

Synthesis and characterization of structural and optical properties of single crystalline a-TiO₂ films on MgAl₂O₄(111) substrate

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Abstract. Anatase phase TiO₂ (a-TiO₂) films have been deposited on MgAl₂O₄(111) substrates by the metal organic chemical vapor deposition (MOCVD) method at the substrate temperatures of 500-650°C. The structural analyses showed that the films were highly (004) oriented with tetragonal anatase structure and the epitaxial relationship was given as a-TiO₂ (004)||MgAl₂O₄ (111). The sample prepared at 600°C exhibited the best crystallization with a single-crystalline epitaxial film. The average transmittance of every TiO₂ film in the visible range exceeded 90% excluding the influence of the substrate. The morphology and composition of the TiO₂ films have also been studied in detail.

1. Introduction

The wide band gap oxide semiconductor material is an important material for the transparent electronic devices and optoelectronic devices. The wide band gap oxide semiconductor material has been widely used in the fields of flat panel display[1], transparent film transistors(TFT)[2], solar cells[3], light-emitting diodes (LED)[4] and UV detectors[5]. High quality epitaxial single crystal oxide films have attracted more and more attentions because of the advantages of the integrity of the structure, few defects and high mobility. The band gap of the titanium dioxide (TiO₂) is about 3.2eV[6], which is relatively close to those of the GaN[7], SiC[8] and ZnO[9] materials. Therefore, TiO₂ is a promising wide band gap oxide semiconductor material with excellent properties of stable physical and chemical properties, completely non-toxic and abundant storage.

Rutile and anatase are the common crystal structures of TiO₂. The rutile TiO₂ has poor adsorption capacity for oxygen, small surface area, easy combination of the electrons and holes and poor catalytic activity. Conversely, the anatase TiO₂ has larger surface area, strong adsorption capacity for oxygen and better photocatalytic activity. Therefore the anatase phase TiO₂ was widely used in the fields of photocatalytic catalysts and dye-sensitized solar cells. The MOCVD method has the properties of good control of the growth parameters and easy commercial production. The TiO₂ films deposited by the MOCVD method normally have good single crystal properties with complete structure. The TiO₂ films prepared on the substrates of Y-stabilized ZrO₂(YSZ)[10], LaAlO₃(LAO)[11], SrTiO₃(STO)[12], α -Al₂O₃[13] and LSAT[14] have been reported, but the a-TiO₂ film deposited on the MgAl₂O₄ substrate is seldom reported until now. The MgAl₂O₄ substrate is suitable for the growth of the a-TiO₂ film with low cost and good matching. In the present work, the high quality a-TiO₂ single crystalline films were deposited on MgAl₂O₄(111) substrates by MOCVD. The structural

properties, surface morphology, optical properties and the growth mechanism of the films were investigated in detail.

2. Experimental

TiO₂ films were deposited on MgAl₂O₄(111) substrates using a high vacuum MOCVD system with two different gas flows. The tetrakis-dimethylamino titanium (TDMAT) was used as the organometallic (OM) precursor and was stored in a stainless steel bubbler maintained at 20°C. The high purity oxygen (5N) is used as the oxidant. Before loaded into the reaction chamber, the substrates were cleaned with ethanol and then ultrasonic cleaned with de-ionized water, followed by compressed N₂ drying. The TDMAT and the oxidant were separately transported into the reaction chamber by ultra-high-purity N₂. During the deposition, the flows rates of OM vapor and O₂ were kept at 25sccm and 68sccm, respectively. The chamber pressure was fixed at 10Torr.

The epitaxial relationships of the obtained samples were examined by a Rigaku D/MAX 2200PC X-ray diffractometer (XRD) with Cu K α radiation. The surface micrograph was obtained using a JSM-6700F scanning electron microscope (SEM). The chemical composition of the TiO₂ film prepared at 600 °C was determined by the X-ray photoelectron spectroscopy (XPS) using an ESCALAB MK II multi-technique photoelectron spectrometer. High-resolution transmission electron microscopy (HRTEM) and selected area electron diffraction (SAED) were performed on the sample by a Tecnai F30 transmission electron microscope operated at 300 kV. The optical transmittance spectra were performed with a TU-1901 double-beam UV-vis-NIR spectrophotometer in the wavelength range from 200 to 800 nm.

