

ELECTROCHROMIC INVESTIGATIONS ON PURE AND NICKEL DOPED TiO₂ THIN FILMS DEPOSITED BY SPRAY PYROLYSIS METHOD FOR DISPLAY DEVICES

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ABSTRACT: The Pure and Nickel doped Titanium oxide (TiO₂) thin films were successfully deposited on the glass substrate and ITO-coated conducting glass substrate with the substrate temperature of 400 °C using Spray pyrolysis technique. The structural, morphological, functional group, optical and electrochromic studies of the prepared TiO₂ films were characterised by X-ray diffraction (XRD), Scanning Electron Microscopy (SEM), Fourier Transform Infra-Red (FTIR) spectroscopy, UV-Vis-double beam spectrometer and Cyclic Voltammeter (CV). From the XRD analysis, the sample shows the amorphous structure. The optical energy gap was determined by transmittance measurement. The uniform grains were observed through the SEM studies. The electrochemical performance of pure and doped thin films was studied in 0.5M H₂SO₄ as an electrolyte. From the Cyclic Voltammograms, the magnitudes of the peak currents are larger for Ni-doped TiO₂ than pure sample.

Keywords: Spray pyrolysis, Thin film, Glass/ITO substrate, Optical properties, Electrochromic properties

1. INTRODUCTION

The transition metal oxides have the potential semiconducting material. Because It has found appeal to many applications including a semiconductor in dye-sensitized solar cell, water and air treatment materials, photocatalytic splitting of water for green-energy hydrogen fuel, display devices [1] etc. Among the various transition metal oxides, Titanium oxide (TiO₂) has the remarkable optical and electronic properties. It has high refractive index and dielectric constant and is transparent to visible light [2]. Apart from this, it has shown interesting Photocatalytic [3] and electrochromic [4] behavior. Further, TiO₂ has poor colouring efficiency (CE), one approach for improving the CE of TiO₂ films is through doping/mixing with other oxides with high electrochromic performance, as many papers reported, electrochromic metal oxide thin films doped with other oxides are superior to pure oxide electrochromes in being more robust than the constituents oxide alone [5]. It is known that the electrochromic effect can be stronger in mixed oxides due to electron transitions between two kinds of metal sites with different valences. As a matter of fact there are many reports on mixed oxide semiconductor thin films based on their electrochromic performance in electrochromic device's (ECD's) [6-9]. The NiO films have received significant attention during the previous years, and they are studied mostly due to their broad industrial application. Mixed oxides of Titanium and Nickel are of great interest due to alteration of structure that affects electrochromic performance profoundly. A higher coloration efficiency is expected, due to increased electron transition between the two kinds of metal sites with different valences, or with different structural surroundings, have shown that NiO doping is found to enhance the electrochromic efficiency of

electrochromic materials like WO_3 , wherein coloration efficiency ‘becomes’ almost double and samples exhibit increasingly high reversibility with NiO doping concentration in the studied range, (13-38 vol%). The mixed oxide system TiO_2 -NiO could be obtained by different deposition methods such as Chemical vapour deposition [10,11], Electrodeposition [12], Sol-gel process [13-15], Sputtering [16-18] and Spray pyrolysis [19-21]. The chemical spray pyrolysis is a simple method, to deposit Thin films and only in few works the formation composition of chemical spray pyrolysis deposited TiO_2 films from acetylacetonate stabilized Ti-alkoxide precursors have been studied [22,23].

In this paper, report that the effect of pure and doping of Ni(2,4,6,8,10%) in TiO_2 thin films prepared by spray pyrolysis technique and its structural, optical and functional group properties are studied. Further, the electrochromic properties are investigated on the 10% Ni doped TiO_2 thinfilms prepared on ITO glass substrate.

