

Thermochromism of titanium–vanadium oxide thin films prepared from peroxotitanate and peroxovanadate solutions

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Abstract

Thin films of vanadium–titanium complex oxides were prepared on glass substrates from the mixture of peroxovanadate and peroxotitanate solutions by the spin coating method. Temperature dependence of the reflectance spectra for the thin films were investigated, and it was found that their reflectivities in the wavelength region from 700 to 1000 nm were reversibly increased over 45 °C. The changes in optical dielectric constants were estimated and discussed from a viewpoint of the practical applications as thermochromic smart windows.

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1. Introduction

Vanadium dioxide VO₂ exhibits a semiconductor-to-metal transition owing to a structural transformation from a monoclinic phase to a tetragonal rutile-type phase at $T_c=67$ °C [1]. This transition accompanies an abrupt change in optical properties, i. e., a significant increase in reflectivities in infrared region [2,3]. Much effort has been made to apply these optical properties to thermochromic smart windows which automatically shade the sunlight at high temperature.

A number of researchers have tried to lower the transition temperature T_c by doping another element. Doping tungsten or molybdenum in VO₂ reduces the T_c [4,5], and the switching performance of double-doped films in the V_{1-x-y}W_xMo_yO₂ and V_{1-x-y}W_xTi_yO₂ systems has been investigated [6]. Phase transitions of V_{1-x}Ti_xO₂ system have been also investigated using the conductivity and DTA measurements [7,8]. The optical switching properties have been reported using thin films deposited from alkoxides [9]. A wet process using solutions is suitable for fabricating thin films from the practical viewpoint, because it is easy to dope another element and to produce a

large-area thin film at a low cost. A vanadium–titanium solution process is highly desirable to achieve the smart window.

We have found a new nonstoichiometric orthorhombic titanium oxide (TiO_x, $x=1.85$ – 1.94) [10] and have investigated its thermochromic properties [11]. We have also reported the thermochromic properties of the solid pellet of vanadium–titanium oxide (V_{0.48}Ti_{0.52}O₂) [12]. The pellet of V_{0.48}Ti_{0.52}O₂ showed a reflectivity increase in the wavelength of 750–1000 nm above 45 °C. The goal of this study is to fabricate thin films of vanadium–titanium oxide through a solution process using peroxovanadate and peroxotitanate solutions and to evaluate their thermochromic properties.

2. Experimental

2.1. Preparation of solutions

Peroxotitanate solution was prepared by mixing metallic titanium powder (0.25 g) with the mixture of hydrogen peroxide solution (30 wt.% aq, 20 g), ammonia solution (28 wt.% aq, 5 g), and citric acid (0.25 g), according to the literature [13]. A transparent light yellow peroxotitanate solution (0.20 mol/kg of Ti) was obtained by a vigorous reaction between the metallic titanium and the hydrogen peroxide. The peroxo and citric

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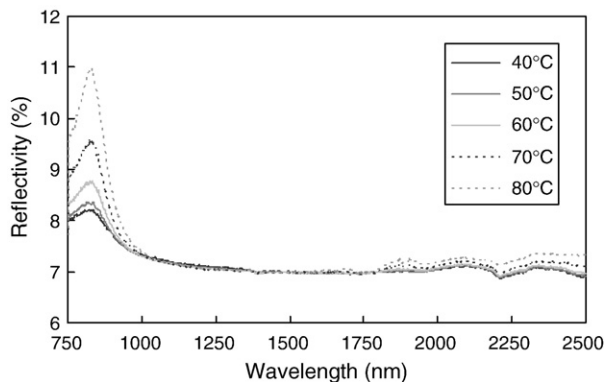


Fig. 1. Reflectance spectra for thin films having the composition of $V_{0.48}Ti_{0.52}O_2$ prepared from the mixture of peroxovanadate and peroxotitanate solutions. The reflectivity change was reversible.

groups are ligands of the titanium to form a stable complex ion, and the ammonium ion is a counter ion.