3. Result and discussion

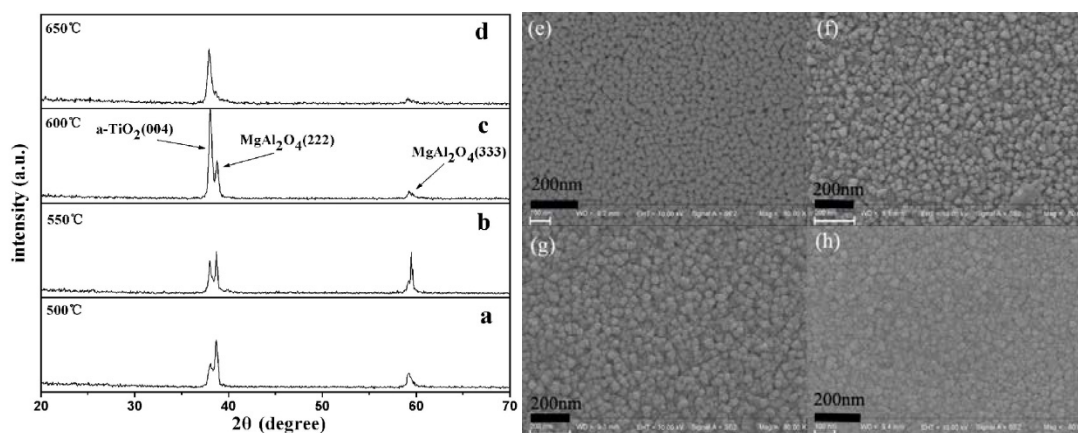


Figure 1. XRD spectra of the TiO₂ samples deposited at different substrate temperatures: (a)500, (b)550, (c)600 and (d)650°C. Plan view SEM micrographs of the TiO₂ films prepared at (e) 500, (f) 550, (g) 600 and (h) 650°C.

XRD patterns of θ -2 θ scan for TiO₂ films deposited on MgAl₂O₄(111) substrates at different substrate temperatures of 500, 550, 600 and 650°C are shown in Figure 1(a), (b), (c) and (d), respectively. The diffraction peak of the MgAl₂O₄(222) is located at about 38.5° and that of the MgAl₂O₄(333) is located at about 59.3° (JCPDS No.21-1152), which can be seen in Figure 1(a)-(d). Only one diffraction peak located at about 37.8° corresponding to a-TiO₂(004) (JCPDS No.21-1272) is observed besides the peaks of the substrates for all the samples, which indicates that the films obtained at all temperatures are single crystalline a-TiO₂ structure. In addition, the full width at half maximum (FWHM) of the peak of the MgAl₂O₄(222) deposited at 500-650°C are 0.651°, 0.430°, 0.411° and 0.487° obtained by the Jade, respectively. Therefore the a-TiO₂ film deposited at 600°C exhibits the best crystal quality with the smallest FWHM. The analyses of XRD θ -2 θ patterns show that the crystal

quality of the TiO_2 films prepared by MOCVD is obviously influenced by the substrate temperature. The out-of-plane growth relationship of the film is $\text{a-TiO}_2(004) \parallel \text{MgAl}_2\text{O}_4(111)$.

Figure 1(e)-(h) show the SEM images of TiO_2 films deposited at 500, 550, 600 and 650 °C, respectively. The SEM images show that the grains become bigger as the substrate temperature increases from 500 to 600 °C, which indicates the crystal quality of the film becomes better. In Figure 1(e), compact grains can be seen, but the grains are small and there is no evident boundary between the grains. The bigger grains are obviously seen in Figure 1(f), but the sizes of the grains are uneven. Figure 1(g) shows uniform grains with evident boundaries, which indicates the film obtained at 600 °C has a excellent crystallization. The surface morphology becomes smooth with unsystematic grains in Figure 1(h), indicating a degradation in the film crystallinity. The analysis of the SEM result shows that the film deposited at 600 °C exhibits the best crystallization, which is consistent with the XRD analyses.

