Fabrication of TiO_2 Nanoscale Thin Films and Its Structural Properties

Titanyum Dioksit Nano Ölçek İnce Filmlerin Üretimi ve Yapısal Özellikleri

Research Article

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ABSTRACT

The photocatalytic properties of titanium dioxide with extraordinary stability have potential application in chemical industry. Titanium dioxide nanoparticles were synthesized by sol-gel method and used dip-coating method for the preparation of thin films on glass substrate. To study the structural and physical characteristics of the samples, the XRD, UV-VIS and an optical microscope were used. The results show that with increasing the annealing temperature and thickness, larger particle size obtained and energy gap is reduced. Thus, by controlling the annealing temperature and thickness can be achieved to the gap-controlled semiconductors.

Key Words
Nanoscale thin film, TiO_2, Semiconductor, Dip-Coating.

ÖZET

Olağanüstü kararlılıktaki titanyum dioksit fotokatalitik özellikleri nedeniyle kimya endüstrisinde potansiyel uygulamalara sahiptir. Titanyum dioksit nanopartiküller sol-jel yöntemi ile sentezlenmiş ve daldırmalı kaplama yöntemi ile cam yüzey üzerine ince film hazırlamak için kullanılmıştır. Örneklerin yapısal ve fiziksel özelliklerini karaterize etmek için XRD, UV-VIS ve optik mikroskop kullanılmıştır. Sonuçlar yakma sıcaklığı ve kalınlık arttıkça, partikül boyutunun arttığını ve enerji aralığının azaldığını göstermiştir. Enerji aralığı kontrollü yarı iletkenler, yakma sıcaklığını ve kalınlığı kontrol ederek üretilebilir.

Anahtar Kelimeler
Nano ölçek ince film, TiO_2, yarı iletken, dip kaplama.

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INTRODUCTION

In recent years, titanium dioxide nanoparticles due to the considerable activity and high chemical stability, have been potential application in environmental and waste water treatment, dyeing, analysis, and in the fabrication of solar cells. For the first time, scientists discovered the effect of titanium dioxide photocatalysis in 1972 [1]. When a semiconductor excited with light, if the energy of light is larger than the energy band gap of the semiconductor, the electrons go from the valence band to the conduction band and positive holes are remind. Titanium dioxide is excited with light wavelengths less than 390 nm, and by creating the pairs of electrons - hole, titania act as a photocatalysts [2]. Studies on the mechanism of photocatalysis has shown that some factors such as crystal structure, particle size and surface characteristics influence on photocatalysis activity [3]. Titanium dioxide surface characteristics play a major role in the photocatalytic behavior. The photocatalytic behavior of titanium dioxide depends on the concentration of active sites on the surface. The transformation of photocatalytic carriers is related to the characteristics of the surface modes such as surface defects [4]. The inherent defects are including the dressing cations that unsaturated such as: Ti^{+3} (oxygen vacancies), anions of oxygen (bridged oxygen) and hydroxyl groups that can be characteristic of acidic or basic and the non-essential defects are including H^+, O_2, CO^+ and formed by the surface interaction with the foreign molecules. The bridging oxygen and hydroxyl groups and O^{-2} has the most advantages in photocatalytic activities [5]. So in this article, the thin films of titanium dioxide nanoparticles which have been prepared by sol-gel method. To determine the size of particles, uses the XRD spectra at different temperatures and to obtain the optical energy gap curves uses the UV-VIS spectrum. Also the optical microscope used to check the cracks on the layer.

EXPERIMENTAL METHOD

The sol-gel method for the synthesis of titanium dioxide nanoparticles is used. First, 10 ml of mixed with 40 ml ethanol and this solution is placed on the mixer. Also, 10 ml of distilled water with 10 ml of ethanol and 4 ml of nitric acid are mixture and shake well. The first solution adds drop by drop to the second solution under stirring. The ultima solution to shake for 3 hours. The solution including the TiO_2 nanoparticles almost white with slightly yellowish gel was obtained.

For the deposition process, the glass slides were used as the substrate. First, put them in glass containers and washed with the alcohol and water in the ratio of 1: 2. The ultrasonic device fill with distilled water and the glass slides put into the chamber for 10 min at 50°C. After the time, they were pulled out and washed with distilled water and dry by heater. Desiccating the substrate until the padding inside the vacuum can be maintained. Then, with using dip-coating method, slide into the solution and draw out from the solution with speed of 30 cm/h, a very thin layer is formed on glass slides. Initially, the samples are dried at room temperature, then they are annealed at different temperatures. It should be noted that the annealing time was one hour at each temperature.

