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Electrically Switchable Nan Crystals-in-Glass Coatings That Dynamically Filter Heat and Light

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Electrically Switchable Nan Crystals-in-Glass Coatings That Dynamically Filter Heat and Light

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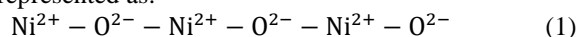
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Abstract: Nickel oxide (NiO) is an electro chromic material that can be used either as a working or counter electrode in solid-state electro chromic devices such as smart windows. In combination with Cerous Titanate ($\text{CeO}_2\text{-TiO}_2$), Titanium-doped Nickel Oxide (NiO:Ti) is a promising coloring material with improved optical, electrical and electro chromic properties. Ti-doped NiO thin films were deposited on fluorine-doped tin oxide coated glass ($\text{SnO}_2\text{:F}$) using sol-gel dip coating technique with different molar concentrations of titanium ranging from 0 to 67%. The results show a decrease in transmittance as the concentration of titanium is increased due to the formation of coloring centers. The electrical properties such as resistivity, conductivity and sheet resistance were measured using four-point probe method. The electro chromic properties of the thin films were investigated using 1M KOH electrolyte for cyclic voltammetry (CV), ion-optics transmittance and chronoamperometry (CA) measurements. An optimized $\text{Ni}_{0.75}\text{Ti}_{0.25}\text{O}$ sample films was found to have enhanced emissivity and electrochromism hence a good candidate for applications in smart windows.

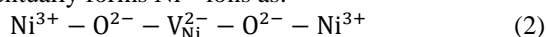
Keywords: Nickel oxide, Coatings, Nan crystals, Electro chromic, Coatings.

1 Introduction

Transition metal oxides such as tungsten and titanium undergo cathodic electrochromism upon intercalation of ions. On the other hand, transition metals such as Nickel, Cobalt and Manganese anodic electrochromism upon extraction of ions. This has enabled scientists to exploit these feature and apply them in various electronic devices. Nonetheless, electrochromism does not only depend on the type of material, but factors such as stoichiometry, morphology, and material phases as well [1, 2]. NiO has a cubic rock salt structure surrounded by six other ions. From one direction, it looks like a chain of alternate Ni and O ions represented as:

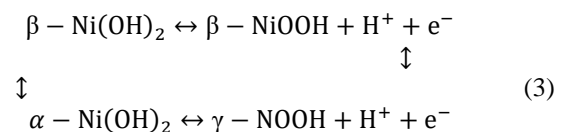


In disordered NiO structure, Ni creates holes around Ni^{2+} and eventually forms Ni^{3+} ions as:

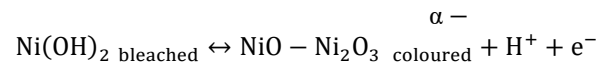
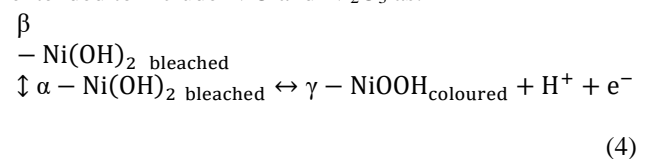


NiO undergoes different phases depending on the amount of oxygen and hydrogen in the structure [3,4]. For instance, non-hydrous Ni_2O_3 is dark-brown, while hydrous $\text{Ni}(\text{OH})_2$ is transparent. $\text{Ni}(\text{OH})_2$ is transparent just like NiO and exists in modifications of α and β , while NiOOH is coloured just like Ni_2O_3 and exists in either β or γ phases.

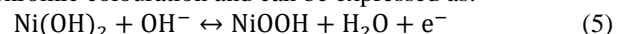
The difference between various phases is the amount of water present for reasons to do with stabilization of ions. Bode reaction is widely used to explain electrochromism of NiO as:



The Bode reaction mechanism illustrates the reaction in different phases of the material, and the reaction can be extended to include NiO and Ni_2O_3 as:



The transformation between NiOOH and $\text{Ni}(\text{OH})_2$ occurs due to intercalation and de-intercalation of protons, normally monovalent (A^+) protons, to achieve electro chromic colouration and can be expressed as:



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2 Experimental

2.1 Substrate Cleaning

Fluorine-doped tin oxide (FTO) glass substrates ($10\Omega/\square$) were purchased from Sigma Aldrich. The substrates were washed in liquid detergent and placed in an ultrasonic cleaner in the presence of pure ethanol for two hours. They were then removed and thoroughly rinsed in distilled water. Thereafter, they were placed in a warm water-bath containing 0.5M hydrochloric acid for 10 minutes. The substrates were then rinsed thoroughly in distilled water and finally dried at 100°C for five minutes before use [5].

