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Effect of Li doping on conductivity and band gap of nickel oxide thin film deposited by spin coating technique

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Abstract
Nickel oxide, a stable inorganic p-type semiconductor with wide bandgap is an attractive hole transport material for the perovskite-based solar cells. Doping the nickel oxide with group-1 elements such as lithium, sodium, and potassium is found to increase the conductivity of the film. In the present work lithium doped and undoped nickel oxide thin films are coated on the glass substrate by spin coating method under ambient conditions, and the effects of doping are investigated. The structural, electrical and optical properties have been studied for different doping concentrations. X-ray diffraction confirms the formation of single-phase cubic nickel oxide. It is found that the conductivity increases nine times as the lithium concentration increases. The UV–vis spectroscopy measurement modulates the bandgap with the increase in the lithium-ion concentration.

1. Introduction

Research on inorganic hole transport materials (HTM) such as CuI, CuSCN, Cu2O, CuO, CuS, NiOx, MoO3, V2O5, and CuGaO2 for perovskite solar cell applications are of current interest. Compared to organic hole transport materials and organic polymers, inorganic HTMs exhibit many advantages such as low fabrication cost [1], high chemical and thermal stability [2–5], high mobility [6] and excellent optical transparency in IR and visible region with large work function. Metal oxides work as a blockade against environmental degradation and have excellent charge transport properties. NiO is proved to be a promising candidate as anode interfacial layer in perovskite heterojunction solar cells [7] owing to its deep valance band edge (∼5.4 eV), wide bandgap (>3.5 eV), work function (∼5.0 eV) [8–10] which are suitable in aligning with the hybrid perovskite material [11] and easy solution processing. The High transparent, non-corrosive and stable crystal structure of NiO HTM in the perovskite solar cell confers high photo and thermal stability to the corresponding perovskite material [11]. Due to their thermoelectric, translucent, catalytic and semiconducting properties, nickel oxide has also been studied for various other applications such as p-type transparent conductors [12, 13], gas sensing [14, 15], organic photovoltaic [16, 17], supercapacitor [18] resistance switching [19], transparent heat mirror [20], electrochromic display devices [21], transparent organic dye-synthesized solar cells [22] etc. The nickel oxide hole transport layer can be synthesized using several methods such as sputtering [23, 24], atomic layer deposition [25, 26], electrodeposition [18] pulsed laser deposition [27], combustion method [28], solution processing method [29–31]. Among these, the solution processing method and the combustion method have the advantages of low temperature and large-area fabrication under ambient conditions at low cost [28, 32]. NiO suffers from disadvantages such as low intrinsic electrical conductivity which leads to charge recombination and reduced hole extraction. The conductivity of intrinsic nickel oxide semiconductor is attributed to the hole states induced by the nickel vacancies. Studies have shown that under the oxygen-rich condition the energy formation is low for nickel vacancies and is high for oxygen vacancies which are hole killers. This results in low concentration and makes nickel oxide an intrinsic p-type semiconductor [33–35]. To increase the conductivity of the nickel oxide, monovalent atoms such as lithium could be added as an impurity to increase Ni vacancies. The lithium-ion donates one hole to the valance band to keep the charge neutral [36–38]. Doping lithium-ion increases the hole extraction level due to its deep valance band edge (∼5.3 eV to −5.4 eV) and increases the
open-circuit voltage [39] in solar cells. Fermi level of the NiO thin film lies far from the valence band maximum which leads to a relatively large energy level offset at the interface between perovskite light absorber layer and NiO layer and weak built-in field strength [11, 40]. This can be resolved by doping lithium to NiO in which the Fermi level shifts towards the valence band maximum [41]. NiO would be even more effective if the bandgap would have reduced. Li doping is found to modify the bandgap in other oxide semiconductors. However, to our best of knowledge effect of Li incorporation on the bandgap of NiO has not been systematically studied for spin-coated thin film. In the present work, the structural, morphological, electrical and optical properties of Li doped NiO thin film processed by spin coating method are investigated. The results indicate a strong correlation between the conductivity, bandgap modulation and the Li-ion concentration in NiO thin film.

