Electrochromism of Niobium Oxide Thin Films Prepared by the Sol-Gel Process

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ABSTRACT

Thin layers of niobium oxide (NbO_x) were accumulated by the sol-gel process, with the sol of NbO_x in ethanol prepared by partial hydrolysis of commercial niobium(V) ethoxide on glass plates coated with transparent conducting tin oxide. Characterization by x-ray diffraction, differential thermal analysis, and thermogravimetry revealed that the as-prepared film, consisting of fully hydrated amorphous niobium oxide, undergoes dehydration into the partially hydrated form and, finally, crystalline niobium(V) oxide (Nb_2O_5) by calcination at the temperature up to 873 K. The films exhibited electrochromic (EC) properties; the reversible color change was observed between colorless and brown-black by alternating anodic and cathodic polarizations, respectively. Among the films used in this study the crystalline Nb_2O_5 film showed the best EC properties and its spectral change, durability for repeated coloration-decoloration cycles, and retentivity of colored states, i.e., memory characteristics under open-circuit conditions were investigated in detail.

Transition metal oxides, e.g., oxides of tungsten (WO_3), molybdenum (MoO_3), and vanadium (V_2O_5) have been extensively investigated as electrochromic devices in the form of a thin film adhering to a conducting substrate. Among them, niobium oxide (Nb_2O_5) is also expected to show electrochromism, and several studies on Nb_2O_5 thin films prepared by thermal oxidation, anodization, sputtering, vacuum evaporation, and the sol-gel process have been reported. Previous work in this laboratory has shown electrochemical properties of WO_3, iron(III) oxide (Fe_2O_3), and titanium(IV) oxide (TiO_2) films prepared by sol-gel process. In comparison with the sputtering or vacuum evaporation technique, the sol-gel process is of advantage for preparation without using specialized instruments such as a vacuum chamber. The preparation of Nb_2O_5 thin film by thermal oxidation and anodization requires the niobium metal plates of desired size and shape of devices. This might be a limitation to these preparation processes, however, the sol-gel process has no such limitation; it is possible essentially to produce the film on the given substrate material in any size and shape. This paper deals with the preparation of Nb_2O_5 thin films by the sol-gel process and the characterization of their properties by x-ray diffraction (XRD), differential thermal analysis (DTA), and thermogravimetry (TG). Their electrochemical (EC) properties are discussed and correlated with the structure.

Experimental

Sol of NbO_x was prepared by partial hydrolysis of niobium(V) ethoxide [Nb(OEt)_5] (Kanto Chemicals) with concentrated hydrochloric acid (HCl); Wako Pure Chemical Industries. Griesmar and co-workers have reported the preparation of clear sol and molliphilic gel of NbO_x by the hydrolysis of niobium(V) pentoxide [Nb(OEt)_5] in the presence of acetic acid. As shown below, however, the addition of HCl also enables the preparation of clear NbO_x sol. A portion of Nb(OEt) (0.036 moles) was dissolved in ethanol (Wako, 99.5%), water (0.4%); 1.7 moles) at room temperature and cooled to 273.5 K in an ice bath. To the solution was slowly added under stirring a mixture of ethanol (0.98 mol) and HCl (0.036 mol). Additional stirring overnight at room temperature led to a slightly yellow clear sol containing 0.21 mol dm^-3 of NbO_x. Glass substrates coated with transparent conducting tin oxide (NESA; 22.3 Ω/sq) were supplied from Nippon Sheet Glass Company Limited in a cleaned state and used just after removal of dust by the blowing of dry air. The plates were dipped in and drawn from the NbO_x sol at a constant rate of 0.6 mm s^-1. After gelation at room temperature for 10 min, the coated substrates were calcined at 423 K for 5 min in an electric furnace. Further calcination at the higher temperature (T_c) was performed for 2 h for every ten-layer accumulation. Hereafter, the entry of NbO_x films is made with the number of the layer and T_c, e.g., 20/733 refers to the film consisting of 20 layers calcined at 733 K.

Electrochemical measurements were performed with an HA-301 potentiostat/galvanostat; an HB-104 function generator, and an HF-202D coulometer (Hokuto Denko). A Pyrex cell with flanges in opposite sides was used. An NbO_x-coated substrate and a Pyrex glass plate were fixed on the flanges in parallel each other with fluorinated rubber (Viton) gaskets. Through these two parallel plates passed the light beam for optical absorption measurements (a Shimadzu UV-2005 spectrophotometer). A plane platinum counterelectrode and an Ag/AgCl reference electrode were fixed in the positions outside the light beam. Electrolyte solutions, 1.0 or 9.0 mol dm^-3 aqueous formic acid solution or 0.5 mol dm^-3 sulfuric acid in the cell were deaerated by bubbling nitrogen for at least 20 min before and during the measurements.

