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Compositional analysis and optical properties of Co doped TiO_2 thin films fabricated by spray pyrolysis method for Dielectric and Photocatalytic applications

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Abstract

Cobalt doped TiO_2 thin films (CTF) deposited by spray pyrolysis has been studied. The compositional analysis has been done using RBS method, while optical spectroscopy has been done by measuring the transmittance and reflectance of the films. The CTF thin films were prepared by doping TiO_2 at different concentration levels of Co which was varied between 0 and 4.51 at. %. The optical transmittance of the thin film has been found to be about 80% in the visible and near infra red regions. The calculated optical band gap has been observed to shift by about 0.22eV, this shows a high potential for application as a dielectric and a Photocatalyst material.

Key words: Cobalt oxide; Titanium dioxide; thin film; optical properties; spray pyrolysis; Dielectric; Photocatalytic applications.

1. Introduction

Doping metal oxides with transition metals (TM) has led to investigation of new materials for photovoltaic applications; TiO_2 is a promising material as a semiconductor having high photochemical stability and low cost [1]. Co-doped TiO_2 has been studied due to the high potential on TiO_2 in photocatalysis [2, 3] and as a dielectric material [2]. Doping TiO_2 is equivalent to introducing defect sites like Ti^{3+} into the semiconductor lattice, where oxidation of Ti^{3+} is kinetically faster than oxidation of the Ti^{4+} species [3].

Co-doped TiO_2 (CTF) thin films have been deposited by various methods including sol-gel [1, 4], dip coating [4], crossed-beam pulsed laser deposition [5], spray pyrolysis [6], magnetron sputtering [7] and atomic layer deposition (ALD) [8]. Compositional analysis studied by X-ray photoelectron spectroscopy (XPS) of CTF thin films showed that Co atoms are bonded to oxygen and that oxygen vacancy in the spin polarization of the structure is responsible for the ferromagnetic behavior of CTF [6]. The transformation of CTF from amorphous to anatase to rutile phases depends on the calcinations temperature and Co concentration. The anatase-rutile transformation occurs at lower temperatures as the Co amount is increased. The strain energy associated with the incorporation of Co into TiO_2 results into lower activation energies, which facilitates the anatase-rutile transformation process [9].

This paper reports a compositional analysis of CTF thin films deposited by spray pyrolysis (SP) from titanium Isopropoxide and Cobalt chloride precursors. SP method has the advantage of being vacuum free hence less costly, it allows for a wide variety of precursor choices and deposition parameters and different precursors can be mixed in different proportions before deposition to effectively dope the samples. The composition of CTF thin films was studied using Rutherford backscattering spectrometry (RBS), which is an absolute method that does not require the use of standards in measurement and analysis. RBS has been effectively used for depth profiling and stoichiometric analysis of different materials [10-12].

Optical properties provide strong directions towards the actual applications at ground level and hence have been studied widely over the period. Optical Properties of not only the oxide materials [22-25] but also of selenides [26] and sulfides [27] has been of great interest recently.

In this paper we report the preparation of different volume percentages of Co-doped TiO_2 nanoparticles by spray pyrolysis.

2. Experiments

TiO_2 thin films were deposited (c-Si substrates for RBS analysis while microscope slides were used for UV-VIS study) by ultrasonic spray pyrolysis method [15] from a precursor of Titanium isopropoxide (TTIP). 19.2 ml of TTIP were added to 28.8 ml of 2, 4-Pentanedione solution with Acetylacetone (Acac) as a stabilizer. The reaction is exothermic [18] therefore the mixture was left to cool for 15 minutes before adding 432 ml of pure ethanol and stirring for 10 min. 43.2 mg of anhydrous $CoCl_2$ was dissolved directly in 50 ml of acetonitrile and stirred for 3 hrs in a closed bottle [19]. To dope TiO_2 thin films, different volumes of $CoCl_2$ solution were added to TTIP precursor solution in volumetric percentages of 0, 5, 10, 20, 30, 40 and 50 %, which corresponded to adding 0, 1.25, 2.5, 5, 7.5, 10 and 12.5 ml of $CoCl_2$ precursor, respectively, into 25 ml of TTIP solution. TiO_2 and Co-doped TiO_2 (CTF) thin films were sprayed from each of these solution mixtures for 5 min at a substrate temperature of 400 ^{o}C.