2. EXPERIMENTAL DETAILS

The precursor solution contained Titanium (IV) Isopropoxide ($\text{C}_{12}\text{H}_{28}\text{O}_4\text{Ti}$)(TTIP), Nickel chloride ($\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$), acetylacetonate ($\text{CH}_3\text{COCH}_2\text{COCH}_3$) (AcAc) and IsoPropylalcohol (IPA) at TTIP:AcAc molar ratio of 1:2. The solution was atomized by a spray system using compressed air as a carrier gas onto cleaned glass substrate and ITO-coated conducting glass substrate. This precursor solution was sprayed in fine droplets using air as carrier gas, the spray rate was fixed at 3ml min^{-1} , and the distance between the nozzle and the substrates at 25cm, the solution sprayed was 30ml. Microglass slides were used as substrates in the present work, and substrate cleaning plays an important role in the deposition of thin films. The glass slides rinsed in acetone and dried in open air before use. This process is to ensure a clean surface, which is necessary for formation of nucleation centres, required for film deposition [24]. TiO_2 thin films were prepared on this glass substrate with the different molarities of Ni like 0M (Pure), 0.02M, 0.04M, 0.06M, 0.08 and 0.1 M. For each deposition 30ml of solution was sprayed onto glass substrates kept at 400°C . The schematic representation of experimental procedure is shown in Fig. 1.

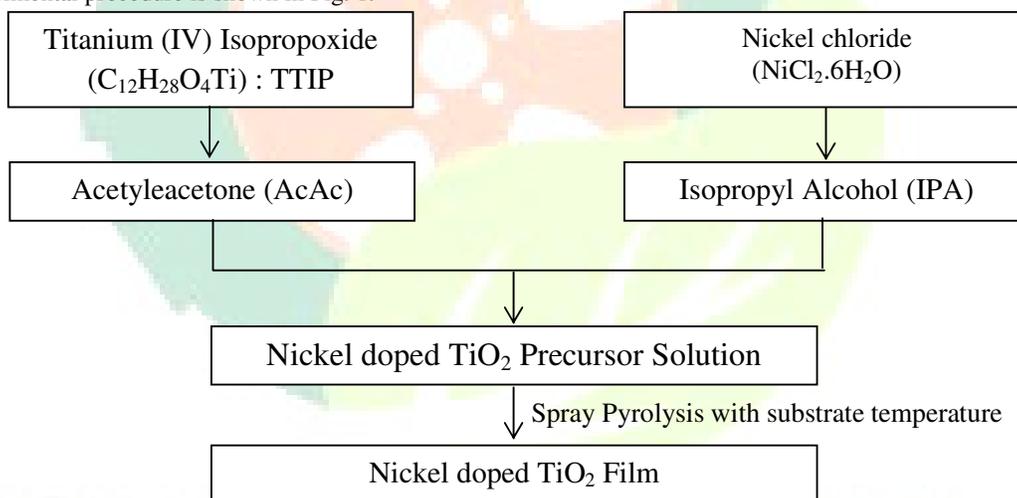


Figure 1. Flowchart of preparation of Ni doped TiO_2 films

The structural behaviour of prepared film are analysed through X-ray diffraction (XRD) studies. XRD patterns of prepared TiO_2 films were recorded by a Rigaku Ultima III X-ray diffractometer using the $\text{Cu-K}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$). The surface morphology, homogeneity and grain size of the deposited films were studied by SEM, model JSM35CFJEOL, Optical absorption measurements were carried out by using a Lambda 35 UV-vis-NIR spectrophotometer. The electrochemical intercalation and deintercalation of electrons and H^+ ions was carried out in a potentiostat [EG & G model verstat – II PAR 362] controlled by a personal computer [Electrochemistry software M 270] in three electrode cell configuration

Glass/ITO/NiO- TiO_2 /0.5M H_2SO_4 /C/SCE

where NiO- TiO_2 thin film act as a working electrode, H_2SO_4 is an electrolyte and H^+ ion source. Saturated calomel electrode (SCE) was used as a reference electrode to which all measured voltages were referred; C is graphite electrode, which acts as a counter electrode. The colouring efficiency (CE) are analysed through the CV devices.

