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The effect of system pressure on microstrain and photoluminescence properties of TiO_2 nanowires

Scientific research paper

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ABSTRACT

TiO_2 nanowires were prepared by a thermal evaporation method at different pressures. The effects of air pressure on morphology, microstructure, and photoluminescence properties were investigated by SEM, XRD, and spectrophotometer. XRD Analysis indicated the presence of rutile phases in samples. The Williamson-Hall method was used for studying micro strain and crystallite size. The results showed that decreasing air pressure leads to increasing micro strain due to increasing tension in the grain boundary with increasing oxygen vacancies as point defects. TiO_2 nanowires prepared at lower pressure indicated weaker intensities in the PL spectrum due to increasing nonradiative centers obtained by oxygen vacancies that as an extinguisher the luminescence may trap photogenerated electron-hole.

1 Introduction

The difference in structure of nanomaterial and quantum size effects is due to changing the synthesis conditions that imply new physical and chemical properties. Micro strain is one of the important factors in identifying the physical properties of nanostructures [1]. Micro strain expands the XRD lines. The additional volume of grain boundaries and dislocations are the basic source of micro strain [2]. The production of optical and electrical devices with high quality and lifetime requires films with perfect structure. Strains and stresses on thin films deposited on substrate change the mechanical properties, electronic structure, chemical stability, etc. [3]. Thus, the information about micro strains can improve structural properties.

A broad field of research has been carried out on the correlation between Photoluminescence and mechanical parameters. The results of researches show dependence of Pl emission on parameters such as: micro strain, defects, oxygen pressure, and the crystallite size. Nevertheless; studies in this area are in progress [4-5].

Semiconducting in one-dimension has attracted attention due to unique physical properties. Among them, the TiO_2 with a wide band gap (3.2 eV for anatase and 3.0 eV for rutile) is a suitable candidate due to chemical stability, non-toxic, and low construction cost [6,7], gas sensors [8], optical devices [9,10], photocatalysis [11-13], and solar cells [14]. Different methods such as sol-gel, chemical vapor deposition, hydrothermal, and thermal evaporation have been employed to prepare TiO_2 nanostructure [15–21].

TiO_2 nanostructures deposited on different substrates create different stress effects. In the study of Shibata, the effect of stress on Tio_2 thin films with different substrates such as mica and glass were investigated [22]. In 2015 Rahmani et al. [23] studied the strain phenomena in Tio_2 nanostructures on porous silicon substrates. In 2022 kumavat et al. investigated the micro strain and photoluminescence intensity on Eu

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doped ZnO thin films and observed that the pl intensity and micro strain reduce with Eu doping [24]. Also, in 2013 Dariani and Nafari [25] studied the microstructure properties of the prepared TiO_2 nanowires by thermal evaporation under Ar different flows. But they reported no correlation between PL emission and micro strain. In our previous work in 2020 the microstructure properties of TiO_2 nanowires on Ti substrate were studied by the hydrothermal method [26]. Due to the importance of the dependence of Pl emission and micro strain, in this project, we have studied the effects of various air pressures on the micro strain and photoluminescence properties of TiO_2 nanowires. The TiO_2 nanowires were produced in two steps by a thermal evaporation method. The effects of various air pressures on the microstructural and photoluminescence properties were studied.

2 Experiment

2.1 Fabrication TiO_2 nanowires

By the thermal evaporation method, TiO_2 nanowires were prepared on a silicon substrate. At first, using the evaporation technique, a Ti layer (50 nm) was deposited on the substrate. The pressure and evaporation rates were 10^{-5} mbar and 1.5 Å/s, respectively. Then by a sputtering method, an Au thin film with a thickness of 3 nm was deposited as a catalyst on the Ti layer. After this step, in a quartz boat, a mixture of Ti and graphite powder (ratio of 1:1) was placed. The boat was located at the center of a horizontal tube furnace with a temperature of 1050 °C, and the Si substrate was placed in the low-temperature zone (800–850 °C). The sample at 1050 °C temperature was held for 1 h in the 1000 mbar pressure. Then, the sample was cooled down to reach room temperature. In another experiment without changing the parameters of experiment; the air pressure inside the furnace reached to 60 mbar and 30 mbar by a vacuum pump.

