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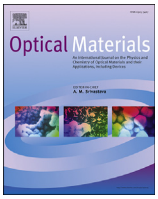

Difference of SERS ability from titanium oxide films by Ti^{3+} self-doping

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ABSTRACT

With the Ti^{3+} self-doping, the surface-enhanced Raman scattering (SERS) ability of titanium oxide films shows difference. In this paper, the titanium oxide films were fabricated by electron beam evaporation under different oxygen flow. The surface morphology, element composition, optical property and SERS ability were characterized, respectively. The X-ray photoelectron spectroscopy reveals the existence of two different valence states of titanium ion in samples. Both the optical absorption and the bandgap shows difference when various quantities of Ti^{3+} was doped, which is related to the SERS ability. As a result, the Raman scattering intensity of RhB molecule increases when the number of Ti^{3+} increases. In conclusion, the SERS ability of titanium oxide films is related to the amount of doped Ti^{3+} in film, which is valuable to the SERS research.

1. Introduction

Raman spectrum is seen as an important way to detect trace amount information. However, when it is used in the practical application, the low signal intensity inevitably influences the accuracy and sensitivity of the measurement result. One such technique, which can improve Raman signal significantly, is surface enhanced Raman scattering (SERS) [1,2]. Two key explanations for the SERS are the electromagnetic (EM) and the chemical contribution. In general, the EM enhancement is regarded as the more important one, and it mainly relies on an effect which is known as localized surface plasmon resonance (LSPR) [3]. SERS ability of both semiconductor and metal has been reported, but there are just few reports on LSPR property of semiconductor material. It means SERS induced by semiconductor material may not mainly rely on EM enhancement.

Sultan Ben-Jaber et al. [4] reported the photo-induced enhanced Raman spectroscopic technique, where the charge transfer from oxygen vacancy of titanium oxide thin film gives rise to large signal enhancement. Cong et al. [5] reported the Raman enhancement on a semiconducting metal oxides by making oxygen vacancies. The $W_{18}O_{49}$ was prepared by a hydrothermal reaction, and it achieved a limit detection as low as 10^{-7} M and EF up to $3.4*10^{5}$. These recent studies suggest that the surface state of semiconductor material is a key to SERS enhancement. Among the numerous methods of tuning the surface states of semiconductor, introducing oxygen deficiency represents one main strategy and may work as an efficient and simple way.

Titanium oxide material has been widely studied because of its interesting and potentially unique physical, mechanical and chemical properties. For example, splitting of water on TiO_2 electrodes has been studied extensively [6]. This catalyst application depends on the ability generating electron–hole pairs in the surface under illumination. Besides, many other applications including gas sensors [7], antireflection coatings [8], solar cells [9,10] and MOS devices [11] have also been reported. More current evidence has demonstrated that oxygen vacancy defects on the TiO_2 surface plays an essential part in acting as electron scavengers when electron–hole pair creation occurs by excitation in the TiO_2 [12]. To change the surface state and create oxygen vacancy, a number of methods like hydrogenation [13], doping, anneal [14] and non-stoichiometric preparation have been studied.

In this research, we prepared the mixed-valence titanium oxide films by electron beam evaporation. Electron beam evaporation, which is widely used in industrial applications, provides very high deposition rate on large deposition areas. It is very convenient and possible to deposit many types of materials into thin films and nanostructures [15]. To create the oxygen deficiency, different flow

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rate of oxygen is introduced during deposition process. The Raman spectra and X-ray photoelectron spectroscopy (XPS) characterizations reveal the existence of the Ti^{3+} dopants in the TiO_2 thin film, which plays the key role of charge transfer at the semiconductor–analyte interface. X-ray diffraction (XRD), atom force microscopy (AFM) and UV-VIS-NIR spectrophotometer results are also been reported in this paper.

2. Experiment

Titanium oxide films were deposited on quartz substrates by electron beam evaporation at 200 °C. The coating material which we used in this experiment is Ti_3O_5. The thickness of the films was about 100 nm and monitored by an in situ quartz crystal microbalance. As a comparative experiment, all parameters are the same apart from four different groups of the oxygen flow rate. The titanium oxide thin film with oxygen flow rate 0, 10, 30 and 50 sccm were denoted as Sample1(S1), Sample2(S2), Sample3(S3) and Sample4(S4), respectively. A simple heat treatment experiment was added for testing stability of sample S1 and the as-annealed sample was denoted as S1'. The anneal condition was 300 °C for 1 h in air.

The crystal structure of samples was characterized by X-ray diffraction using a Bruker AXS/D8 Advance system, with CuKα radiation ($\lambda = 0.15408$ nm). Surface morphology of the films were studied by the atom force microscopy. The scanning area is 1 μm*1 μm. Thermo Scientific K-Alpha+ was used to study on the X-ray photoelectron spectroscopy. Optical transmittance and absorption spectra of samples were performed by using an integrating sphere setup mounted on a dual-beam UV-VIS-NIR spectrophotometer (Lambda 1050, Perkins Elmer) at normal incidence. The scanning step and integration time are 2 nm and 0.24 s, respectively. While Rhodamine B (RhB) was used as probing molecules (concentration = $1*10^{-3}$ mol/L), the Raman spectrum was studied by a confocal microprobe Raman system (inVia Raman Microscope, Renishaw) operated with a 633 nm laser. All the measurements were carried out at room temperature.