2.2 Chemical Composition

Different molar solutions of Ti-doped NiO thin films were prepared by dissolving nickel (II) acetate tetra hydrate, $\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$, in ethanol and then the solution subjected to continuous stirring at room temperature for 1 hour. On the other hand, different molar solutions of titanium isopropoxide, $\text{Ti}(\text{C}_3\text{H}_7\text{O})_4$, were dissolved in ethanol and stirred for 1 hour. The two solutions were then mixed together and stirred for further 6 hours. Thereafter, the sol was filtered using a $0.2\ \mu\text{m}$ Teflon filter to remove any suspended particles. Using dip coating system, the thin films were deposited on cleaned FTO substrates before the samples were taken for annealing in air between 300 and 500°C at a heating rate of 4°C per min for one hour before cooling them down to room temperature. Using the same procedure, other film samples were deposited by varying the concentrations as shown in table 1.

2.3 Characterization Procedures

The optical characterization of the thin films was done using 3700 UV-VIS-NIR Solid Spectrophotometer in the wavelength range 300 - 1200 nm. The electrical properties of the thin films were investigated using the four-point probe method. The electrochromic properties of the thin films were investigated in aqueous alkaline electrolyte (1M KOH) with the help of a three-electrochemical cell, where the substrate material was used as the working electrode, platinum as the counter electrode and Ag/AgCl as the reference electrode. Cyclic voltammeteries of the thin films were carried out in potential between 0 mV and $+1000$ mV with different scan rates. Transmittance modulation (ΔT) and colouration efficiency (CE) measurements were also investigated using constant-current measurement technique. A constant charge density of $10\ \text{mC}/\text{cm}^2$ and current density of $0.05\ \text{mA}/\text{cm}^2$ were applied to substrates measuring $2\ \text{cm}$ by $3\ \text{cm}$ for 20 s. The transmittance spectra in bleached and coloured states were recorded at a wavelength range of 300 - 1200 nm using transmittance measurement setup.

3 RESULTS

3.1 Electrical Properties

The results of electrical resistivity for $\text{Ni}_x\text{Ti}_{1-x}\text{O}$ thin films are presented in figure 1. The results show that electrical resistivity of $\text{Ni}_x\text{Ti}_{1-x}\text{O}$ thin films decreases from $141.69 \pm 2.83\ \Omega\text{cm}$ ($x=1$) to $108.21 \pm 2.17\ \Omega\text{cm}$ ($x=0.5$) before it rises again to $114.87 \pm 2.3\ \Omega\text{cm}$ ($x=0.33$).

It is observed that as the concentration of Ti is increased, the resistivity of $\text{Ni}_x\text{Ti}_{1-x}\text{O}$ thin films decreases. This can be attributed to scattering of charge carriers residing at the grain boundary. The incorporated titanium ions occupy the native Ni 2p vacancies and gradually at high doping concentrations, there is an increase in total hole concentration. Thus, the resistivity of the thin films decreases.

The electrical conductivity of the thin films increases as the concentration of Ti is increased. Non-stoichiometric NiO is known to be a p-type extrinsic conductor, and in most cases, the Ni^{2+} ions are the defects that act as holes and make it possible for the thin films to conduct electricity. The holes are replaced by Ni^{3+} ions that are taken to be electron acceptors. The conductivity of highly doped $\text{Ni}_{0.33}\text{Ti}_{0.67}\text{O}$ thin films was found to be $8.7055 \times 10^{-3}\ \Omega^{-1}\text{cm}^{-1}$. This behaviour suggests that titanium ions in the NiO:Ti composition contributes dopants that enhance conductivity. In other words, the donor atoms occupy the Ni 2p vacancies at the lattice sites for shallowly doped films, while for highly doped films the Ti atoms occupy the interstitial sites. Additionally, Ni^{3+} ions are created when Ti^{2+} ions are incorporated into the NiO matrix, which increase acceptor centers ($\text{Ti}^{2+}\text{-Ni}^{3+}$) leading to an increase in electrical conductivity of the films as shown in figure 2 [6].

