Annealing Induced Red Shift in the Absorption Edge of TiO_2 Films Prepared by Sol-gel Technique

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We report the formation of sol-gel spin coated TiO_2 films on corning glass substrates. The XRD spectra revealed the predominance of anatase phase in the films with annealing temperature from 250 to 450 °C. The FE-SEM studies showed dense distribution of nanocrystallites in the deposited films. Elemental analysis by EDAX measurement also confirmed the formation of TiO_2 films. Most interestingly, annealing at 250 to 450 °C for 1 h in air produced a red shift in the absorption edge from 353 to 374 nm. This red shift was attributed to annealing-induced reduction in carrier confinement linked to enhancement in nanocrystallite sizes in the annealed films.

Keywords: Red shift, Absorption edge, TiO_2, Sol-gel, Thin films.

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1. INTRODUCTION

Metal oxides have important technological applications in the fabrication of various kinds of sensors, piezoelectric devices, solar cells, transparent conducting electrodes, fuel cells, and coatings for passivation of surfaces against corrosion and as photo-catalysts. There are several methods of producing thin film of metal oxides like sputtering [1, 2], electron-beam evaporation [3, 4], nanocluster deposition [5], molecular beam epitaxy [6, 7] etc. One of the cheapest and up scalable synthesis method amongst them is wet chemical deposition by sol-gel technique [8-10]. Sol-gel technique has several advantages like low processing temperature, large area coatings, good homogeneity of the film etc.

TiO_2 is a wide band gap semiconductor and thin films of TiO_2 on supported material are known to be a good photocatalytic material under UV radiation [11, 12]. The Anatase phase of TiO_2 is rare and show more photocatalytic activity than the Rutile phase [12, 13]. Generally, the precipitates derived in sol gel method are amorphous in nature and further heat treatment is required to induce crystallization [14, 15]. Homogeneous and compact TiO_2 film attached to the substrate can only be obtained if we anneal the as-deposited sol-gel film. But, there should be a trade-off, as annealing alters the crystal structure leading to the degradation of optical properties of the film due to out diffusion of oxygen species from the lattice. Thus, it becomes imperative to study the effect of annealing on the crystal transformation of TiO_2 film and its impact over optical properties. It is to be noted here that TiO_2 film transforms from amorphous state to anatase structure before it is converted to rutile structure. Sol-gel synthesis route in acidic medium has been adopted in the present work to prepare a sol containing nanoparticles which is aged and subsequently spin coated over the substrates at room temperature. In this work, we have deposited thin films of TiO_2 on corning glass substrates by spin coating the precursor derived by sol-gel method. The structural properties and band edge absorption of the annealed films is studied via X-ray diffraction (XRD) and UV-Vis spectroscopy. Field emission scanning electron microscopy (FE-SEM) and energy dispersive X-ray analysis (EDAX) have been also carried out to support the results of the current work.

2. EXPERIMENTAL

Prior to deposition, the glass substrates for coating were cleaned by sonication with acetone and de-ionized water which is necessary for good adherence of the film to be deposited. Titanium (IV) isopropoxide (TIP), propanol, hydrochloric acid (HCl) and deionized water were taken as initial materials to synthesize the sol. Firstly, solution of TIP in propanol was added to a solution of HCl in propanol under high speed stirring at room temperature. The molar ratio of HCl/TIP was maintained to be 0.54. Afterwards, a solution of water in propanol was added drop-wise using a burette to the above solution under continuous stirring. The molar ratio of the TIP:H_2O was maintained at 1:4. A white gel was formed which finally was spin coated on already cleaned corning glass substrates. To ensure high homogeneity as well as considerable thickness of resultant TiO_2 thin films, we adopted multi-step coating process. Thin films were coated on the substrates at 3000 rpm for 20 s and every layer, after coating, was dried at 200 °C for 5 min. The process was repeated 5 times to achieve appreciable thickness. The films thus obtained were finally annealed in a horizontal quartz tube furnace at three separate temperatures varying from 250 to 450 °C in the steps of 100 °C, for 1 h in ambient air. One separate film with all the same parameters was deposited by repeating the coating process 10 times and then it was finally annealed at 450 °C.

