

Addition Effect of Rare-Earth (Pr, Nd, Sm, Dy) on Electrochromism of Vanadium Oxide Films

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V/M (Pr, Nd, Sm, Dy) oxide films were deposited onto ITO glass by vacuum evaporation. The effects of 25% rare earth addition on the electrochromism, the structure, and the optical properties of the vanadium oxide films were analyzed by in-situ UV-VIS-NIR spectroelectrochemical measurement, spectrofluorometric measurement, XRD, and cyclic voltammetry. The high transmittance and the small coloration efficiency of the V/M films suggested their utilization as a counter electrode in electrochromical (EC) devices. V/Sm and V/Dy oxide films, which were composed of MVO_4 (revealed by XRD), showed better cyclic reversibility, ionic conduction and electronic than other V/M oxide films. The different addition effects of Pr, Nd, Sm, Dy on the electrochromism, the structure, and the optical properties of the mixed oxide films were found to be closely related to the radius of M^{3+} .

Keywords: electrochromism, evaporation, film, rare earth, V_2O_5 .

1. INTRODUCTION

Vanadium oxide films have been widely investigated as the counter electrode of WO_3 in electrochromic devices. By now vanadium oxide films have been prepared by vacuum evaporation, sol-gel processes, sputtering and chemical vapor deposition. Vanadium oxide films prepared by above methods exhibit less reversibility than tungsten oxide films (beyond 1200 cycles), of which cyclic reversibility has been demonstrated through FT-IR by Macek and Orel [1]. Another drawback of vanadium oxide films is that they show mixed anodic/cathodic electrochromism because of the combined effects of band gap widening and appearance of a polaron absorption extending from the visual to near and mid-IR [2]. In order to solve these problems, researchers have attempted to minimize the near infrared coloration of reduced V_2O_5 films by adding dopants such as Ce [3]. The CeO_8 units in the formed $CeVO_4$ -W prevent direct kinematic coupling of different VO_4^{3-} ions in the D_{4h} unit consequently there is a negligible cathodic coloring in the VIS [3].

The rare-earth orthovanadates MVO_4 except for $LaVO_4$ have the same structure as $CeVO_4$ and are formed easily. In order to decrease the coloration of the V_2O_5 film and to improve the reversibility of the V_2O_5 film, Pr^{3+} , Nd^{3+} , Sm^{3+} and Dy^{3+} were added into the V_2O_5 film. Another aim of this paper is to identify the relationship between the addition effects and the radius of M^{3+} . The analyses about the electrochromism, the structure, and the optical properties of these films were carried out by in-situ spectroelectrochemical measurement,

cyclic voltammetry, spectrofluorometric measurement, XRD and cyclic voltammetry.

2. EXPERIMENTAL

High purity V_2O_5 powder was mixed with Pr_2O_3 , Nd_2O_3 , Sm_2O_3 and Dy_2O_3 powders respectively with the V/M molar ratio of 1:0.25. Then they were heated at $900^\circ C$ for two hours. After being grinded they were evaporated onto the ITO (Indium Tin Oxide) glass substrates. The vacuum in chamber was maintained at 5×10^{-4} Torr during the evaporation. The films were annealed in a controlled furnace at $400^\circ C$ for 0.5h and 2h. As references, V_2O_5 , Pr_2O_3 , Nd_2O_3 , Sm_2O_3 and Dy_2O_3 films were prepared in the same way.

The composition of the films was analyzed by EDX and ICP. The thickness and the surface morphology of the films were observed by SEM. Voltametric cycling was performed at the voltages between $-2.0V$ and $+2.0V$ relative to Ag/AgCl with a sweep rate of $200 mV/s$. The in-situ spectroelectrochemical measurements were carried out using a three-electrode cell with two Pt counter and reference electrode installed in a compartment of scanning spectrophotometer (Shimadzu RF-5300PC). The spectral region used in this work was 300-1050 nm. The microstructures of the films were determined by XRD. The photoluminescence spectra were recorded by UV-VIS-NIR spectrofluorophotometer (Shimadzu UV-3100PC) at the wavelength range of 300-650 nm.

3. RESULTS AND DISCUSSION

According to the result of SEM and EDX of the surface of the V/M oxide films, it was verified that uniform V/Pr, V/Nd, V/Sm and V/Dy oxide films were synthesized by vacuum evaporation. The ICP result showed that the molar ratio of V to M was about 1:0.25. The as evaporated films were brown, but became yellow-green after being heated at 400 °C. The same color change has been observed in vacuum-evaporated vanadium oxide film. The absorption spectra of those as-evaporated films showed a large amount of V^{3+} , being oxidized into V^{4+} and V^{5+} after heating at 400 °C.

