



Regular Article

Preparation and characterization of single crystalline anatase TiO₂ epitaxial films on LaAlO₃(001) substrates by metal organic chemical vapor deposition



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ARTICLE INFO

Article history:

Received 16 April 2016

Received in revised form 26 June 2016

Accepted 26 June 2016

Available online 8 July 2016

Keywords:

TiO₂ films

MOCVD

TDMAT

LaAlO₃

ABSTRACT

Anatase phase TiO₂ (a-TiO₂) films have been fabricated on LaAlO₃(001) substrates at the substrate temperatures of 500 to 650 °C by the metal organic chemical vapor deposition (MOCVD) method using tetrakis-dimethylamino titanium (TDMAT) as the organometallic (OM) source. The structural studies revealed that the TiO₂ film prepared at 600 °C had the best single crystalline quality with no twins. The out-of-plane and in-plane epitaxial relationships of the films were a-TiO₂(004)||LaAlO₃(001) and TiO₂[100]||LaAlO₃[100], respectively. The optical band gap of the films ranged from 3.30 to 3.37 eV. The morphology and composition of the TiO₂ films have also been studied in detail.

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1. Introduction

Titanium dioxide (TiO₂) have attracted much attention for the past two decades from viewpoints of applications and basic science study as a wide band gap oxide material. TiO₂ has many excellent properties such as a large refractive index, a high dielectric constant, a high photochemical activity [1] and stable physicochemical properties, which are widely used in the fields of photocatalysts [2], transparent conducting oxides (TCOs) [3], photovoltaic cells [4], gas sensors [5] and field effect transistors (FETs) [6]. The powder, thin film and bulk are three common forms of TiO₂, among which the form of nanoparticles has the highest surface area to volume ratio. The photocatalytic reactions, such as hydrogen generation, organic substance decomposition and photoinduced hydrophilicity occur only on the contact surface. Therefore, a thin solid film is also the suitable form for a photocatalyst [7].

Rutile (tetragonal), anatase (tetragonal) and brookite (orthorhombic) are the three different crystallographic structures of TiO₂, among which the rutile with the space group of P4₂/mnm [8] is most stable and has been widely studied. As a metastable phase, the anatase with the space group of I4₁/amd [9] can be transformed into rutile at high temperatures. The anatase phase TiO₂ has good catalytic activity and large specific surface area which is caused by its lower specific density [10], which has been widely studied in degradation of organic pollutants and dye-sensitized solar cells (DSSCs) [11] since the photocatalysis of water found by Fujishima and Honda in 1972 [12].

The lattice mismatch between the LaAlO₃[001] and a-TiO₂[001] direction is about 0.94% and the thermal expansion coefficients of those two are very close, indicating the LaAlO₃ is a suitable substrate to grow a-TiO₂ film. Some methods have been used for the preparation of TiO₂ films on LaAlO₃. The TiO₂ films with twin domain were obtained by A. Lotnyk using electron beam evaporation at substrate temperatures ranging from 500 to 1000 °C [13]. The TiO₂ films prepared by S. Kitazawa using pulsed laser deposition (PLD) were polycrystals [7]. The TiO₂ films with many crystal defects were prepared by M. Zhu using laser ablation, for which the optical and compositional properties were not studied [14]. But the a-TiO₂ film deposited on LaAlO₃ by MOCVD is seldom reported as far as we know. Unlike other methods, the TiO₂ films prepared by means of MOCVD normally will have good single crystal properties with seldom defects and no twins. In addition, MOCVD has excellent characteristics of easy commercial production and good control of the growth parameters. In this paper, high quality a-TiO₂ single crystalline films without domain structure have been successfully deposited on LaAlO₃ substrates by MOCVD. The crystalline structural, surface morphology, compositional and optical properties of the obtained films have been discussed in detail.

