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Structural, Morphological, and Optical Investigation of Undoped and Nickel Doped Titanium Dioxide Thin Films

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ABSTRACT

Titanium dioxide and Ni doped titanium dioxide thin films were prepared from titanium isopropoxide in isopropanol solution and nickel nitrate hexahydrate salt solution by spin coating method. Films were prepared with varying percentage of nickel doped (0%, 1%, and 2%) titanium dioxide on a glass substrate (2.5 cm x 2.5 cm film area). The films were characterized by XRD and SEM to analyze the crystallinity and morphology respectively. XRD study results of the fabricated films confirmed that the undoped films were amorphous and improved crystallinity was found with nickel doping in titanium dioxide. The doped films exhibit a closer proximity to transitioning from the amorphous phase to the polycrystalline phase compared to the undoped film. SEM micrographs revealed that the titanium dioxide thin films, despite undergoing high-temperature annealing, retained significant porosity due to particle agglomeration in the crystalline nanoparticle suspensions used in the spin coating method. The optical characterization was carried out by UV-Visible spectrophotometer. The transmission spectral analysis showed that the films were transparent. Transparency of the film at the doping level of nickel 2% was highest (about 75-85%) in the visible range of spectra. And the corresponding band gap energy was 3.96 eV. With decreasing the nickel percentage, the transparency decreased from 75-85% to 50-65% in the visible range and the band gap energy also shifted to 3.89-3.95 eV.

Keywords: Thin Film, titanium dioxide, spin coating, doping.

1. Introduction

Thin film is an example of advanced technology which has been introduced especially for the modification of surface properties. The importance of discovering a mean by which it is possible to grow a layer of desired material over the surface of a predetermined object became significantly important. In order to modify and control the properties of the surface at an atomic level, thin film became a subject of great importance. So far, a wide range of research works has been done in this sector which includes researches on the electrical properties of thin film semiconductors [1], their optical properties [2], applications in solar cells [3], tissue engineering [4], and so on. Thin films have a variety of applications and among these applications, Transparent Conducting Oxides (TCO) are of great importance in modern times for their usage in especially solar cells, heat mirrors, windows, etc. [5]. In recent times, titanium dioxide has received more attention because of its photocatalysis properties. TiO_2 is widely used for many applications such as the purification of water, dyes of sensitized solar cells, self-cleaning, and antifogging applications [6]. TiO_2 is the most chemically stable, non-toxic, and eco-friendly photocatalyst. Its low-cost production and eco-friendly nature make it suitable for biomedical applications. TiO_2 has a wide bandgap of 3.0 to 3.2 eV. TiO_2 absorbs ultraviolet light only which constitutes approximately 5% of the solar spectrum and reflects the maximum percentage of visible light [7]. To develop the properties of TiO_2, several tactics have been engaged in research work like morphological alterations to increase the surface area, addition of metals and/or nonmetals, and so on [8, 9]. Supardan S.N. et al. modified the structural properties of TiO_2 nanoparticles by metal doping [10]. Nanocomposites of metal doped titanium dioxide and Fuller's earth was studied for effective photocatalysts for environmental applications [11]. Metal doping in titanium dioxide is also effective for the application of sensing devices [12]. Current research work involves the fabrication of pure and metal like nickel doped titanium dioxide thin films and investigation of the modification of structural, morphological, and optical properties with nickel doping.

There are a number of methods to deposit thin films among which spin coating, spray pyrolysis, and chemical bath deposition are the most widely used. In this work, the spin coating method has been implemented to deposit doped and undoped TiO_2 thin films. This method has been chosen because of its low-cost requirement, easy-to-operate procedures, and ease of changing the parameters of the production of the films [5]. Our first and foremost target was to find an optimum condition to deposit the film which would carry the desired properties as close as possible, to study the properties, and to improve certain optical, morphological, and structural properties as well.