3. RESULTS AND DISCUSSION

3.1 STRUCTURAL PROPERTIES

The Pure and Ni-doped (like 0M, 0.02M, 0.04M, 0.06M, 0.08 and 0.1 M) TiO₂ : NTO thin films deposited at 400 °C on glass substrate and ITO substrate are subjected to the phase analysis studies using XRD. The obtained X-ray diffraction patterns are shown in Figure 2 (a). Suhail et. al. reported that the X-ray diffraction patterns obtained for the as-deposited films at ambient temperature are amorphous structure [25]. From the X-ray diffraction studies the absence of the peaks confirms their amorphous nature. Figure 2 (b) also includes the XRD spectra of sample (0.1M NTO) prepared on ITO glass substrate. The Ni and Ti have comparable ionic radii ($\text{Ni}^{4+}=0.60\text{\AA}$ and $\text{Ti}^{6+}=0.62\text{\AA}$), substitutional doping is presumed. This structure is advantage for the electro-chromic devices as it offers open channel-like conduits for easy intercalation and deintercalation of the ions. The observed structure is in agreement with the reported value. Hence, Ni doping is projected to be favourable for the electrochromic property.

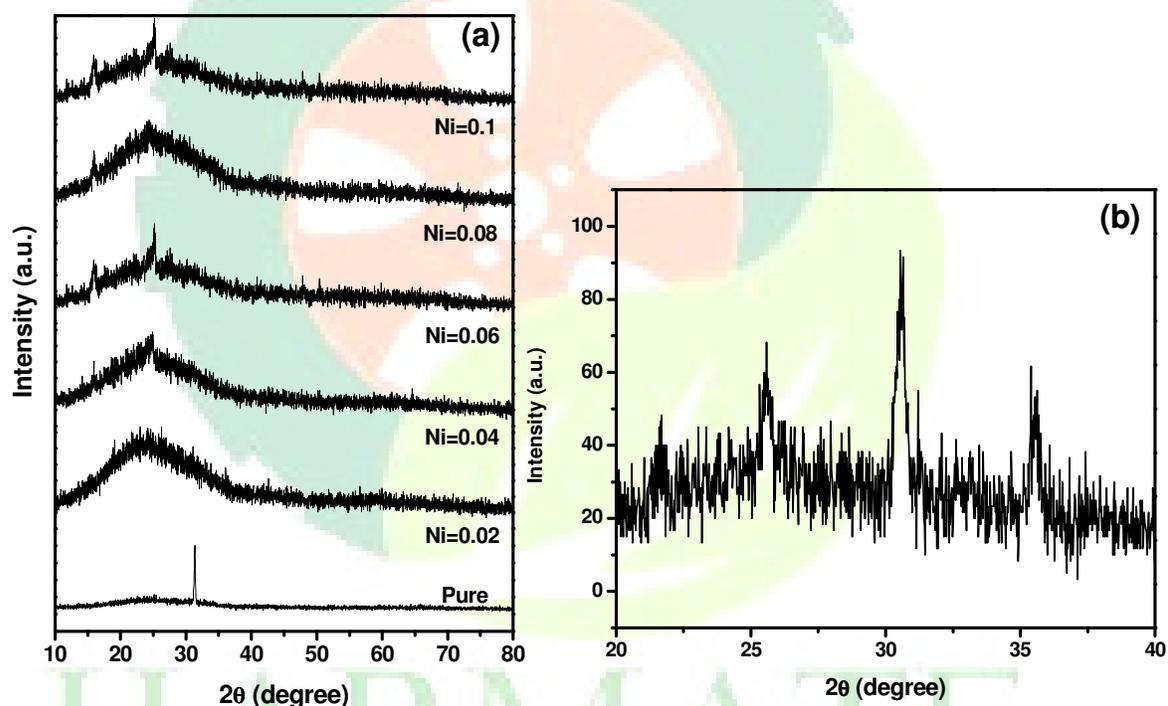


Figure 2. XRD patterns of (a) Pure and Ni doped (0.02M, 0.04, 0.06, 0.08 and 0.1M) TiO₂ thinfilms deposited on glass substrate (b) Ni doped TiO₂ thinfilms (0.1M) deposited on ITO substrate

The substitution of Ni at TiO₂ film was further confirmed by Energy Dispersive Analysis with X-ray (EDAX) technique and the results are shown in Figure 3. The peaks related to Titanium and other elements can be clearly observed. Based on these results, it can be deemed that Ni doped TiO₂ films with 0.1M has occurred at TiO₂ films.