2. Experimental

TiO₂ films were prepared on LaAlO₃(001) substrates (double-face polished) by a high vacuum MOCVD system at different temperatures of 500–650 °C. The tetrakis-dimethylamino titanium (TDMAT) was used as the organometallic (OM) precursor and was stored in a stainless steel bubbler maintained at 21.33 °C. The TDMAT and high purity

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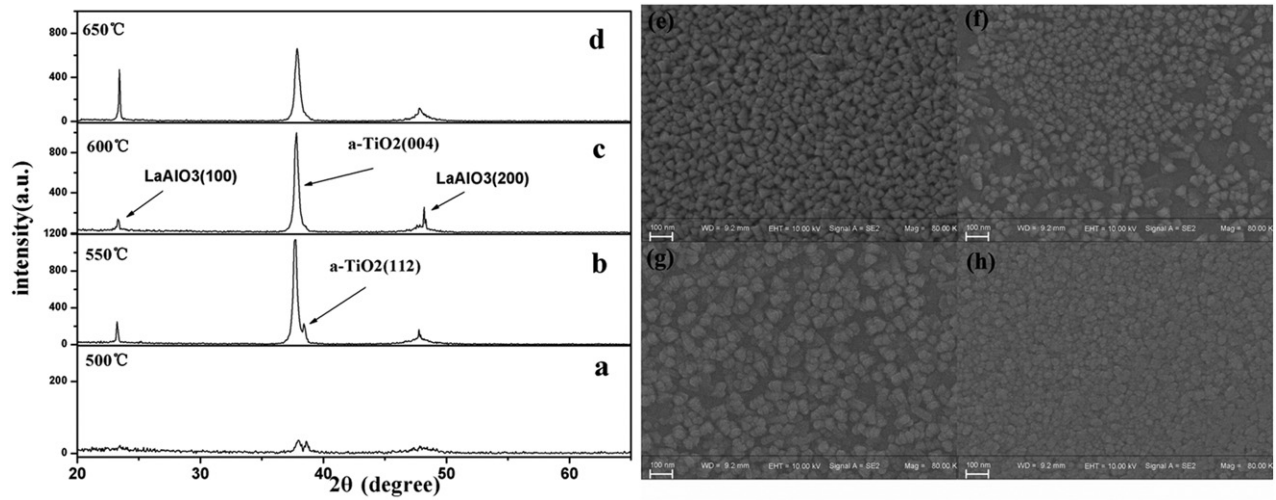


Fig. 1. XRD spectra of the TiO_2 samples deposited at different substrate temperatures: (a) 500, (b) 550, (c) 600 and (d) 650 °C. Plan view SEM micrographs of the TiO_2 films prepared at (e) 500, (f) 550, (g) 600 and (h) 650 °C.

oxygen (5 N) used as the oxidant were delivered into the reactor chamber by ultrahigh purity N_2 as the carrier gas in two separate lines. Before taken into the reactor chamber, the substrates were ultrasonically cleaned with ethanol and de-ionized water and then dried with high purity nitrogen. The flow rates of TDMAT and oxygen were 23 and 70 sccm, respectively. The pressure of the reactor chamber was kept at 10 Torr.

Crystalline structure and epitaxial relationship of the obtained films were examined by the Rigaku and Philips X'Pert PRO X-ray

diffractometers. The surface morphology and thickness of the films were researched using a JSM-6700F scanning electron microscope (SEM). The atomic force microscope (AFM) was employed to study the roughness of the samples with a Dimension Icon scanning probe microscope. Chemical composition of the film prepared at 600 °C was examined by the X-ray photoelectron spectroscopy (XPS) using an ESCALAB MK II multi-technique photoelectron spectrometer. The high-resolution transmission electron microscopy (HRTEM) and selected area electron diffraction (SAED) were used to further study the