2. Experimental details

Titanium dioxide and nickel doped titanium dioxide thin film was prepared by the spin coating technique from transparent TTIP solution (Titanium isopropoxide, $Ti(OCH(CH_3)_2)_4$) and nickel nitrate hexahydrate salt solution ($Ni(NO_3)_2.6H_2O$). This process involves first to spread the TTIP solution and doped precursor solution containing nickel

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nitrate hexahydrate on to a glass substrate where the solution decomposes into titanium dioxide and nickel doped titanium dioxide interact with the substrate as a film. The glass substrates were first immerged into ethanol for a few minutes to prepare it ready to deposit. After removing from alcoholic solution, those were ringed with distilled water and were cleaned ultrasonically for about 20-25 minutes. Then again ringed with water and were dried into an oven. Finally, the substrates were preserved for use. For preparing such a solution for titanium dioxide and nickel doped titanium dioxide thin film, TTIP (Titanium isopropoxide) and nickel nitrate hexahydrate was dissolved separately with required amount of isopropanol. Before preparing a solution concentration of solution in molarity was getting fixed like 0.2 M. Then for a specific volume (0.2 M) of the solution what amount of TTIP and nickel nitrate hexahydrate were required. Titanium oxide and nickel doped titanium oxide thin film was deposited from 0.2 M aqueous solution of titanium dioxide and nickel nitrate hexahydrate ($Ni(NO_3)_2.6H_2O$). First, a suitable drying annealing temperature was found out by preparing the film at 80 °C - 100 °C and annealed the sample at 500 °C. While the other parameters were constant: concentration 0.2 M, rotation speed was 500 rpm, and distance between substrate and dropper was 10-12 cm. Then keeping the determined temperature and other parameter to obtain a film with good structural and optical properties.

After spin coating, the film was dried at a temperature of 100 - 150 °C on a hot plate or in an oven for 30 minutes to evaporate the solvent. Drying removes the solvent from the thin film. The substrate was heated in a furnace or a hot plate at a temperature of 500 °C for about 2 hours to remove any residual organics and to promote the formation of a pure titanium oxide film.

3. Results and discussion

The deposited undoped and Ni doped TiO_2 thin films on glass substrate were characterized by different characterization technique to analyze the properties.

3.1 Structural analysis

Structural properties of the prepared films were analyzed by X-ray Diffraction (XRD) with CuKα radiation. The films were annealed at the temperature of 500 °C. The three X-ray Diffraction (XRD) patterns are given in Fig.1.

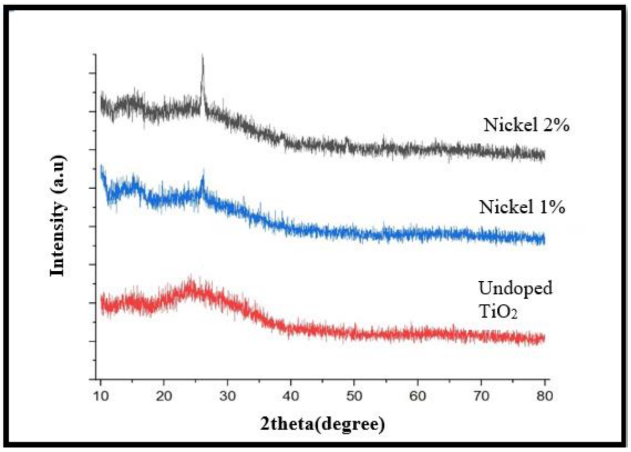

Fig.1 XRD patterns of undoped and Ni doped TiO_2.

We can observe a broad peak at 2θ = 26° in undoped TiO_2 XRD pattern, which is due to glass substrate. The lack of distinct peaks in the XRD pattern of undoped TiO_2 indicates that the films are amorphous. In 1% Ni doped TiO_2 XRD pattern, we can observe that the intensity increases at 2θ = 26.06° and the intensity also increases in 2% Ni doped TiO_2 at 2θ = 26.06°. A sharp peak is observed for 2% Ni doped TiO_2 which indicates that the doped films are likely to become crystalline from amorphous phase.