2.2 Characterization

The morphology and structure of the samples were characterized by scanning electron microscopy, with a voltage of 17 KV and a working distance of 15 mm (SEM: XL130, Philips) and X-ray diffraction (XRD: JEOL JDX- 8030), respectively. The room temperature photoluminescence (PL) spectra of the samples were measured with a Cary Eclipse spectrophotometer.

3 Results

3.1 morphology properties

Figure 1 indicates the SEM images of TiO_2 nanowires at air different pressures. Figure 1a shows the nanowires with a diameter of around 60 to 120 nm. With decreasing air pressure to 60 mbar, the diameter of the nanowires became smaller (60 to 100 nm) (Fig. 1b), and at pressure equal to 30 mbar, the diameter of nanowires reached 40 to 100 nm (Fig. 1c). For explaining the effect of various air pressures on morphology, the growth mechanism of the prepared TiO_2 nanowires by the thermal evaporation method was considered. Since Au was used as a catalyst, therefor TiO_2 nanowires are grown by the vapor-liquid- solid (VLS) mechanism. According to the VLS mechanism at evaluated temperature, the Ti middle layer is oxidized to TiO_2 by air oxygen. Ti vapour (included source Ti and middle layer Ti) was diffused into the Au catalyst and then a liquid alloy is formed as a nucleation site to grow TiO_2 nanowires. Figure 2 shows the growth process of TiO_2 nanowires schematically. Oxygen plays a basic role in the growth of TiO_2 nanowires. According to the SEM images with reducing air pressure and oxygen, nanowires became thinner. In higher air pressures, increasing oxygen, reaction of the vapor of Ti and O_2 before being absorbed on alloy droplet takes place. Therefore, an increase of oxygen causes a reduction in the growth of TiO_2 nanowires. Also, at lower pressures, the mean free path of particles increases thus, the transfer of gas to the deposition surface is easier.

Table1. The constants of lattice and FWMH of TiO_2 nanowires at different pressures.

pressure(mbar)	unit cell constants		FWMH (degree)
	a(Å)	C(Å)	
1000	4.589	2.961	0.16
60	4.595	2.961	0.19
30	4.599	2.961	0.21