The sheet resistance of undoped NiO thin films was found to be $1.52 \times 10^7\ \Omega/\square$. As the concentration of Ti was increased from 0 to 67% , sheet resistivity of the thin films decreased gradually taking a polynomial shape as shown in figure 3. The polynomial fit of sheet resistivity against concentration reveals residual sum of squares and the adjusted root square, which can be used to explain the decrease in sheet resistance.

After doping, Ti^{2+} ions create hole centers, which together with polarons in the 3d band of Ni^{2+} form trap near the Fermi level. Consequently, electrons are excited from the 3d band of Ni^{2+} to 2p of O^{2-} . This leads to a decrease of ionized impurity scattering centers, and an increase of mobility charge carriers on further doping; hence, a decrease in sheet resistance [7].

Table 1: Masses of Nickel (II) Acetate and Ti-iso propoxide used in 40ml and 20ml of ethanol respectively.

Sample no.	Composition	Nickel (II) acetate (g)	Ti-isopropoxide (g)
1	NiO	9.96	0
2	Ni _{0.9} Ti _{0.1} O	8.96	1.04
3	Ni _{0.8} Ti _{0.2} O	7.96	2.28
4	Ni _{0.75} Ti _{0.25} O	7.46	2.84
5	Ni _{0.5} Ti _{0.5} O	6.46	3.48
6	Ni _{0.33} Ti _{0.67} O	5.76	4.42

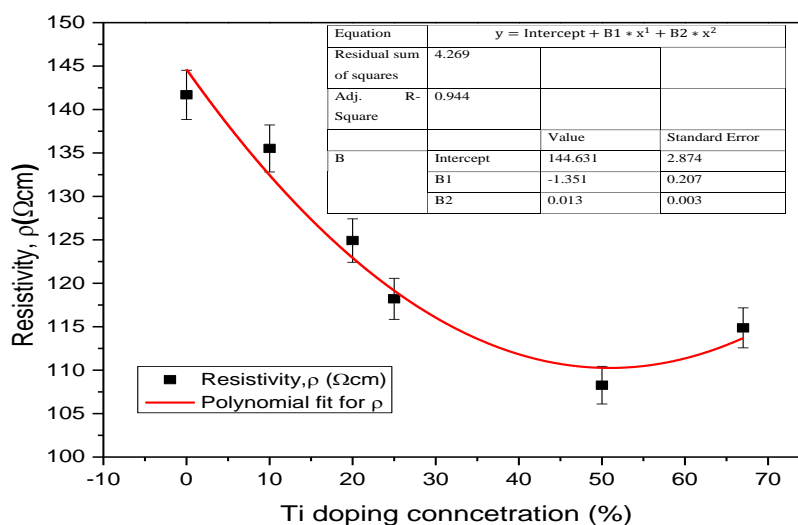


Fig.1: Electrical resistivity against concentration x in Ni_xTi_{1-x}O thin films.

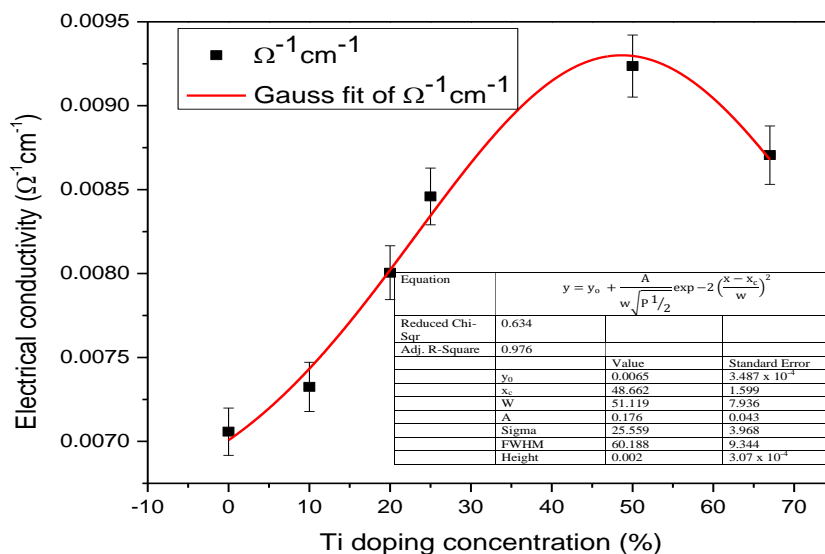


Fig. 2: Electrical conductivity against concentration x in Ni_xTi_{1-x}O thin films.