Peroxovanadate solution was prepared in a similar manner by mixing metallic vanadium powder (0.25 g), hydrogen peroxide solution (30 wt.% aq, 20 g), ammonia solution (28 wt.% aq, 5 g), and citric acid (0.25 g). This reaction yielded a transparent orange solution containing the complex ion of vanadium.

2.2. Fabrication of thin films

The mixture of the two solutions (peroxotitanate and peroxovanadate) was spin-coated on a soda-lime glass substrate at the spinning rate of 8000 rpm, and a thin film of precursor of $V_{1-x}Ti_xO_2$ was formed. In order to remove ligands, counter ion, and water, the film was heated in air at 400 °C for 2 h. Although in the synthetic procedure used in the earlier report, reduction in a hydrogen stream was essential to obtain VO_2 [6], hydrogen gas was unnecessary in our procedure to obtain thermochromic films. The composition of the thin film was estimated at $V_{0.48}Ti_{0.52}O_2$.

2.3. Measurement of thermochromic properties

The reflectance spectra in the wavelength range of 750–2500 nm were measured using a spectrophotometer (Ubest

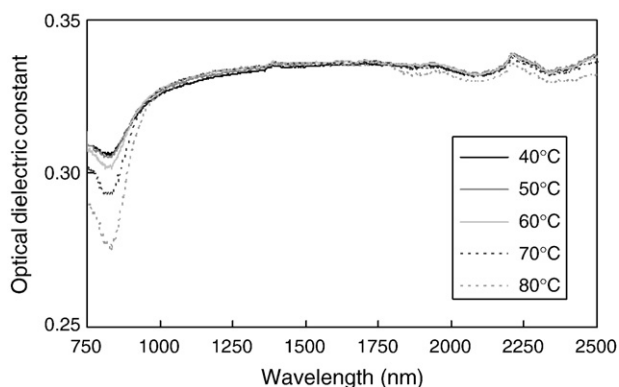


Fig. 2. Optical dielectric constant of the thin film estimated from the reflectivity.

V-570DS, JASCO corporation). The temperature of the sample was controlled by a rubber heater. The incident angle was 5°.

2.4. XPS measurement

XPS spectra were taken for two samples: the dry residue of the mixture of peroxotitanate and peroxovanadate solutions and its reduced form heated in hydrogen stream at 400 °C for 2 h. This measurement was performed to compare the valance states between before and after the hydrogen reduction, because the hydrogen reduction was found to be unnecessary for our sample.

3. Results and discussion

3.1. Thermochromism measurement

Fig. 1 shows reflectance spectra for thin film of vanadium–titanium oxide on a glass substrate heated in air at 400 °C for 2 h. Reversible reflectivity change was observed distinctly in the wavelength region of 700–1000 nm and slightly in the wavelength region of 1500–2500 nm. The reflectivity began to increase at 45 °C and ceased to increase around 80 °C. We found that the thin films having the composition of $V_{0.48}Ti_{0.52}O_2$ show reversible reflectivity increase above 45 °C. These properties have not been observed for the VO_2 samples, which show an abrupt increase in reflectivity at $T_c=67$ °C. The starting temperature at which the reflectivity began to increase is much lower than that of the VO_2 . It is important to note that the reflectivity increase of the present thin films was gradual unlike the VO_2 . These thermochromic properties of the thin films are similar to those of powder compact of the present vanadium–titanium oxides which we have already reported previously [13]. The reflectivity of the powder compact was changed in the range of 1.6–3.0%, whereas that of the thin