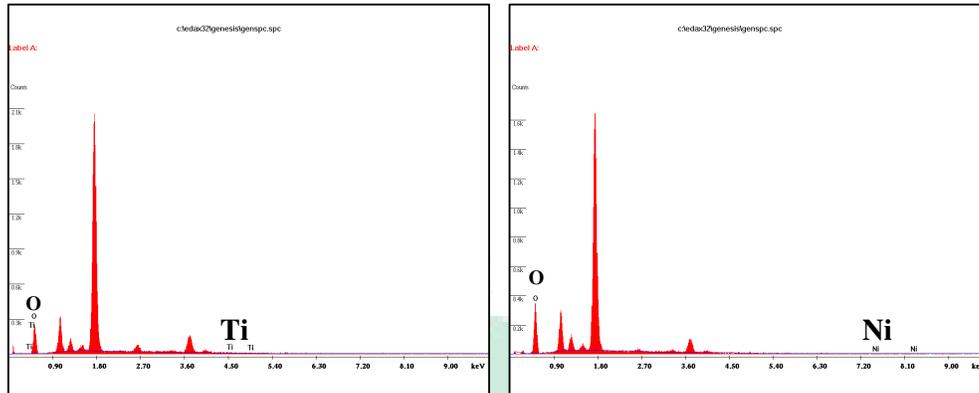


Figure 3.EDAX spectrum of Pure and Ni doped TiO₂ thin films

3.2 SURFACE MORPHOLOGICAL STUDIES

The scanning electron micrographs (SEM) of undoped and Ni doped TiO₂ films were studied to understand and identify the surface morphology. Figure 4 (a) and (b) shows the images of the surface morphology of Pure TiO₂ films. From this, the grains are having the uniform size and distributed. It is attributed to small account of crystallization in the phase. Images show that deposited film is compact. Figure 4 (c) and (d) shows the Ni doped TiO₂ films are having the uniform size of grains but unequal distribution due to the amorphous phase. It can be explained that the different morphologies of the films might be related to the lattice structure and defects generated during deposition governed the chemical adsorption, subsequent nucleation and growth.

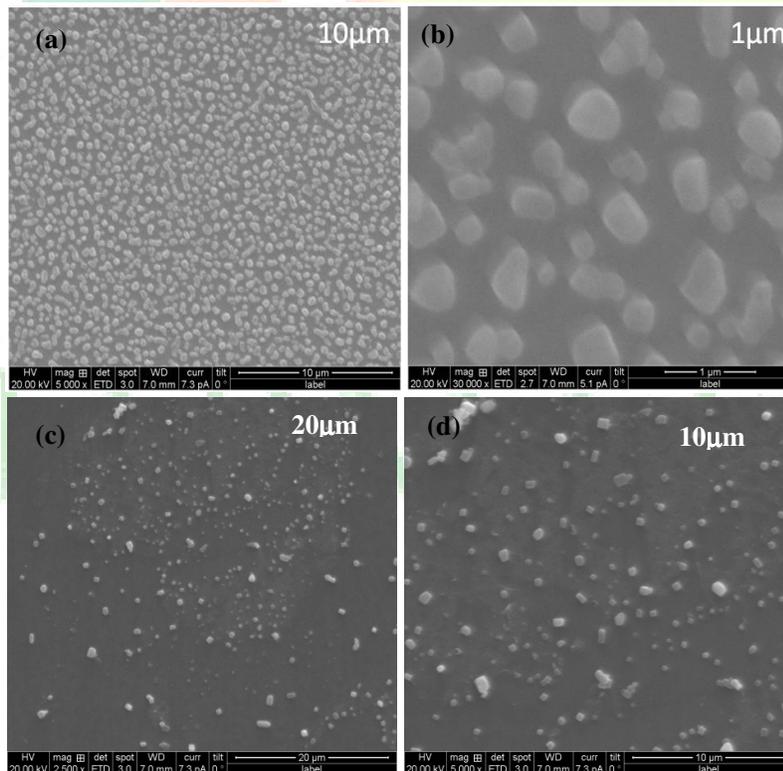


Figure 4. SEM micrographs of (a,b) Pure TiO₂ thin films (c,d) Ni doped TiO₂ thinfilms