Fig. 1 shows XRD pattern of V/M oxide films, which were evaporated in three steps (thickness about 700nm). The XRD pattern of V/Pr oxide film revealed formation of V_5O_9 ; the V/Nd oxide film, V_6O_{11} ; the V/Sm oxide film, $SmVO_4$; the V/Dy oxide films, $DyVO_4$. Comparing the lattice constant of these crystals with the radii of Pr^{3+} , Nd^{3+} , Sm^{3+} and Dy^{3+} , it was found that the lattice constant became smaller with the radius of M^{3+} (Fig. 2), and the smaller M^{3+} ions enable the formation of MVO_4 . The relationship between the ionic radius and lattice constant is shown in Fig. 2.

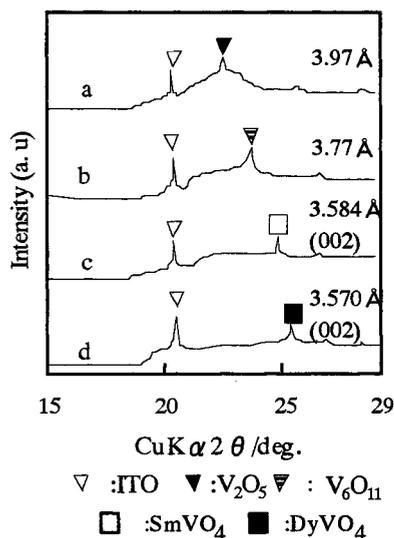


Fig. 1 The XRD pattern of V/M oxide films (a: V/Pr; b: V/Nd; c: V/Sm; d: V/Dy) heated at 400 °C for 2h (thickness about 700 nm).

The UV-VIS-NIR spectra of V/M oxide films and V oxide film heated at 400 °C are shown in Fig. 3. V/M oxide films were observed to have weak absorption in VIS and NIR, which are similar to the V oxide film. These absorptions of V/M oxide film can be attributed to the absorption of V oxides. The relationship between the addition effect and the ionic radius were also found here, the absorption peaks of V/M oxide films in the visual and near infrared

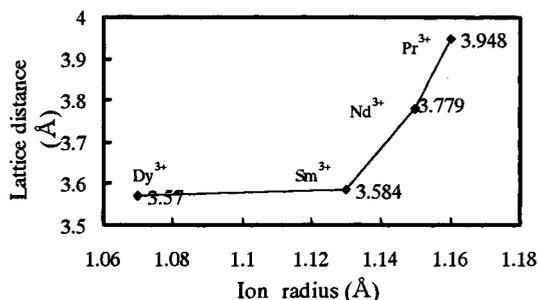


Fig. 2 The relationship between the lattice constant of crystal in V/M oxide films and the ionic radius of M^{3+} .

were observed to shift to the short wave with the increasing of the ionic radius of M^{3+} . This result agrees with that of XRD. The relationship between the wavelength and the ionic radius is illustrated in Fig. 3.

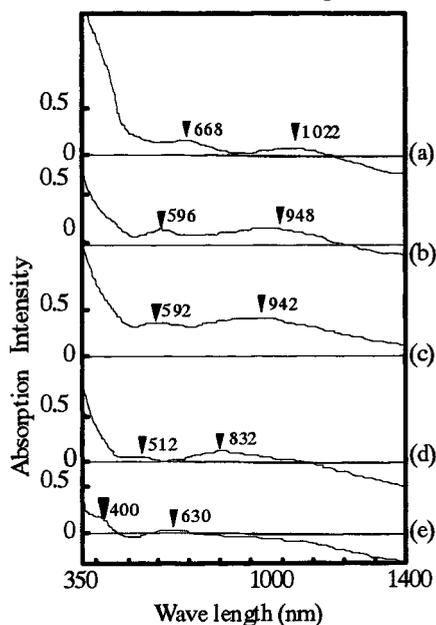


Fig. 3 The absorption spectra of the vacuum evaporated oxide films (a: V, b: V/Pr, c: V/Nd, d: V/Sm, e: V/Dy) heated at 400°C for 0.5h.

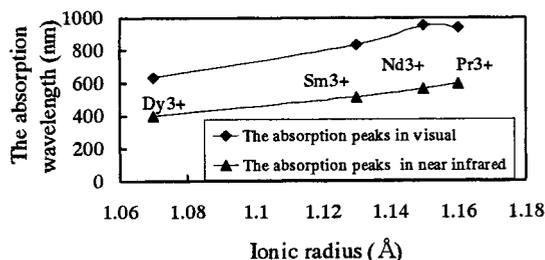


Fig. 4 The relationship between the absorption wavelength of V/M oxide films and the ionic radius of M^{3+} .