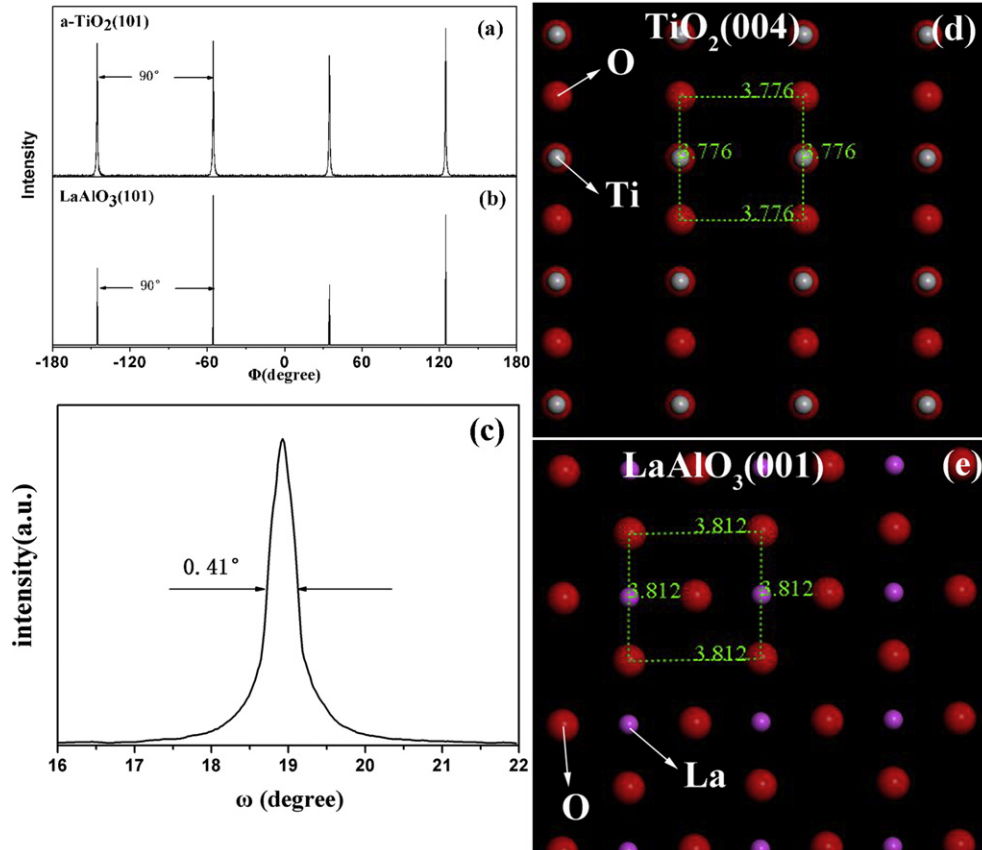


Fig. 2. XRD patterns of off-specular Φ scan for (a) $\text{a-TiO}_2\{101\}$ planes and (b) $\text{LaAlO}_3\{101\}$ planes. (c) ω -rocking curve of $\text{a-TiO}_2(004)$ reflection for the film. (d) and (e) the schematic diagram of geometrical epitaxial relationship between the $\text{TiO}_2(004)$ and $\text{LaAlO}_3(001)$ planes.

microstructure and epitaxial relationship of the sample which is prepared by gluing two pieces together with the thin films facing each other with a Tecnai F30 transmission electron microscope operated at 300 kV on the cross-section of the sample. The optical transmittance spectra were measured by a TU-1901 double-beam UV–vis–NIR spectrophotometer.

3. Results and discussion

Fig. 1 shows the XRD θ - 2θ patterns of the TiO₂ films deposited on LaAlO₃(001) substrates at temperatures of (a) 500, (b) 550, (c) 600 and (d) 650 °C, respectively. In Fig. 1, the substrate diffraction peaks can be identified as LaAlO₃(100) and (200) located at about 23.45° and 47.98° (JCPDS No.85-0848), respectively. Only two weak peak can be seen for the sample prepared at 500 °C from Fig. 1(a), which are identified as a-TiO₂(112) and (004) (JCPDS No.21-1272), indicating poor crystalline quality. In Fig. 1(b), the peak of a-TiO₂(004) becomes sharper with smaller full width at half maximum (FWHM) while the peak of a-TiO₂(112) is small, indicating the preferred orientation is a-TiO₂(004). In Fig. 1(c) and (d), only one sharp peak of a-TiO₂(004) located about 37.8° is observed besides the substrate peaks, which means the obtained films are a-TiO₂ with a single orientation along [001]. As the substrate temperature increases from 600 °C to 650 °C, the FWHM of the film increases from 0.446° to 0.625°, which demonstrates degeneration in the film crystallinity. The XRD θ - 2θ analyses demonstrate that the crystal quality of TiO₂ films deposited by MOCVD is obviously influenced by

the substrate temperature and the sample deposited at 600 °C has the best crystallinity with an out-of-plane growth relationship of a-TiO₂(004)||LaAlO₃(001). For the a-TiO₂ film deposited at 600 °C, the lattice parameter *c* calculated from the XRD result is about 0.944 nm, which is close to the standard value 0.95 nm.