X-ray diffraction patterns of NbO_x films on NESA glass substrate were recorded on a Mac Science MXP18 diffrac-
Results and Discussion

Figure 1 shows parts of XRD patterns of NbO$_x$ films (a) and powders (b) prepared by the gelation of Nb$_2$O$_5$ sol and subsequent heat-treatment. Only less intense peaks corresponding to the NESA layer (20; 27.0, 38.0, 52.0 deg) appeared in the pattern of films calcined at $<733$ K, suggesting their amorphous structure. Similar amorphous structure was observed in the case of powder. Heat-treatment at higher temperatures ($\geq733$ K) led to the crystallization of Nb$_2$O$_5$, as seen for both films and powders; intense peaks (20; 22.5, 28.0, 37.0 deg) are assigned to Nb$_2$O$_5$ crystallites. The relatively smaller intensity of the powder at 733 K may be due to the shorter duration (5 min) of heat-treatment during the in situ XRD measurement compared with that for films (2 h). Calcination at elevated temperature (773 to 873 K) reduced the intensity of Nb$_2$O$_5$ peaks for the film, while it enhanced them for powder; peaks (29; 46.0, 50.0, 55.0 deg) newly appeared. These facts suggest the partial decomposition of NESA layer occurring at the higher temperature. Thus, the Nb$_2$O$_5$ layer obtained by calcination at the lower temperature consists of amorphous oxide, and of crystalline Nb$_2$O$_5$ at the higher ($\geq733$ K) temperature.

Such a structural change was followed by TG and DTA of Nb$_2$O$_5$ powders (Fig. 2). On heating up to 850 K, the weight of the powdered Nb$_2$O$_5$ sample decreased to ca. 81% of the original (a), accompanied by a significant endothermic DTA peak with the maximum at ca. 400 K. The weight loss due to the elimination of water is most plausible. Subsequent heating up to 700 K induced negligible change in the weight of sample, suggesting the metastable structure of Nb$_2$O$_5$ in this temperature region (b). Further weight decrease was observed at around 750 K. Characteristic exothermic peak appeared at 780 K. Neither change in weight nor DTA shift was observed at the temperature region higher than 800 K (c). The total weight loss during the heating from room temperature to 1273 K was 24%. On the assumptions that NbO$_x$ consists of Nb$_2$O$_5$ and that only the dehydration causes the weight loss, the composition of Nb$_2$O$_5$ ($\cdot$5H$_2$O or [Nb(OH)$_5$]) and of Nb$_2$O$_5$ ($\cdot$H$_2$O or Nb$_2$O$_5$(OH)) account for the results in TG. At present we have no experimental results to distinguish the hydrated oxides (Nb$_2$O$_5$ ($\cdot$5H$_2$O and Nb$_2$O$_5$ ($\cdot$H$_2$O) from the hydroxides [Nb(OH)$_5$] and Nb$_2$O$_5$(OH)). The Nb$_2$O$_5$ gel prepared from Nb(OEt)$_4$ showed a similar, but somewhat shifted (to higher temperature), DTA curve. However, the above-mentioned double-step TG curve is a unique characteristic of Nb$_2$O$_5$ sol from Nb(OEt)$_4$; sharp decrease in weight could be seen between 473 and 523 K for the gel from Nb(OEt)$_4$.

On the basis of the results of XRD, TG, and DTA, the structure of Nb$_2$O$_5$ could be described as follows. The as-prepared gel (a) in a fully hydrated amorphous phase is dehydrated by the calcination at lower than 550 K into a metastable amorphous phase of partly hydrated oxide. Further dehydration into crystalline Nb$_2$O$_5$ proceeds at temperature higher than 700 K. The exothermic peak in DTA at 780 K may correspond to the accompanying amorphous-crystal transition.

The Nb$_2$O$_5$ films were almost colorless and transparent. An example is shown in Fig. 3. This spectrum was recorded in transmission mode, not in reflection mode, and therefore included the concurrent absorption by a NESA glass substrate. The undulations seen in a whole range of spectrum are the interference pattern due to reflections of the front and back surfaces of the film. Difference in such optical characteristics due to the calcination temperature was not so marked. The films exhibited negligible change in these ultraviolet and visible range spectra by the contact with an aqueous formic acid solution (9.0 mol dm$^{-3}$).