3.3 FTIR ANALYSIS

Figure 5 shows that IR spectra for an undoped and Ni doped TiO₂ films prepared with the substrate temperature of 400 °C. Strong absorption in the frequency region of 400-1000 cm⁻¹ corresponds to Ti-O-Ti bonding and indicates the formation of a titaniumoxide network [26]. The transmittance spectrum of the undoped TiO₂ films shows a main absorption band centered at 433 cm⁻¹ and several small features located at 638, 804 and 1076 cm⁻¹. The absorption band at near 900cm⁻¹ corresponds to the vibration mode for the peroxy group, -O-O-. Partial electron transfer from hydroxo, peroxy ligands to the coordination sphere Ti⁴⁺ ion, which has empty d-orbitals, occurs in the early stage of the sol formation. Hence, the partial positive charges are built up on the hydrogen atoms of hydroxo, peroxy ligands with the electron transfer. The absorptions at 1545, 1452 and 1415 cm⁻¹ belong to asymmetrical and symmetrical vibration of M-O-C groups [26,27] and CH₂ or CH₃ groups, respectively [28].

On the other hand, it should be remarked that, in both spectra, there are no absorption signals between 2600 and 3800 cm⁻¹ related to incorporated OH groups as reported for overstoichiometric titanium oxide [29]. This fact indicates that both the undoped and Ni doped TiO₂ films are formed by dense materials without porous.

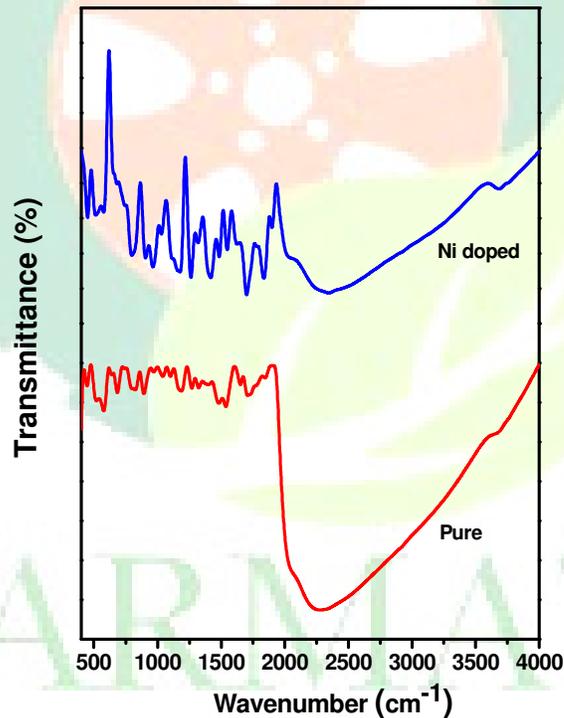


Figure 5. FTIR spectra of Pure and Ni doped TiO₂ thinfilms

3.4 OPTICAL STUDIES

The optical transmission spectra of TiO₂ films are measured in the wavelength range 350-900 nm at room temperature. The nature of transition involved in oxide semiconductors can be determined on the basis of dependence of absorption coefficient (α) of the material on incident photon energy ($h\nu$). The energy band gap of the film is evaluated from the relation

$$(\alpha h\nu)^2 = A(h\nu - E_g)$$

where A is a proportionality constant and E_g is the direct transition band gap. The optical absorption coefficient is of the order of 10⁴ cm⁻¹[29,30].

Figure 6 shows the plot of $(\alpha h\nu)^2$ versus photon energy ($h\nu$) for all the samples. Since there is not sharp absorption edge, band gap energy of the films is obtained from the intersection of extrapolation of the

linear region (higher photon energy region) to zero absorption coefficient, i.e. at $\alpha = 0$ and the horizontal baseline [18]. The band gap energy of TiO₂ increases from 3.28 to 3.48 eV with Nickel doping concentration. The change in the Burstein-Moss effect can be explained in terms of Burstein-Moss band gap widening [19]. According to the Burstein-Moss effect, the increase in the Fermi level in the conduction band leads to the band gap energy broadening with increasing carrier concentration.