Fig. 1(e), (f), (g) and (h) show the plan view SEM images of TiO₂ films deposited at 500, 550, 600 and 650 °C, respectively. The thicknesses of films deposited at 500, 550, 600 and 650 °C were measured as 91, 84, 79 and 60 nm by cross-sectional SEM. In Fig. 1(e), small and compact grains are observed, which is in agreement with the polycrystalline structure of film prepared at 500 °C. The well-defined loose grains are observed as the substrate temperature increases to 550 °C as shown in Fig. 1(f). In Fig. 1(g), well-defined grains become more uniform and larger, indicating an improvement in the film crystallinity. For the film deposited at 650 °C as shown in Fig. 1(h), smaller grain with irregular shape and fuzzy boundary is observed, indicating degradation in the film crystallinity. The RMS surface roughness of films deposited at 500, 550, 600 and 650 °C were 2.94, 3.90, 4.66 and 2.59 nm as obtained by the AFM. The SEM results demonstrate obviously that the substrate temperature has obvious influence on the film crystallinity and the film deposited at 600 °C has the best crystallization, which is consistent with the XRD analyses.

Fig. 2(a) shows the off-specular Φ -scans of TiO₂{101} planes ($\psi = 68.3^\circ$) for the film deposited at 600 °C. Four diffraction peaks separated by 90° of the a-TiO₂{101} planes indicate a good in-plane alignment inside the film. The {101} plane of a-TiO₂ is four-fold symmetrical along a-

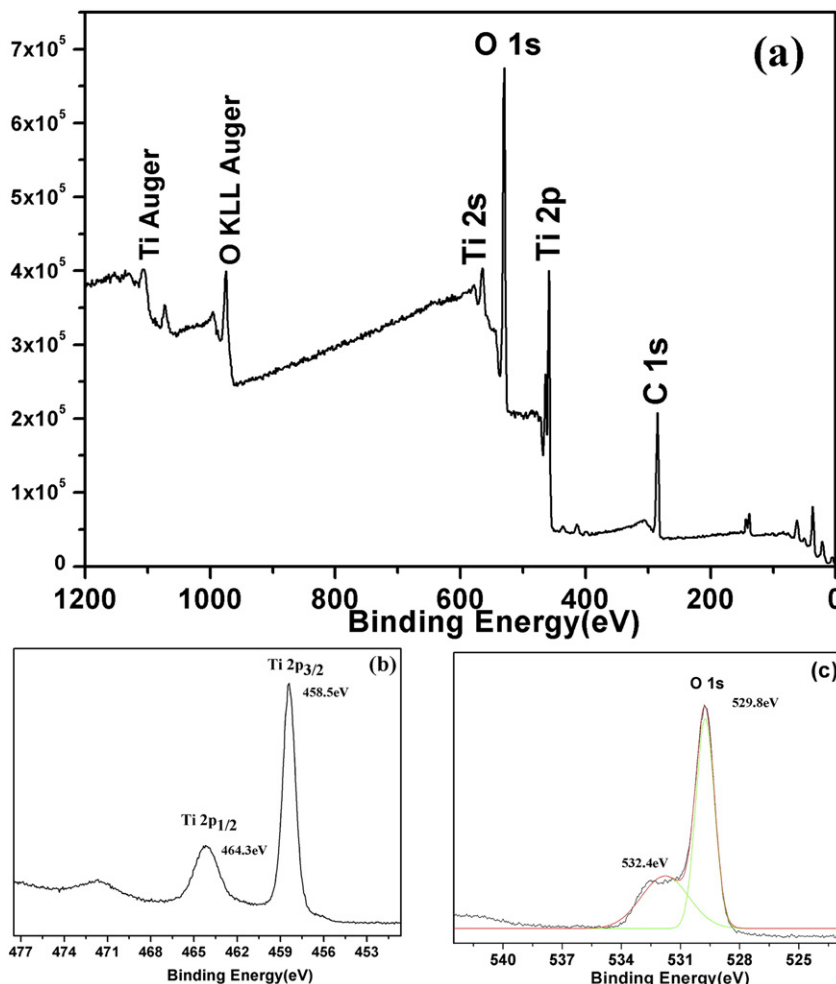


Fig. 3. XPS spectra of the TiO₂ film grown at 600 °C: (a) survey, (b) Ti2p and (c) O1s core level.

