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Multiple-mode Responsive Device. Photo- and Electro-Chromic Composit Thin Film of Tungsten Oxide with Titanium Oxide

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Optically transparent thin film of tungsten oxide and its composit film with titanium oxide, prepared on the glass plates by repeated dip-coating method, exhibited dual ability of photo- and electro-chromism in an aqueous formic acid solution.

In order to design highly functionalized display and memory device, the thin film which responds to multiple types of stimulation, such as photoirradiation or potential change, is one of the most useful materials. Metal oxides have generally long-term durability under the usual atmospheric conditions. Among them tungsten oxide and titanium oxide are known as an electrochromic[1] material and a photoresponsive[2] material, respectively. Photochromic ability may arise from the combination of an electrochromic material with a semiconductor, as exhibited previously.[3] This paper describes the photo- and electro-chromism of composit thin films of the thermally and chemically stable metal oxides, tungsten and titanium oxides, deposited on glass plates.

Tungsten hexaethoxide ($W(OEt)_6$) was prepared by refluxing the benzene solution of tungsten hexachloride with sodium ethoxide for 6 h followed by centrifugation to remove sodium chloride and evaporation.[4] Indium tin oxide (ITO) deposited glass (9.5 mm × 50 mm, 20 Ω/□) was supplied from Yoneda Garasu Kogei Co. Ltd. To the ethanol solution of $W(OEt)_6$ or titanium tetra-2-propoxide (Wako Pure Chemicals Co. Ltd.) was dipped the ITO glass at the rate of 1 mm s^{-1} and calcined in air for 10 min.[5] Change in optical density of the prepared thin film being immersed in a rectangular quartz cell (10 mm), together with Ag/AgCl reference and counter electrodes, was measured under Ar atmosphere with a Shimadzu MPS-2000 spectrophotometer equipped with a Xe-lamp cross-illumination apparatus and a Hokuto HA-301 potentiostat/galvanostat. An aqueous solution of formic acid (9 mol dm^{-3}) was used as electrolyte.[6]

The prepared tungsten oxide film and its composit film with titanium oxide were apparently transparent and slightly colored due to the optical interference. From the X-ray diffraction (XRD) pattern (Rigaku Geigerflex 2013 ($Cu\text{-}K_\alpha$), Fig. 1), it is revealed that the tungsten oxide layer calcined at below 673 K is amorphous, and that at above 673 K is in crystalline structure. The XRD patterns of these crystalline tungsten oxides did not coincide with those of previously reported tungsten oxides and their hydrates.[7] Similar unusual XRD patterns were observed by Tada and coworkers in the preparation of tungsten oxide thin film

from potassium tungstate and oxalic acid.[8] The titanium oxide films prepared at below 673 K were amorphous, and those at 773 K and 873 K contained crystallites. Because of the resemblance of XRD patterns of anatase and brookite, the form of these crystallites could not be determined. The effect of such thermal treatment of titanium oxide films has been reported.[5,9]

The tungsten oxide film exhibited electrochromism (between blue and colorless) as shown in Fig. 2; optical density in the wavelength region of visible and near infra-red was increased to be ca. 1 by applying negative

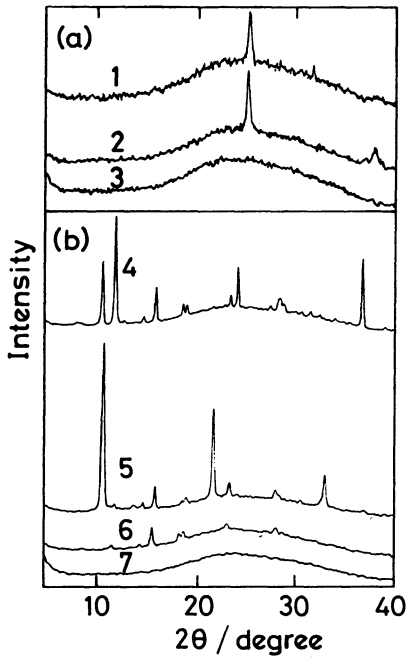

Fig. 1. X-Ray Diffraction patterns of (a) titanium oxide and (b) tungsten oxide films calcined at 873 K (1, 4), 773 K (2, 5), 723 K (6), and below 673 K (3, 7).

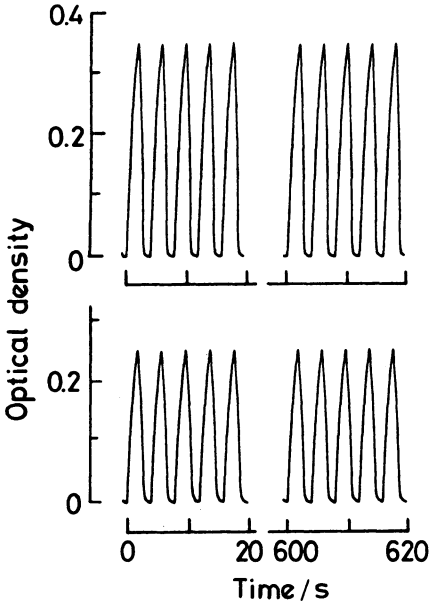

Fig. 3. Change in optical density of (a) tungsten oxide film (run 1 in Table 1) and (b) composit film of titanium oxide with tungsten oxide (run 6) by rectangular wave (0.25 Hz, +1.5 — -1.0 V).

