Effect of Fluorine doping on the Optical properties of NiO thin Films deposited by Spray Pyrolysis

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ABSTRACT

Thin films of undoped Nickel oxide and fluorine doped Nickel oxide have been deposited utilizing easy and cheapest technique, which is chemical spray pyrolysis. Absorbance and transmittance spectra were achieved by double beam spectrophotometer in the wavelength range (300-900) nm. Direct electronic transition for the deposited films, the optical energy gap was evaluated to be increase as the doping ratio increase. All the optical constants such as reflectance and refractive index, are affected by increase their value with the increase in F content. The calculated skin depth was found to decrease upon the increase of fluorine.

Keywords: NiO Thin Film, Chemical Spray Pyrolysis, Optical Properties. Energy Gap

I. INTRODUCTION

Transparent conducting oxides (TCO) thin films are attracting more and more attention due to their widely applications such as liquid crystal displays, light-emitting diodes, solar cells and detector [1-2]. Transparent conducting oxides (TCO) are well known and have been widely used in optoelectronics and transparent electronics as well as in different research fields. Most of the existing TCOs are n-type, where as it is very difficult to prepare binary metal oxides with p-type conductivity [3]. Bulk NiO has a cubic rock-salt crystal structure (Fm-3m) undergoing a weak cubic-to-rhombohedral distortion (R-3m) below the Néel temperature $T_N=523$ K due to the magnetostriction effect [4].

Non-stoichiometric nickel oxide (NiO) thin films can exhibit p-type semiconducting properties and possess wide band gap (3.6 - 4.0eV) and simultaneously low electrical resistance, when film growth conditions lead to generating nickel vacancies and/or forming interstitial oxygen atoms in NiO crystallites [5-6]. NiO films can be prepared by multiple physical and chemical methods such as: spray pyrolysis [7-8], electron beam evaporation [9] pulsed laser deposition [10], plasma-enhanced chemical vapor deposition [11] and reactive sputtering [12]. Among various methods, spray pyrolysis is one through which the films can be coated for large area.

In the present work, the influence of the F-doped on the optical properties of NiO films deposited by chemical spray pyrolysis is considered.

II. EXPERIMENTAL

Thin films of Nickel oxide have been prepared by chemical pyrolysis method. The spray pyrolysis was done by using a laboratory designed glass atomizer, which has an output nozzle about 1 mm. The films were deposited on preheated glass substrates at a temperature of 380°C, the starting solution was
achieved by an aqueous solutions of 0.1 M of nickel chloride (NiCl₂.6H₂O) provided from Merck company/Germany. The doping agent was Fluorine trichloride (FCl₃) (provide by PubChem India) dissolved in deionized water, few drops of HCl were added to the solution in order to get clear solution, used as a doping agent with a concentration of 2% and 4%; these materials were dissolve with deionized water and ethanol, formed the final spray solution and a total volume of 50 ml was used in each deposition. With the optimized conditions that concern the following parameters, spray time was 10 sec and the spray interval (3min) was kept constant. The carrier gas (filtered compressed air) was maintained at a pressure of 105 Nm⁻², distance between nozzle and substrate was about 28 cm ±1 cm, solution flow rate 5 ml/min. Thickness of the sample was measured using the weighting method and was found to be around 0.3 μm. Absorbance and transmittance spectra were obtained using double beam spectrophotometer in the wavelength range (300-900) nm.

III. RESULTS AND DISCUSSION

Transmittance spectra of the prepared films were presented in Fig.1 represent the relationship between transmittance and wavelength of F:NiO thin films. From this figure, it can notice that the transmittance decreased with increasing contain of F in NiO thin films, this may be attributed to the creation of levels at the energy band by increasing F contain.

**Figure 1**: Transmittance with wavelength for NiO thin films and different doping of F concentration.

Absorption coefficient (α) was evaluated from absorbance using the relation [13];

\[ \alpha = \frac{2.303A}{t} \] (1)

Where (A) is Absorbance, (t) is thickness. Fig (2) Shows the relation of α versus wavelength. It can be noticed that absorption coefficient increases by increase F content and progressively increased with wavelength.

**Figure 2**: α against wavelength for NiO thin films and different doping of F concentration

In high absorption region, the form of absorption coefficient with photon energy was given in a more general term for direct transitions [14, 15]:

\[ \alpha h\nu = A(\alpha h\nu - E_g)^n \] (1)

Where ν is the frequency of the incident photon, h is Planck’s constant, A is a constants, Eg is the optical energy gap and n is the number which characterizes the optical processes. n has the value 1/2 for the direct allowed transition, 3/2 for forbidden direct allowed transition and 2 for the indirect allowed transition. Portion of the graph of (αhν)n against hν is extrapolated to α= 0 the intercept gives the transition band gaps. The plot of (αhν)² versus hν shown in Figs. (3-5). These figures shows that the energy gap decreases with increasing F-doped NiO thin films.
from 3.15 eV for undoped NiO film to 2.9 eV for 3% F-doped NiO thin films.

**Figure 3**: $(\alpha h\nu)^2$ against photon energy for NiO thin films.

**Figure 4**: $(\alpha h\nu)^2$ against photon energy of NiO2% F concentration.

**Figure 5**: $(\alpha h\nu)^2$ against photon energy of NiO:4% F concentration.

The extinction coefficient ($k$), which is related to the exponential decay of the wave as it passes through the medium, is defined as [16]:

$$k = \frac{\alpha \lambda}{4\pi}$$

Where $\alpha$ is the absorption coefficient and $\lambda$ is the wavelength. Fig. 5 represents the relationship between extinction coefficient and wavelength. From this figure, it can be noticed that the extinction coefficient increases with increasing content of F in the F: NiO thin film.

**Figure 6**: $k$ for NiO with different doping concentration of F: NiO thin films versus wavelength.

Reflectance ($R$) was obtained by the next formula [17]:

$$A + T + R = 1$$

Where $T$ is the transmittance. Reflectance spectra of NiO with different doping of F: NiO thin films are shown in Fig. 6. It shows that reflectance increases with increasing F contents.
The refractive index \((n)\) depend on the reflectance \((R)\) and extinction coefficient as in the following relation \([18]\):

\[
n = \left[ \left( \frac{4R}{(R - 1)^2} \right) - K_0^2 \right]^{1/2} \frac{R + 1}{R - 1}
\]  

\(\text{(4)}\)

Fig. (7). It shows that refractive index increases with increasing F contents.

The skin depth \((\chi)\) represents the electromagnetic wave will have amplitude reduced after traversing a thickness that calculated from the following relation \([19]\):

\[
\chi = 1 / \alpha
\]  

\(\text{(4)}\)

Fig. 8 showing the variation of skin depth with wavelength. Skin depth increased with increasing F contain in F:NiO thin film.

The NiO thin films were deposited on glass substrates with different concentrations of F using spray pyrolysis technique. From this study optical properties were calculated. Transmittance decreased with increasing contain of F. The energy gap for F-doped was decrease from 3.15 eV for undoped film to 2.9 eV for 3% F content, also reflectance absorption coefficient, extinction coefficient, reflectance and Skin depth were increased via F contents.

IV. CONCLUSION

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