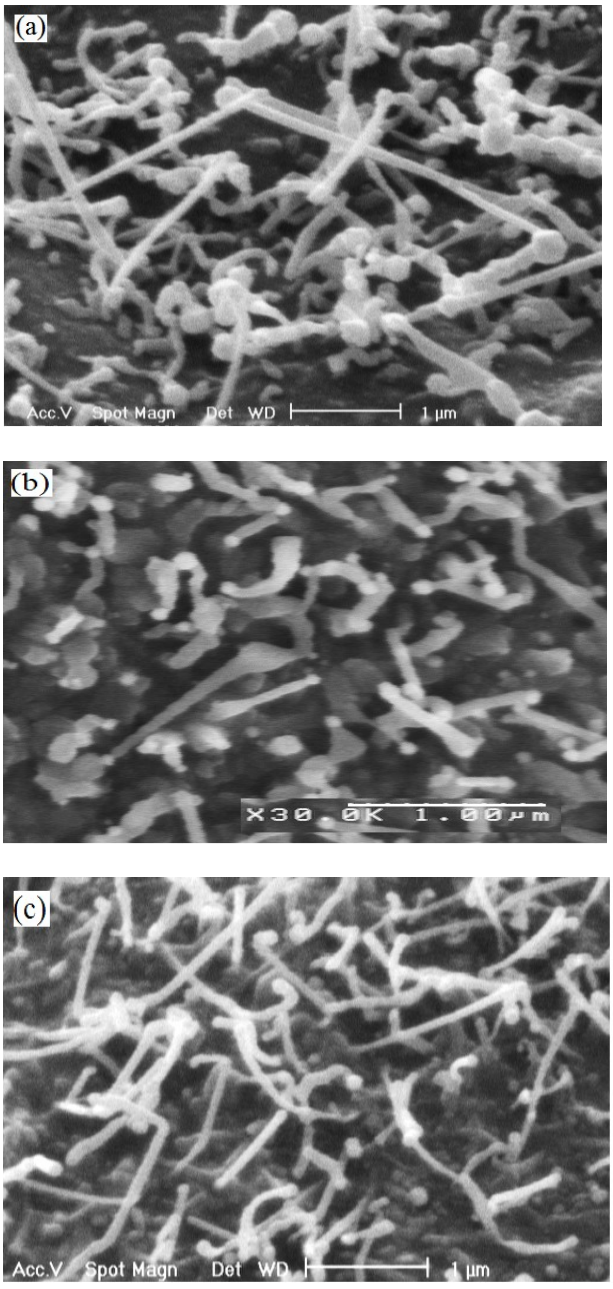

Figure 1. SEM images of TiO_2 nanowires (a) 1000 mbar pressure, (b) 60 mbar pressure, (c) 30 mbar pressure. The Scale bar is 1µm.

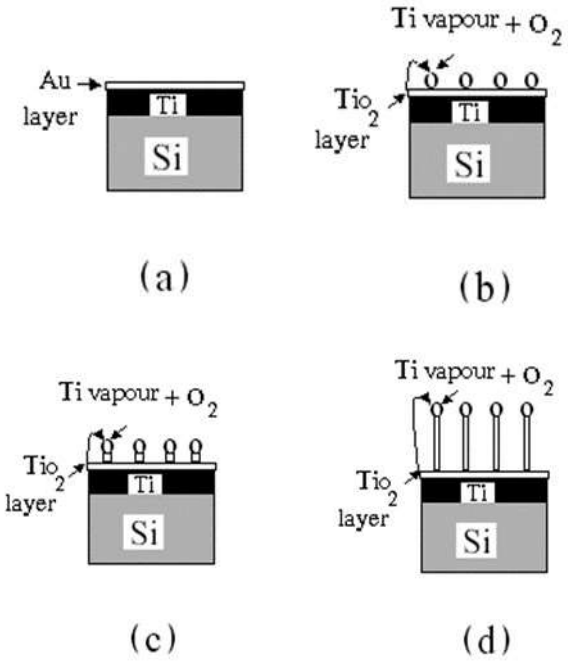

Figure 2. The schematic illustration of the growth process of TiO_2. nanowires.

3.2 microstructure properties

3.2.1 XRD patterns

Figure 3 shows the XRD patterns of TiO_2 nanowires deposited on Si substrate at various air pressures. All the samples show a rutile phase with predominant reflection (101). The constants of the lattice of each sample and the fullwidth at half-maximum (FWMH) were calculated and shown in Table 1, which are in agreement with the value database of (JCPDS #73-1765). Our results showed that with decreasing pressure, the FWMH of (101) peak increases. Also, the intensity of the peak becomes lower. Commonly, in the crystalline with high quality, the FWHM is smaller. With the enhancement of oxygen and reduction of the defects such as oxygen vacancies and titanium interstitials, stoichiometric structures appear. Increasing the pressure from 30 mbar to 1000 mbar creates a high oxygen environment therefore more crystallinity is obtained.

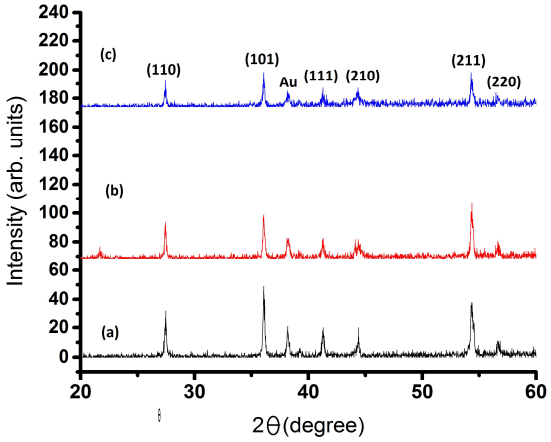

Figure 3. XRD patterns of TiO_2 nanowires (a) 1000 mbar pressure, (b) 60 mbar pressure, (c) 30 mbar pressure.

The crystallite size of the nanowires was obtained by the Scherrer equation [27]: (D=kλ/(β cos θ)). Where K is the shape factor, λ is the X-ray wavelength, θ is the Bragg angle and D is the crystallite size. the obtained results are shown in Table 2. It was found with decreasing air pressure the crystallite size decreases.

