V and Ga Co-doping Effect on Optical Absorption Properties of TiO₂ Thin Films

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Abstract. In this work, V and Ga co-doped TiO₂ thin films were obtained by pulsed laser deposition (PLD) using sintered ceramic targets, followed by short term annealing at 1000°C. The structures of the thin films were characterized by X-ray diffraction (XRD) and the optical absorption properties of the films were investigated using UV–VIS spectrophotometer. A narrow energy band gap of about 1.5 eV was obtained in a typical co-doped film with 1 at.% V and 0.5 at.% Ga as dopants. The analysis on the chemical states of Ti and Ga elements by X-ray photoelectron spectroscopy (XPS) revealed that the Ga doping plays an important role in the band gap narrowing.

1. Introduction

Among various oxide semiconductor materials, titanium dioxide (TiO₂) is most widely studied because of its promising application in photocatalysis [1], solar cells [2], and so on. However, as it has a energy band gap of 3.0 eV (rutile TiO₂) and 3.2 eV (anatase TiO₂), it is activated only under UV light irradiation which accounts for only a small fraction (~5%) of the solar irradiance compared to the visible region (~45%) [3]. In recent years, many studies focused on the process of shifting the optical response of active TiO₂ from the UV to the visible spectral range. An efficient approach is doping TiO₂ with metal [4],[5] and nonmetal elements [6],[7]. Anpo et al. modified TiO₂ catalysts by bombarding it with high-energy metal ions, such as V, Cr, Mn, Fe, etc. They found that among them V ion implantation had the highest effectiveness in the red shift of TiO₂ absorption edge [8]. Wu and Chen narrowed the band gap of TiO₂ to 2.8 eV with 8% V-doping [9]. Likewise, simultaneous incorporation of V and Pd in TiO₂ by magnetron sputtering results in the decrease of the band gap of TiO₂ to 2.09 eV [10].

Our previous theoretical calculation showed that the bandgap of TiO₂ could be reduced gradually by increasing the Gallium doping level. However, gallium has very low solubility in the crystal lattice of TiO₂, which leads to considerable difficulty to increase the Ga doping amount. In order to overcome this problem, we deliberately co-doped TiO₂ thin films with both V and Ga elements, expecting to enhance redshift in the band gap of TiO₂.

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2. Experimental details

The TiO₂ thin films were prepared by PLD-IV (KrF laser wavelength: 248 nm) using ceramic targets. The targets were made by pressing TiO₂ powder with various V and Ga ratios added as V₂O₅ and Ga₂O₃ powder into disks and then baked at 1200 °C for 2 h.

Deposition processes were performed on quartz substrates at room temperature for 60 min. The substrate was placed at a distance of 5 cm from the target. The laser output power was 200 mJ per pulse at a frequency of 5 Hz. The base pressure of the vacuum chamber was kept at lower than $3 \times 10^{-4}$ Pa in all deposition process. After deposition, the samples were thermal treated at 1000 °C in air for 10 min.

X-ray diffraction spectra of the samples were measured by Bruker D8 Advance X-ray Diffractometer (Cu Kα, $2\theta = 20$–$60^\circ$). Transmission spectra of the TiO₂ films were obtained by a Lambda UV-VIS spectrometer (UV-2500, Shimadzu, Japan) in the range of 326–1500 nm to study the optical absorption properties. X-ray photoelectron spectroscopy (XPS) measurements were carried out using a Kratos XSAM800 XPS system with Cu Kα source and a charge neutralizer. All the binding energies were referred to the C 1s peak at 284.6 eV of the surface adventitious carbon.

3. Results and Discussion

3.1. XRD analysis

Figure 1 shows the XRD spectra of the films without and with V, Ga doping, the peaks were identified by comparing them with JCPDS cards. Only one characteristic XRD peak at $2\theta = 27.3^\circ$ corresponding to (110) plane of rutile phase TiO₂ was detected. With the addition of V 1% and Ga 0.5%, the intensity of the (110) diffraction peak became sharper than that of the pure TiO₂ film, suggesting that the film with V and Ga co-doping experienced better crystallization. Other co-doped samples were also rutile TiO₂ and no sign of metal or oxides of Vanadium or Gallium was detected.

