

Elaboration and Characterization of Doped NiO Thin Films Prepared by Spray Pyrolysis and Their Application in Gas Sensor Devices

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Abstract—NiO thin films were deposited on glass substrates using the spray pyrolysis technique at a fixed temperature of 450 °C, employing nickel nitrate hexahydrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) as the precursor. The primary objective of this study is to compare fluorine-, copper-, and aluminum-doped NiO thin films prepared via spray deposition. To achieve this, ammonium fluoride (NH_4F) was used with an F/Ni ratio of 0.05 for fluorine doping, copper acetate ($\text{Cu}(\text{CH}_3\text{COO})_2$) with a Cu/Ni ratio of 0.03 for copper doping, and aluminum nitrate ($\text{Al}(\text{NO}_3)_3$) with an Al/Ni ratio of 0.03 for aluminum doping. Using a fixed NiO solution volume of 5 mL, we examined the structural, optical, and electrical properties of the thin films. The F-, Cu-, and Al-doped NiO films all crystallized in a monocrystalline cubic phase with a preferred (111) orientation, and the largest crystallite size (12.51 nm) was observed for the Al-doped samples. Optically, every doped film exhibited high transmittance in the visible region, with the F-doped NiO reaching about 84%. Furthermore, the F-doped films showed the smallest optical band gap (3.55 eV) and the lowest electrical resistivity 231 $\Omega \cdot \text{cm}$.

Keywords— Nickel oxide, Thin films, Spray pyrolysis, Optical gap energy, Monocrystalline structure.

I. INTRODUCTION

Nickel oxide is one of the most important semiconductor materials in the environmental field due to the detecting ability of toxic gases .

Nickel oxide is considered one of the most significant semiconductor materials in the environmental field due to its

ability to detect toxic gases. NiO is a p-type semiconductor material with an optical band gap ranging from 3.6 to 4 eV. Its chemical stability and durability, along with low toxicity, high optical density, cost-effectiveness, and excellent thermal stability, make it one of the most valuable oxide materials. These physical properties make NiO a key base material for the fabrication of various technological devices, including solar cells, gas sensors, ... etc.

NiO thin films can be fabricated using various techniques such as spray coating, thermal evaporation, reactive spraying, sol-gel, and laser ablation, among others. Among these, the spray pyrolysis technique stands out as a simple, cost-effective, and efficient method for thin film deposition. NiO films produced using this technique exhibit excellent optical and structural properties.

II. EXPERIMENTAL DETAILS

The samples used in this study were deposited using a spray deposition system fabricated. The solutions used are Nickel nitrate hexahydrate $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$. In this work, we have used a F, Cu and Al doping with various concentrations in the range $\text{F}/\text{Ni} = 0.05$ and $\text{Cu}/\text{Ni} = 0.03$ and $\text{Al}/\text{Ni} = 0.03$ at.%. Then, we have added a drop of HCl to stabilize heating solution. The mixture solution was stirred at room temperature and heated at 40°C for 2 h to yield a clear and transparent solution. The coating was made 1 day after the precursor was prepared.

The spraying of the liquid is then carried out through a pyrolysis system that transforms it into fine droplets. These precursors are ejected on glass substrates placed below a substrate holder heated to a fixed temperature of 450°C



Fig. 1 A photograph of the experimental setup for the deposition of doped NiO thin films.

III. RESULTS AND DISCUSSION

A. Structural Properties

The structural characterization of the NiO thin films prepared is carried out by X-ray diffraction method that is shown in figure 1. XRD spectra indicate that the films exhibit a single crystal structure that belongs to the cubic type of NiO (JCPDS) No. 47-1049). Figure 1 shows that the XRD peak at 37.17538° corresponding to (111) crystal plane.

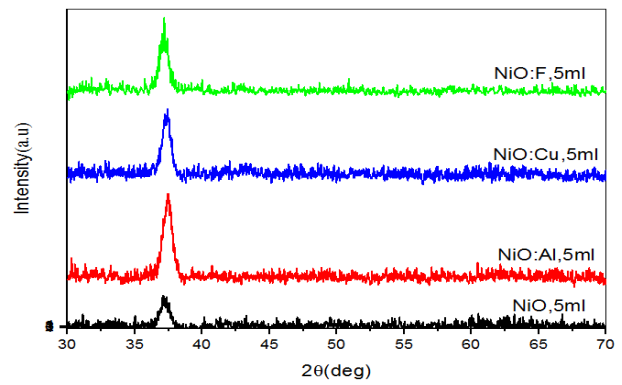


Figure -1: The results of X-ray diffraction spectra of doped NiO thin films

Table 1 shows the various structure parameters structural parameters of the undoped and doped NiO thin films.

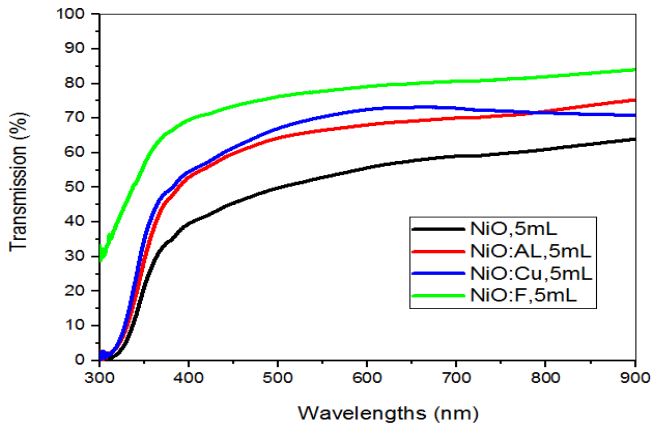
TABLE I: the structural parameters of the undoped and doped NiO thin films.

