Influence of annealing temperature on the structure and optical properties of TiO_2 nanoparticles

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The effect of annealing temperature on structure and optical properties of TiO_2 nanoparticles prepared by thermal evaporation was investigated. Nanoparticles were annealed with O_2 for 2h at different temperatures from 300^0C-900^0C. The optical constants were deduced by using effective medium approximation (EMA). Polycrystalline nanoparticles with rutile crystal structure, as evidenced from X-ray diffraction pattern, were obtained with major refraction along (110).Refractive index decreases with decreasing annealed temperature. The direct energy band gap increases with decreasing annealed temperature and decreasing grains size.

(Received December 10, 2010; accepted February 17, 2011)

Keyword: Optical properties, TiO_2 nanoparticles, Effective medium approximation, Annealed temperature

1. Introduction

Performance of devices based on semiconductor nano materials can depend sensitively on the nanostructure morphology. The emergence of nano sciences in the recent years can be explained by the great potential of nano scaled materials. TiO_2 is an inert, non-toxic and widely used material because of its multiple applications like solar cell [1-2] and photocatalyst [3-4]. These types of applications are based on surface phenomena. It therefore is of particular interest to use nanostructures like nanoparticles or nanowires which exhibit large specific surface. Determination of the optical constants of nanostructures, refractive index and band gap energy is a topic of fundamental and technological importance. The evaluation of refractive indices of optical materials is of considerable importance for application integrated optic devices [5].

The aim of this study is to investigate the effect of annealing on structure and optical properties of thermal evaporated TiO_2 nanoparticles. One of the successful models for electronic structure of nanostructures is effective medium approximation (EMA). This model provides a better description of the energy-level structure of nanoparticles and is able to incorporate the interconnectivity of the systems. In this paper we apply EMA analysis to calculate the optical properties of nanoparticles of TiO_2 by a written FORTRAN program.

2. Experimental details

2.1 Samples preparation and annealing process

Thermal evaporation technique has been used to obtain TiO_2 nanoparticles. Prior to deposition, the Si substrates were sequentially cleaned for 10 min in ultrasonic bout with acetone and ethanol. Finally, they were rinsed with distilled water and dried. Then substrates were coated with thin layer of gold (5 nm) before introducing in to vacuum system. The distance between Ti source and substrate was 8.5 cm. The nanoparticles were deposited by evaporation rate of 2 A^0/s and pressure was 10^{-5} mbar.

After deposition, samples were annealed at different temperature for 2h with O_2 gas. The samples were annealed at the temperature from 300^0C to 900^0C by a step of 10 $^0C/\min$ and were cooled by a rate of 5 $^0C/\min$.

2.2 Calculation method of optical constants

When size particles are much smaller than the wavelength of light, it can be modeled by effective medium theories (EMA) [6-7]. We used the Bruggman method in our EMA analyses.The Bruggman method is given by [6]:

$$f\left(\frac{\varepsilon_p-\varepsilon}{\varepsilon_p+k\varepsilon}\right)+(1-f)\left(\frac{\varepsilon_m-\varepsilon}{\varepsilon_m+k\varepsilon}\right)=0 \qquad (1)$$

where f is the particles volume fraction, ε is the composite permittivity, ε_m is the matrix permittivity, ε_p is the particles permittivity, and k is a geometric factor. k is 1 for an array of cylinders with its axis collinear with the incident radiation and 2 for spherical nanoparticles.

In equation (1), if we take ε_m equal to unity for air, and k=2 for spherical nanoparticles, then we have:

$$f\left(\frac{\varepsilon_p-\varepsilon}{\varepsilon_p+2\varepsilon}\right)+(1-f)\left(\frac{1-\varepsilon}{1+2\varepsilon}\right)=0 \qquad (2)$$

where ε_p is the permittivity TiO_2 bulk and ε is TiO_2/air composite permittivity. By using equation 2, the real part of permittivity, ε_1, and imaginary part of permittivity , ε_2 , are obtained.

The real and imaginary part of refractive index can be taken in terms of ε :

$$\varepsilon_1 = n^2 - k^2 \quad , \quad \varepsilon_2 = 2nk \tag{3}$$

The absorption coefficient, α , is defined as:

$$\alpha = \frac{2E}{\hbar c} k \tag{4}$$

Consequently, the optical parameters of a material are determined from EMA analyses.

3. Results and discussion

3.1 Structural information

X-Ray diffraction patterns (XRD) was used to investigate the structure of TiO_2 nanoparticles at different annealed temperatures. Fig 1 shows the XRD patterns of TiO_2 nanoparticles at different annealed temperatures. It can be seen that for the temperature 300^0c the film is still amorphous phase and there is no any crystalline phase. As the annealing temperature is increased up to 700^0c or above a clear signal of diffraction peaks start to appear, the intensity of these diffraction peaks increases with an increase of annealed temperature, these results are matching with that of the reported results by others [8]. X-Ray diffraction results show that the TiO_2 nanoparticles are mainly composed of rutile phase (JCPDS: 73-1765), where reflect (110) is the most predominant [9]. The unit cell constants of TiO_2 rutile phase are a=b=4.56Å, c=2.98Å

Fig 2 shows typical scanning electron microscopy (SEM) images of TiO_2 nanoparticles with different annealed temperatures. The average of grain size is 51, 58, 77 nm in Fig 2a, 2b, 2c, respectively. It can be seen that with increasing annealing temperature the size of nanoparticles increases, which is in agreement with the result obtained by XRD. XRD patterns show with increasing annealed temperature, the intensity of diffraction peaks increase and full width at half maximum (FWMH) decrease. With decreasing FWMH due to Debye Scherrer's formula [10], the size of nanoparticles increases.