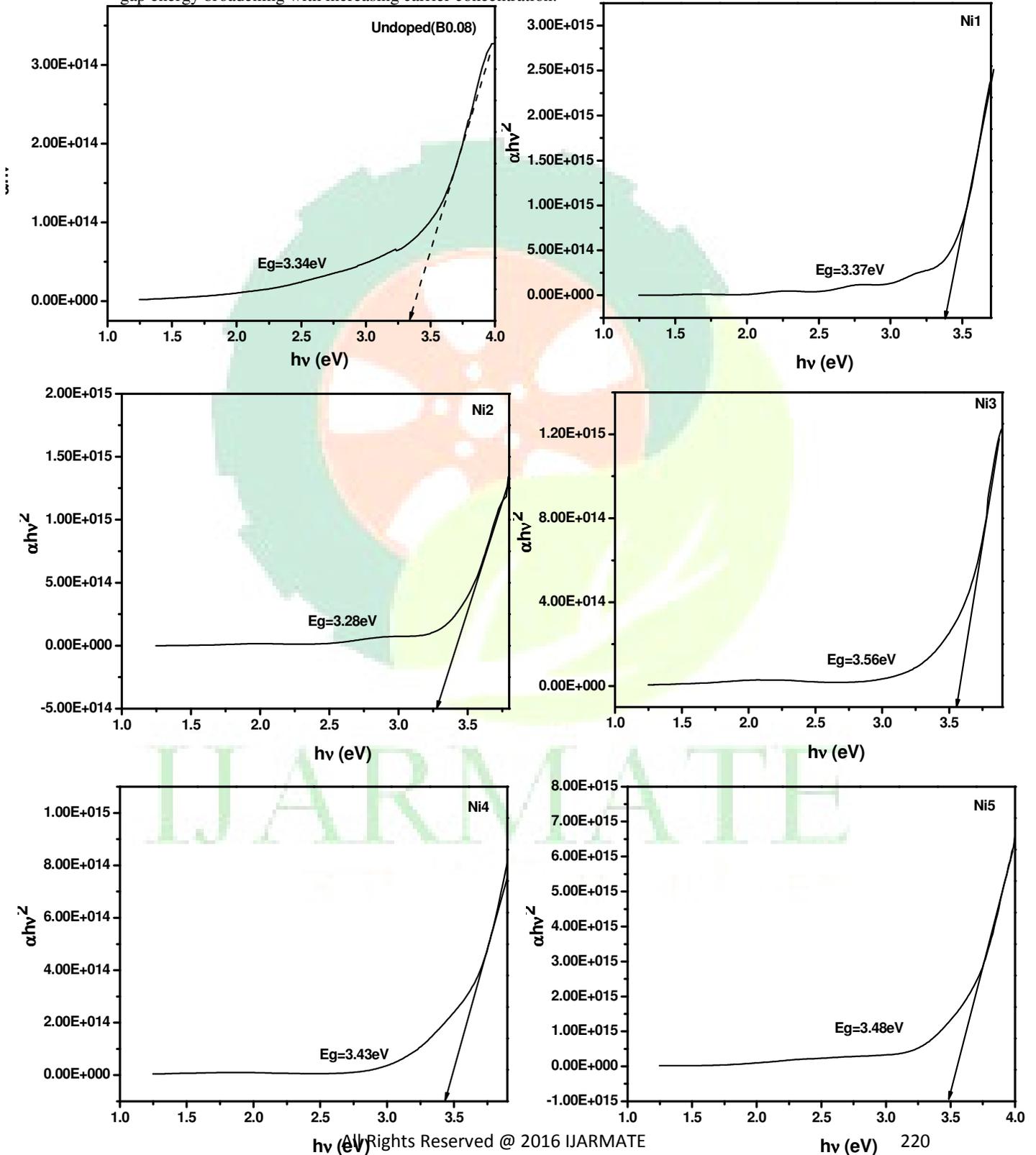


Figure 6. UV spectra of Pure and Ni doped TiO₂ thinfilms

3.5 CYCLIC VOLTAMMETRY MEASUREMENTS

Figure 7 shows the Pure and Ni doped TiO₂ film's cathodic electrochromism. The variation of x from -0.2 to 0.2 was attributed to the amorphous phase. The reversal of the potential, the anodic current peaks, corresponding to the deintercalation process are observed. The magnitudes of the peak currents are larger for Ni-doped TiO₂ than pure sample. Hence, from the improvement in overall CV performance we assume that Ni⁴⁺ is supporting the Ti⁶⁺ to Ti⁵⁺ reactions. The charge intercalation-deintercalation capability of Ni doped TiO₂ sample is larger than other samples. Hence, Ni doped TiO₂ sample offers excellent host matrix for intervalency charge transfer process.