2. Experimental section

The nickel oxide thin film deposition on the glass substrates is done by the spin coating method under ambient conditions. The glass substrates were cleaned using liquid detergent followed by soaking of the glass substrate in the chromic acid for 24 h. The substrates were then sonicated for 15 min in acetone, Isopropl alcohol, ethanol, and double-distilled water respectively then dried at 60 °C for 1 h. The materials involved in the preparation of precursor solution involves nickel acetate tetrahydrate (99% purity, SRL) as a solute, 2-methoxy ethanol as solvent, monoethanolamine as a stabilizer and lithium nitrate as the dopant. The precursor solution was prepared by dissolving the calculated amount of nickel acetate tetrahydrate to 60 ml of 2-methoxy ethanol and stirred continuously for four hours at 75 °C. Monoethanolamine was added dropwise into the solution to obtain a homogeneous, clear solution. After continuous stirring for 4 h, the solution was separated into six different beakers and the lithium nitrate was added at five different concentrations (1 wt%, 2 wt%, 3 wt%, 4 wt% and 5 wt%) of lithium doped nickel oxide thin films respectively.

The as-prepared solutions were coated on the glass substrate by the spin coating method at 3000 rpm for 30 s and were dried at 100 °C on a hot plate for 15 min. This coating and drying process was repeated seven times to obtain the desired film thickness. The prepared films were then annealed at 350 °C for four hours. The films are named as NiO, LiNiO-1, LiNiO-2, LiNiO-3, LiNiO-4, and LiNiO-5 which corresponds undoped NiO, 1 wt%, 2 wt%, 3 wt%, 4 wt% and 5 wt% of lithium doped nickel oxide thin films respectively.

3. Results and discussion

3.1. Structural analysis

The XRD analysis was performed for structural characterization of undoped and Li doped nickel oxide coating over the glass substrate and the XRD patterns are shown in figure 1. The (111), (200), (220), (311) and (222) diffraction peaks are observed for undoped and Li doped NiO samples. The XRD pattern shows that all the thin films have polycrystalline nature with a single-phase cubic structure [42, 43]. The deposited films exhibit XRD peaks at \(2\theta = 37.115^\circ, 43.219^\circ, 62.784^\circ, 75.469^\circ\) and \(79.124^\circ\) corresponding to lattice planes (111), (200), (220), (311) and (222) respectively which agrees with the ICDD card no:04–5840. The peak width is observed to be broadened as the lithium concentration increases, which indicates that the crystalline size decreases as the lithium concentration increases [44]. The lattice constant values of the nickel oxide films deposited with different lithium concentrations are found to be nearly the same and match well with the standard value 0.418 nm (ICDD card no:04–5840, table 1). The strain (\(\varepsilon\)), crystallite size (D), and the dislocation density (\(\delta\)) of the deposited films were calculated for the plane (200) from the relation, \(\varepsilon = (\beta / \cos \theta) / 4, D = 0.9 \lambda / (\beta \cos \theta)\) and \(\delta = 1 / D^2\) respectively, where \(\beta\) is the full width half maximum in radian, and the values are presented in table 1. It is observed that the crystalline size of the nickel oxide thin films decreases as the lithium concentration increases [44]. The obtained crystalline size for the undoped NiO is 106.25 nm, LiNiO-1 is 99.51 nm, LiNiO-2 is 75.39 nm, LiNiO-3 is 49.97 nm, LiNiO-4 is 48.06 nm, LiNiO-5 is 46.14 nm. The strain and the dislocation density gets increases from \(3.4 \times 10^{-3}\) to \(7.5 \times 10^{-3}\) and from \(8.8 \times 10^{14}\) to \(43.2 \times 10^{14}\) respectively as lithium is doped to it.