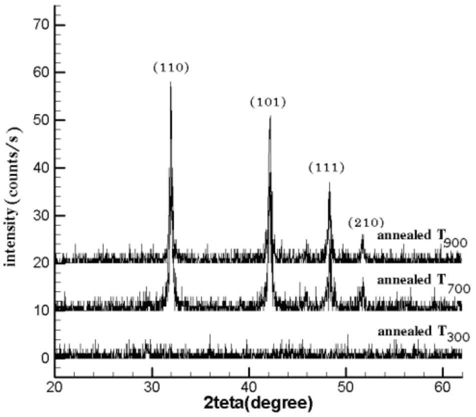

Fig. 1. X-ray diffraction pattern of TiO_2 nanoparticles at different annealing temperatures

3.2 Optical properties

Optical properties of samples were calculated by EMA. It estimated from SEM images that particles volume fraction in different annealed temperatures 300^0, 700^0 and 900^0 is 13%, 39% and 51% respectively. In EMA method, it needs to know the real and imaginary of bulk TiO_2 dielectric constant. Complex dielectric constant of $TiO_{2/}$/air composite was calculated with equation 2, by using bulk TiO_2 optical constant [11] and given f_v from software measurement. Then index refraction and absorption coefficient were calculated by equations 3 and 4. The results of calculation will be explained in following:

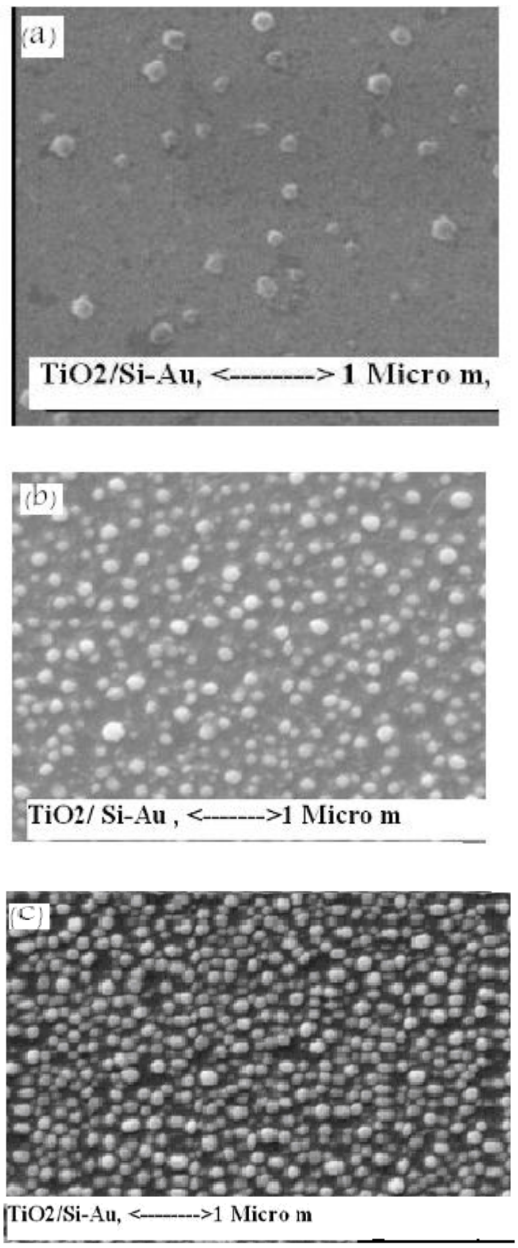

Fig. 2. Top view SEM images of TiO_2 nanoparticles at different annealing temperature a) 300^0C; b) 700^0C; c) 900^0C.

From Fig 3, we see that the refractive index decreases with decreasing annealed temperature. This may be attributed to the variation of the packing density [12]. The packing density of TiO_2 nanoparticles decreases with decreasing annealed temperature. The decreasing of refractive index and packing density in TiO_2 nanoparticles with different annealing temperature can be ascribed to the porous structure as shown in SEM images.

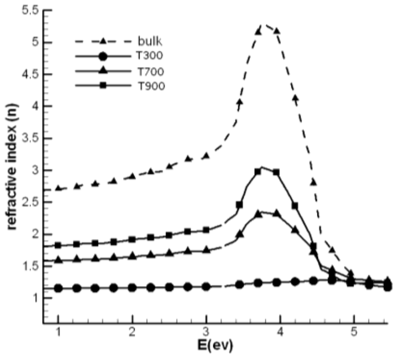

Fig. 3. Refractive index of TiO_2 nanoparticles at different annealing temperatures.

