Preparation of Nickel Oxide Films by Sol-Gel Process

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The films have been prepared by the dip-coating technique using nickel nitrate hexahydrate, Ni(NO₃)₂•6H₂O, as starting material and ethylene glycol as solvent. In order to obtain uniform films the withdrawal speed should not exceed 12 cm/min. The crystalline phase formed after firing at 500°C for 2 h is nickel oxide, NiO, which belongs to the cubic system with lattice parameter \( a₀ = 4.1769\text{Å} \). The conductivities of NiO films are on the order of \( 10^{-6}\text{S}\cdot\text{cm}^{-1} \) in our measurements.

Key-words: Nickel oxide, Thin film, Ethylene glycol, Sol-gel process, Dip-coating

1. Introduction
Since the work of Dislich in 1971,¹) the sol-gel process has become an interesting and rapidly growing method in the field of new ceramic materials. One of the most interesting applications of the dip-coating technique based on sol-gel process is the deposition of thin films on glass, ceramic or metal substrates for many different purposes.²⁻⁶) The dip-coating technique is particularly advantageous for the preparation of thin oxide films, because of (i) the extreme homogeneity on a molecular scale since it involves the mixing of precursors in the liquid state; (ii) the fact that complex shapes or large substrates can be coated easily; (iii) the simpler production facilities and processing than other methods, e.g., the vacuum evaporation or sputtering method.

Nickel oxide was thought to be a model of p-type semiconductor. Films of nickel oxide have been prepared by vacuum evaporation,⁷) reactive sputtering⁸) methods. However no sol-gel process for preparation of NiO films has been reported yet. In the present work, nickel oxide films were deposited on glass slides by the dip-coating technique.

2. Experimental procedure
2.1 Preparation of films
Nickel nitrate hexahydrate, Ni(NO₃)₂•6H₂O, was used as starting material, and ethylene glycol as solvent. For preparing the coating solution, the reagent-grade Ni(NO₃)₂•6H₂O (10 g) was dissolved into the reagent-grade ethylene glycol (30 ml). The solution was vigorously stirred in covered beaker at room temperature for 4 h. The coating solution formed after ageing for 3 days was obtained.

The substrate used in this study was glass slides. The glass slides were washed with a basic detergent, cleaned in an ultrasonic bath for 30 min, rinsed with distilled water and dried. The cleaned glass slides was dipped into the coating solution, drawn up vertically at different withdrawal speed, and dried in air at 100°C for 10 to 30 min. The gel films obtained were subsequently heated at a heating rate of 5°C/min to 500°C with 2 h soaking, and then furnace cooled to room temperature.

2.2 Characterization of films
Morphology of the films was observed with an optical microscope (MF3 Type, Austria). The crystalline phases precipitated during heat treatment were examined by the X-ray diffraction technique using Cu Kα radiation (XD-3A Type, Shimadzu, Japan). The thickness of films were measured by interferometer. Finally, the measurement of the absorption spectrum \( \alpha (\lambda) \) was made using spectrophotometer (UV-365 Type, Shimadzu, Japan).

3. Results and discussion
3.1 X-ray analysis
Figure 1 shows the X-ray diffraction pattern of the film after firing at 500°C for 2 h. The calculated d-values are very consistent with that of JCPDS card as indicated in Table 1. The crystalline phase formed is NiO of fcc structure.

3.2 Relation of film thickness versus withdrawal speed
The variation in thickness of the films formed on glass slides by different withdrawal speed is shown.

Fig. 1. X-ray diffraction pattern of the NiO film formed on glass slide at 500°C for 2 h.
in Fig. 2. The thickness of films was found to increase with increasing the withdrawal speed. It is generally accepted that the relationship between thickness \( t \) and withdrawal speed \( u \) has been given as \( t = au^x \). The \( x \) is theoretically \( 2/3 \).\(^9\) The experimental results gave \( x \) values ranging from 0.1 to 1.10\(^{10-13}\).

In the present work, the change in thickness of the films with withdrawal speed conform with a power equation with exponent value \( x \approx 0.61 \).

### 3.3 Effect of withdrawal speed on film formation

Figure 3 shows the optical microscope photographs of films. Figure 3(A) shows a uniform film, the withdrawal speed is slow (6.5 cm/min); (B) shows a defective film, the withdrawal speed is fast (12 cm/min). As shown in Fig. 3(B) the film is defective, as the glass slides had been withdrawn too fast. This may be due to the gel films being thick and the drying rate being high.

In the drying process, the conversion of a wet gel into a dry gel consists of removing as large a proportion of the remaining liquid phase as possible. During this drying stage, crack is more likely if the gel films are thick and the drying rate is high.\(^14\)

In the present work, the maximum thickness obtained without cracking after heating is about 2000Å for single coating, i.e. films crack if thickness exceeds a critical value 2000Å. Thinner NiO film (\( \leq 2000Å \)) do not crack regardless of the drying rate.

### 3.4 Optical and electrical properties

In the absorption spectrum of nickel oxide films as shown in Fig. 4, at approximately 3400Å (~4 eV) the absorption spectrum of the nickel oxide films is characterized by a rapid increase in absorption coefficient.

Nickel oxide is p-type semiconductor, its conductivities are on the order of \( 10^{-6} \) S·cm\(^{-1} \) as measured by the four-probe method at room temperature.
4. Conclusions

(1) Thin films of NiO with lattice parameter $a_0 = 4.1769\,\text{Å}$ have been successfully prepared on glass slides by the dip-coating technique using Ni(NO$_3$)$_2$•6H$_2$O as starting material, and ethylene glycol as solvent.

(2) Withdrawal speed should not exceed 12 cm/min for preparing uniform films.

(3) The conductivities of NiO films are on the order of $10^{-6}\,\text{S/cm}$.

(4) The absorption spectrum of the NiO films is characterized by a rapid increase in absorption coefficient at approximately 3400 Å ($\sim 4\,\text{eV}$).

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References