3.2.2 The Williamson -Hall method and micro strain

In the W-H method, the effect of crystal size and micro strains is considered in line with the broadening of XRD. Micro strains correspond to atom displacements to their position in crystals [27]. With separating micro strain and the crystalline size contributions, the sum line breadth is $\beta = \beta_D + \beta_t$. Where, β_D is the breadth related to the crystalline size and β_t is the breadth related to micro strain. Therefore the W-H equation is obtained as [28]:

$$\beta = \beta_D + \beta_t = \frac{\lambda}{\beta cos\theta} + 4\varepsilon sin\theta \,. \qquad (1)$$

Micro strain can be measured from the slope of the curve $\beta cos\theta$ vs. $4sin\theta$ and the crystallite size can be calculated from the value of the vertical axis that is cut off by linear fit.

Figure 4 shows the W-H curve of TiO_2 nanowires at various air pressures. It can be seen a positive strain for TiO_2 nanowires at various air pressures which indicates the tensile stress in lattice.

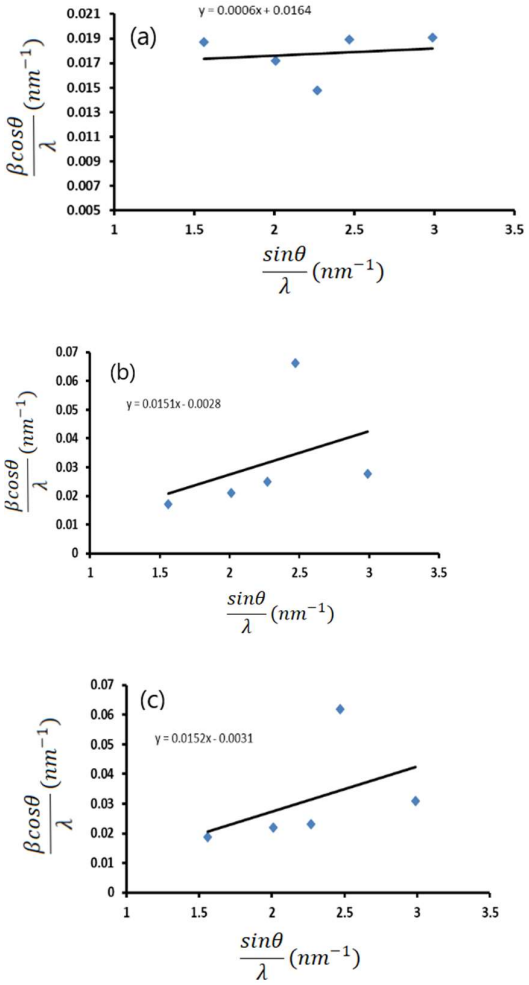

Figure 4. Williamson -Hall curve of TiO_2 nanowires (a) 1000 mbar pressure, (b) 60 mbar pressure, (c) 30 mbar pressure.

The obtained value for crystallite size and micro strain of TiO_2 nanowires are shown in Table 2. According to Table 2, A decreasing air pressure leads to an increasing micro strain. The micro strain is proportional to the concentration of defects [2]. With decreasing pressure, oxygen vacancies as point defects can be increased. Thus, increasing the content of oxygen vacancies leads to an increasing tension in the grain boundary and micro strain. Another hypothesis that may confirm increasing micro strain with decreasing air pressure is the enhancement of elastic energy. All of the evaporated particles have a certain kinetic energy. A decreasing air pressure causes reduced collision between evaporated particles, therefore it can increase their velocity and energies and also micro strain.