Compositional analysis of the TiO_2 and CTF thin films was investigated by RBS using JULIA accelerator in Friedrisch-Schiller University Jena. The samples were probed using a He^+ ion beam of energy 2.0 MeV at zero incidence and exit angle of 12^o. The backscattered ions were detected at a scattering angle of 168^o. The charge was 5 coulombs with measurement time of about 12 min. The analysis of the RBS data was performed using spectral management software (Spewa) based on the Nuno Data Furnace (NDF) code [12]. Optical transmittance and reflectance data were measured in the wavelength range of 200 – 2000 nm using Perkin Elma Lambda 35 UV-VIS-NIR spectrophotometer equipped with an integrating sphere.

3. Results and discussion

3.1. Compositional analysis

The RBS spectra for the TiO_2 and CTF thin films are presented in figure 1. The signals/peaks from Co, Ti, Si substrate and O are indicated accordingly. The position of the peaks with respect to the channel number depends on the atomic number or mass of the elements detected. The heavier elements appear with higher channel numbers corresponding to higher energy of backscattered He^+ ions after collision with the nucleus of that specific atom. The height/yield of the peaks is proportional to the amount of material present in the sample and which depends also on the scattering cross section of the detected element. The width of the peak is proportional to the thickness of the probed sample and depends on the energy loss per unit depth of the detected element [13].

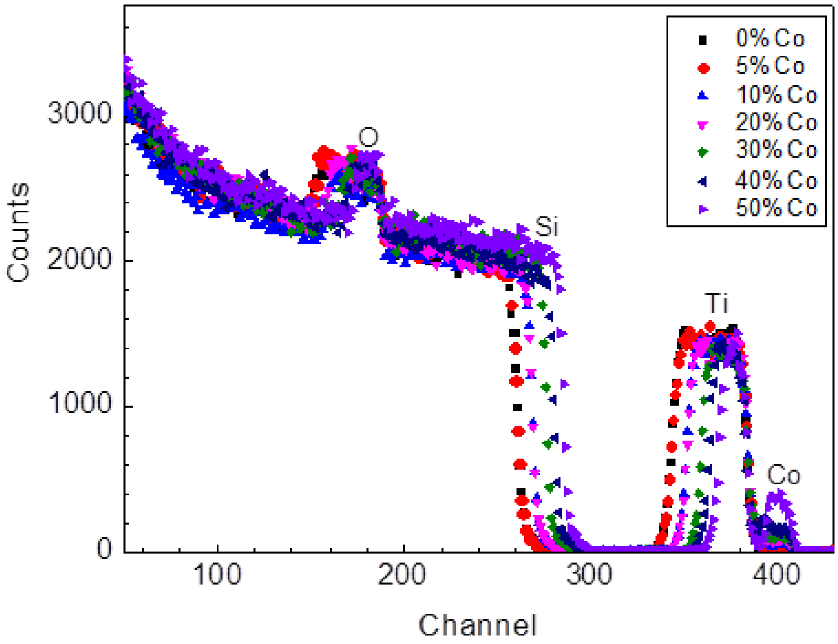

Figure 1: RBS spectra from TiO_2 and CTF thin films deposited from precursor solutions with 0, 5, 10, 20, 30, 40 and 50 % volumetric ratio of $CoCl_2$ solution.

From figure 1, it can be seen that the width of the Ti signal decreases with an increase in the percentage volume of $CoCl_2$ precursor used. This means that by increasing the amount of $CoCl_2$ in the precursor solution, the deposition rate and hence the thickness of the deposited films decreased. The signal from Co increased in height with increasing $CoCl_2$ volume in the precursor solution as expected. This corroborates the increase of the concentration of Co in the CTF film with the volume of $CoCl_2$.