RESULTS and DISCUSSION

The XRD pattern of the TiO_2 nanoscale thin films was recorded by using a Philips powder X-ray diffractometer in diffraction temperature. The crystallite size was determined from the broadening of corresponding X-ray Peaks. The XRD pattern of the TiO_2 nanoscale thin films dried at room temperature is shown in Figure1. The observed peaks in angle $2\theta=25.765^{o}$ corresponding to results reported in the literature [5, 6], attributed to the crystal phase of anatase titanium dioxide. The average nano-crystalline size (D) was calculated using the Scherrer formula:

$$D = 0.9\lambda / \beta.\cos\theta \quad (1)$$

where λ is the X-ray wavelength (CuKα radiation and equals to 0.154060 nm), θ is the Bragg diffraction angle, and β is the FWHM of the XRD peak appearing at the diffraction angle θ. The average crystalline size that was calculated from X-ray line broadening peak and Scherrer equation was found to be about 71.22 nm.

In the XRD spectrum of the sample dried at 200°C (Figures 1 and 2), we can see a peak at angle

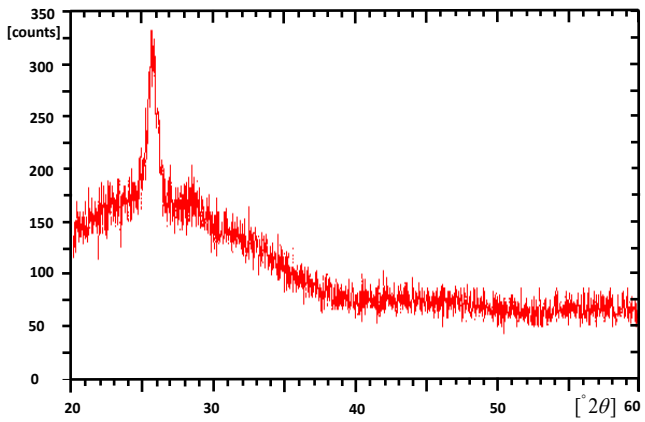

Figure 1. XRD spectrum of TiO_2 nanoscale thin films annealed at room temperature.

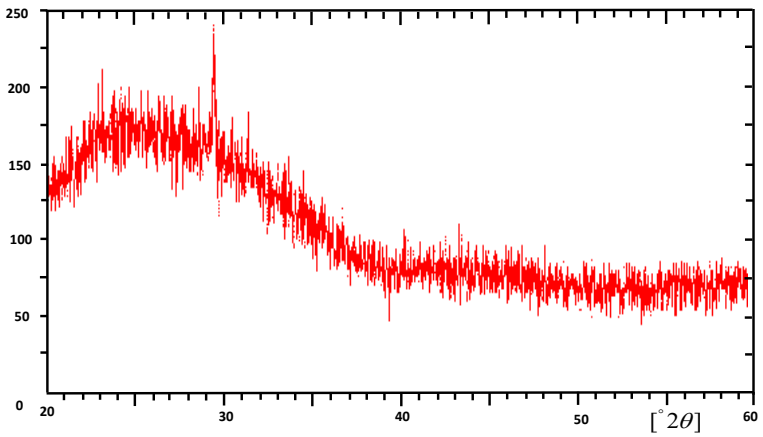

Figure 2. XRD spectrum of TiO_2 nanoscale thin films annealed at 200°C.

2θ=29.560°. However, due to the peak of the rutile crystalline phase at 2θ=27.42°, this peak to be likely that the peaks above the rutile crystalline phase, is concerned that shifted of its locations. This shift can be caused by the impurities in the sample. According to photocatalytic properties of titanium dioxide, it is expected that these defects are created due to the presence of impurities in the air. Also, the particle size of the sample is 49.931 nm. Also, in the XRD spectrum range of third sample that annealing at 400°C (Figure 3), two peaks are observed (at 2θ=25.455° and at 2θ=47.935°). According to the literature cited in [5, 6], these peaks are related to the anatase phase of titanium dioxide and the particle size are 13.326 nm and 11.21 nm, respectively. However, in the above range, one pick at 2θ=29.525° is exists, there probably can be attributed to the rutile crystalline phase that shifted of its locations. This was likely to be correct, because the transition from the anatase to rutile crystalline phase, occurs at temperatures from 350°C to 450°C and the sample was annealed in this period. The particle size of this sample is 70.26 nm.