3. RESULTS AND DISCUSSION

XRD patterns of the TiO_2 films are shown in the Fig. 1. The peak positions in the XRD spectra reveal that all samples consist of anatase phase only and

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higher annealing temperature results in change in intensity and width of the anatase (101) peak. Occurrence of long range order i.e. improved crystallinity in the deposited TiO_2 films with annealing temperature can be concluded, as enhancement in the intensity of (101) peak is observed. Emergence of (200) and (105) peaks of anatase phase which are of feeble intensity, in the samples annealed at higher temperature i.e. 350 and 450 °C, is another evidence to support the improved crystallinity [16]. The average crystallite size is calculated from broadening of most intense line (101) in the XRD data using Debye-Scherrer formula [8]. The calculations reveal that the crystallite size is ~ 9 nm for the sample annealed at 350 °C and ~ 11 nm for the sample annealed at 450 °C. Thus, the predominance of long range order in the nanocrystalline film with heat treatment is further confirmed from the enhancement in average particle size with annealing temperature.

FE-SEM image of the film which was annealed at 450 ºC is presented in Fig. 2. Similar pictures are obtained for other two samples as well. The image shows a dense distribution of nanocrystallites in the deposited film. From the FE-SEM image, which is similar for all the samples, as presented in Fig. 2, it can be concluded that all the annealed films have nearly similar surface morphologies. The elemental composition of the same TiO_2 film as determined by EDAX measurements is shown in Fig. 3. The EDAX spectra confirm the presence of both Ti and O suggesting thereby the formation of TiO_2 films.

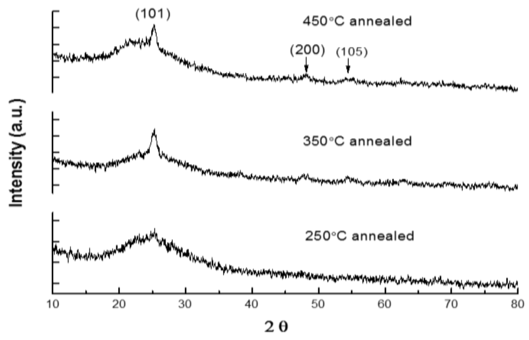

Fig. 1 – XRD patterns of 5 layered coated TiO_2 film annealed at different temperatures

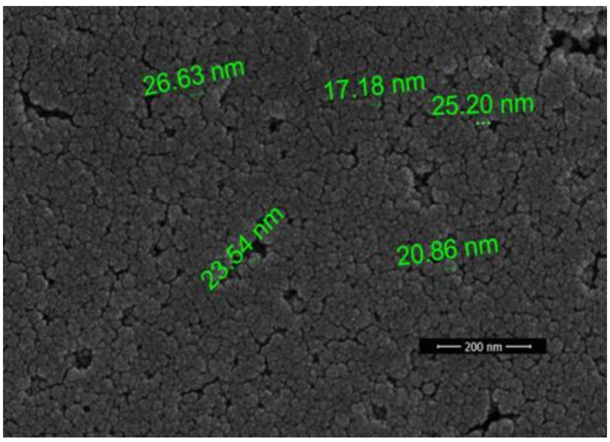

Fig. 2 – SEM image of the deposited 5 layered TiO_2 film annealed at 450 °C

Further, the presence of Ca, Ba, Si and Al peaks in the EDAX data is possibly due to the presence of these elements in the compounds used for making the corning glass which is well-known as a calcium barium glass.

The surface morphology of a film generally modifies optical absorption spectrum. The transmittance spectra in UV-Vis range as shown in Fig. 3 depict the transparency of films in visible region (380-700 nm). A characteristic absorption at a wavelength of around 350-380 nm is seen which falls under UV region. The absorption edge for the samples shifts from ~ 353 nm for the sample annealed at 250 °C to 368 nm for the sample annealed ~ 350 °C. Finally, it is shifted to ~ 374 nm for the sample annealed 450 °C. It can be attributed to reduced carrier confinement in the TiO_2 thin films with annealing temperature. The reduced carrier confinement happens because of enhancement in particle size constituting the films, due to heat treatment, as is evident from the XRD data. On the other hand, the red shift of absorption edge suggest a reduction in band gap. Such reduction in band-gap of TiO_2 films may find potential applications in optoelectronics.

For further understanding, optical transmission characteristics of 10 layered TiO_2 film is compared with 5 layered film, annealed at the same temperature i.e. 450 °C. The transmission spectra plotted in Fig. 5 shows that the transmission decreases from 80 to 55 percent in a 10 layered film as compared to that of 5 layered film, due to increased thickness, keeping the absorption edge unaltered in both cases.