Measured and fitted RBS data from Ti and Co in CTF thin films deposited from precursor solutions containing $CoCl_2$ volumetric percentages of 0, 5, 10, 20, 30, 40 and 50 % are shown in figure 2.

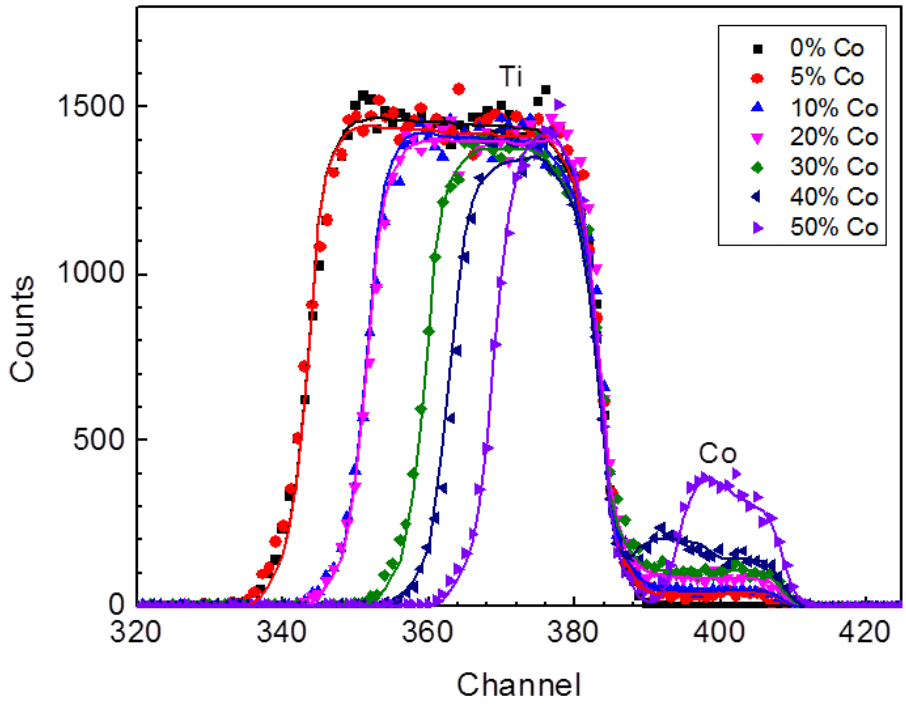

Figure 2: Measured and fitted RBS spectra showing Ti and Co signals from CTF thin films deposited from precursor solutions with 0, 5, 10, 20, 30, 40 and 50% volumetric percentages, measured data is represented by symbols while fitted data is represented by lines

The depth distribution of Co in the CTF thin films shows non-uniform concentration for thin films deposited from precursor solutions with $CoCl_2$ volumetric percentages higher than 30% with accumulation of Co at the internal interface with c-Si substrate. CTF thin films prepared by pulsed laser deposition also showed non-uniform depth distribution but with Co accumulating at the surface instead. Thin films with smaller Co content did not show this inhomogeneity [10]. Other authors have observed the presence of clusters in CTF thin films [10, 14], but these observations could be due to different deposition and characterization techniques employed.

To obtain quantitative information, the RBS spectra were fitted using Spewa software based on the NDF code [12]. The thicknesses of the CTF thin films were extracted from the width of the peaks using the energy loss per unit depth for each element [13]. The thicknesses (*d*) and total concentrations (atomic density) (*N*) of O, Ti and Co were obtained by integrating the respective peaks and calculating the areal densities (atoms/cm^2) using the expression [13]

$$A = \sigma.\Omega.Q.Nd \tag{1}$$

Where *A* is the integral of the peak, σ is the scattering cross-section, **Ω** is the detector's solid angle, Q is the charge and *Nd* is the areal density of the detected element.