According to the Figure 4, the annealing temperature and particle sizes is related together and for obtaining to the small particles, the annealing temperature must be below room temperature. We analyze the optical spectrum of crystalline solids and amorphous, because of it is very effective tool to understand the electronic structure. Titanium dioxide as a semiconductor has the optical band gap. The ultraviolet spectrophotometry has been used to obtain information about the band structure. Thus, we use a UV-VIS Agilent 8453 in the range of 290 to 110 angstrom wavelength of the radiation. The relationship between absorption $\alpha(\omega)$ and photon energy $\hbar\omega$ is $\alpha\hbar\omega = const(\hbar\omega - E_{opt})^n$

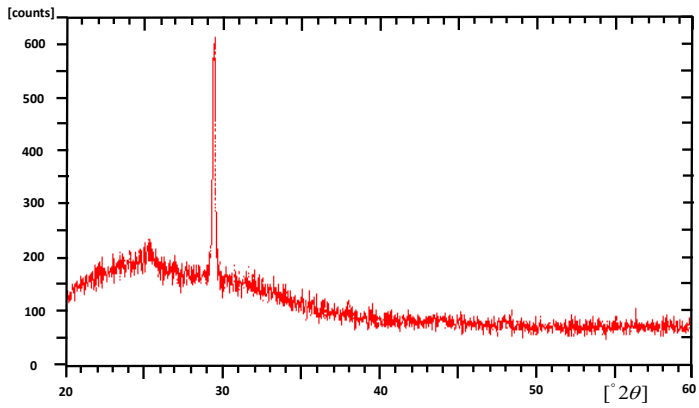

Figure 3. XRD spectrum of TiO_2 nanoscale thin films annealed at 400°C.

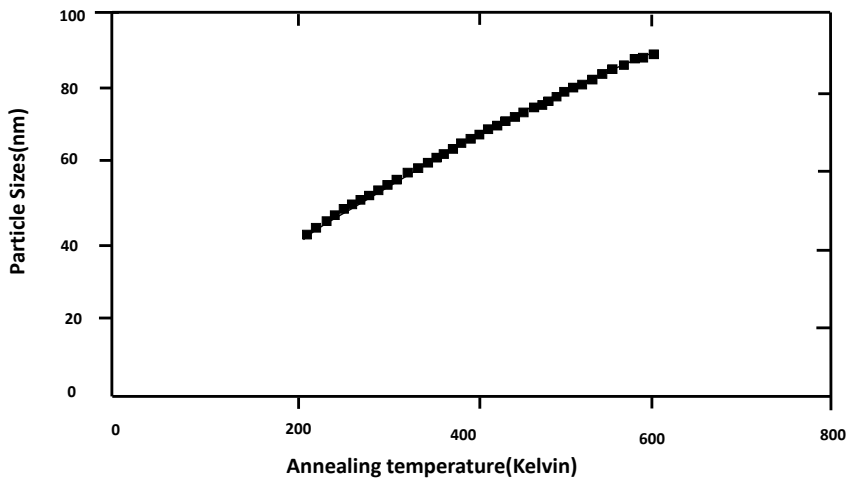

Figure 4. Versus of annealing temperature with particles sizes.

that E_{opt} the optical energy gap and n is the number that defines the optical absorption processes. To analyze the factors of n, curves of $(\alpha\hbar\omega)^{\frac{1}{n}}$ for different n versus versus energy should be drawn. Each of the curves that are more linear, n will determine appropriate. According to Figure 5, the energy gap of TiO_2 nanoparticles have been 3.65 eV. Also, for annealing temperatures of 400°C and 600°C, it can be seen that the energy gaps were obtained from these curves are 3.62 eV and 3.47eV. Curves of the energy gap in the reheating temperature for the three above samples are shown in Figures 6 and 7. With increasing the annealing temperature, the energy gap gets smaller and particle sizes become larger. Since the gel-like solution that is more rigid over time, with the passage of time, the thicker layer solution obtained. By increasing the thickness, it should be expected that the energy gap is smaller. An example of that is at the beginning of the construction of padding solution (here shown with zero time) of the energy gap is 3.75 eV.

The surface of sample was studied using an optical microscope Olympus SZX. According to the prediction of previous studies [7], fractures are clearly visible. Many fractures can be seen in the samples due to that stress during the drying time or the annealing process. Because of the difference in thermal coefficient between the substrate and thin film, according to Figure 8 can be seen that with increasing annealing temperature, the fractures between together are high. This indicates that the aggregation occurs at higher temperatures annealing, in other words, with increasing the annealing temperature, particle size gets larger. The thin films with high fractures have uneven surface, which makes for activity photocatalytic activity is an advantage.

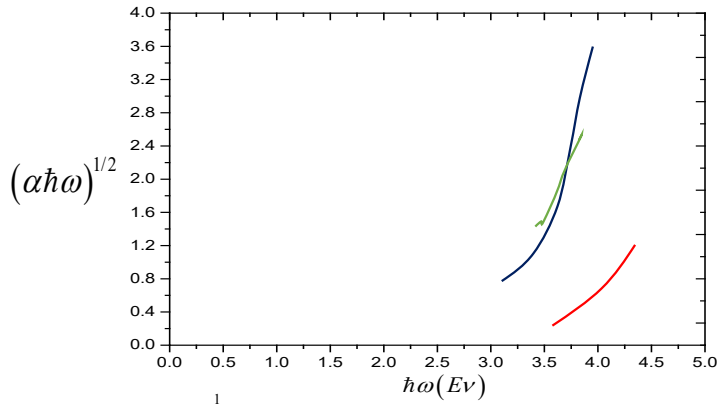

Figure 5. Diagram $\hbar\omega$ based on $(\alpha\hbar\omega)^{\frac{1}{2}}$, for sample, prepared by dip - coating after 40 minutes making the solution and at a) 200°C, b) 400°C, C) 600°C are annealed.