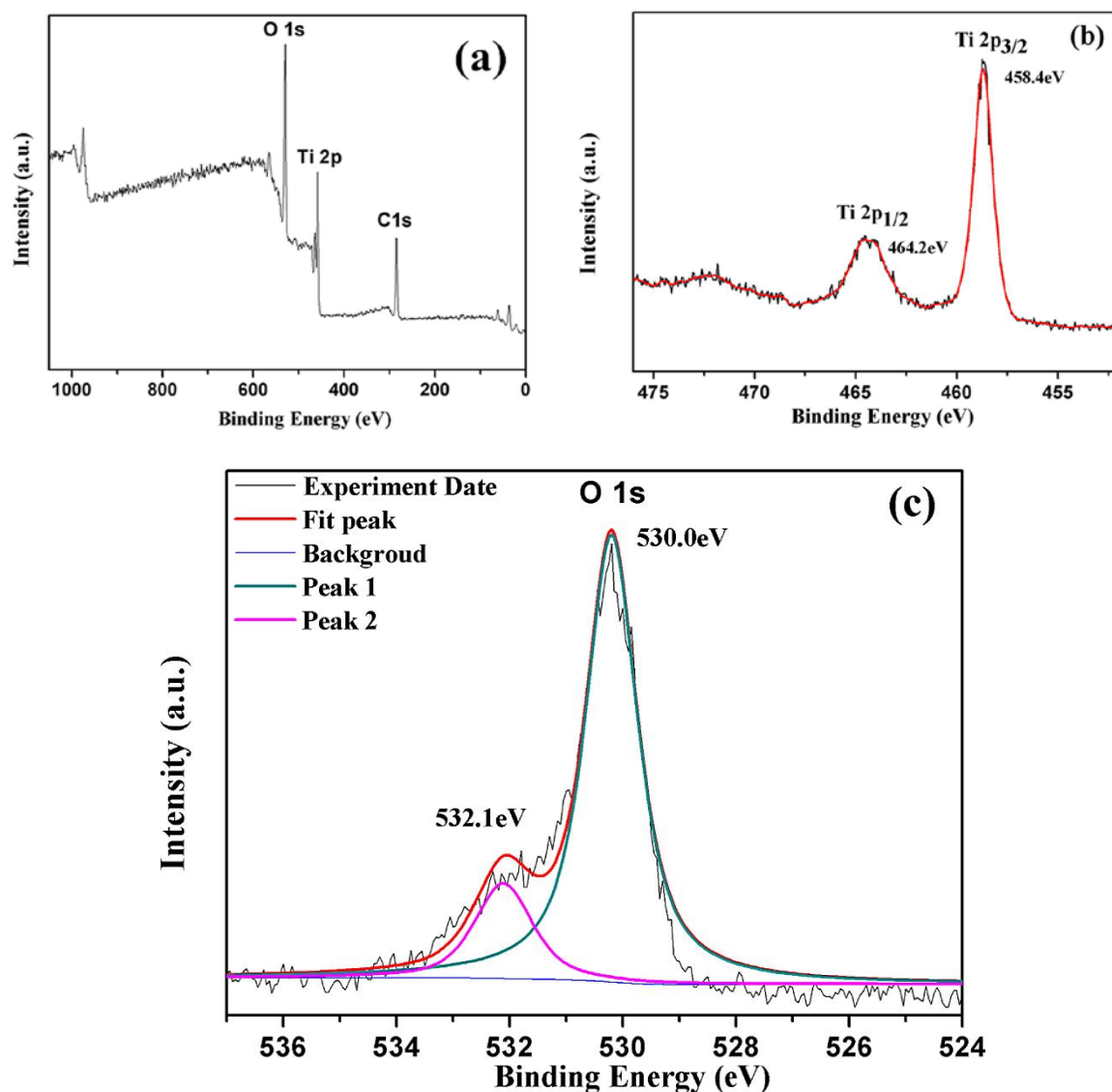


Figure 2. XPS spectra of the TiO_2 film grown at 600 °C: (a) survey, (b) Ti2p and (c) O1s core level, respectively.