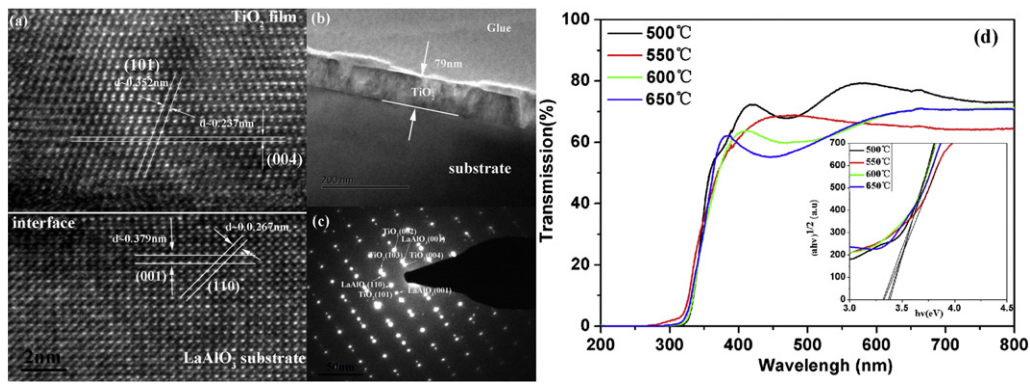


Fig. 4. The cross-sectional (a) HRTEM micrographs, (b) low magnification TEM and (c) SAED micrographs of the interface between TiO_2 film grown at 600°C and LaAlO_3 substrate. (d) The optical transmittance spectra of a- TiO_2 samples prepared at different temperatures with the plot of $(\alpha hv)^{1/2}$ vs. hv shown in the inset.

$\text{TiO}_2[001]$, which is consistent with Fig. 2(a), indicating a complete single crystalline structure without any domains in the obtained film. Fig. 2(b) shows the off-specular Φ -scans of $\text{LaAlO}_3\{101\}$ planes ($\psi = 45^\circ$) for the substrate, from which four diffraction peaks separated by 90° with the same Φ -angles as the $\text{TiO}_2\{101\}$ can be seen. Fig. 2(c) shows the ω -rocking curve of a- $\text{TiO}_2(004)$ reflection for the film deposited at 600°C , in which the FWHM is about 0.41° . A schematic diagram has been dealt for further explanation of the relationship between the film and substrate. Fig. 2(d) and (e) are geometrical configurations of a- $\text{TiO}_2(004)$ and $\text{LaAlO}_3(001)$ planes from the top-view perspective, respectively. In Fig. 2(d) and (e), the big balls present the O^{2-} since the radius of O^{2-} is larger than that of Ti^{4+} and La^{3+} . The lattice structure of LaAlO_3 is cubic with lattice parameter of $a = 3.812 \text{ \AA}$ and that of a- TiO_2 is tetragonal with lattice parameters of $a = b = 3.776 \text{ \AA}$, $c = 9.5 \text{ \AA}$. The lattice mismatch between the $\text{LaAlO}_3(001)$ and $\text{TiO}_2(001)$ direction is about 0.94% as shown in Fig. 2(d) and (e), which means a good lattice match. These results reveal that the TiO_2 film deposited at 600°C is epitaxial single crystal with no twins and the in-plane epitaxial relationship is $\text{TiO}_2[100]||\text{LaAlO}_3[001]$.

Fig. 3(a)–(c) show the XPS spectra of the survey, Ti 2p and O 1s core levels, respectively, for the TiO_2 film deposited at 600°C . From the survey spectrum shown in Fig. 3(a), photoelectron peaks of O1s, O Auger, Ti Auger, Ti2p, Ti2s and C1s can be observed, without any other elements detected, indicating the formation of titanium oxide. The C1s peak caused by adventitious hydrocarbon contamination on the surface of the film located at about 285.0 eV [15] is used as a reference for the calibration of other peaks. The titanium core levels Ti2p_{1/2} and Ti2p_{3/2} shown in Fig. 3(b) are observed at binding energies of 464.3 and 458.8 eV, respectively, with a peak-to-peak separation of 5.8 eV, which is consistent with the value of TiO_2 . In addition, there is no indication of Ti^{3+} (456.7 eV) [16]. In Fig. 3(c), the O1s core level is consistent of one sharp peak located at 529.8 eV and one weak peak located at 532.4 eV. The peak located at 529.8 eV originates from the OH^- adsorption on the film surface and the Ti–O bonding is taken to be at about 532.4 eV [17]. A quantitative analysis of the film composition can be performed based on the estimated areas of the XPS spectral lines using the atomic sensitivity factor analytical procedure [18]. The atomic ration of O/Ti calculated using the XPS data is about 2.0, which is consistent with the stoichiometry of TiO_2 . The XPS results reveal that the film prepared at 600°C is high purity TiO_2 .