Samples	Diffraction angle 2θ ($^\circ$)	FWHM β ($^\circ$)	Crystallite size D (nm)	Lattice parameter a (nm)	Main strain ϵ
NiO, 5 ml	37,37	0,54	18,51	0,4414	0,00308
NiO:Al, 5 ml	37,42	0,68	12,42	0,41593	0,00388
NiO:Cu, 5 ml	37,34	0,67	12,51	0,4168	0,00383
NiO:F, 5 ml	37,21	0,80	12,47	0,44266	0,00459

B. Optical Properties:

The Optical characterizations of fabricated NiO thin films doped were performed by measuring the transmittance in the wavelength region 300 to 900 nm as it is shown in Figure 2. As we can see, the developed samples showed a high transmission ranging between 53.9 and 83.9% in the UV-Visible region the value of the average transmission of spray NiO thin films is about 76% in the visible region. However, the prepared F doped NiO thin films

exhibit good transmission approximately 80 % in the visible region the region of the absorption edge was located



between 330 and 360 nm in. It is related region between of the valence band and the conduction band.

Figure -2: the transmittance of the thin films prepared.

Figure-3: determination the optical gap of doped NiO layers prepared. The UV-Vis spectroscopy revealed a band gap of E_g (3.55 to 3.76 eV) eV for the NiO. This result is in agreement with prior reports for similar NiO oxide.

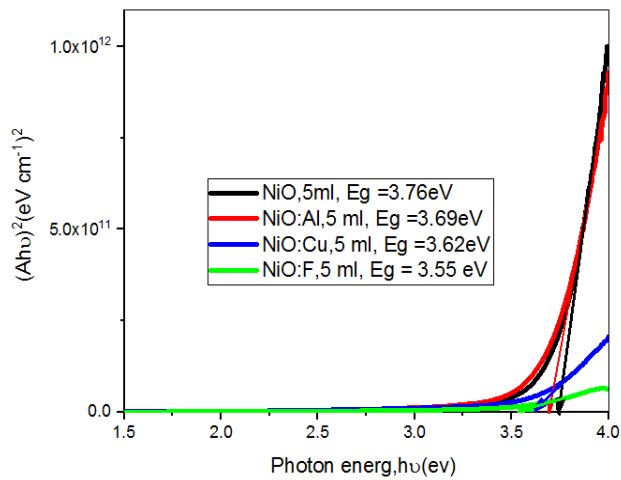


Figure-3: determination the optical gap of doped NiO layers prepared.

Figure-4: the variation of $\ln A$ as a function of $h\nu$ of undoped NiO thin films prepared. From Figure 4, we were able to determine the value of the Urbach energy of doped NiO layers prepared, which ranged between (310 meV to 632 meV).

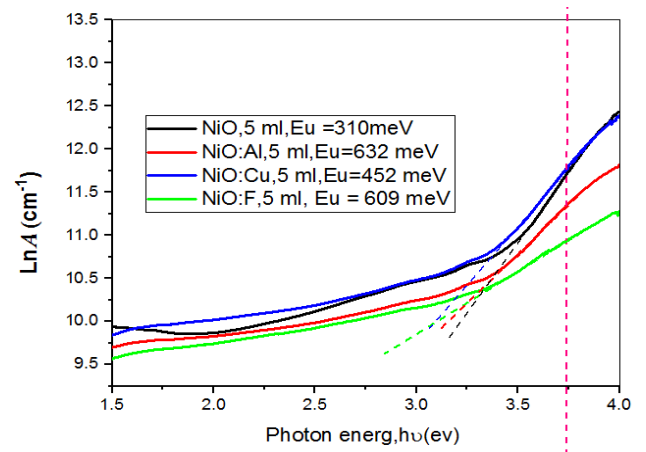


Figure-4: the variation of $\ln A$ as a function of $h\nu$ of undoped NiO thin films prepared.

C. Electrical Properties

TABLE II: Shows the electrical characterizations such as the variation of measured current and voltage and the sheet resistance of doped NiO thin films prepared.

It can be seen that the undoped NiO thin film has a highest electrical resistivity of $1.5 \times 10^5 \Omega \cdot \text{cm}$ and the F doped NiO thin film has a minimum the electrical resistivity of $231 \Omega \cdot \text{cm}$

TABLE II: Shows the electrical characterizations such as the variation of measured current and voltage and the sheet resistance of doped NiO thin films.

Samples	Measured Current I (nA)	Measured voltage V (mV)	Sheet resistance R_{sh} (Ω)	Electrical resistivity ρ ($\Omega \cdot \text{cm}$)
NiO, 5 ml	0.011	5	1.1×10^{10}	1.5×10^5
NiO:Al, 5 ml	0.5		4.5×10^{10}	6.4×10^5
NiO:Cu, 5 ml	0.164		1.4×10^8	1.6×10^3
NiO:F, 5 ml	10.80		2.1×10^7	$231 \Omega \cdot \text{cm}$

IV. CONCLUSIONS

The doped NiO thin films were deposited by pyrolysis spray on glass substrates. The effect of doping on optical and structural properties of films was studied. XRD spectra

indicate that the films exhibit a singlecrystal structure that belongs to the cubic type. The deposited NiO films showed a preferential orientation following the plane (111) along the c-axis perpendicular to the substrate surface. The developed samples showed a high transmission ranging between 53.9 and 83.9% in the UV-Visible region. However, the prepared F doped NiO thin films exhibit good transmission approximately 80 % and the obtained optical gap values are in good agreement with the literature data (3.55~3.76eV). The F -doped NiO thin films deposited exhibit a minimum optical band gap energy of 3.55 eV, and it has a minimum the electrical resistivity of 231Ω.cm, which can be used as a gas sensing.

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