

Characterization of niobium-doped titania epitaxial films deposited by metalorganic chemical vapor deposition



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ABSTRACT

Titania (TiO₂) films with different niobium (Nb) doping concentrations were deposited on SrTiO₃ (STO) (100) substrates by metalorganic chemical vapor deposition (MOCVD). The crystal structures, surface morphologies, electrical and optical properties of the Nb-doped TiO₂ (TiO₂:Nb) films varying with Nb content were investigated. The single crystal TiO₂ films with anatase structure were obtained at low Nb doping levels. The highest Hall mobility of the prepared films reached as high as 16.50 cm² V⁻¹ s⁻¹. The lowest resistivity of 5.75 × 10⁻² Ω cm with a Hall mobility of 7.40 cm² V⁻¹ s⁻¹ and a carrier concentration of 1.47 × 10¹⁹ cm⁻³ were obtained from the 1.20% Nb-doped TiO₂ film. This resistivity was about 6 orders of magnitude lower than the undoped TiO₂ film. Moreover, all the deposited films exhibited high average transmittances of over 88% in the visible wavelength range.

1. Introduction

Titania (TiO₂) has attracted considerable attentions due to its superior properties such as bio-compatibility [1], nontoxicity [2], an excellent physicochemical stability [3], a high transparency in visible light [4] and an outstanding photo-catalytic efficiency [5]. TiO₂ naturally has three main phases, including brookite (b-TiO₂), rutile (r-TiO₂) and anatase (a-TiO₂) [6]. B-TiO₂ mainly concomitantly exists with rutile or anatase phase TiO₂ [7]. R-TiO₂ has been widely used as UV absorber [8], white pigment and dielectric layers in MOS devices [9]. Nevertheless, the conditions for the synthesis of r-TiO₂ materials are rather demanding. Although Wu et al. reported the low-temperature growth of monolayer r-TiO₂ nanorod films using the wet chemistry routes [10], a high temperature exceeding 800 °C is usually requisite for most of the other methods to synthesize pure r-TiO₂ [11]. The preparation conditions of a-TiO₂ are relatively accessible compared with those of b- or r-TiO₂. Literatures on the preparation of pure a-TiO₂ materials using various methods such as PLD [12], MBE [13,14] and MOCVD [15] with easily feasible conditions have been reported, which lays a good foundation for the further investigations of a-TiO₂.

In spite of the superior properties and simple acquisition methods, a-TiO₂ also possesses some disadvantages which may severely restrict its applications in many fields. For example, due to the wide band gap of 3.2 eV [16], a-TiO₂ is active only under the radiation of ultraviolet light, which merely covers 5% of sunlight spectrum, leading to a low

photo-catalytic activity [17]. Another serious drawback is the high resistivity of intrinsic a-TiO₂, which will significantly limit its applications in the microelectronic and optoelectronic fields [18].

Doping has been acknowledged as an effective way to adjust or improve the conducting properties of metal oxide semiconductor materials [19]. By incorporating various dopants, mainly including non-metals and transition metals, the optical absorption edge of a-TiO₂ could be extended to the longer wavelengths, which makes the doped system sensitive to visible light and therefore the photo-catalytic and photochemical performances are significantly enhanced [20]. Wu et al. synthesized W, N co-doped TiO₂ and Ni-doped TiO₂ nanobelts, both of which showed excellent photo-catalytic activity in assisting the photodegradation of rhodamine B in water [21,22]. Sharotri et al. reported the preparation of Mn, S co-doped TiO₂ using ultrasonic wave and verified its high photo-catalytic activity under visible light for the degradation of organophosphate pesticide, quinalphos [23]. Belver et al. synthesized Zr-doped TiO₂ clay materials and exhibited their potential application in dealing with emerging pollutants [24]. However, very few literatures are about the remarkable improvements of electrical properties of a-TiO₂ films through doping because it is much harder to be realized. Kafizas et al. reported a 0.21 Ω cm resistivity for the F-doped TiO₂ thin films deposited by an atmospheric pressure chemical vapor deposition (APCVD) process [25]. Kumar et al. synthesized the Mg-doped TiO₂ thin films using the sol-gel method, the lowest resistivity of which was 4.9 × 10⁴ Ω cm [26]. Akbar et al. prepared V-