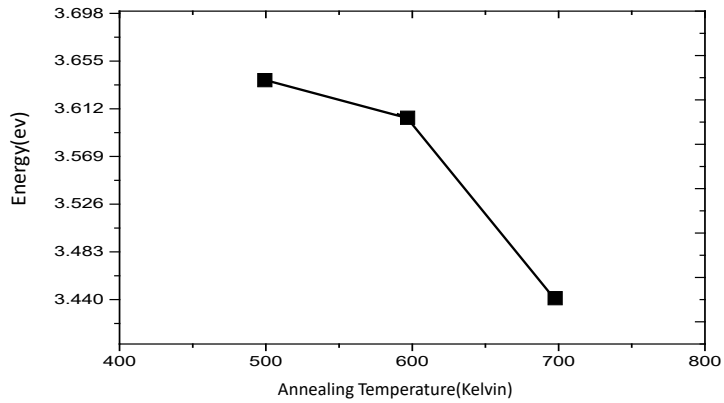

Figure 6. The plot of the energy gap in terms of reheating temperature.

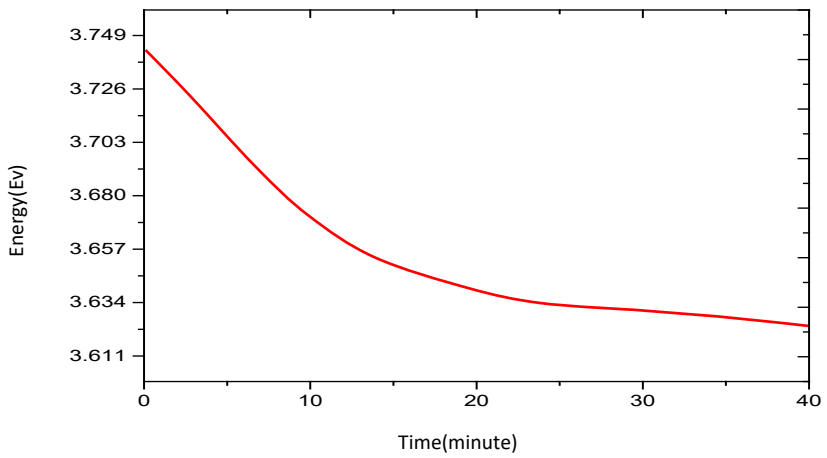

Figure 7. Versus the energy gap with time at 400°C.

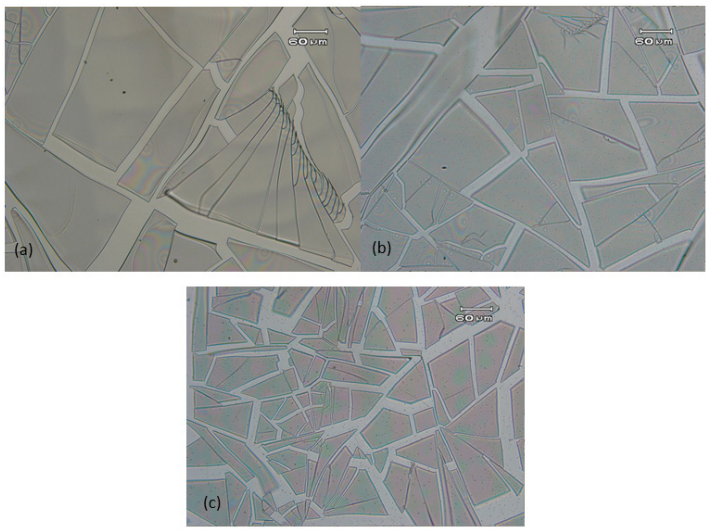

Figure 8. The samples prepared by dip-coating method and dried at a) 20˚C, b) 100˚C and c) 200˚C temperature.

CONCLUSION

According to the result of optical curves, it can be concluded that with increasing the annealing temperature and thickness, energy gap gets smaller, that this result is correct, because of with these reasons particle size gets larger and the energy gap is decrease. By controlling the annealing temperature and thickness can be achieved to the semiconductors with controlled gaps, because with increasing annealing temperature, the activation energy is reduced and helps to crystallize the crystal.

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