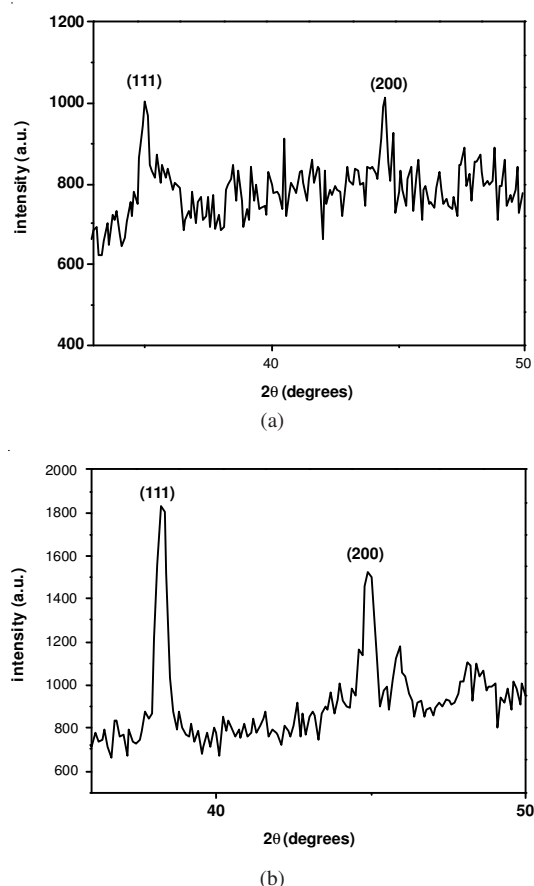
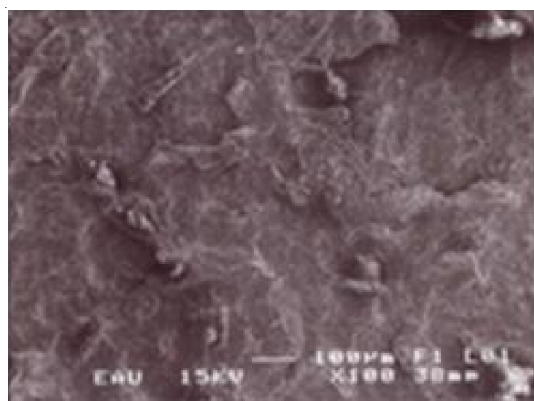


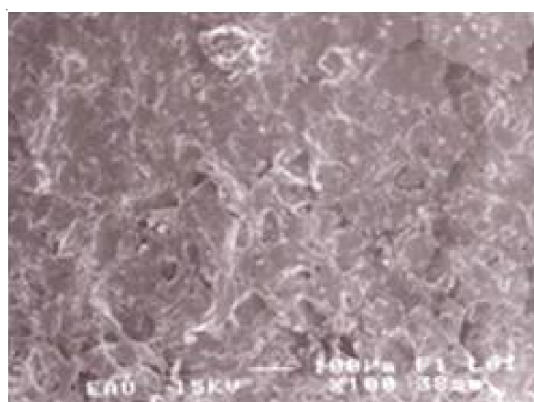
Fig. 2. XRD patterns of the (a) as-deposited NiO and (b) annealed NiO thin film on glass substrate

All of the visible peaks in Fig. 2 belong to the cubic NiO phase¹. The diffraction pattern of as-deposited thin film shows the presence of weak diffraction peaks from (111) and (200) lattice planes (Fig. 2a). However, the annealed NiO thin film were brown in colour and the XRD pattern exhibited intense peaks corresponding to the (111) and (200) orientation of cubic NiO as shown in Fig. 2b.

The SEM photographs of as-deposited and annealed thin films shown in Fig. 3 corroborate XRD results.