In-site spectroelectrochemical measurements

showed that the transmittance (T) (75% -90%) of V/M oxide films is much higher compared to that of V_2O_5 film in the range of 500 -1050 nm. The color of V/Pr, V/Nd, V/Dy oxide films show yellow-green in the cathodic state and black-green in the anodic state, which corresponds to the V_2O_5 film. The color of the V/Sm oxide film changes from yellow-green in the cathodic state to red-brown in the anodic state. The V/Sm oxide film may be expected being used as the electrochromical film for its special cathodic coloration. Coloration efficiency (CE) is defined as $CE = (.D/Q) = \log(T_b/T_c)/Q$, where b: bleached, c: colored. The CE of V/M oxide films in the range of 500-1050 nm are shown in Table I. The CEs of V/M oxide films (0.6-4.5) were almost two times smaller than that of V_2O_5 film. It could be considered that as the counter electrode in EC device, the V/M oxide films are comfortable than V oxide film.

Table I The coloration efficiencies of V/M oxide films in the range of 500-1050 nm

Film	V	V/Pr	V/Nd	V/Sm	V/Dy
CE (cm ² /C)	9	4.2	1.1	0.6	3.4

The cyclic voltammogram of M_2O_3 films indicated little ionic and electronic conduction in PC solution. The CV curves of the V/M oxide films were observed to be similar to that of the V_2O_5 film. This suggests that redox processes just occurred in the same manner as V oxide film. V/Sm and V/Dy oxide films exhibited better ionic and electronic conduction and reversibility than V/Pr and V/Nd oxide films. This might be contributed to the formation of $SmVO_4$ and $DyVO_4$. The Fig. 6 showed the CV curves of V, V/Sm and V/Dy oxide films. It can be found that ionic and electronic conductivities of V/Sm and V/Dy oxide films may be less than V oxide films, but the reversibility of formers than that of V oxide film.

The photoluminescence of V and V/M oxide films were measured. The as-evaporated films did not show any peaks. The films heated at 400°C for 2h showed photoluminescence peaks near 520 nm except for V/Sm oxide film (Fig. 6). It was also found that the photoluminescence peaks of V/M oxide films shifted to shorter wavelengths, and the intensities became weaker with decreasing ionic radius of M^{3+} . Because only a low amount of M^{3+} was added, the peaks near 520 nm in V/M oxide films were considered to

belong to $V=O$ which have been reported by M. Anpo *et al.* [4]. The addition effect on the $V=O$ bonding were considered to increase with decreasing ionic radius. In the V/Sm oxide spectra, a new peak appeared at 490 nm. The peaks near 470 nm were testified to attribute to the installation.

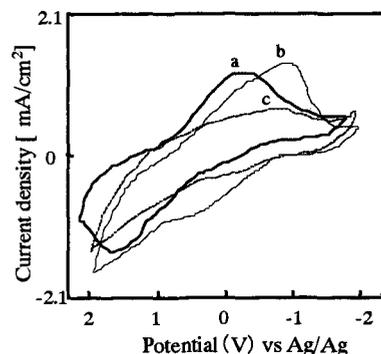


Fig. 5 Cyclic voltammogram curves for the oxide films (a: V cycled 10 times; b: V/Dy cycled 140 times; c: V/Sm cycled 70 times) heated at 400°C for 0.5h (thickness about 700 nm).

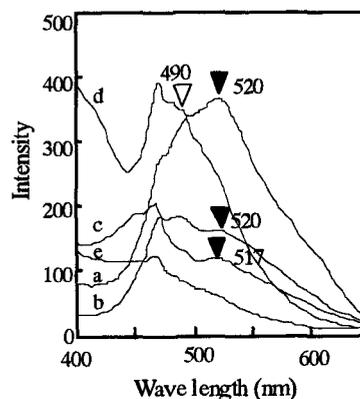


Fig. 6 The luminescence spectra of V/M oxide films (a: V, b: V/Pr; c: V/Nd; d: V/Sm; e: V/Dy) heated at 400°C for 2h (thickness about 700 nm).

4. CONCLUSION

The V/M (Pr, Nd, Sm and Dy) oxide films were successfully prepared by vacuum evaporation. It can be concluded that:

1. The V/M oxide films showed higher optical transmittance and smaller coloration efficiency suggesting their utilization as counter electrodes in electrochromical (EC) devices.
2. The formation of MVO_4 in the V/M oxide film corresponded to improve ionic and electronic conductivities and reversibility.
3. The lattice constant of the V/M oxide films became smaller with the increasing of

- ionic radius of M^{3+} ;
4. The absorption peak of the V/M oxide film in the visual and the near infrared were found to shift to the longer wavelengths with increase of ionic radius of M^{3+} .
 5. The photoluminescence peaks shift to shorter wavelengths, and the intensities become weaker with decreasing ionic radius of M^{3+} .

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