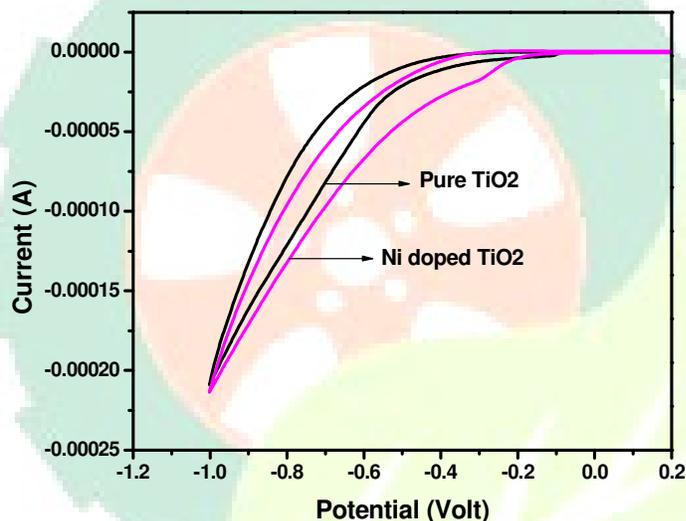


Figure 7. Cyclic voltammograms of the Pure and Ni doped TiO₂ films

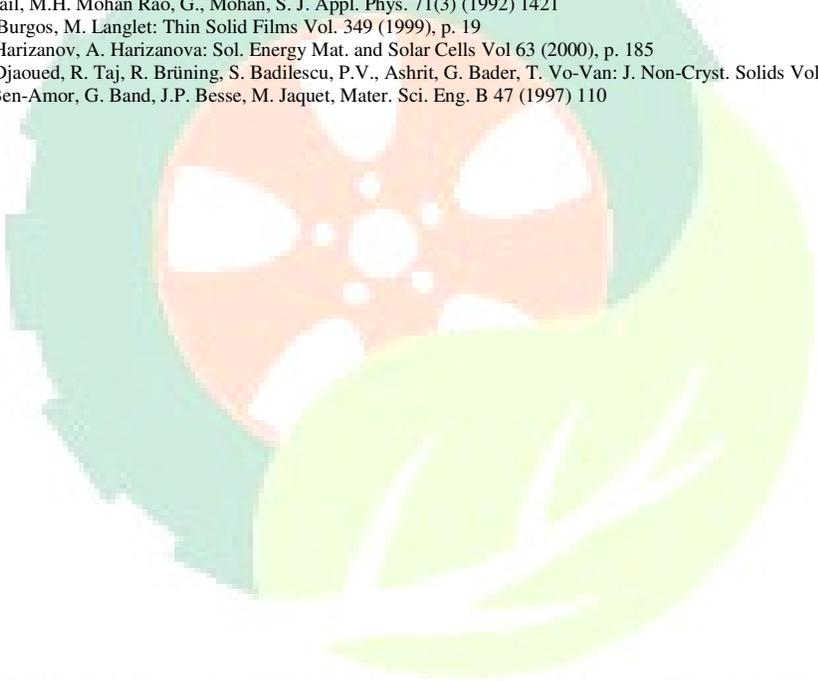
4. CONCLUSION

In conclusion, effect of Ni doping on electrochromic performance of TiO₂ thin films deposited using spray pyrolysis deposition technique was investigated. With increasing Ni doping concentration, the structure of TiO₂ having the amorphous state. It was seen that Ti doping could lead to significant morphological changes in TiO₂ films. The functional groups are analysed through FTIR studies. The UV visible study showed that the band gap are varied with increasing of doping concentration of Ni. From the Cyclic Voltammograms, the magnitudes of the peak currents are larger for Ni-doped TiO₂ than pure sample. The improvement is attributed to the amorphous nature of the doped samples that favors easy intercalation and deintercalation processes. Hence the Ni doped TiO₂ film host for electrochromic devices.

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