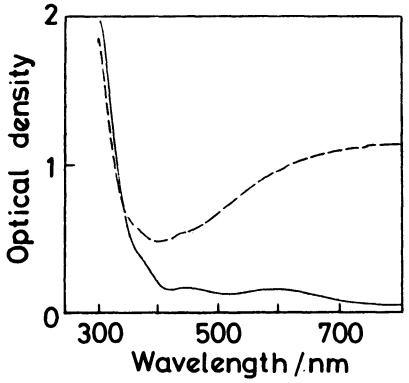

Fig. 2. Absorption spectra of tungsten oxide films calcined at 473 K. Dashed line shows the spectrum of film colored by applying cathodic potential.

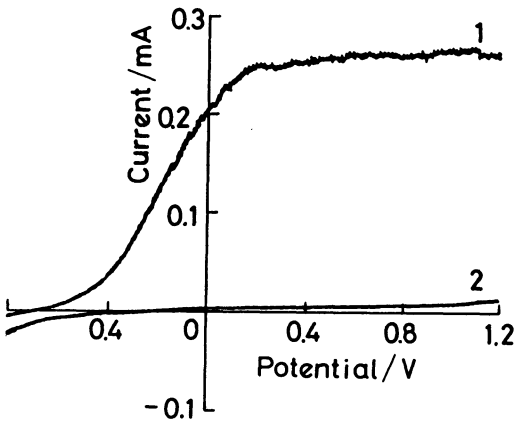

Fig. 4. Potential-current curves of titanium oxide film (1) on irradiation and (2) in the dark.

potential, and decreased to be ca. 0 by positive potential. As shown in Fig. 3, the electrochromism was apparently reversible; no difference in the pattern of optical density change at 800 nm could be observed after 150 cycles of the coloration-bleaching.

Table 1 summarizes the result on the chromism of tungsten oxide alone and tungsten-titanium oxides composit films. The chromic ability was evaluated as a rate of change in optical density by the potential step from +1.5 V to -1.0 V or by the photoirradiation at 320 nm. It is clear from this table that the amorphous tungsten oxide (calcined at 473 K) showed markedly higher ability of electrochromism than the crystalline analogue (773 K). The tungsten oxide film immersed in an aqueous solution of formic acid also turned blue when irradiated by monochromatic light at 320 nm and turned back colorless by applying the potential at +1.5 V.[1] The rate of this photoinduced change in optical density is also collected in Table 1. The photochromic ability of tungsten oxide film seems to be poor, though it was improved by the crystallization at higher calcination temperatures. In this relation, negligible photocurrent through the tungsten oxide film was observed when irradiated at > 300 nm with a 200-W high-pressure mercury arc at a given potential of -0.4 – +1.2 V, suggesting the existence of recombination centers for electron - hole pairs in the tungsten oxide film.

As shown in Fig. 4, photoinduced anodic current which is characteristic of an n-type semiconductor was observed with the titanium oxide film electrode (calcined at 773 K). Similar results have been reported by Yokoo and co-workers.[5] Although the titanium oxide film itself showed neither electro- nor photo-chromism, the composit film of titanium oxide with tungsten oxide showed the electrochromic ability comparable to the tungsten oxide film (Table 1). The ability also markedly depended on the calcination temperature; the rate of optical change in the film obtained by the 473 K calcination (run 3) was > 30 times faster than that at 773 K (run 4). This difference is attributable to the

Table 1. Electro- and Photo-Chromic Properties of Oxide Films

Run	Composition[a]	Temp[b]/K	Thickness/nm	Rate of OD change[c]		
				by Potential step[d] /ΔOD s^{-1}		by Photoirrad.[e] /ΔOD h^{-1}
				Color[f]	Bleach[g]	Color[f]
1	ITO/W	473	41	0.17	0.25	0.012
2	ITO/W	773	63	0.005	0.001	0.039
3	ITO/W/T	473	92	0.14	0.25	0.036
4	ITO/W/T	773	114	0.003	<0.001	0.318
5	ITO/W/T	473/773	——[h]	0.06	0.016	——[h]
6	ITO/T/W	773/473	——[h]	0.08	0.13	0.114

a)W and T refer tungsten oxide and titanium oxide, respectively. b)Calcination temperature. c)Change in optical density at 800 nm. d)Applied potential: +1.5 – -1.0 V vs. Ag/AgCl. e)Monochromatic light at 320 nm from a 500-W Xe lamp. f)Coloration. g)Bleaching. h)Not measured.

structure of tungsten oxide, whether amorphous or crystal. On the other hand, there is a trend that the higher-temperature calcination gives higher photochromic ability to the composit film, presumably owing to the change in photosensitivity of titanium oxide rather than tungsten oxide. Reduction of tungsten oxide by the photogenerated electron of titanium oxide is most likely for the appearance of the photochromism; the simultaneously generated positive hole would oxidize formic acid to CO_2.[6)]

On the basis of these results, the combination of crystalline titanium oxide and amorphous tungsten oxide is promising for the design of dual ability of photo- and electro-chromism. For such a purpose, the composit film was prepared by successive depositions of titanium oxide layer at 773 K and tungsten oxide layer at 473 K to prevent the higher-temperature treatment of tungsten oxide.[10)] The prepared composit film remained about 50% of electrochromic ability of the tungsten oxide film and, furthermore, about 10 times enhanced photochromic ability (Table 1). This composit film also showed the high reproducibility in coloration-bleaching cycles (Fig. 3).

In conclusion, we have shown that amorphous tungsten oxide film shows sufficient electrochromic ability with high reproducibility, and that the combination with titanium oxide film enhances the photochromic ability. Although we have at present no mechanistic details on coloration and bleaching, these results provide novel trends of functionalization of metal oxides.

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10) If the suitable preparation is possible, the composit film of ITO/W/T is rather promising because the titanium oxide, an n-type semiconductor, works as an photoanode which oxidize formic acid on the outer surface.

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