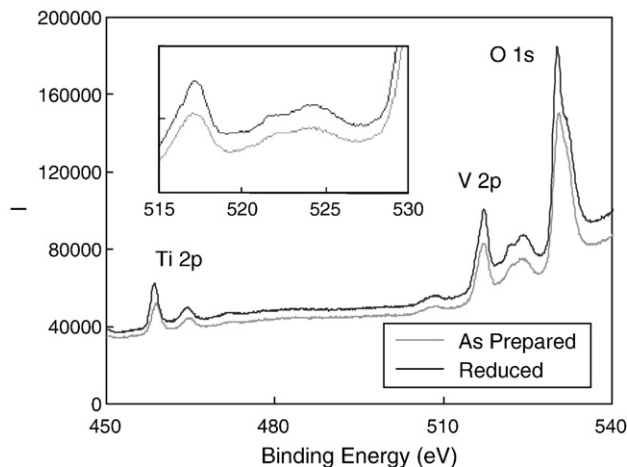


Fig. 3. XPS spectra (Ti 2p, V 2p, O 1 s) for the dry residue of the mixture of peroxotitanate and peroxovanadate solutions and its reduced form heated in hydrogen stream at 400 °C for 2 h. The inset is the magnified figure of the V 2p spectrum.

film was changed in the range of 8–11%. This is due to the difference of surface roughness between the powder compact and the thin films on glass substrate.

The change in optical dielectric constant of the thin film was estimated from the reflectance spectra observed using s-polarized light (Fig. 2). The result suggests that the reflectivity increase was attributed to the decrease in the dielectric constant. In our previous study, we have concluded from SEM and EDX observations that the present thermochromic property is owing to an amorphous vanadium–titanium oxide phase generated by the new method. The optical dielectric constant is considered to be changed due to a gradual structural change in the amorphous phase.

Thicker thin films were also fabricated by repeating a set of spin coating and drying. However, increasing the thickness of the thin films did not bring about an increase in reflectivity. The reflectivity is dependent on the optical dielectric constant, i.e., complex refractive index, $n+ik$. Strategy for increasing the change in n is required in order to enhance the reflectivity change.

3.2. XPS analysis

XPS spectra for the dry residue of the mixture of peroxotitanate and peroxovanadate solutions and its reduced form heated in hydrogen stream at 400 °C for 2 h are shown in Fig. 3. The V 2p peaks for the two samples were almost coincident with each other, indicating that the valence states of V for the two samples were the same. Vanadium in the dry residue was already tetravalent before the hydrogen reduction [14]. This is the reason why the present material shows the thermochromism without hydrogen reduction. The Ti 2p peaks slightly shifted to lower binding energy by 0.3 eV, suggesting only a slight reduction of Ti, since the reduction from Ti^{4+} to Ti^{3+} accompanies the decrease of binding energy by ca. 2 eV [15]. The O 1s peaks consist of OH^- and O^{2-} , and the peak intensity ratio of OH^-/O^{2-} was decreased from 1.30 to 1.00 by hydrogen reduction. This indicates the change from hydroxyl group ($-OH$) to terminal oxygen ($=O$) by heating. In the hydrogen reduction at 400 °C, the reduction only slightly occurred in Ti. As for the present dry residue, the valence states were almost

the same as those after the hydrogen reduction. This point is advantageous because the reduction using explosive hydrogen is unnecessary.

4. Conclusions

Thin films having the composition of $V_{0.48}Ti_{0.52}O_2$ was prepared through a wet process using peroxovanadate and peroxotitanate solutions. The reflectance spectra for the thin films showed a reversible reflectivity increase in the wavelength region of 700–1000 nm above 45 °C. The reflectivity change is attributable to the change in the optical dielectric constant, which is considered to be changed owing to a gradual structural change in the amorphous phase. The XPS spectra showed that the valence state of vanadium in the dry residue of mixture of the peroxovanadate and peroxotitanate solutions were tetravalent, same as that after hydrogen reduction at 400 °C for 2 h. This is the reason why hydrogen reduction is unnecessary for the present vanadium–titanium oxides to exhibit the thermochromism unlike the conventional vanadium oxide.

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