The X-ray photoelectron spectroscopy (XPS) technique was performed to research the chemical compositions of the sample deposited at 600 °C. Figure 2(a) shows a full scan in the energy ranging from 0-1200eV, from which the Ti2p, C1s and O1s core levels can be seen without the perks of any other elements detected, indicating the formation of titanium oxide. The C1s peak is located at about 285.0eV, which is used as a reference for the calibration of Ti2p and O1s core levels. The presence of C1s peak is related to surface pollution of the sample when it is exposed to the air before the XPS experiments. The Ti2p spectra of the TiO₂ film deposited at 600°C is shown in Figure 2(b). The peak of Ti2p_{1/2} is located at about 464.2eV and that of Ti2p_{3/2} is located at about 458.4eV, which is the characteristic of TiO₂ with a separation of 5.8eV[15]. No Ti³⁺ signal located at 457eV is observed on the surface of the film[16]. In Figure 2(c), the O1s core level located at about 532.1eV and 530.0eV after gaussian fitting were assigned to oxygen from OH⁻ adsorption and TiO₂, respectively[17]. The stoichiometry of the film can also be calculated by the relative areas of the total Ti2p and O1s XPS peaks corrected by the relative sensitivity factors, the result of which is about 2.0. The analyses of the XPS indicates the film deposited at 600°C is high-purity TiO₂.

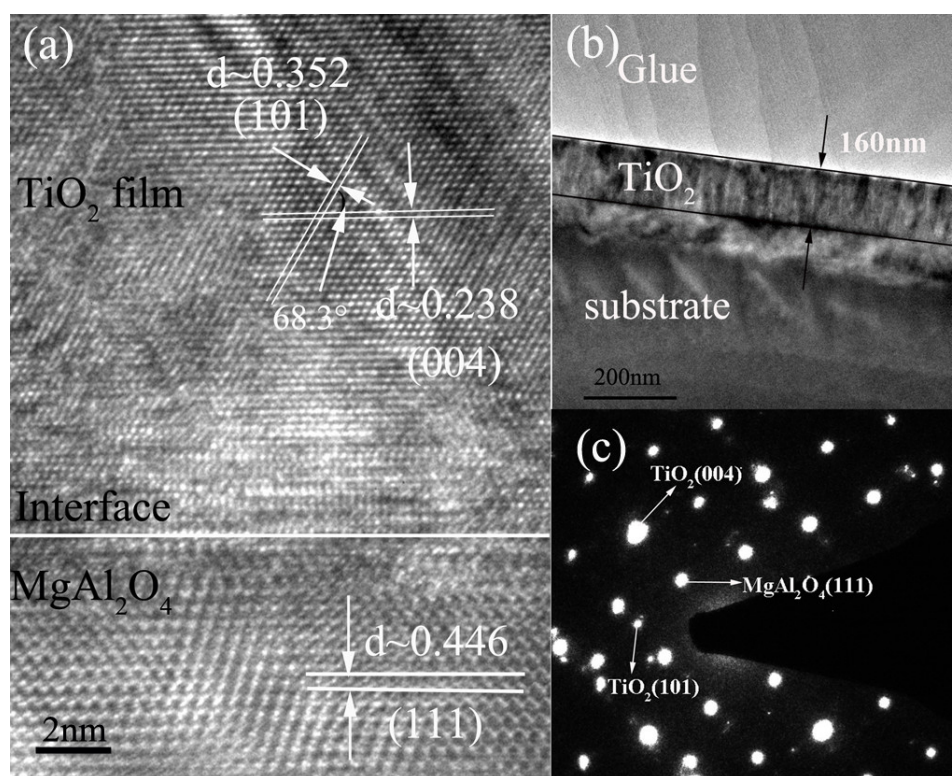


Figure 3. The cross-sectional (a) HRTEM micrographs, (b) low magnification TEM and (c) SAED micrographs of the interface between TiO₂ film grown at 600°C and MgAl₂O₄ substrate.