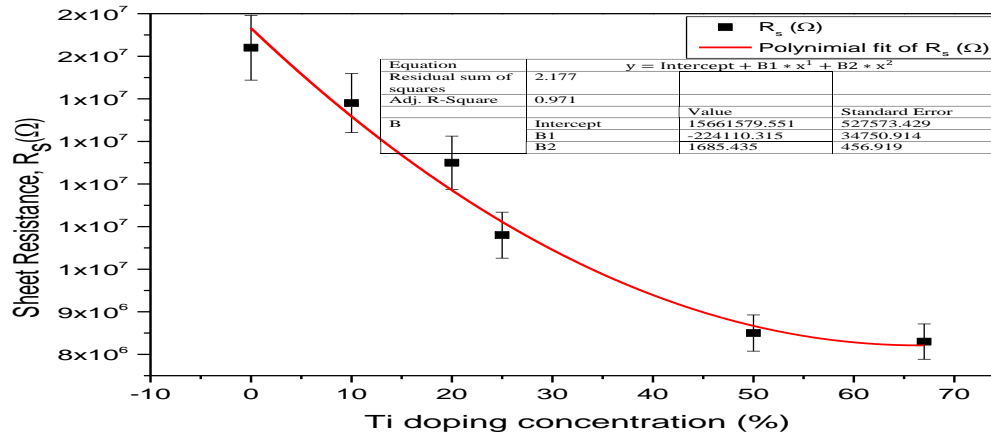


Fig. 3: Sheet resistance against concentration x in $\text{Ni}_x\text{Ti}_{1-x}\text{O}$ thin films.

3.2 Optical Properties

The decrease in transmittance with increase in doping of titanium can be attributed to the increase in cluster size and surface roughness that enhance multiple and diffuse reflections at the surface thus enhancing reflection and absorbance [8, 9].

3.2.1 Energy Band-gap

The energy bands of different doped $\text{Ni}_x\text{Ti}_{1-x}\text{O}$ thin films annealed at 400°C were obtained by simulating transmittance data in the scout software. Figure 4 shows the extrapolated energy band gap of thin films whose value was found to be 3.61 eV.

The energy band gaps of the other samples were extrapolated and are presented in table 1. From the table, the energy band-gap of the thin films decreases as the concentration of titanium is increased. This can be explained as follows: shallow doping of impurities create energy levels in the energy band-gap around the donor level, which is near the conduction band edge. On the other hand, shallow acceptor impurities create new energy levels at the acceptor level that is close to the valence band. However, upon increasing concentration of the dopants, a continuum of states is formed around the donor or acceptor level that resembles that of the bands, and effectively the energy band-gap decreases.

3.3 Electrochemical Properties

To investigate electrochemical properties of titanium-doped NiO thin films, cyclic voltammetry (CV) was used. Cyclic voltammetry is an electrochemical technique that is used to

To investigate electrochemical properties of titanium-doped NiO thin films, cyclic voltammetry (CV) was used. Cyclic voltammetry is an electrochemical technique that is used to study information about the analyte by measuring current (i) against applied potential (E) in an electrochemical cell. Figure 5 represents the cyclic voltammograms of titanium doped NiO thin films at different scan rates. When voltage is applied, the K^+ ions move and diffuse into the thin films. This leads to colouration. The withdrawal of voltage leads to the movement of K^+ ions from the thin films into the electrolyte and the thin films bleaches. During colouration, oxidation takes place (Ni^{2+} to Ni^{3+}), while during bleaching, reduction takes place (Ni^{3+} to Ni^{2+}) leading to bleaching [10]. The role of Ti ions is to enhance cyclability of NiO thin films. Since titanium ions also undergo redox reactions i.e. change of Ti^{3+} to Ti^{4+} and vice versa. From figure 5, it can be observed that the anodic peak current density (j_a) and the cathodic peak current density (j_p) vary as the scan rate is also varied. The current peak densities increase with increase in scan rates. This behaviour compliments the Randles-Servcik equation that is also used to calculate the diffusion coefficient of the ions in the thin films.

$$j_p = 2.72 \times 10^5 \times n^{\frac{3}{2}} \times D^{\frac{1}{2}} \times C_0 \times V^{\frac{1}{2}} \quad (6)$$

Where j_p is current peak current, D is the diffusion coefficient in cm^2/s , n is number of electrons (taken as unity), C_0 is concentration of active ions in electrolyte in mol/cm^3 , and V is potential scan rate mV/s . Table 2 presents the peak current densities and diffusion coefficients of different molar concentrations at different Scan rates.