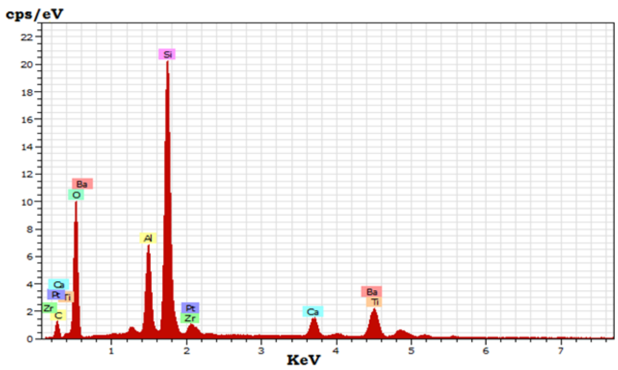

Fig. 3 – EDAX spectra of the 5 layered TiO_2 annealed at 450 °C

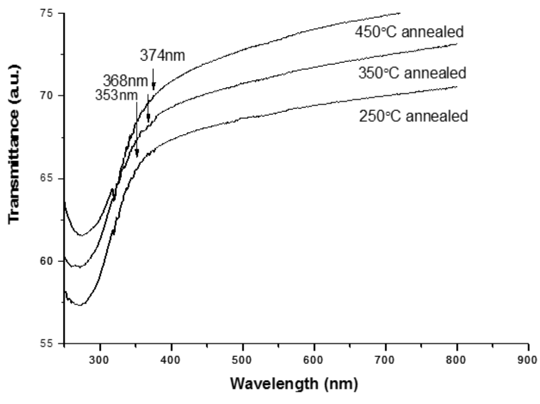

Fig. 4 – Transmittance spectra of 5 layered TiO_2 film annealed at different temperatures

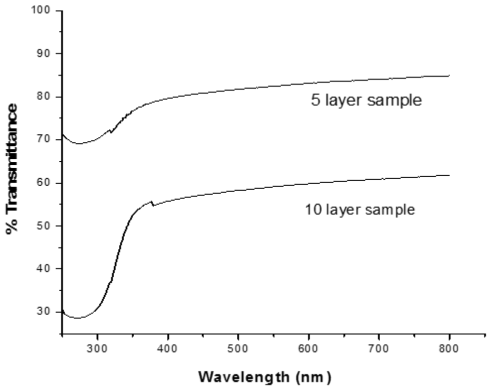

Fig. 5 – Transmittance spectra of 5 layered and 10 layered TiO_2 films annealed at 450 °C

4. CONCLUSIONS

The present work reports the deposition of TiO_2 nanocrystalline thin films on corning glass substrate by sol-gel spin-coating technique. As revealed by the XRD spectra the deposited films exhibit a preferential (101) orientation corresponding to anatase phase of TiO_2. The prominence of the (101) orientation increases with increase in annealing temperature from 250 to 450 °C. Further, the nanocrystallite size as calculated from the XRD data increases with annealing temperature. A red shift in the absorption edge within UV domain is revealed in the nanocrystalline films with increase in the annealing temperature. This red shift is attributed to annealing induced reduction in carrier confinement in the deposited films. This red shift of absorption edge is also indicative of reduction in band gap. Such reduction in band-gap of TiO_2 films may find potential applications in optoelectronics.

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Індукований відпалом червоний зсув краю поглинання плівок TiO_2, підготовлених технікою золь-гелю

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Представлені результати про формування плівок TiO_2 золь-гелевим спін-покриттям на підкладках з гранульованого скла. Спектри XRD виявили переважання фази анатазу у плівках із зміною температури відпалу від 250 до 450 °C. Дослідження FE-SEM показали щільний розподіл нанокристалітів у нанесених плівках. Елементний аналіз за допомогою вимірювання EDAX також підтвердив утворення плівок TiO_2. Найцікавіше, що відпал при температурі від 250 до 450 °C протягом 1 год на пояснюється впливом індукованого відпалу на зменшення обмеження носіїв, пов'язаного із збільшенням розмірів нанокристалітів у відпалених плівках.

Ключові слова: Червоний зсув, Край поглинання, TiO_2, Золь-гель, Тонкі плівки.