Table 2. Micro strain and crystallite size of TiO_2 nanowires by the Scherrer equation and W-H methods.

pressure(mbar)	W-H methods		Size using Scherrer equation(nm)
	Size(nm)	Micro strain	
1000	60.97	0.0006	56.60
60	35.71	0.0151	47.53
30	32.25	0.0152	44.29

3.2.3 Volume strain

Change of volume due to strain is [29]:

$$\theta = \frac{\Delta V}{V} = 2\varepsilon_a + \varepsilon_c \,, \qquad (2)$$

where ε_a and ε_c are the horizontal and vertical strains, respectively. ε_a and ε_c can be calculated from [24]:

$$\varepsilon_a = (a - a_0)/a_o \;\; and \; \varepsilon_c = (c - c_0)/c_o \quad , \quad (3)$$

where a and c are the strained lattice constant of TiO_2 nanowires while a_0=4.587 Å and c_0 =2.954 Å are reference values for TiO_2. Table 3 shows horizontal and vertical strain and volume strain for TiO_2 nanowires at different pressures. It can be seen that the volume strain is positive for all of the samples which indicates the TiO_2 nanowires have been exposed to tensile strain duo to tension in the grain boundary with increasing oxygen vacancies as point defects. Comparing the micro strain obtained from the W-H curve and the volume strain calculated from the lattice constant showed that the micro strain and volume strain are same order and positive.

Table 3. Horizontal and vertical strain and volume strain for TiO_2 nanowires at different pressures.

pressure(mbar)	ε_a	ε_c	θ(%)
1000	0.000436	0.00236	0.32
60	0.00174	0.00236	0.58
30	0.00261	0.00236	0.75

3.3 Photoluminescence properties

Figure 5. shows the room-temperature photoluminescence of the spectrum of TiO_2 nanowires at various air pressures. The excitation wavelength was 370 nm. According to Fig. 5 there is a strong peak at 435 nm and three weak peaks at 486, 506, and 541 nm. The major peak is due to free exactions emission and weaker peaks can be ascribed to the vacancies of oxygen. [30,31]

Comparing the PL spectra indicated that the relative intensity of all of the peaks has been decreased by changing the pressure from 1000 mbar to 30 mbar. The photoluminescence emission is proportional to both the stoichiometry and the crystallite of the nanostructure [32]. The intensity of emission is estimated using irradiative and non-radiative transmission by $\eta = I_R / I_R + I_{NR}$ [33]. Where η is luminescence efficiency, I_R and I_{NR} are irradiative and non-radiative transmission, respectively. The crystal imperfections, such as defects, grain boundaries, and dislocations cause the nonradiative transfer. With reducing air pressures and increasing oxygen vacancies, non-radiative centers increase that as an extinguisher the luminescence may trap photogenerated electron-hole [34].

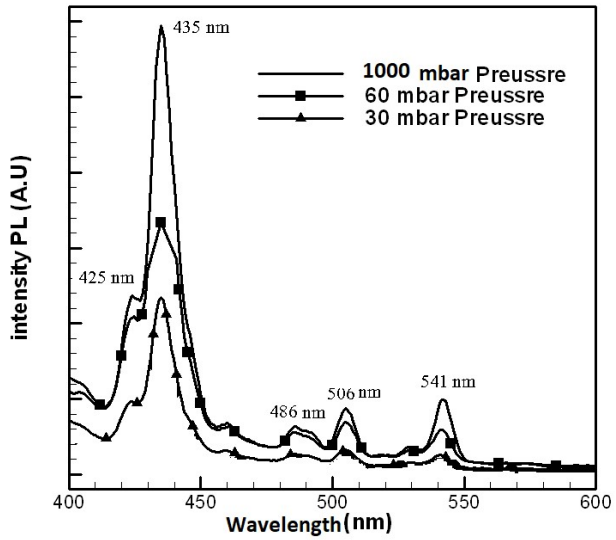

Figure 5. photoluminescence spectrum of TiO_2 nanowires at different system pressures.

4 Conclusion

TiO_2 nanowires are fabricated by an evaporation method at different pressures. SEM images showed with decreasing the air pressure, the nanowires become thinner. XRD patterns indicated the rutile phases in the samples. Our results showed that as the air pressure decreases, FWMH of (101) peak increases which leads to weaker crystalline. Also obtained micro strain from the W-H method increases with reducing air pressure. With decreasing pressure, oxygen vacancies as point defects can be increased. Thus, increasing the content of oxygen vacancies leads to an increasing tension in the grain boundary and micro strain due to an increasing tension in the grain boundary. Comparing PL spectra indicated that the relative intensity of all of the peaks has been decreased by changing the pressure from 1000 mbar to 30 mbar. Due to increasing non-radiative centers that as an extinguisher, the luminescence may trap photogenerated electron-hole.

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