Preparation and characterization of p- NiO:Li thin films as Schottky photodiode

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Abstract. Nickel oxide was prepared using the chemical method. Li-doped NiO thin films with concentrations (0.04) were deposited on glass substrate using drop casting technique with thickness 150nm, and then the annealing at 300 °C for 60 sec. The effect of the lithium doping on the structural and optical properties of Li: NiO films were examined. The structure of the prepared films were described by x-ray diffraction (XRD) and Atomic Force Microscopy (AFM). The results of X-ray pattern showed the NiO and Li: NiO films to have a polycrystalline structure of a cubic type and preferred orientation (111). (AFM) data indicated that the structure was nanoscale and surface of the films is highly smooth. The study of optical properties included the transmittance spectrum of the prepared films of the wavelengths of (300-900) nm, It was found that the transmittance of pure nickel oxide is 79% in the visible area after doping by Li. The transmittance decreases and the absorption increases. The energy gap was also calculated and found to be decreasing by increasing the doping concentration. Other important optical properties of the absorption coefficient and extinction coefficient were calculated. The electrical properties of the prepared films were studied, It was found that the concentration of the carriers increases with increasing doping concentration and mobility decreases. The thin films were deposited on a substrate of FTO to make of Schottky diode. The characteristics of I-V, C-V were studied. A solar cell was found the efficiency of the cell was increased by doping.

Keywords: nickel Oxide, XRD, AFM, Transmittance, photodiode

Introduction:

The distinction in semiconductor junctions and their functions has been restricted to some extent compared to standard semiconductors, although semiconductors have good stability in harsh environments and have special properties such as optical transparency functions, [1] such as photovoltaic. To take advantage of the total potential of semiconductors from oxide, the composition of p-type semiconductors with semi-conductive type Ni oxidation is formed for electronic and electronic applications, like rectification of diodes, transistors, optical detectors and optical diodes [2–6]. Most of oxidizing semiconductors contain n-type properties due to the donors are more than receptors [7]. Therefore, the manufacture of semiconductors that rely upon sort p-type Oxide poses a significant challenge within the formation of p-n intersections. The oxides of transition metals, like NiO-doped Li [8] and related copper oxide compounds [8-10] are exceptional as a result of those oxides are mostly p-type semiconductors, as transition metal ions can be easily oxidized with that's from NiO and Copper vacancies[9]. Like Li-doped NiO, excess O2 within the NiO film has similar properties and is additionally a p-type semiconductor[10]. though the conducting mechanism within the NiO has long been the topic of much controversy, resistivity of...
the NiO film will be lowered by a rise of the Ni$^{3+}$ ions ensuing from the excess oxygen in the NiO crystallite [11]. Recently, a heterogeneous relationship with oxide and nitrogen with the properties of photon fusion oxide [5, 6, 11] has been reported. These innovative materials and applications are driving the progress of semiconductor-based semiconductors steadily. During this work, p-n heterogeneous diodes were manufactured on the basis of NiOx / indium Tin oxide ITO / glass nickel oxide with different O$_2$ ratios in the anarchic NiOx films on the corresponding ITO glass.

2. Experimental works

7.48 g of NiCl$_2$ were melted (BDH Chemicals Ltd Pool England) in 50 ml of 1WT (Sigma Aldrich USA) PVP. Distilled water was used and reused in all stages of the experiment. The solution was added in a round flask with flipping. The colour of the mixture was green. Then we add about 30 mL NaOH (1M) to the mixture rapidly. The nanoboder solution was formed as shown in Figure 1. The prepared film was annealing at about 300 ° C for one hour. and then cooling them till reach to room temperature, NiO particles were separated using centrifugation and washed by distilled water to eliminate any contamination.