The thicknesses of the CTF thin films are plotted as a function of the volumetric percentages of $CoCl_2$ in the precursor solution as shown in figure 3 (a). The graph shows an inverse proportionality between the volumetric percentage (*p*) and the layer thickness (*d*) indicating a decrease in the deposition rate with an increase in the $CoCl_2$ volume. The relationship could be expressed in a mathematical form as

$$d = (176 \pm 5) - (2.3 \pm 0.2)\, p \tag{2}$$

The slope implies that the film thickness decreases at the rate of 2.3±0.2 nm per unit percentage increase of the volume of $CoCl_2$ in the precursor solution, this is consistent with other researchers that showed Cobalt doping reduces the nucleation process in TiO_2 [9]. Equation (2) can be used to determine the film thickness for a given precursor ratio, which controls the doping level in the CTF thin films.

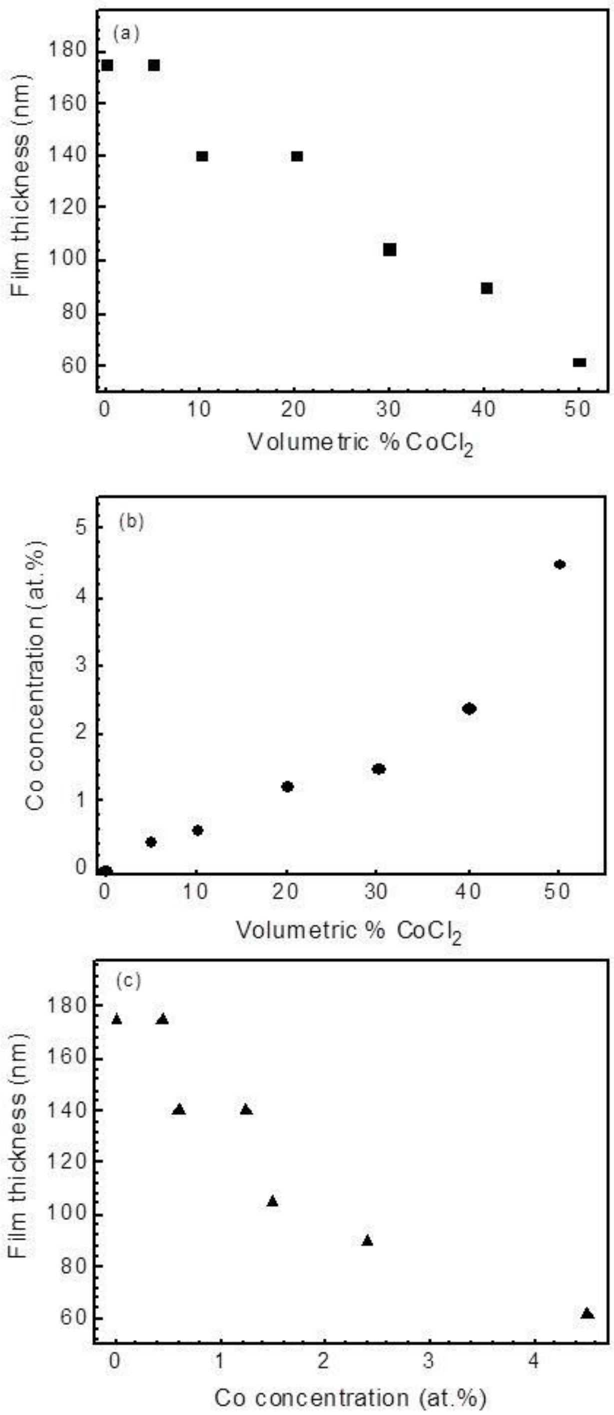

Figure 3: (a) CTF film thickness (b) Co concentration as a function of the volumetric percentage of $CoCl_2$ and (c) the layer thickness as a function of the Co concentration.