3. Results and discussion

3.1. Film structure & morphology

Fig. 1 shows the X-ray diffraction (XRD) pattern of the titanium oxide films which were prepared under different oxygen flow. It can be seen that all samples are amorphous structure, which can be explained by the structure zone model which is put forward by Barna and Adamik [16]. This classic model points out that there are three stages during a deposition process which are transport, surface diffusion and bulk diffusion. Here, we define $\mathbf{T}$ as the depositing temperature and $\mathbf{T_m}$ as melting point temperature of coating material, the value of $\mathbf{T/T_m}$ is used to show the effect of temperature on the diffusion fluxes. When depositing temperature $\mathbf{T}$ is high enough, bulk diffusion will dominate over all other processes and the atoms prefer moving according to the lattice structure [16,17]. When $0.3 < \mathbf{T/T_m} < 0.5$, surface diffusion works as an important role since the width of grain boundaries subject to activation energies typical of surface diffusion. When $\mathbf{T/T_m} < 0.3$, there is little surface diffusion and every atom essentially sticks to where it arrives. In this work, substrate temperature $\mathbf{T}$ is 200 °C, $\mathbf{T_m}$ relative to titanium oxide almost equals to 2180 °C in the atmosphere. Therefore, amorphous structure film samples which we prepared in this paper are reasonable with zone model theory.

Fig. 2 represents the surface morphology images which is captured by the AFM. As is shown in Fig. 2(a), the particle size of S1 is small. Then, the particle size start to become larger with oxygen flow increasing (Fig. 2(b)~(d)). According to the structure zone model, little surface diffusion took place in deposition process. It means the particles were limited at small size, which is supported by surface morphology of S1. When oxygen flow was introduced into the vacuum chamber, the molecule combination of oxygen and coating material increased the particle size. It should be attributed to the combination with oxygen molecule during the deposition process. The root mean square roughness (RMS) values are also shown in Fig. 2. It is seen as that all samples have similar RMS values in the scale of picometer (pm), which reveals that the surface roughness is independent of the oxygen flow.

3.2. Composition and valence state

In order to further identify sample composition with different oxygen flow rates, X-ray photoelectron spectroscopy of samples was measured. As is shown in Fig. 3 (a), a strong peak at around 529.7 eV for all samples which corresponds to the O *1s* can be found. After peak-fitting, two independent peaks were deconvoluted from the spectra and marked as O *1s* (I) and O *1s* (II). Q. Chen et al. [18] reported that peaks at 529.6 eV is assigned to the lattice oxygen (O^{2-}) of titanium oxide. The peak at 530.9 eV can be attributed to hydroxyl group species [19]. Due to the anhydrous environment for film preparation, the hydroxyl group here should be attributed to the quartz substrate.

The Ti *2p* core-level spectra of S1 is shown in Fig. 3 (b). Four peaks at around 458eV, 458.6eV, 463.7eV and 464.3eV which was marked as Ti *2p* 3/2(I), (II) and Ti *2p* 1/2(I), (II) have been achieved after peak-fitting. According to the study of I. Bertoti et al. [20], the species of Ti *2p* 3/2(I) and Ti *2p* 3/2(II) should be regarded as Ti^{3+} and Ti^{4+}, respectively. Obviously, there are two valence states in these samples. Instead of Ti^{4+}, two trivalent titanium ion can only combine three oxygen ion. Unexpectedly, all samples contain a large amount of Ti^{3+}. It should be attributed to the coating material Ti_3O_5 which can be seen as $Ti_2O_3 \cdot TiO_2$. In the other word, the Ti^{3+} was doped into titanium oxide film automatically. The composition ratio of various titanium species is shown in Table 1, which is calculated by the area of different peaks. Among all samples, the S1 has the largest percentage of Ti^{3+}, which means the most oxygen deficiencies were involved.

3.3. Optical properties

Optical absorption spectra of the samples were verified by

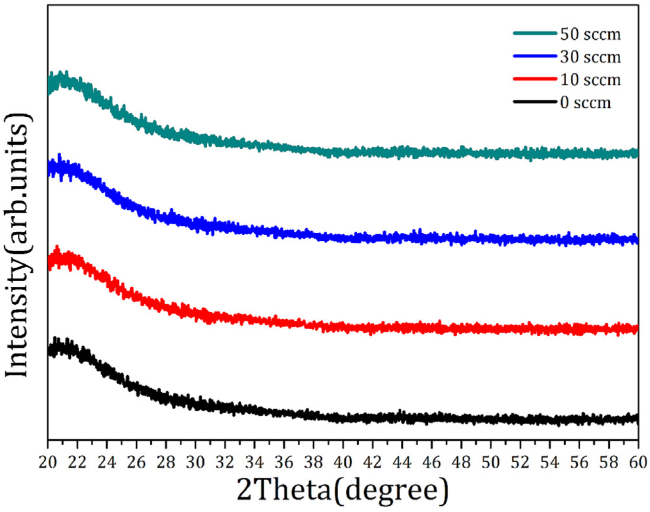

Fig. 1. XRD pattern of samples which are deposited under different oxygen flow.