The doped films are nearer to transitioning from the amorphous phase to the polycrystalline phase compared to the undoped films. The broad hump of undoped TiO_2 is disappearing with the increasing concentration of Ni doping.

3.2 Surface morphology

Scanning Electron Microscopy (SEM) image was used to examine the morphological features of the undoped and Ni doped thin film samples. Fig.2 shows the SEM images of the undoped TiO_2, 1% Ni doped TiO_2, and 2% Ni doped TiO_2 samples.

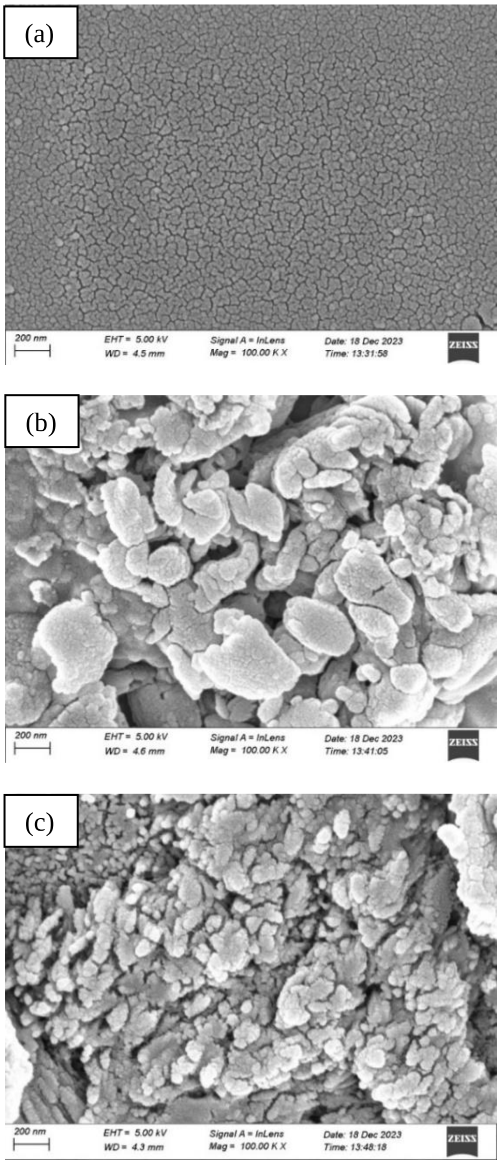

Fig.2 Surface micrograph of (a) undoped, (b) 1% Ni doped, and (c) 2% Ni TiO_2 thin films.

The results of SEM images were analyzed using ImageJ software to calculate the average particle size. The average particle size is in close proximity to the nanometer region. The titanium oxide thin films prepared exhibited a structure characterized by numerous cracks evenly distributed throughout the material. SEM images confirmed the presence of these cracks, indicating that the thin films were not densely packed. Despite annealing at high temperatures, the significant porosity of the thin films produced by the spin coating method remained unchanged. This was attributed to the agglomeration of particles in the crystalline nanoparticle suspensions. 1% nickel doped titanium dioxide and 2% nickel doped titanium dioxide thin films show the average surface grain size about 59 nm and 47 nm. The cracks were eliminated from the surface when titanium oxide was doped with nickel, resulting in a denser surface than before. SEM analysis of the surface morphology of doped samples reveals that the overall nanograin size tends to decrease as the Ni content increases.