The dependence of Co atomic concentration in the CTF thin films on the volumetric percentage of $CoCl_2$ in the precursor solution is given in figure 3 (b). The amount of Co in the deposited films increased parabolically with an increase in the $CoCl_2$ volume in the precursor solution. From figure 3(b), the dependence of the atomic concentration of Co on the volumetric percentage of $CoCl_2$ in the precursor solution is given by equation (3) as

$$n(at.\%) = (0.03 \pm 0.02)\, p + (0.0012 \pm 0.0005)\, p^2 \qquad (3)$$

Where n is the Co concentration in at. % and p the volumetric percentage as shown in equation (2). Figure 3 (c) shows the relationship between the layer thickness and concentration of Co in the CTF thin films. The film thickness and hence deposition rate decreases parabolically with increasing Co content in the deposited films. The relationship satisfies the expression

$$d = (180 \pm 10) - (50 \pm 13)\, n + (5 \pm 3)\, n^2 \qquad (4)$$

Equations (2), (3) and (4) obtained from the relationships between volumetric percentage of $CoCl_2$ in the precursor, the film thickness and Co concentration can be utilized to predetermine the deposition parameters for specific applications of CTF thin films for example in photocatalysis or ferromagnetism where CTF films are mostly used [2,3].

3.2. Optical properties

The optical transmittance of CTF thin films deposited at 400 ^{o}C from precursor solutions containing 0, 5, 10, 20 and 40 % by volume of $CoCl_2$ are presented in figure 4. The spectrum from the substrate is also included as a reference. The films were highly transparent up to above 80 % in the visible and near infrared spectral range. There was no significant change in the transmittance of the CTF thin films with increase in the volume of $CoCl_2$ in the precursor. Similar observations were reported by Sharma *et al* for spray pyrolysed CTF thin films [15].

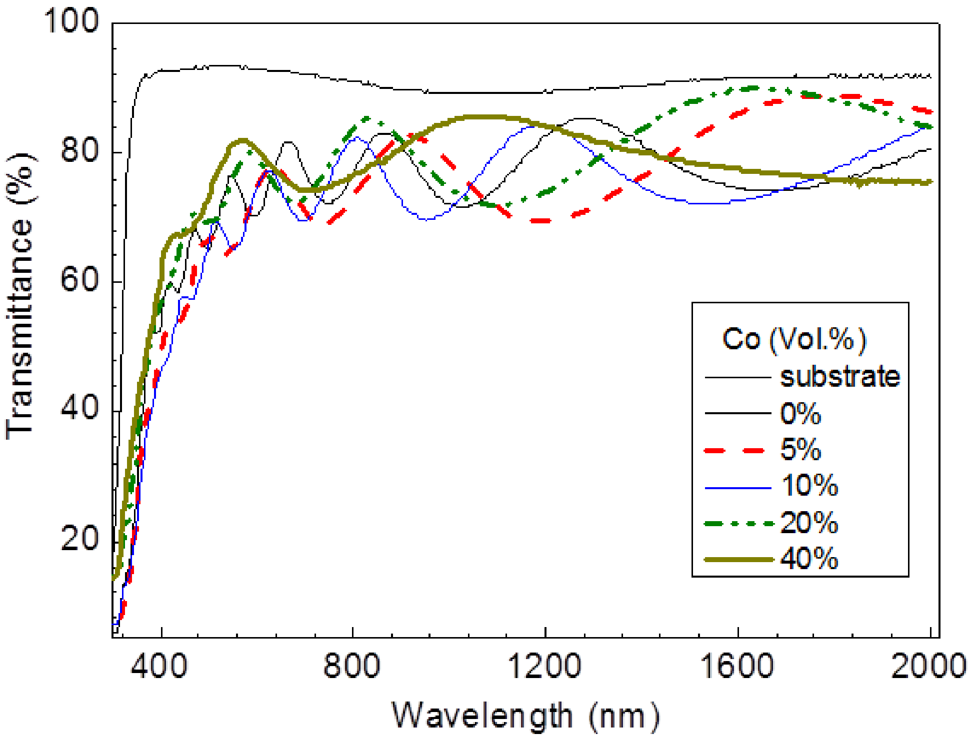

Figure 4: Optical transmittance of CTF thin films deposited by spray pyrolysis from precursor solutions with 0, 5, 10, 20 and 40 volumetric percentage of $CoCl_2$.