The Raman analysis was performed for the spin-coated nickel oxide thin film with different lithium concentrations using the 532 nm laser and the spectra are shown in figure 2. The Raman scattering is observed between the range of 200 cm\(^{-1}\) and 1400 cm\(^{-1}\). The peaks obtained below 1200 cm\(^{-1}\) are due to the first and the second-order Raman scattering by the photons and the peak observed above 1200 cm\(^{-1}\) spectra are originated by scattering of two magnons [45]. The vibrations (568 cm\(^{-1}\), 783 cm\(^{-1}\), 1095 cm\(^{-1}\), and 1330 cm\(^{-1}\)) corresponds to one photon longitudinal optical (PLO), two-photon transverse optical (2PTO), two-photon longitudinal optical (2PLO), two-magnon (2 M) band associated with \(\text{Ni}^{2+}-\text{O}^{2-}\)–\(\text{Ni}^{2+}\) [46–48]. Magnons are quantized excitations of electron spin waves occurring in magnetically ordered materials [45]. Scattering due to two-magnon occurs when the incoming laser and the excited charges subsequently return to the ground orbital emitting a scattered phonon [45, 49] and cause excitation of pairs of spin fluctuations [49]. The intensity of the Raman peaks is increased as the concentration of lithium-ion in the nickel oxide thin film increases, this is due to...
Figure 1. XRD pattern of NiO film deposited with different lithium concentrations.

Table 1. Structural parameters of undoped and lithium doped thin films.

| Film   | 2θ  | XRD peak (hkl) | d value (Å) | D (nm) | ε × 10^3 ln m^2 | δ × 10^13 ln m^−2 | Lattice constant (Å) |
|--------|-----|----------------|-------------|--------|-----------------|--------------------|-----------------------|
| NiO    | 43.2| (200)          | 2.09        | 106.2  | 3.407           | 8.86               | a = b = c = 4.2732   |
| LiNiO-1| 43.1| (200)          | 2.09        | 99.51  | 3.912           | 10.09              | a = b = c = 4.1872   |
| LiNiO-2| 43.2| (200)          | 2.09        | 75.59  | 4.789           | 17.50              | a = b = c = 4.2732   |
| LiNiO-3| 43.1| (200)          | 2.09        | 49.97  | 7.244           | 40.05              | a = b = c = 4.1872   |
| LiNiO-4| 43.1| (200)          | 2.09        | 48.06  | 7.533           | 43.29              | a = b = c = 4.1912   |
| LiNiO-5| 43.2| (200)          | 2.08        | 46.14  | 7.847           | 46.97              | a = b = c = 4.1792   |

Figure 2. Raman analysis of NiO film deposited with different lithium concentrations.
the decreased crystalline size when lithium is doped. Smaller the crystalline size tends to increase the intensity of the Raman peak [48, 50].

3.2. Morphological properties
The surface morphology of the prepared NiO thin films was characterized by scanning electron microscopy (SEM). The surface scanning image of the undoped and the lithium doped nickel oxide thin films are shown in figure 3. The SEM analysis reveals that polycrystalline continuous film is formed in all cases i.e. undoped and all lithium doped NiO thin films. Further, all the films found to have porous structure and cracks can also be seen on the surface of films. The crystallites of the film do not exhibit any preferential oriented which is also confirmed from XRD analyses.

3.3. Optical analysis
The optical absorbance and transmittance spectra are obtained using Agilent’s Cary 5000 UV–vis- near IR Spectrometer. Figure 4(a) shows the optical transmittance of undoped and doped nickel oxide thin film ranged from 300 nm to 800 nm. The transmittance increases gradually to 85% as the wavelength of the light increases to 707 nm. This is almost similar for undoped and doped nickel oxide up to 4 wt%. But when nickel oxide thin film is doped to 5 wt%, the transparency decreases to 70% and also found that transparency tends to decrease as the concentration of lithium increases. The scattering effect is observed in higher lithium concentrations [51]. All the samples show absorption at wavelength 300 nm as shown in figure 4(b). The nickel oxide is a semiconductor with a direct bandgap. The bandgap of the samples was calculated by applying the Kubelka- Munk (K-M) relations. One of the important applications of K-M relation is the calculation of the remission function (equation (1)), which is proportional to the absorption coefficient $\alpha$ [52].
Where $R$ is reflectance

$$f(R) = \frac{(1 - R)^2}{2R}$$  \hfill (1)
**Figure 5.** IV characteristics of nickel oxide thin films with various lithium concentration.