3.3 Optical characteristics

The transmission spectra of the titanium dioxide and nickel doped Titanium dioxide thin films on glass substrate were studied by using UV-Visible spectrometer at room temperature. The optical transmittance spectra of the annealed thin films at temperature 500 °C in the wavelength range 300–900 nm is shown in Fig.3. The spectra indicate that TiO_2 thin films are transparent in the visible region but show a sharp decline in transparency in the ultraviolet region. All Ni-doped TiO_2 films are transparent and colorless, just like pure TiO_2 films. Doping TiO_2 with Ni increases the average transmittance due to the structural distortion of the TiO_2 thin films. Undoped TiO_2 shows 60-75% transparency in the visible range of spectra. Here, 1% Ni doped TiO_2 shows 50-65% transparency and 2% Ni doped TiO_2 shows 75-85% Transparency. Higher transparency of 2% Ni doped TiO_2 is due to the improved crystallinity observed at 2% Ni doping.

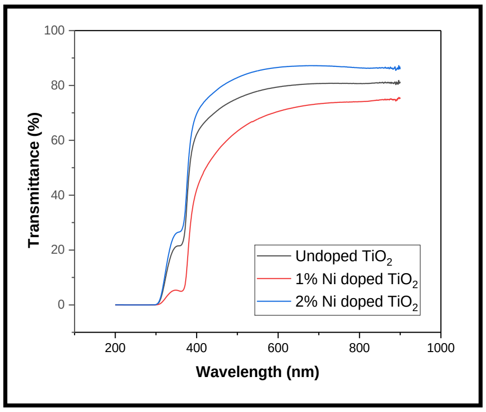

Fig.3 Spectral variation of transmittance with increasing percentage of dopants.

The optical absorbance of the annealed thin films measured through UV-Vis Spectroscopy in the wavelength range 300–900 nm is shown in Fig.4. From the figure, we can observe that undoped TiO_2 shows 2.9% absorbance, 1% Ni doped TiO_2 shows 3.5% absorbance, and 2% Ni doped TiO_2 shows 2.6% absorbance at lower wavelength of spectra.

The absorbance of the films is gradually decreasing at higher wavelength and 2% Ni doped TiO_2 shows lesser amount of absorbance than the other two films at higher wavelength. The materials exhibit prominent absorption spectra around 300 nm, possibly attributed to the transition of charged particles from the valence to the conduction bands. The absorption edge of all doped films (except for 1% Ni doped) shifts towards shorter wavelengths, suggesting a rise in the bandgap (Eg) of the deposited films.

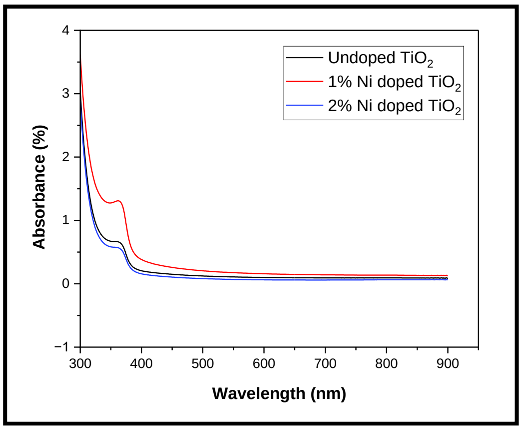

Fig.4 Spectral variation of absorbance with increasing percentage of dopants.

The absorption coefficient (α) dictates how deeply light of a specific wavelength can penetrate a material before being absorbed. A material with a low α value exhibits poor light absorption, and if it is thin enough, it will appear transparent at that particular wavelength. Absorption coefficient (α) of the films was calculated from the absorbance data using Beer-Lambert's formula as presented in Eq. (1).

$$\alpha = (2.303A)/d \quad (1)$$

where, d is the film thickness and A is the optical absorbance of the film. To finalize the calculation of the optical constants, the α value for both undoped TiO_2 and TiO_2 thin films fluctuate in tandem with changes in absorbance, indicating the presence of Ni content in the TiO_2 films. This improves the transparency of the materials in the visible light and near-infrared range, indicating that this material could be a promising option for optoelectronic devices.