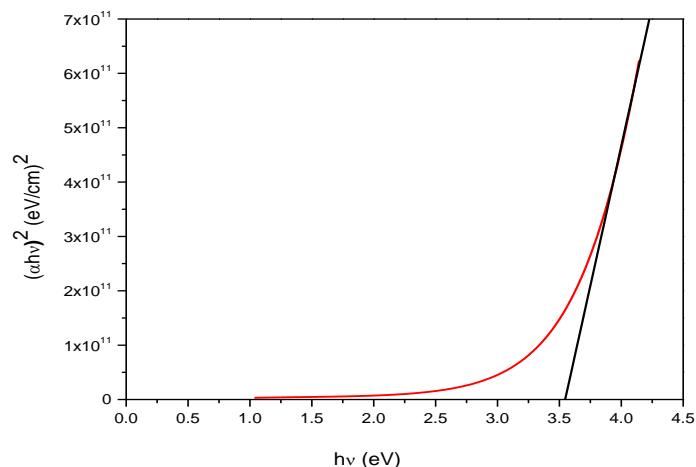


Fig. 4: Energy band-gaps of Ni_xTi_{1-x}O thin films with concentration x.

Table 1: Thin films with their corresponding energy band-gap values.

Sample	Band gap
NiO	3.92 ± 0.22
Ni _{0.9} Ti _{0.1} O	3.88 ± 0.24
Ni _{0.8} Ti _{0.2} O	3.84 ± 0.22
Ni _{0.75} Ti _{0.25} O	3.61 ± 0.11
Ni _{0.5} Ti _{0.5} O	3.51 ± 0.35
Ni _{0.33} Ti _{0.67} O	3.35 ± 0.07

Table 2: Electrochemical parameters anodic peak current density (*j_{pa}*), cathodic peak current density (*j_{pc}*) and diffusion coefficient (*D*) of Ti-doped NiO thin films in 1M KOH at scan rate of 20 mV/s.

Sample	Anodic current density <i>j_{pa}</i> (A)	Cathodic current density <i>j_{pc}</i> (A)	Diffusion coefficient <i>D</i> (cm ² /C)	
			<i>D</i> for <i>j_{pa}</i>	<i>D</i> for <i>j_{pc}</i>
NiO	5.127 x 10 ⁻⁴	8.626 x 10 ⁻⁴	5.053 x 10 ⁻²¹	1.431 x 10 ⁻²¹
Ni _{0.9} Ti _{0.1} O	6.891 x 10 ⁻⁴	9.334 x 10 ⁻⁴	9.128 x 10 ⁻²¹	1.675 x 10 ⁻²²
Ni _{0.8} Ti _{0.2} O	7.926 x 10 ⁻⁴	1.068 x 10 ⁻⁵	1.532 x 10 ⁻²²	2.193 x 10 ⁻²³
Ni _{0.75} Ti _{0.25} O	8.475 x 10 ⁻⁴	3.679 x 10 ⁻⁵	4.182 x 10 ⁻²³	2.602 x 10 ⁻²⁵
Ni _{0.5} Ti _{0.5} O	8.145 x 10 ⁻⁴	6.599 x 10 ⁻⁶	1.275 x 10 ⁻²⁵	8.371 x 10 ⁻²⁶
Ni _{0.33} Ti _{0.67} O	8.827 x 10 ⁻⁵	6.828 x 10 ⁻⁷	1.498 x 10 ⁻²⁶	8.962 x 10 ⁻²⁷