The heteroepitaxial growth mechanism of the TiO₂ film grown on MgAl₂O₄(111) substrate was further studied using the cross-section TEM measurements. The HRTEM, low resolution TEM images and the SAED pattern of the interfacial region between the MgAl₂O₄ substrate and the TiO₂ film grown at 600°C are shown in Figure 3 (a)–(c), respectively. From Figure 3(a), the crystal lattice of both the TiO₂ film and MgAl₂O₄ substrate can be seen clearly with a well-defined interface. For the film, the as-marked interplane spacings are 0.352nm and 0.238nm, corresponding to a-TiO₂ (101) and (004) planes, respectively. The as-marked interplane spacings for the substrate is 0.466nm, which is corresponding to MgAl₂O₄(111) planes. The low resolution TEM image shows that the thickness of the film is about 160nm as is shown in Figure 3(b). The SAED pattern of the corresponding interface

area is shown in Figure 3(c), from which the diffraction spots of a-TiO₂ (101) and (004) as well as MgAl₂O₄ (111) and (222) can be seen clearly. The regular diffraction spots array implies good single crystallinity. From the HRTEM image and SAED pattern, the epitaxial relationship between a-TiO₂ film and MgAl₂O₄ substrate can be given as a-TiO₂(004)||MgAl₂O₄(111), which is consistent with the XRD analyses.

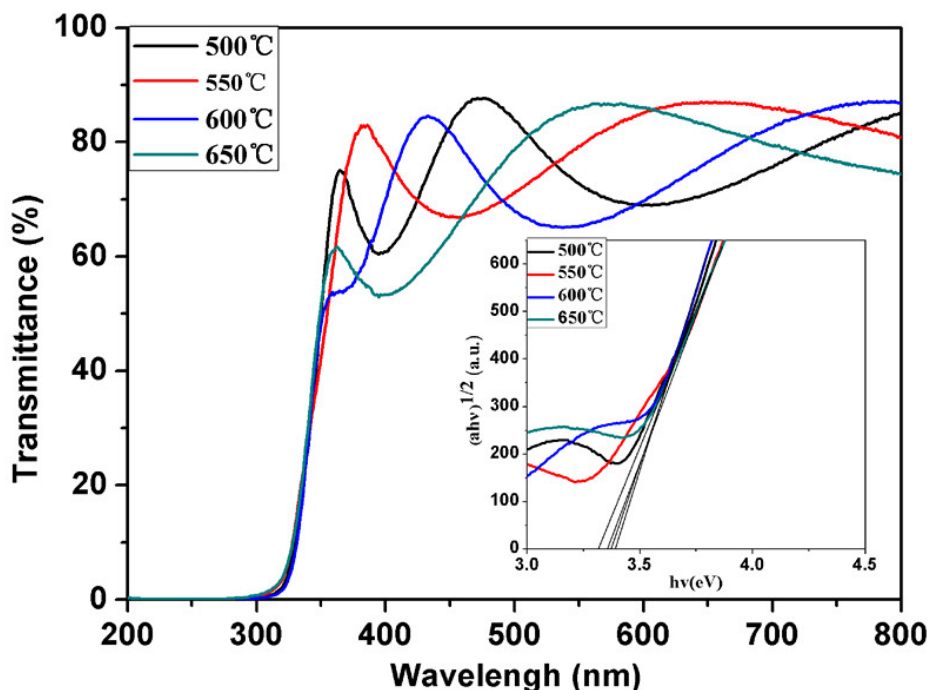


Figure 4. The optical transmittance spectra of a-TiO₂ samples prepared at different temperatures with the plot of $(\alpha h\nu)^{1/2}$ vs. $h\nu$ shown in the inset.