Structural details of the TiO_2 film grown at 600°C was further studied using the cross-section TEM measurements. The HRTEM, low resolution TEM images and the SAED pattern of the interface between the TiO_2 film and LaAlO_3 substrate are shown in Fig. 4(a)–(c), respectively. The incident electron beam was parallel to the $[\bar{1}10]$ direction of the LaAlO_3 substrate. From Fig. 4(a), the uniform and ordered array crystal

lattice of both the TiO_2 film and LaAlO_3 substrate can be seen clearly. The fringe separation of the observed lattice planes in the TiO_2 film area are about 0.237 nm and 0.352 nm, corresponding to a- $\text{TiO}_2(004)$ and (101) planes, respectively, with an standard angular separation of 68.0° . For the HRTEM, the lattice parameter c is about 0.948 nm. For the substrate, the as-marked interplane spacings is consistent with $\text{LaAlO}_3(001)$ and (100) plane, respectively. Fig. 4(b) shows the cross-section low magnification TEM image and the thickness of the film is about 79 nm. In the SAED pattern shown in Fig. 4(c), the a- $\text{TiO}_2(101)$, a- $\text{TiO}_2(004)$, $\text{LaAlO}_3(110)$ and $\text{LaAlO}_3(001)$ spots are clearly observed. The regular diffraction spots array implies good single crystallinity. From the HRTEM image and SAED pattern, the epitaxial relationship between a- TiO_2 film and LaAlO_3 substrate can be obtained as a- $\text{TiO}_2(004) || \text{LaAlO}_3(001)$ with an in-plane epitaxial relationship of $\text{TiO}_2[100]||\text{LaAlO}_3[001]$, which is consistent with the XRD analyses.

The transmittance spectra as a function of wavelength in the range of 200–800 nm is shown in Fig. 4(d). The average transmittances of the samples deposited at 500, 550, 600 and 650°C in the visible range are 75%, 68%, 67% and 65%, respectively. The different film thicknesses in our study have direct impact on the different transmittances. In addition, due to the variation in the film crystallinity with various substrate temperatures, the scattering of light will differ in the films, which will also have a subsequent influence on the light transmittances. As an indirect-band gap semiconductor, the optical band gap (E_g) of a- TiO_2 can be estimated by the equation $\alpha hv = A(hv - E_g)^2$ [19], where hv is the energy of the incident photon, A is a material dependent constant and α is the adsorption coefficient. Therefore the E_g can be determined by plotting $(\alpha hv)^{1/2}$ vs. hv and then extrapolating the straight-line portion of this plot to the energy axis. As shown in the inset, the optical band gaps of the TiO_2 films deposited at 500, 550, 600 and 650°C are about 3.37, 3.32, 3.35 and 3.30 eV, respectively.

4. Conclusions

In summary, a- TiO_2 films were deposited on $\text{LaAlO}_3(001)$ substrates at 500 – 650°C by MOCVD. The substrate temperature has an obvious impact on the film crystallinity. The XRD θ - 2θ analyses indicated that the film prepared at 600°C had the best crystallization with an out-of-plane growth relationship a- $\text{TiO}_2(004) || \text{LaAlO}_3(001)$ and the off-specular Φ scan showed that the in-plane orientation relationship was $\text{TiO}_2[100]||\text{LaAlO}_3[001]$. The XPS results confirmed that the film prepared at 600°C is stoichiometric TiO_2 with high purity. The average transmission of every sample in the visible range exceeded 65% while the average transmission of the substrate was about 50.8% and the optical band gaps of the TiO_2 films deposited at 500, 550, 600 and 650°C were calculated as 3.37, 3.32, 3.35 and 3.30 eV, respectively.

Acknowledgment

This work was financially supported by the National Natural Science Foundation of China, China (grant no. 51472149).

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