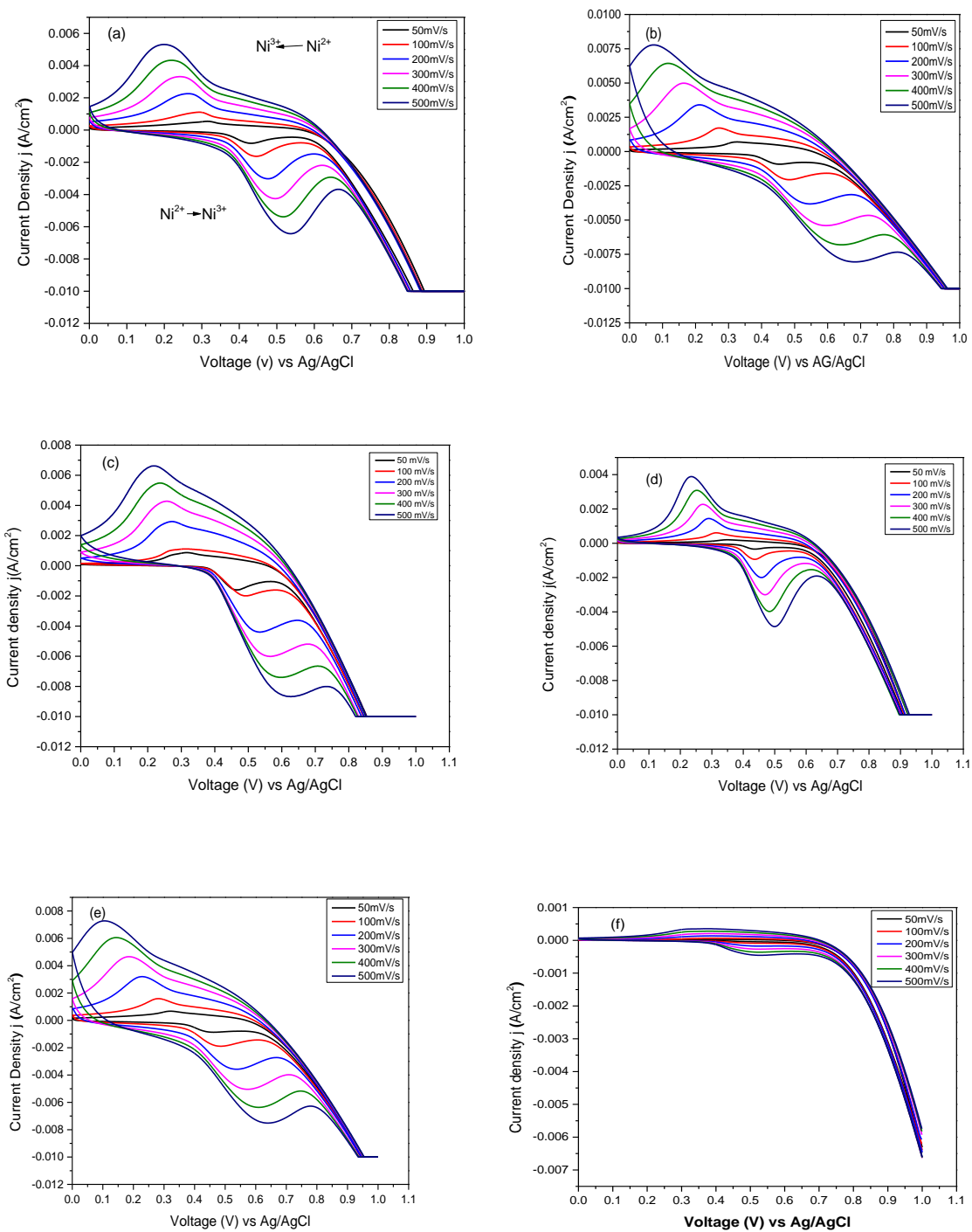


Fig. 5: Cyclic voltammograms for (a) NiO (b) $\text{Ni}_{0.9}\text{Ti}_{0.1}\text{O}$ (c) $\text{Ni}_{0.8}\text{Ti}_{0.2}\text{O}$ (d) $\text{Ni}_{0.75}\text{Ti}_{0.25}\text{O}$ (e) $\text{Ni}_{0.5}\text{Ti}_{0.5}\text{O}$ (f) $\text{Ni}_{0.33}\text{Ti}_{0.67}\text{O}$ thin films at different scan rates.