**Figure 6.** (a) Resistivity of undoped and lithium doped nickel oxide thin film (b) Variation of conductivity of pure and lithium doped nickel oxide thin film.
The graph is plotted between $h\nu$ versus $(\alpha h\nu)^2$ and the bandgap is calculated by extrapolating the linear part of the graph as shown in figure 4(b). The optical bandgap of doped NiO thin films tends to get narrowed as the lithium concentration increases. The bandgap observed to be 3.94 eV for undoped NiO, 3.93 eV for LiNiO-$\delta$, 3.92 eV for LiNiO-$\delta$-2, 3.90 eV for LiNiO-$\delta$-3, 3.89 eV for LiNiO-$\delta$-4 and 3.85 eV for LiNiO-$\delta$-5 (figure 4(d)). Bandgap narrowing has also been observed in Cu doped NiO thin film prepared by the sol-gel technique [32]. Ching et al studied Li doped NiO thin films prepared by a modified spray pyrolysis method. They reported a similar reduction of optical bandgap in Li doped NiO (2.75 eV) compared to undoped NiO (3.08 eV) [33] and attributed to the reduction of carrier mobility due to Li doping [33]. The bandgap of the above doped nickel oxide is similar and is suitable as the hole transport material in perovskite solar cells.

3.4. Electrical analysis

Figure 5 shows the IV characteristics of Li doped NiO film in the presence of visible light using Keithley Source Meter. The linear IV characteristics indicate good ohmic behavior for all the thin film samples. Further, the conductivity is observed with increasing Li concentration. It is found that the increase in the lithium concentration could increase carrier density and reduces the activation energy that tends to increase the conductivity of the film. This is due to the increase of hole density in the nickel oxide lattice as the Li$^+$ ions occupy the Ni$^{2+}$ [54]. The Incorporation of lithium with nickel oxide lattice involves two main processes. Initially, lithium substitutionally enters the nickel oxide lattice creating oxygen vacancies which result in the absorption of oxygen by the lattice from the surroundings [55]. This increase in the hole concentration increases the conductivity of the films [54]. The current increases to four times at an applied voltage of 5 V as the concentration of the lithium increases to 5 wt% from 0 wt%. The increase in conductivity is due to the high carrier concentration.

The resistance profile of the lithium doped thin film is obtained using the Keithley Source Meter for a 1 × 1 inch substrate. It is found that the resistivity decreases eight times as the concentration of lithium increases to 5 wt% as shown in figure 6(a) which in turn results in a higher conductivity in Li doped thin films as shown in figure 6(b). As the maximum drop in resistance is observed for 5 wt% doping we considered it as optimum for our case. This decreased resistance helps in increasing the power conversion efficiency of the perovskite solar cells [56]. The resistivity of the Li doped NiO thin in the present study found to be much lower compared to the resistivity of Li doped NiO thin films reported by Ching et al [50].

4. Conclusion

Undoped and Li doped nickel oxide thin films are synthesized on the glass substrate by the spin coating method and structural, morphological, optical and electrical studies have been performed. The undoped and Li$^+$ doped NiO thin films are found to have a single-phase cubic structure. The electrical analyses show decreased resistance when lithium is doped to 5 wt% which enhances the conductivity. The optical bandgap is found to decrease with increasing the Li$^+$ concentration. The Li$^+$ doping found to improve the electrical property and reduced the band of NiO thin films and therefore doped NiO could act as hole transport material in the perovskite solar cells.

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