![Figure 1. NiO freshly colloidal nanoparticles which is prepared by a chemical method (left) and the solution (right)](image)

Figure 2 shows that colloidal nanoparticles were chemically prepared. A sufficient amount of Li was added to the previous solution. In this experiment, the radiation level were determined about 100_ [Li] / [Li + NiO], which was changed from 0 to 4% mol. They are grounded using drop casting technique on the glass substrate. The solution was take using pipette and then was dropped on the glass surface only 3 drops, the samples are then dried using a heater at 80 ° C, after which the film becomes ready. X-ray-6000, Shimadzu (XRD-6000) was analysed by XRD to determine the crystallization of NiO films. Surface and mass morphology was examined by the Hitachi S-4300 electron microscopy scanner (SEM). Electric resistance was defined by a four-point verification method. We performed optical permeability measurements using a (UV-Vis) spectrometer. PL spectra were recorded at room temperature using the He-Cd laser at wavelength of 500 nm as the excitation source.

![Figure 2. Schematic diagram showing drop casting method.](image)
3- Results and discussion
XRD patterns of 4mol% NiO: Li-thin films appear at 300 ° C in Figure. 3. XRD spectra show that NiO: Li films appeared without forming phases and secondary groups such as LiNi2O4 and NiO pure. The film shows peaks (111), (200), (220), indicating that they have (111) favorites because of the phenomenon of self-composition. From this figure, it is readily observed that the intensity of the diffraction peak (111) will increase with the distortion. This indicates the increased crystallization of the films and the reduction of the crystalline defects in the grid, where it is observed from Table (1) that the crystal size increases because of FWHM reduction. Either intensity of dislocation, decreased with an increase in crystalline volume. [12]

![X-ray diffraction patterns for pure NiO and NiO:4%Li films measured at thickness of 150nm](image)

**Figure 3. X-ray diffraction patterns for pure NiO and NiO:4%Li films measured at thickness of 150nm**

| Samples     | 2 Theta (deg) | (hkl) plans | β (deg) | D_g (nm) | η x10^4 (lines2×m^-2) | δ x 10^4 (lines/m^2) |
|-------------|---------------|-------------|---------|----------|------------------------|-----------------------|
| NiO Pure    | 37.02         | NiO(111)    | 1.74    | 4.79     | 72.32                  | 4792.7                |
| NiO Pure    | 42.98         | NiO(200)    | 1.6     | 5.31     | 65.24                  | 399.3                 |
| NiO Pure    | 62.5          | NiO(220)    | 1.46    | 6.34     | 54.65                  | 2736.3                |
| NiO : Li 4% | 31.88         | LiNi_2O_4(220) | 0.208  | 39.51    | 8.76                   | 70.44                 |
| NiO : Li 4% | 33.54         | Li_2NiO_2(100) | 0.192  | 42.99    | 8.05                   | 59.50                 |
| NiO : Li 4% | 36.88         | NiO(111)    | 0.222   | 37.52    | 9.23                   | 78.10                 |
| NiO : Li 4% | 43.4          | NiO(200)    | 0.22    | 38.67    | 8.95                   | 73.52                 |
| NiO : Li 4% | 49.38         | LiNi_2O_4(331) | 0.1975 | 44.07    | 7.86                   | 56.63                 |
| NiO : Li 4% | 62.92         | NiO(220)    | 0.173   | 53.50    | 6.47                   | 38.42                 |

Table 1. Structural parameters for pure NiO and NiO:4%Li films measured at thickness of 150nm

Figure 4. shows that Atomic force micrographs allow us to get topographic information about the surface structure which represented by the surface relief. This technique along with a special software, offers digital images which allow a quantitative measurement of surface features, such as, roughness average and (RMS) which were equal to (1.47nm) and (2.01) respectively, see figure (4) and the
average grain size was equal to (84.51 nm) for pure NiO but on the other side the average grain size is small for NiO:Li (61.76 nm). The ball shaped particles were highly shaped and the grains were homogenous and aligned vertically.