Absorption coefficient and extinction coefficient of the undoped TiO_2, 1% Ni doped TiO_2, 2% Ni doped TiO_2 was calculated. Both coefficients vary depending on the incident wavelength. Their values fluctuate with the energy of the incident rays. Each monochromatic light possesses its own photon energy. Longer wavelength rays signify lower energy in the spectrum, while shorter wavelength rays indicate higher energy. Absorption coefficient for the films with different doping concentration are shown in Fig.5. At higher wavelength region the values of absorption coefficients are low that means lesser amount of light are absorbed. In the visible range of spectra, the coefficients begin to increase slightly from longer wavelength to shorter wavelength region. Absorption increases sharply in the shorter wavelength region (320-340 nm). This is the region at which the energy of the incident rays is enough for the transition of electrons from valance band to conduction band.

The extinction coefficient k was estimated from the values of absorption coefficient and wavelength of the incident rays, using the mentioned Eq. (2).

$$\kappa = \alpha\lambda/4\pi \quad (2)$$

Where, k = Extinction coefficient, α = Absorption coefficient, and λ = Wavelength of the incident light.

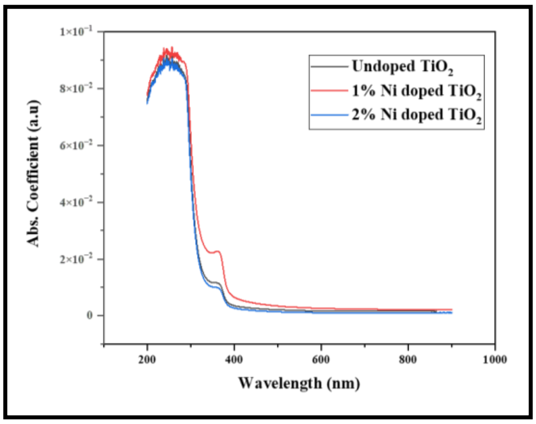

Fig.5 Change of absorption coefficient with photon wavelength of thin films.

The extinction coefficient is an alternative measure of absorbance, quantifying the degree to which a chemical species absorbs light within a specified wavelength range. The extinction coefficient values vary across different spectral ranges for films with varying doping concentrations are shown in Fig.6. It is noted that the extinction coefficient values are elevated in visible range 230 nm-380 nm range which represents higher absorptivity of light by the molecules present in the film. At higher wavelength region 720-900 nm these values slightly decrease. This could occur because of the absorption of higher energy light for molecular vibrations. The spectral analysis also indicates that the extinction coefficient values decline as the concentration of the nickel precursor solution increases. The decrease and increase in the extinction coefficient, as well as the corresponding decline and rise in the absorption coefficient, align with the introduction of impurity atoms.

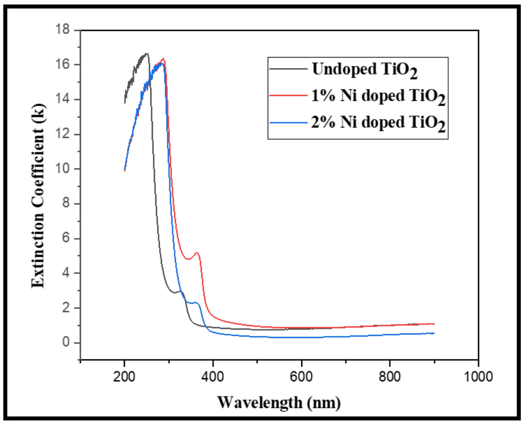

Fig.6 Change of extinction coefficient with photon wavelength of thin films.

To determine the optical band gap value, a straight line was plotted as a tangent from the most linear portion of the curve in the absorption region. At which points, the tangent intersects to the horizontal axis were noted. Each intersection point on the graph corresponds to the specific band gap of the film as shown in Fig.7. The optical band gap energies for the samples were computed. It was observed in this plot that as the nickel percentage in the solution increases, the band gap of the film decreases. Specifically, from the optical band gap measurement, it was noted that the band energy gap decreases with 1% Ni doping and increases with 2% Ni doping as shown in Table 1.