The optical transmittance spectra of the TiO₂ samples deposited at the temperatures ranging from 500 to 650 °C are shown in the Figure 4. Deducting the influence of the substrate, the average transmittance of the TiO₂ films in the visible range exceeds 90%. The a-TiO₂ film is an indirect-band gap semiconductor, so the optical band gap(E_g) of the a-TiO₂ can be estimated by the equation $\alpha h\nu = A(h\nu - E_g)^2$ [18], where ν is the frequency of the incident photon, h is the Planck's constant, A is a material dependent constant and α is the adsorption coefficient ($\alpha = (-1/d)\ln T$, where d and T are the thickness and transmittance of the film, respectively). The energy gap of the a-TiO₂ films can be estimated by plotting $(\alpha h\nu)^{1/2}$ vs. $h\nu$. The optical band gaps of the TiO₂ films deposited at 500-650 °C are in the range of 3.2-3.38 eV.

4. Conclusions

Anatase TiO₂ films have been deposited on MgAl₂O₄(111) substrates at the substrate temperatures of 500-650 °C by MOCVD. The structural analyses showed that the film deposited at 600 °C was single crystalline a-TiO₂ with the epitaxial relationship of a-TiO₂(004)||MgAl₂O₄(111). The HRTEM and SAED measurements further confirmed the single crystal structure and epitaxial relationship of the film prepared at 600 °C. The average transmittance of all the samples prepared at different temperatures exceeded 90% in the visible range. The optical band gap of the TiO₂ film deposited at 600 °C was calculated as about 3.3 eV. Due to the excellent structural and optical properties, the TiO₂ films prepared on MgAl₂O₄(111) will be used widely in the fields of photovoltaic devices after doping Niobium or Tantalum element.

Acknowledgment

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References

- [1] Lewis B G and Paine D C 2000 *Mrs Bulletin* **25(08)**: 22-27.
- [2] Zhang H, Uochi H and Takayama T 1996 *U.S. Patent* 5,563,426[P] **10-8**.
- [3] Wan J, Liu R and Tong Y 2016 *Nanoscale Res. Lett.* **11** 1-9.
- [4] Mont F W, Kim J K and Schubert M F 2008 *J. Appl. Phys.* **103** .
- [5] Basak D, Amin G and Mallik B 2003 *J. Cryst. Growth* **256** 73-77.
- [6] Tang H, Prasad K and Sanjines H 1994 *J. Appl. Phys.* **75** 2042-2047.
- [7] Matsuoka T, Okamoto H and Nakao M 2002 *Appl. Phys. Lett.* **81** 1246-1248.
- [8] Mattausch A and Pankratov O 2007 *Phys. Rev. Lett.* **99** 076802.
- [9] Srikant V and Clarke D R 1998 *J. Appl. Phys.* **83** 5447-5451
- [10] Wang W, Ma J and Wang W, 2015 *Mater. Lett.* **161** 9-12.
- [11] Kurita D, Ohta S and Ohta H 2006 *J. Appl. Phys.* **100** 096105-1.
- [12] Hsieh C C, Wu K H and Juang J Y 2002 *J. Appl. Phys.* **92** 2518-2523.
- [13] Chang H L M, You H and Gao Y 1992 *J. Mater. RES.* **7** 2495.
- [14] Wang M, Wang W and Li Z 2016 *RSC Adv.* **6** 4867-4871.
- [15] Stefanov P, Shipochka M and Stefchev P 2008 *J. Phys. Conference Series. IOP Publishing* **100**.
- [16] Sandell A, Anderson M P and Alfredsson Y 2002 *J. Appl. Phys.* **92** 3381-3387.
- [17] Lu Z, Yip C T and Wang L 2002 *ChemPlusChem* **77** 991.
- [18] Bernardi M I B and Lee E J H 2001 *Mat. Res.* **4** 223.