![Figure 4. 2 and 3 D images with chart distribution for pure NiO and NiO:4%Li films measured at thickness of 150nm](image)

Figure 4. 2 and 3D images with chart distribution for pure NiO and NiO:4%Li films measured at thickness of 150nm

Figure 5. SEM micrographs for pure NiO films and doping abuse are shown by me at 4% at 300 °C. The microscopic structure of the thin film contains many round particles. The surface forms of the membranes reveal remarkable transitions, the films contain minute grains and the particle size (30-40) nm for the NiO film is smaller than NiO: 0.04Li, about 20-30 nanometers

![Figure 5. SEM micrographs for pure NiO and NiO:4%Li films measured at thickness of 150nm](image)

Figure 5. SEM micrographs for pure NiO and NiO:4%Li films measured at thickness of 150nm

Figure 6. shows the effect of wavelength (λ) on the spectrum of transmittance within the range 300-900 nm for pure NiO and Li-doped NiO thin films measured at thickness of 150 nm respectively. For pure NiO film the transmittance value is larger than (79%) in the visible and NIR scopes. The optical transmittance of the samples doped by Li, Noted that the transmittance was decreased. This behavior would be also attributed to microstructural status of prepared films, such as the photon scattering which cause increasing the crystal defects[12,13]
Figure 6. Optical transmittance spectra VS. wavelength for undoped NiO and Li-doped NiO films

Figure 7. The short wavelength takes the absorption coefficient to a higher value (>104 cm⁻¹) and then decreases sharply with increasing wavelength, and then the change becomes slightly. This sharp or low increase is due to the band absorption bands that correspond to the transition between the highest filled energy range to the lowest empty range, which transmits the electron to ions O₂ or also corresponds to the density of absorption centers such as absorption, dumping, excitation transmission, and other defects.

Figure 7. The absorption coefficient for pure NiO and NiO:4%Li films measured at thickness of 150 nm

Figure 8. Show the optical energy gap could be acquired from the object of (αhv)² versus photon energy (hv) for direct allowed transformations. The experimental values of (αhv)² conspire against (hv) of pure NiO and doped NiO (0.04 mol %) of Li deposited at a glass substrate temperature (Ts=298k). The band gap energy is determined by extrapolated straight line of the plots to the x axis, (αhv)²=0. The linear nature of the plots at the absorption edge has been confirmed that all deposited films NiO and Li:NiO are a semiconductor with direct band gap. The amount of optical energy gap, which have been obtained by extrapolating the curves to (αhv)²=0 for NiO and Li doped NiO films thicknesses of 150 nm, found that the band gap of NiO film reduced from 2.3 to 2.0 eV for the Li doping. The change in the optical band gap energy with doping is occurred because of the changes in homogeneity and density of the localized states, which increases due to doping of Li in the deposited films.[14]
Figure 8. Plot of $(\alpha h\nu)^2$ VS. photon energy $(h\nu)$ for pure NiO film and Li-doped NiO.

Figure 9. Shows the variation of extinction coefficient with the wavelength for as-deposited films with doping (0.04mol) % of Li and thicknesses of 150 nm. From these Figures, the general behavior of the extinction coefficient increases as the doping of Li in all samples in the wavelength range (300-900)nm. The difference in extinction coefficient values is directly related to light absorption [14].

Figure 9. Variation of extinction coefficient VS. wavelength for pure NiO and Li-doped NiO film

We have also investigated the suitability of NiO and NiO:Li films as p-type layer via invented a p-n junction diode structure. And for this purpose, we have chosen NiO:Li film which is devoid of any secondary phases. NiO:Li films with optimum conductivity were employed in the fabrication of heteroepitaxial p-n junctions using the configuration of NiO / FTO. The measurement (C-V) one of the electrical measurements adopted for calculating the interior construction voltage $(V_{bi})$, and display the charge carrier concentration and depletion region. the $V_{bi}$ was calculated by drawing a relationship between inverted square capacity $(1/C^2)$ With reverse bias voltage range (0-6)Volt ,frequency(10KHz) as in figure 10. Noting that the relationship is linear between voltages and inverted square capacitance

This indicates that the plant is a junction of the sharp type, and from the intersection of a straight line with the axis of the voltages $(1/C^2=0)$ figure 11 relationship between applied voltage and capacity the table (3) changing values $(V_{bi})$ hybrid junction. Where there was a decrease in the $(V_{bi})$ when doping due to decrease of depletion area obtained as a result of improving the crystalline structure of the film.
Figure 10. Characteristics $I/C^2$ as a function of the reverse bias voltage

Figure 11. The relation between applied voltage and capacity.