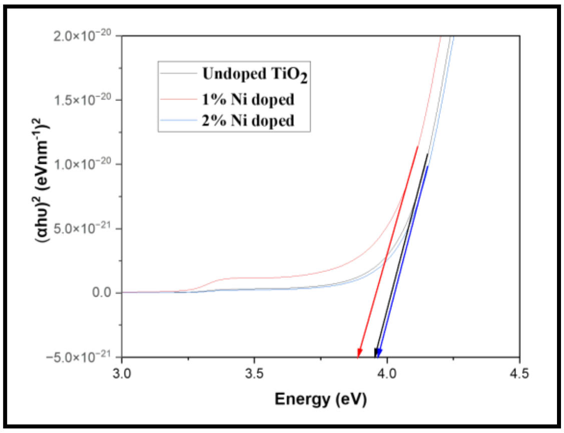

Fig.7 Plots of $(\alpha h\upsilon)^2$ vs. $(h\upsilon)$ for undoped, 1%, and 2% Ni doped TiO_2 thin films.

Table 1 Optical bandgap of undoped and Ni doped TiO_2 thin films.

Concentration (wt. %)	Band Gap (eV)
Undoped	3.95
1% Ni doped	3.89
2% Ni doped	3.96

Here, undoped TiO_2 thin films obtain 3.95 eV band gap energy, 1% Ni doped films obtain 3.89 eV, and 2% Ni doped films obtain 3.96 eV energy. The decrease in band gap energy observed in the film doped with 1% Ni is explained by the emergence of a new energy level below the TiO_2 conduction band, resulting from the Ni^{2+}/Ni^{+} transition positioned beneath it. The appearance of this new energy level arises from a charge transfer between the dopant and either the valence or conduction bands of TiO_2. Furthermore, the inclusion of Ni in the TiO_2 framework could prompt the creation of an oxygen vacancy, aiding in the reduction of Ti^{4+} to Ti^{3+} and probably influencing the band gap energy of the samples [13].

4. Conclusions

The purpose of our work was to prepare and characterize titanium dioxide and nickel doped titanium dioxide thin film on glass substrate. Titanium dioxide and nickel doped titanium dioxide thin film was prepared from titanium isopropoxide, isopropanol solution and nickel nitrate hexahydrate salt solution by spin coating method. Films were prepared with varying percentage of nickel (undoped, 1% nickel doped, 2% nickel doped) on a glass substrate (2.5 cm x 2.5 cm film area). XRD result of the films confirmed that the films were amorphous and improved crystallinity was found at 2% nickel doped titanium dioxide. The doped films are nearing the transition from the amorphous phase to the polycrystalline phase more closely compared to the undoped film. The SEM micrograph revealed that the titanium oxide thin films prepared exhibited a structure riddled with uniformly distributed cracks throughout the substance. The presence of these cracks was evident in the SEM images, indicating that the thin films lacked density. Despite annealing at high temperatures, the significant porosity of the thin films resulting from the spin-coating method persisted due to the agglomeration of particles in the crystalline nanoparticle suspensions. Nonetheless, the film surface appeared relatively even. In the case of 1% nickel-doped and 2% nickel-doped titanium dioxide, the average surface grain sizes were approximately 59 nm and 47 nm, respectively. The optical characterization was carried out by UV-Visible spectrophotometer. The transmission spectral analysis showed that the films were transparent. Transparency of the film at the percentage of nickel 2% was very high (about 75-85%) in the visible range of spectra. And the corresponding band gap energy was 3.96 eV. With decreasing the nickel percentage, the transparency decreased from 75-85% to 50-65% in the visible range and the band gap energy also shifted to 3.89-3.95 eV. Further investigation may be fascinating to know the influence of Ni doping on the electrical conductivity and mobility of charge carriers in TiO_2 thin films.

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