(a)



(b)

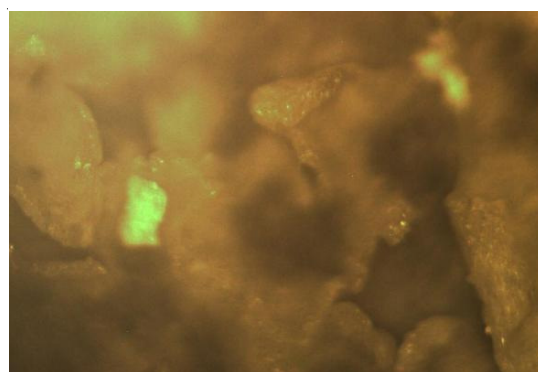
Fig. 3. SEM photographs of (a) as-deposited (b) annealed NiO thin film

Nickel oxide thin film morphology after annealing under vacuum, the roughness of the thin film surface increases; it means that porosity of the films increases²⁻⁴.

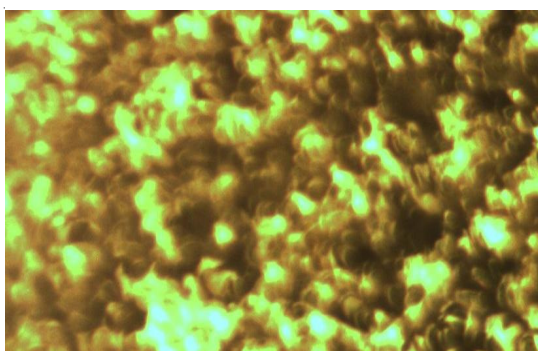
Figs. 4 and 5 shows optical microscopy images of as-deposited and annealed NiO thin films. The images of deposited and annealed NiO thin films characterized by two and three dimensional optical microscopy scans of the sample surfaces. These were recorded from 100 times enlarged surfaces. The optical microscopy images of as-deposited and annealed thin films corroborate SEM and XRD results. According to the images, NiO thin film crystallinity after annealing under vacuum is better than NiO thin film crystallinity before annealing.

Conclusion

Nickel oxide thin films were deposited by chemical spray pyrolysis. Bare glass was used as a substrate. 350 °C substrate temperature and 0.3M precursor concentration were used for having NiO thin film in the experiment. After deposition, NiO thin films were annealed at 425 °C for 3 h under vacuum by using a PLD system. Properties of as-deposited and annealed nickel oxide thin films were evaluated by XRD, SEM and optical microscopy. The XRD pattern exhibited intense peaks corresponding to the (111) and (200) orientation of cubic NiO. The SEM photographs of as-deposited and annealed thin films and the optical microscopy images of as-deposited and

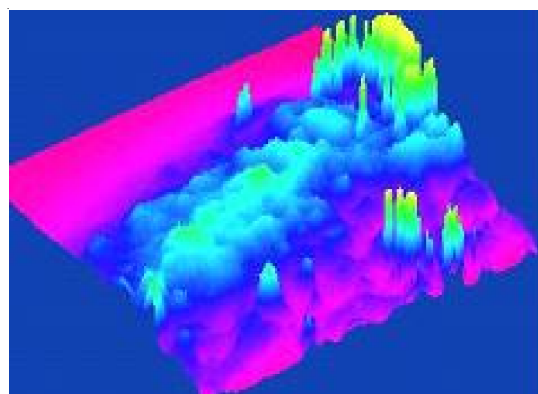


(a)

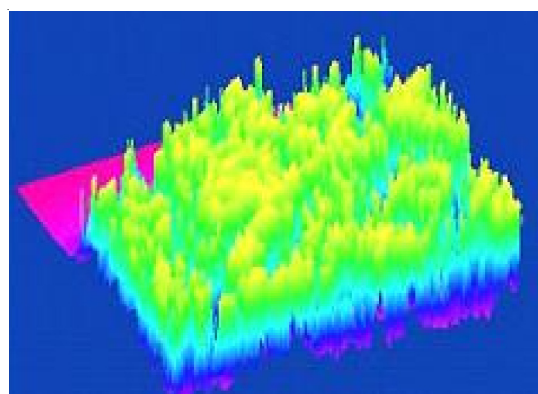


(b)

Fig. 4. Two-dimensional optical microscopy images for (a) as-deposited (b) annealed NiO thin film



(a)



(b)

Fig. 5. Three-dimensional optical microscopy images for (a) as-deposited (b) annealed NiO thin film

annealed thin films corroborate XRD results. According to the photographs, NiO thin film crystallinity after annealing under vacuum is better than NiO thin film crystallinity before annealing.

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