The photon energy dependent complex dielectric constants are shown in Fig 4 for TiO_2 nanopaericles with different annealing temperatures. It can be seen that bout the real of dielectric constants and the imaginary of dielectric constant, decrease with decreasing annealing temperature. We see that with decreasing annealing temperature and increasing porosity, the peak of energy 4eV decreases and confirm TiO_2 nanostructureals properties.

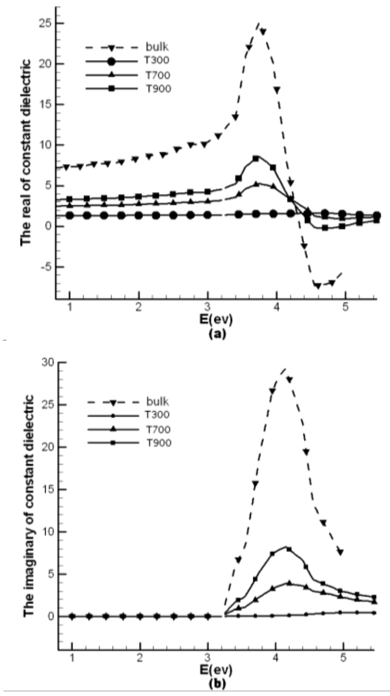

Fig. 4. Dielectric constants of TiO_2 nanoparticles at different annealing temperatures. (a) The real part of dielectric constants; (b) the imaginary part of dielectric constants

Fig. 5 shows absorption spectrum TiO_2 nanoparticles. For semiconductor materials, the quantum confinement effect is expected if the semiconductor dimension becomes smaller than bohr radius of excition, and the absorption edge will be shifted to a higher energy [13]. With increasing annealed temperature, due to the improved grain size of TiO_2 nanoparticles, the absorption edge appears red-shift to some extent.

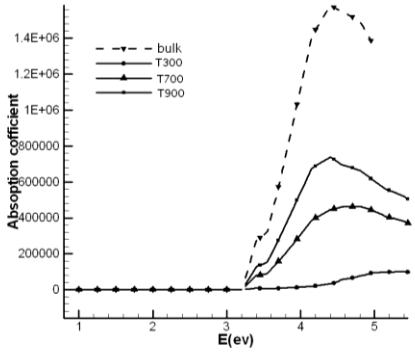

Fig. 5. Absorption spectrum of TiO_2 nanoparticles for different annealing temperatures.

The optical band gap energy can be estimated by using the following equation for a semiconductor:

$$(\alpha h\upsilon)^{n/2} = k(h\upsilon - Eg)$$

where α is the absorption coefficient, k is a constant, Eg is the band gap, and n is equal to 2 for an direct transition. The band gap can be estimated from a plot of $(\alpha h\upsilon)^2$ versus photon energy $(h\upsilon)$. The intercept of the tangent to the plot will give a good approximation of the band gap energy for direct bang gap materials (shown in Fig 6). It is easy to observe that the direct energy bang gap increases from 3.15 to 3.20 when annealed temperature decreases from 900^0C-700^0C. It can be ascribed that with decreasing annealed temperature, grains size decreases and this confirms increasing energy band gap. These values are well matched with that of band gap determined by others [14]. The band gap of the TiO_2 nanoparticles is slightly larger than the value of 3.05 ev for the bulk TiO_2 due to the contribution of quantum size effect of the present TiO_2 [15].

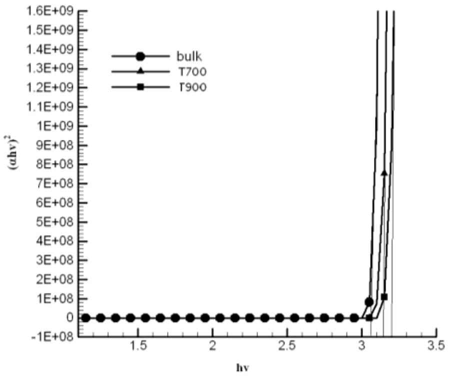

Fig. 6. Dependence of $(\alpha h\upsilon)^2$ on the photon energy $(h\upsilon)$ for TiO_2 nanoparticles at different annealing temperatures

4. Conclusions

We study the effect of annealing temperature on structure and optical properties of TiO_2 nanoparticles. X-Ray diffraction patterns showed that for the annealing temperature 300 ^oC, nanoparticles are amorphous and with increasing annealing temperature at 700 ^oC appears rutile phase. Optical properties were calculated by EMA. Our results show that the refractive index decreases with decreasing annealing temperature. Also the real and imaginary parts of dielectric constants decrease with decreasing annealing temperature.

Absorption edge was shifted to a smaller energy, due to the improved grain size of nanoparticles .A direct band gap energy was estimated from a plot of $(\alpha h\upsilon)^2$ versus photon energy $(h\upsilon)$. We observed that the direct energy band gap increases from 3.15 to 3.20 eV with reduction annealing temperature nanoparticles.

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