From the table, it is established that the peak current densities slightly decrease with the increase in concentration. The diffusion coefficient of the ions also decreases with increase in the doping percentage of titanium [11, 12]. The presence of more Ti^{3+} ions reaches a state where it is difficult for intercalation or de-intercalation to occur fully. This leads a decrease in anodic and cathodic peak current densities, and diffusion coefficient.

The iono-optical study of the thin films was investigated in order to estimate transmittance modulation (ΔT) and colouration efficiency. The transmittance spectra of the thin film samples in bleached and coloured states were measured in the wavelength range of 300-1200 nm as shown in figure 6.

The colouration efficiency (CE), change in transmittance spectra (ΔOD) with charge per unit area (Q) were estimated using the equation:

$$CE(\lambda) = \frac{\Delta OD}{Q} = \frac{\log\left(\frac{T_b}{T_c}\right)}{(q/A)} \quad (7)$$

where, CE is the coloration efficiency, ΔOD is change in optical density, T_b and T_c are transmittance in bleached and coloured states respectively, and Q is charge per unit electrode area of the thin film.

From figure 6, all the thin film samples exhibit transmittance in both bleached and coloured states. It is shown that the variation in the coloured and bleached state is more pronounced in NiO and Ni_{0.75}Ti_{0.25}O as compared to the rest of the samples. Transmittance modulation (ΔT) and colouration efficiency (CE) at wavelengths 550 nm and 1000 nm of thin films grown at 400°C are shown in Table 3. From the table, except Ni_{0.75}Ti_{0.25}O thin films, the other sample show a decrease in transmittance modulation and colouration efficiency as compared to NiO films. This can be attributed to improved crystallinity, which does not favour ion diffusion through the material easily [13, 14]. However, as compared to NiO thin films (21.31cm²/C), Ni_{0.75}Ti_{0.25}O have the highest colouration efficiency of 36.83 cm²/C. The average optical density of Ni_{0.75}Ti_{0.25}O thin film is 0.1588.

Table 3: The transmittance modulation and CE for Ni_xTi_{1-x}O thin films.

Sample annealed at 400°C	Transmittance modulation, ΔT (%)		Colouration efficiency, CE (cm ² /C)	
	$\lambda=550$	$\lambda=1000$	$\lambda=550$	$\lambda=1000$
NiO	25	23	21.31	14.75
Ni _{0.9} Ti _{0.1} O	15	11	10.23	9.92
Ni _{0.8} Ti _{0.2} O	12	12	8.42	4.66
Ni _{0.75} Ti _{0.25} O	48	24	36.83	18.97
Ni _{0.5} Ti _{0.5} O	10	15	12.34	13.51
Ni _{0.33} Ti _{0.67} O	6	10	4.04	7.18