The optical transmittance (T), reflectance (R) and absorption coefficient (α) are related by the equation [16]

$$\frac{T}{(1-R)} = e^{-\alpha d} \qquad (5)$$

The optical band gaps (E_g) of the CTF thin films were determined from a Tauc plot using the relation [17]

$$(\alpha h v)^2 = A\left(hv - E_g\right) \qquad (6)$$

Where hv is the photon energy and A is a constant of proportionality. The values of E_g were obtained by extrapolating the linear part of the graph of $(\alpha hv)^2$ against hv down to the photon energy axis as shown in figure 5.

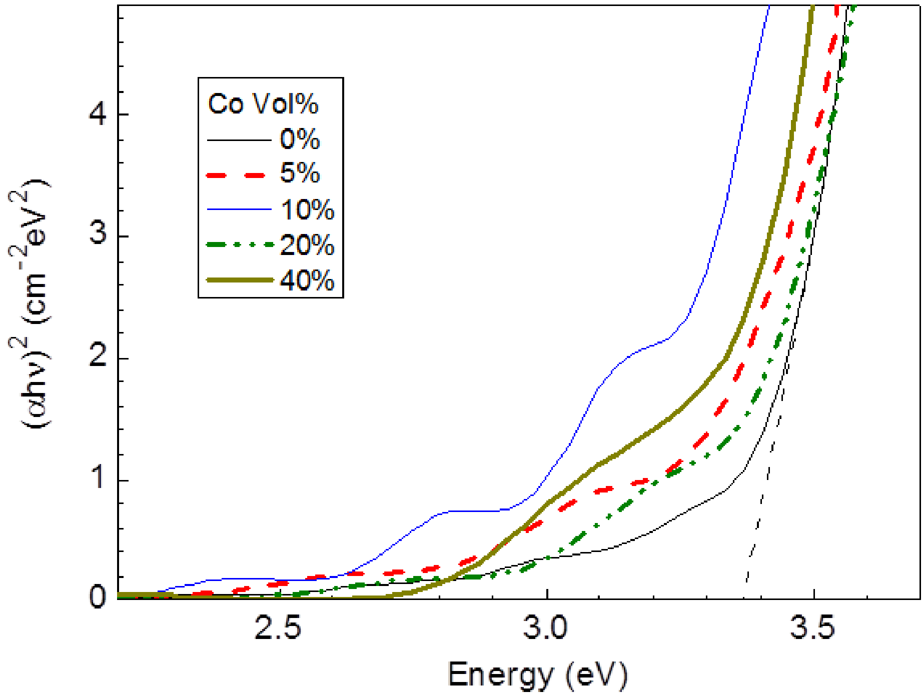

Figure 5: Determination of direct band gap of CTF thin film for thin films deposited from precursor solution with 0, 50, 10, 20 and 40 volumetric percentage of $CoCl_2$.

The values of $x = Co/(Co + Ti)$, Co concentration (at. %), CTF film thickness and E_g are summarized in table 1 as a function of the percentage volume of $CoCl_2$ in the precursor solution.

As expected, the values of x increased with the percentage $CoCl_2$ volume. E_g decreased from 3.37 eV for pure TiO_2 down to 3.15 eV for $CoCl_2$ volume percentage of 10 % and then increased to 3.32 eV for higher volumes. The variation in the value of E_g is about 0.22 eV, which is still small. Similar shift on the optical band gap of CTF thin films due to Co doping have been reported in literature, which agrees well with our results [20].

Table 1: Summary of x, Co concentration, layer thicknesses and optical band gap values as a function of the $CoCl_2$ solution volumetric percentage in the precursor solution.

