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Properties and Photocatalytic Application of Electronbeam Evaporated Titanium Dioxide (TiO_2) Thin Films

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Abstract: This work presents the photocatalytic property of electron beam evaporated titanium dioxide (TiO_2) thin films prepared at room temperature. The films were investigated for decomposition of methylene blue – eosin dye solution under visible light irradiation. The effect of annealing on structural, optical and decomposition properties was studied in detail. X-ray diffraction study revealed the amorphous nature of the film. Transmittance of the as deposited and annealed samples was good in the entire visible region. Suppressed recombination rate upon annealing enhanced the degradation of dye molecules to 32 %.
Keywords: Titanium dioxide, electron beam evaporation, photocatalysis, dye decomposition, visible light.

Introduction and Experimental:

Titanium dioxide (TiO_2) has wide range of applications, especially the photocatalysis. It is being researched for controlling harmful pollutants like bacteria, disease causing moulds and gases such as CO_2, NO_X, SO_X in the environment [1]. Thin films do a better job of photocatalysis compared to powder, in terms of easier separation from the dye solution, reusability even though it has lower surface area than nano powder [2]. In this context, the present work is devoted to investigate the photocatalytic (PC) property of electron beam evaporated TiO_2 thin films in decomposition of methylene blue (MB) – eosin dye solution under visible light irradiation. There is no condition like controlled environment is considered here. Hence this serves as a fundamental study to understand the photocatalytic application of TiO_2 thin films in normal day to day life. The structural and optical properties are studied in detail, in order to understand the mechanism involved with catalysis.

The source material was the palletized pure TiO_2 [titanium dioxide] powder. The substrates were cleaned microscopic glass plates. The titanium dioxide thin films were prepared at room temperature (300K) by the electron beam (e-beam) evaporation using a commercial vacuum unit (Hind Hivac 12A4D). The electron gun was operated at 6kV and 10mA (Hind Hivac model EBG-PS-3K). The evaporation was carried out for 15 mins and the chamber pressure is maintained between 4-6 x 10^{-6} mbar. Then the source material was deposited as a thin film on the glass substrates. The prepared sample was further annealed at 450°C for about 3 hrs in air.

The prepared TiO_2 thin films were examined for their crystalline nature by a Philips X'Pert- Pro diffractometer [Copper Kα radiation, λ = 1.5406 Å]. The thickness was measured using Stylus Profilometer. The optical absorption and transmission in the wavelength range 300 – 1100 nm were recorded by using a double beam spectrophotometer UV-2450, UV-VIS spectrophotometer (Shimadzu). The photoemission measurements were taken with the use of RF-5301 PC spectroflurophotometer (Shimadzu). For photocatalysis, the films were immersed in desired amount of solution in a petri dish. The reaction was allowed under normal sunlight for 4 hrs. The degradation ratios were calculated using concentration of dye solution before and after the light irradiation [3]. Where, the concentrations were obtained using Beer-Lambert's law.

Results and discussion:

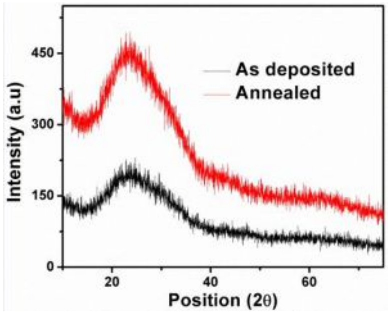

Figure 1: X-ray diffraction pattern of e-beam evaporated and annealed films

Presence of no peak in X-ray diffraction (XRD) pattern (Figure 1) revealed that the sample even after post-heat treatment at 450 °C shows amorphous nature. This indicates the above mentioned synthesis conditions could not produce crystalline TiO_2. Figure 2 (a) shows UV-Vis transmittance spectra of as deposited and annealed films. It indicates both the samples have good transparency in the entire visible region. The decreased transmittance for the annealed film reveals the increase in particle size due to annealing.

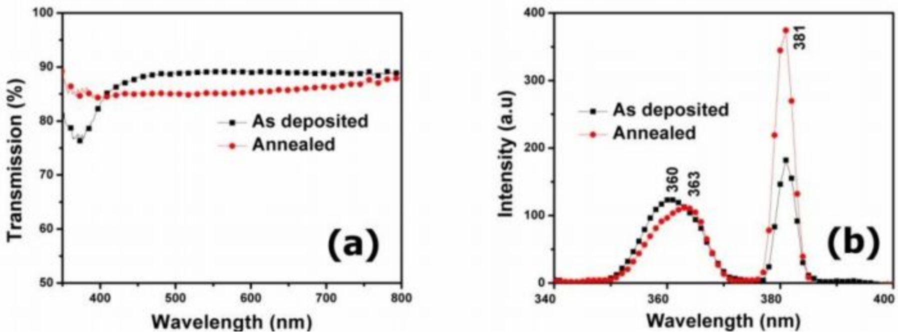

Figure 2: Transmittance and photoluminescence spectra of e-beam evaporated and annealed films

PL spectra of the samples were obtained by exciting at a wavelength of 320 nm. Two prominent peaks were observed at 360 and 381 nm for the as deposited sample. The absence of peaks at visible region indicates the samples are free from any structure defects or impurities [4]. When the film gets annealed, the peak at 360 nm slightly red-shifts to 363 nm, which indicates the particle size dependent interaction of electrons – holes [5]. The increase in intensity at 381 nm for the annealed film indicates the enhancement in recombination process due to annealing.

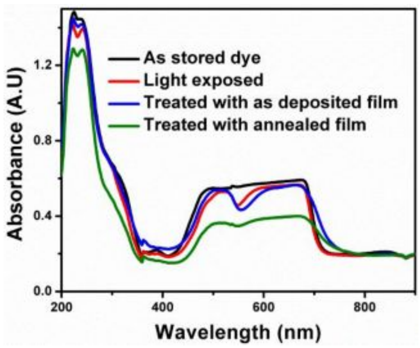

Figure 3: Absorbance spectra of methylene blue – eosin dye solution under different conditions

Figure 3 shows the UV-Vis absorbance spectra of the dye solution with/without the prepared films under normal sunlight irradiation. The spectra behave similar for the solution stored in dark condition and the one irradiated with visible light, except a hump observed at 549 nm (corresponds to yellowish green color). Moreover, as deposited sample did not show any notable decomposition [6]. The absorbance minimum observed in the region of 359 – 412 nm indicates that the color of the solution lies in purple to violet region. The calculated degradation efficiencies of the as deposited and annealed films at 600 nm are 7 and 32 %, where mere light irradiation causes an efficiency of 3%. From the above observations we can conclude that the degradation of dye solution is due to catalytic effect, not due to thermal effect [7].

Conclusion:

The photocatalytic properties of e-beam evaporated titanium dioxide thin films were studied. Degradation efficiency of the annealed film is about 32 % for the MB – eosin dye solution. The obtained results were related with the microscopic properties, in order to understand the mechanism involved behind catalysis. The decomposition reaction is a catalytic one, which is proved by observing the dye in normal sunlight and dark conditions. The results prove that with improved crystallinity these films can have potential application in waste water treatment.

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