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doped TiO₂ films via the sol–gel dip coating method and the resistivity of the films was in the range of 1.7 to $16.7 \times 10^7 \Omega \text{ cm}$ [27]. Ta and Nb are also the frequently investigated dopants aiming to reduce the high resistivity of a-TiO₂ film materials. However, the experiment conditions in relevant literatures were considerably harsh and most of the deposited films were polycrystalline [18,28,29]. Metalorganic chemical vapor deposition (MOCVD) is a very suitable method for epitaxial growth of doped TiO₂ films. Gao et al. reported the deposition of Nb-doped r-TiO₂ films on sapphire by MOCVD, but only the structural properties of the films were studied [30]. Takahira et al. deposited Nb-doped a-TiO₂ films by MOCVD and the photocatalytic activity was investigated [31]. Therefore, it is very necessary and urgent to deposit doped a-TiO₂ epitaxial films with good electrical properties to extend their applications in the microelectronic and optoelectronic fields.

In this paper, a simple yet effective method to improve the electrical properties of a-TiO₂ epitaxial films by Nb incorporating is reported. The undoped and Nb-doped TiO₂ (TiO₂:Nb) films with various Nb contents were deposited on SrTiO₃ (STO) (100) substrates using MOCVD. The structural, electrical as well as optical properties of the deposited films were systematically studied.

2. Materials and Methods

The undoped and Nb-doped TiO₂ films were synthesized on double-side polished STO (100) substrates (size of $10 \text{ mm} \times 10 \text{ mm} \times 0.5 \text{ mm}$) via a high vacuum MOCVD system. The substrates were ultrasonically cleaned with ethanol and then dried with pure N₂ before being placed into the reaction chamber. Commercially available niobium ethoxide [Nb(OCH₂CH₃)₅] and tetrakis-dimethylamino titanium [Ti[N(CH₃)₂]₄] were applied as the organometallic (OM) sources. High purity O₂ (5N) was used as the oxidant. During the deposition, the OM and O₂ vapors were transported into the reaction chamber with high purity N₂ (9N) through separate pipelines. The flow rate of O₂ was kept at 50 sccm. The pressure of the reaction chamber was maintained at 10 Torr and the substrate temperature was kept at 550 °C. The bubbler pressure of Ti OM source was kept at 170 Torr and the vapor flow rate was kept at 32 sccm, resulting in a molar flow rate of Ti OM vapor as $6.77 \times 10^{-7} \text{ mol/min}$. By manipulating the bubbler pressure and vapor flow rate of the Nb OM source, the molar flow rate of Nb OM vapor was controlled in the range of 1.10×10^{-9} – $2.19 \times 10^{-8} \text{ mol/min}$. The experimental set values of Nb/(Ti + Nb) atomic ratio were 0, 0.15%, 0.30%, 0.60%, 1.20%, 1.50% and 3.00%, corresponding to the samples marked from S₀ to S₆, respectively. The deposition time of the films was 2 h.

The crystal quality of the deposited films was studied by X-ray diffraction (XRD) θ - 2θ scan via the Rigaku D/MAX- γ B X-ray diffractometer with Cu K α radiation. The thicknesses of the films were measured via scanning electron microscopy (SEM) with an S-4800 ultra-high resolution scanning electron microscope. The chemical composition and the corresponding atomic ratio of the films were measured by X-ray photoelectron spectroscopy (XPS) using the ESCALAB MK II multitechnique electron spectrometer. The surface roughness and morphology were obtained using the peak force error mode of atomic force microscopy (AFM) with a Dimension Icon scanning probe microscope. The room-temperature electrical resistivity, carrier concentration and carrier mobility were determined by the Hall measurement with Van der Pauw technique. Using a Tecnai F30 transmission electron microscope, the high-resolution transmission electron microscopy (HRTEM), selected area electron diffraction (SAED) and energy dispersive X-ray spectroscopy (EDX) were performed to further study the crystal quality and verify the chemical composition of the film, respectively. The optical transmittances and diffuse reflectance spectra of the films were measured using the TU-1901 double-beam UV–vis–NIR spectrophotometer with an integrating-sphere accessory.