	0%	**5%**	**10%**	**20%**	**30%**	**40%**	**50%**
X=Co/(Co+Ti)	0	0.014	0.020	0.042	0.050	0.078	0.14
Co (at.%)	0	0.43	0.60	1.25	1.50	2.40	4.51
Thickness (nm)	175	175	140	140	105	90	62
Bandgap (eV)	3.37	3.21	3.15	3.32	-	3.30	-

Some authors have reported insignificant changes in the optical band gap for Co ≤ 10 at% [7,14,15, 16] The band gap narrowing is mainly due to the interaction between the band electrons of TiO_2 and the localized d electrons of Co^{2+} ions substituting Ti^{4+} cations [14]. Some groups have reported that incorporation of Co into TiO_2 does not actually reduce the band gap but introduces mid band gap states which result in the red shift of the band gap. Some have suggested that the reduction in the band gap is due to the *sp-d* exchange interactions between the *sp* electrons of the host and *d* electrons of the dopant [4, 14].

Figure 6 shows anatase to rutile phase transitions with higher Cobalt doping of TiO_2 making the films less crystalline. These transformations are known to be a nucleation and growth process during which rutile nuclei form within the anatase phase and grow in size eventually consuming the surrounding anatase phases. The film crystallites increase in size due to Cobalt incorporation and the cobalt ions are uniformly spread in the composite film. The effective ionic radii of Ti^{4+} and Co^{3+} are 0.605 and 0.685Å respectively the difference in lattice constants cause distortions during Cobalt incorporation in TiO_2, consistent with reported work [21].

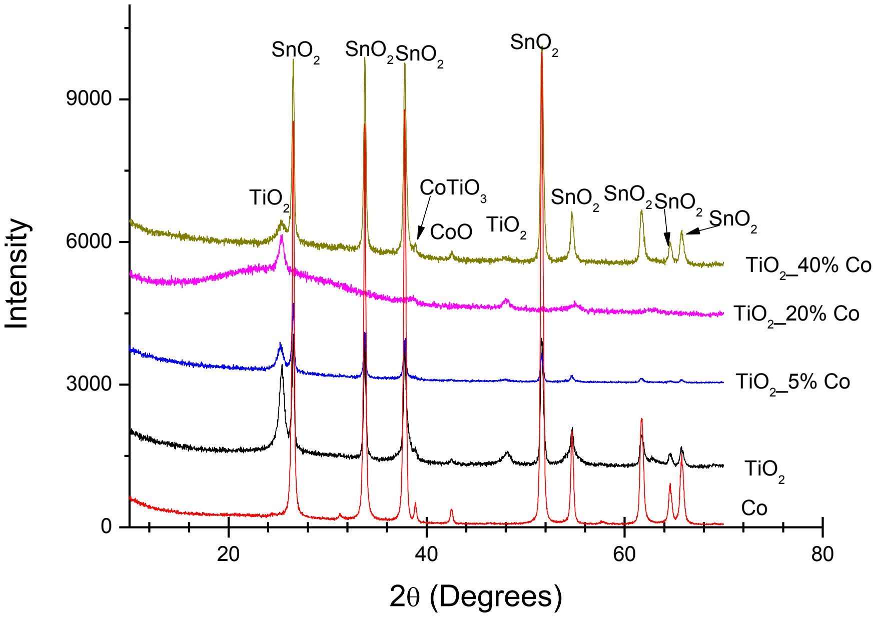

Figure 6: XRD patterns showing Cobalt ions and TiO_2 implanted in the composite film

The strain energy associated with the incorporation of Co results in lower activation energies which facilitate the anatase-rutile phase transformation, this is consistent with RBS results.

4. Conclusion

The concentration of Co dopant in TiO_2 host matrix was varied by increasing the volume of $CoCl_2$ in TTIP precursor solution between 0 and 50%. The resulting concentration of the Co into the CTF thin films ranged between 0 and 4.51 at. %. An inverse relationship between the CTF film thickness and the volumetric percentage was obtained while the relationship between the Co content and the volumetric percentage of $CoCl_2$ in the precursor solution was parabolic. The CTF thin films exhibited high transmittance in the visible and near infrared regions and the change in the optical band was about 0.22 eV.

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