![Figure 1. XRD spectra of the pure and V1%-Ga0.5% co-doped TiO₂ films](image)

3.2. Absorption properties

Transmission spectra of the TiO₂ films were measured by UV-VIS spectrophotometer to study the optical absorption properties. The absorption coefficient $\alpha$ of the films was calculated as follows:

$$\alpha(\lambda)d = \ln[1/T(\lambda)]$$
where $d$ is the thickness of the thin film, and $T(\lambda)$ is the transmittance directly measured by UV-VIS spectrometer.

Figure 2 presents the optical absorption spectra of the pure and doped TiO$_2$ films. The linear dependence of $\alpha^2$ on the photon energy over an adequate energy range indicates that all these films have a direct band property, which is consistent with other reports about rutile TiO$_2$ [11]. The band gap of the co-doped rutile TiO$_2$ film can be estimated by extrapolating the linear part of the $\alpha^2$ versus photon energy curve to zero area as shown in figure 2. The band gap of pure rutile TiO$_2$ and the films with V 1% or Ga 0.5% solely doped is approximately 3.5 eV, while the V 1% and Ga 0.5% co-doped film has a forbidden band energy as small as 1.5eV as shown in figure 2a. The results reveal that V and Ga co-doping rather than sole V or Ga doping can alter the band gap of TiO$_2$ significantly. Figure 2b compares the $\alpha^2$-$h\nu$ curves of the co-doped V1%-Ga0.5% film with other diverse V and Ga contents (V 0.5% -Ga 0.5%, V 0.5% -Ga 1%, and V 1% - Ga1%). The band gap of the co-doped films with other V and Ga contents appears at around 3.5 eV. These results indicate that the content and proportion of V and Ga play a dominant role for narrowing the forbidden band gap of TiO$_2$.

![Figure 2](image.png)

(a) (b)

**Figure 2.** Dependence of $\alpha^2$ on photon energy for pure, V, Ga co-doped and solely doped TiO$_2$ thin films

### 3.3. XPS analysis

X-ray photoelectron spectroscopy was used to analyze the states of Ti and Ga on the surface of the as-obtained films. The peaks were determined by Gaussian fitting after a Shirley background subtraction. There are two sets of Ti core levels observed in the pure TiO$_2$ film as shown in figure 3a. One set locates at 458.9 and 464.6 eV, related to the Ti 2p$_{3/2}$ and Ti 2p$_{1/2}$ binding energies of Ti$^{4+}$ in TiO$_2$ [12]. The other set of core binding energies at 457.0 and 462.6 eV are assigned to Ti$^{3+}$ as reported in previous studies [13], showing that there are O vacancy in the film due to the oxygen deficient environment during deposition. The simultaneous Ti$^{4+}$ and Ti$^{3+}$ chemical states were observed in the V1%-Ga0.5% co-doped film in figure 3b. Figure 3c shows the corresponding Ga 2p$_{3/2}$ XPS spectrum. Two Ga 2p$_{3/2}$ peaks located at 1116.5 and 1118.8 eV corresponding to Ga$^{3+}$ and Ga$^{4+}$, respectively. There are about 80% Ga ions taking Ga$^{4+}$ state, which means that most of the Ga ions were doped at Ti$^{4+}$ sites rather than separated out to form Ga$_2$O$_3$. This is consistent with XRD result that no sign of Ga metal or oxide phase was observed due to the little content.
According to the previous report, V doping has an effect on the TiO₂ band narrowing, but 1% V can redshift the band edge for only 0.2 eV [9]. Combined with the above discussion, it is reasonable to attribute the large band narrowing effect to Ga ions doped at Ti⁴⁺ sites instead of oxygen vacancy observed in both pure and doped films or films doped solely by V.

4. Conclusion
Rutile TiO₂ thin films with and without V and Ga doping were obtained by the PLD method. The addition of V and Ga improved the crystallization of the TiO₂ film. V and Ga co-doping rather than V or Ga sole doping can induce significant reduction of the band gap of TiO₂, from 3.5eV to 1.5eV. XPS revealed Ti⁴⁺ and Ti³⁺ chemical states in both the pure and V-Ga co-doped films, showing that there are oxygen vacancies in the films due to the oxygen deficient environment during deposition. The dominance of the Ga⁴⁺ states indicates that Ga ions are doped at Ti⁴⁺ sites rather than separated out to form Ga₂O₃, which accounts for the band narrowing effect.

Acknowledgments
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