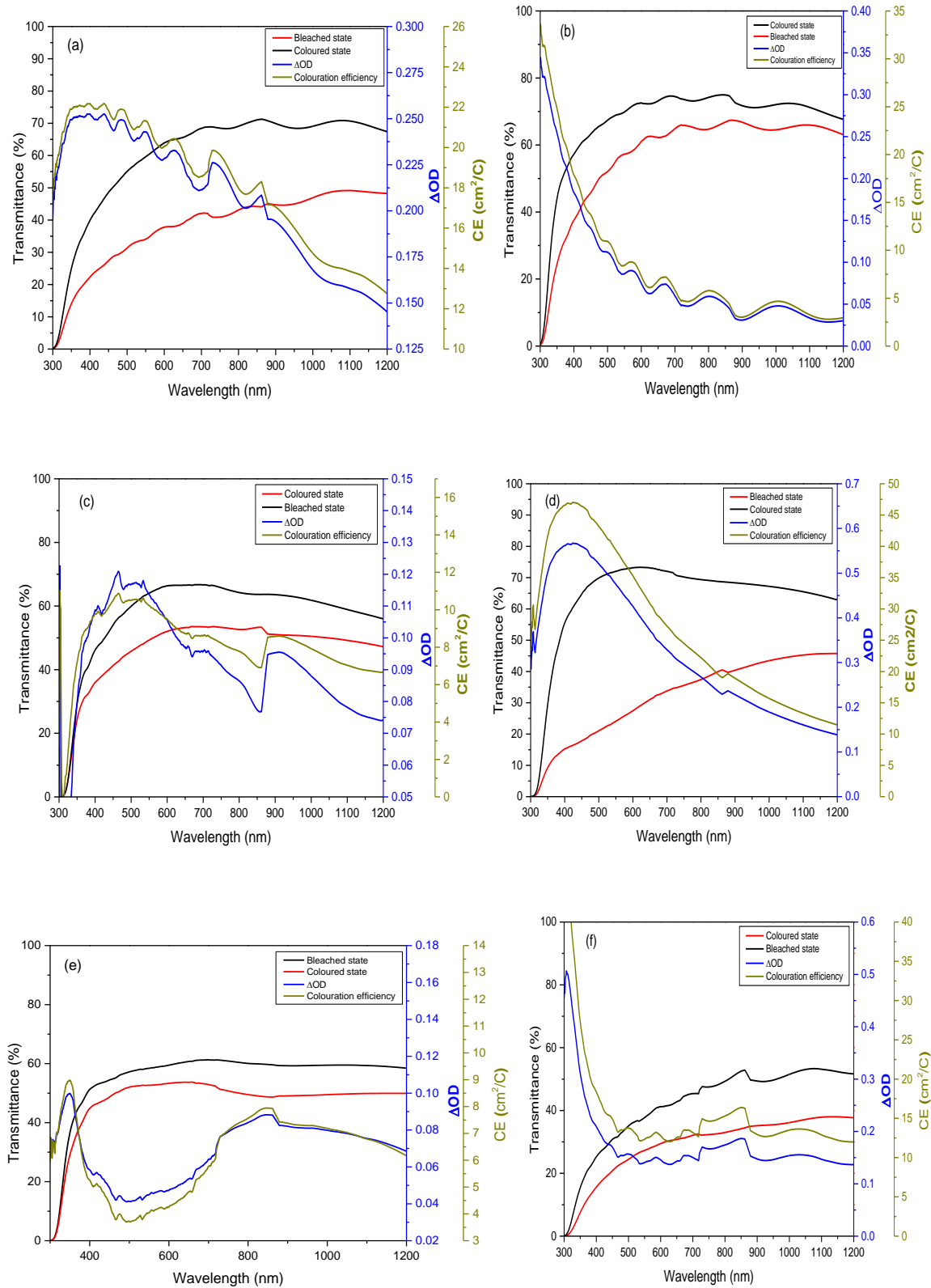


Fig. 6: The transmittance spectra in bleached and coloured states, the ΔOD and CE of (a) NiO (b) $Ni_{0.9}Ti_{0.1}O$ (c) $Ni_{0.8}Ti_{0.2}O$ (d) $Ni_{0.75}Ti_{0.25}O$ (e) $Ni_{0.5}Ti_{0.5}O$ (f) $Ni_{0.33}Ti_{0.67}O$ thin films annealed at $400^{\circ}C$.

4 Conclusions

The electrical, optical and electrochromic properties of $\text{Ni}_x\text{Ti}_{1-x}\text{O}$ thin films have been investigated in this study. The electrical resistivity of pure NiO thin films was measured and found to be 141.69 Ωcm . On doping, as the concentration of Ti was increased, there was a decrease in resistivity up to 108.27 Ωcm . This can be attributed to scattering of the charge carriers by the Ti ions residing at the grain boundary. The transmittance of $\text{Ni}_x\text{Ti}_{1-x}\text{O}$ with varying concentrations of NiO (from 100 to 33%) was performed as well. Transmittance increases as the percentage of titanium is increased. The electrochromic properties of $\text{Ni}_x\text{Ti}_{1-x}\text{O}$ thin layers were tested using cyclic voltammetry, constant-current measurement and chronoamperometry electrochemical techniques in 1M aqueous KOH solution in the potential range -1 V to +1 V. For pure NiO thin films, the peak cathodic and anodic peak current single cycles at 500 mV/s are $5.334 \times 10^{-3} \text{ A/cm}^2$ and $6.436 \times 10^{-3} \text{ A/cm}^2$ respectively. The corresponding diffusion coefficients are $5.469 \times 10^{-20} \text{ cm}^2/\text{C}$ and $7.963 \times 10^{-20} \text{ cm}^2/\text{C}$ respectively. The results show that $\text{Ni}_x\text{Ti}_{1-x}\text{O}$ thin films experiences redox reactions with high ion diffusion coefficients.

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