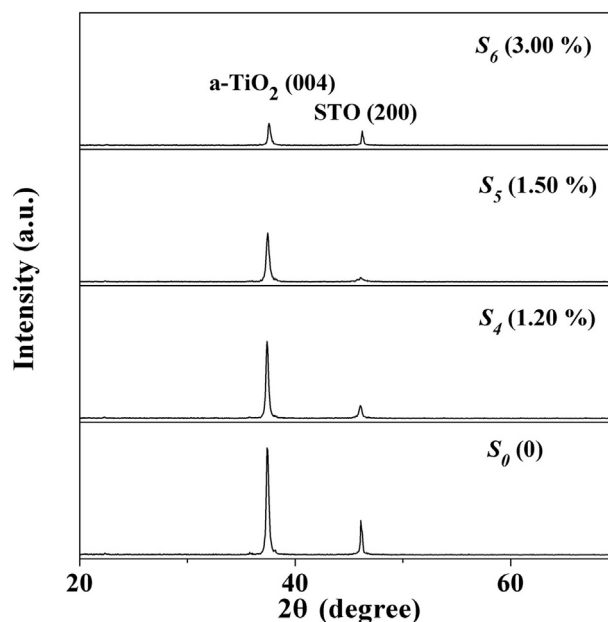


Fig. 1. XRD θ - 2θ patterns of the S₀, S₄, S₅ and S₆ samples.

3. Results and Discussion

Fig. 1 shows the XRD θ - 2θ scan spectra for the samples with various Nb contents. Since the TiO₂:Nb films with low Nb concentrations present similar patterns, here only the undoped and Nb-doped TiO₂ samples with relatively high Nb concentrations are depicted in Fig. 1. The thicknesses of the S₀, S₄, S₅ and S₆ samples are 177.3, 190.2, 195.1 and 212.3 nm, respectively. Besides the STO (200) diffraction peak centered at $2\theta = 46.5^\circ$ (JCPDS NO. 21–1272), all curves exhibit a single film diffraction peak centered at 37.8° corresponding to a-TiO₂ (004) (JCPDS NO. 21-1272), indicating that the deposited films are all pure anatase phase TiO₂ with an out-of-plane epitaxial relationship of a-TiO₂ (001)||STO (100). Nb⁵⁺ is reported to present a very high solid solubility in TiO₂ materials [32] and the ionic radius of Nb⁵⁺ (0.69 Å) is very close to that of Ti⁴⁺ (0.68 Å). When the doping concentration is low, Nb⁵⁺ tends to distribute uniformly into the TiO₂ lattice as substitutional impurity and it is difficult to aggregate and form a niobium oxide phase, so no niobium oxide peak is detected. The position of a-TiO₂ (004) peak shows no obvious shifts with the variation of Nb doping content, which can also be ascribed to the numerical proximity of the ionic radii of Nb⁵⁺ and Ti⁴⁺. The full-widths at half-maximum (FWHMs) of the a-TiO₂ (004) peaks are 0.26° , 0.27° , 0.31° and 0.32° corresponding to the TiO₂:Nb films with Nb contents of 0, 1.20%, 1.50% and 3.00%, respectively, indicating that the crystalline quality of the films slightly degrades with the increase of Nb doping content.

XPS analyses are performed to determine the chemical states of the film elements and to ascertain their relative concentrations. Fig. 2(a) illustrates the survey scan of the 1.20% Nb-doped TiO₂ sample (S₄) in the binding energy range of 0 to 1000 eV, from which only the Ti, O and Nb related core levels can be detected besides the C 1s peak caused by the adventitious hydrocarbon contamination and the O KLL Auger lines. Fig. 2(b) displays the XPS spectrum of O 1s core level. The main peak centered at 529.4 eV is attributed to the lattice oxygen in TiO₂ and the other weak peak centered at 532.3 eV may be due to the OH– and/or C/O adsorptions on the film surface. Fig. 2(c) and (d) show the high resolution spectra of the Ti 2p and Nb 3d peaks, respectively, which confirm that titanium is present only in Ti⁴⁺ state and niobium merely exists as Nb⁵⁺, without any other low valence titanium and niobium states detected. By using the atomic sensitivity factor analytical procedure, quantitative analyses of element proportions based on the XPS peak areas have been performed for the S₄, S₅ and S₆ samples. The

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