Table 3. Changing values ($V_{bi}$)

| Sample      | $C_o$ (nF) | $V_{bi}$ (Volt) |
|-------------|------------|-----------------|
| NiO (Pure)  | 0.22       | 2.4             |
| 4% Li       | 0.37       | 0.2             |

Figure 12. Shows the measured dark current as a function of the front and invers bias of the junction (NiO/FTO) and the effect of doping on the dark current in two biases. The result of $I$-$V$ characteristics the junction is (Anisotype Heterojunction) Due to the different behavior of the current in front for his bias in reverse bias.

Figure 12. $I$-$V$ characteristic of NiO/FTO Schottky junction at room temperature

Figure 13. Shows an increase in the value of the photo current with increased voltage reverse bias due to the first two reasons because of increasing the width of the depletion zone and the second reason
increases the internal electric field with the increase of reverse bias voltage, increasing of possibility of separation (electron – hole)

Figure 13. illustrates the I-V characteristic for forward and reverse biasing applied to NiO/FTO with illumination

Also From Figure 14, showing the open circuit voltage \((V_{oc}, I=0, R=\infty)\) the increasing in \((I_{sc})\) and \((V_{oc})\), resulting in an increasing output power. This leads to increasing efficiency of solar cells when doping by Li, that’s due to the doping operation caused reducing the recombination then improved the value of \((I_{sc} \text{ and } V_{oc})\) , then the Fill Factor \((F.F)\) is that the rate of maximum power output \((V_m \text{ and } I_m)\) respectively to the product of \(V_{oc} \text{ and } I_{sc}\). From these parameters, efficiency can be rated. The diversion efficiency \((\eta)\) is defining as ratio of \(\eta = (P_m/P_{in})100\%\) and \(F.F = (I_mV_m/I_{sc}V_{oc})100\%\). Studied parameters of solar cell for NiO/FTO is listed in Table (4).

| Sample         | \(I_{in}\) (mA) | \(V_{oc}\) (mV) | \(I_{sc}\) (mA) | \(V_{m}\) (mV) | F.F\% | \(\eta\)% |
|----------------|-----------------|-----------------|-----------------|----------------|-------|-----------|
| Pure (NiO)     | 56.6            | 3.38            | 36              | 2.2            | 41.39 | 6.6       |
| 4% Li          | 4.1             | 5.65            | 31.2            | 4.4            | 59.36 | 11.44     |

Figure 14. I-V characteristics for solar cell with illumination, for NiO/FTO/Ag

Figure 15. represents the lifetime of charge carriers, which describes the recombination process in semiconductor devices, which can be defined as the cancellation of an electron-hole pairs. It can be seen from the figure that \((\tau)\) for the NiO/FTO heterojunction has decreased from 0.39 msec to 12msec for NiO:Li/FTO.
Figure 15. shows measurements of the lifetime of charge carriers by Open-Circuit Voltage Decay Photograph method

Conclusions:

From the obtained results of the present work, we conclude the following:

1- Chemical method is very promising and suitable to produce Nickel Oxide thin film.

2- The doping of NiO with 0.04Li didn't show any effect on the nature of crystal structure.

3- Drop casting technique is also a simple one rather than giving the required intent.

4- Deposited Nickel Oxide on a conductive matter (FTO) produces a schottky photodiode with high efficiency that can be used; in turn, to produce the desired electrical power.

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