Cathodic polarization in acidic electrolyte induced the change in color. The Nb$_2$O$_5$ film turned brown or black and was bleached readily by anodic polarization. As Fig. 3 shows, an almost constant increase in absorption by cathodic polarization was observed in visible to the near infrared region. Thus, the thin films of Nb$_2$O$_5$ exhibited the EC activity. Early studies suggested that electrochromism of Nb$_2$O$_5$ is based on simultaneous injection of cations (proton, H$^+$) and electrons, thereby reversible change occurs between Nb$_2$O$_5$ and H$_2$NbO$_4$. Although the color blue in the reduced form was reported previously, a somewhat different result was obtained in the present experiments. These facts might suggest a different morphology of Nb$_2$O$_5$ films related with the method of preparation.

Although the Nb$_2$O$_5$ film exhibited the above EC properties, unrelated with $T_c$, the degree of coloration under given conditions of cathodic polarization depended considerably on $T_c$ as shown in Fig. 4. The change in absorbance ($\Delta$OD) by the cathodic polarization was monitored at 700 nm and plotted against $T_c$. The as-prepared film ($T_c$ = 425 K) showed larger $\Delta$OD, which was reduced by elevating $T_c$ up to 700 K. At $T_c > 700$ K, $\Delta$OD was drastically enhanced to attain its maximum at 733 K, and gradually decreased by the further calcination at higher $T_c$. In several experiments of different potentials of cathodic polarization, similar dependences

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Fig. 3. Absorption spectra of Nb$_2$O$_5$-coated NESA glass (20/733) immersed in an aqueous formic acid solution (1.0 mol dm$^{-3}$), (a) before and (b) after polarization at $-0.9$ V.
were observed (Fig. 4). Comparison of these Tc dependents with the presumed structure of NbOx indicates that the fully hydrated amorphous oxide (a) showed relatively higher EC property and it was reduced by dehydration into partly hydrated form (b). Further dehydration and crystalization (c) enhanced the EC property markedly. The lower EC property of the (b) state, assigned to be Nb205-9H2O, should be correlated with its poor electronic and ionic conductivity.8

Figure 5 shows the variations of ΔOD, current, and potential as a function of time during the repeated potential stepping at intervals of 20 s between -0.6 and +1.0 V. Reversible change in ΔOD was observed, and its maximum was kept almost constant during a few tenths of cycles. A relatively large cathodic current, which induces the coloration, was seen just after the step of potential to -0.6 V and gradually decreased. Appreciable residual cathodic current flowed even at 20 s after the cathodic step. On the contrary, the decay of anodic current was rather sharp; both ΔOD and current became negligible within 5 s. This behavior of cathodic and anodic currents seems to depend on neither the potential nor the concentration and kind of electrolytes (data not shown). Figure 6 shows relationship between ΔOD and passed charge, the latter of which was calculated by integration of the current profile, for both cathodic (coloration) and anodic (bleaching) processes. The linear relation for both processes at various cathodic potential clearly shows that the EC property of the present NbOx films is attributed to a unique reversible electrochemical reaction. From the slope of the linear plot, ΔOD per unit charge density, corresponding to efficiency of coloring, is estimated to be 38 C⁻¹ cm² (at 700 nm). This coulombic efficiency is superior to that reported for Nb2O5 thin film via the sol-gel process (6 C⁻¹ cm² at 800 nm) and sputtering (<10 C⁻¹ cm²).15 However, the efficiency is ca. four times smaller than that for a WO3 film prepared by sol-gel process (167 C⁻¹ cm² at 800 nm).17 Stability of NbOx films was studied in prolonged periods as shown in Fig. 7. In these experiments, the duration of anodic potential (+1.0 V) step was expanded to 180 s to bleach completely. In the experiment with the duration of a given cathodic potential (-1.2 V) for 40 s, the maximum ΔOD after the 104th cycle was considerably decreased.
interpreted without the flow of the current through the electrode. Such tool dm\(^{-3}\) lithium fluoroborate was also unsuccessful for ing cathodic potential which determines the rate of col-

ter in the film. In this relation, Mohapatra reported that durability under 40 s duration is inferior to that under 20 s duration, as described above. The faster the cathodic coloring, the faster the

color bleached; the decrease in ΔOD of NbO\(_2\) film colored at the potential of −0.8 V was negligibly small. On the assumption that the EC properties of NbO\(_2\) in the present study are also based on the reversible electrochemical reaction between NbO\(_2\) and H\(_2\)NbO\(_4\), the spontaneous bleaching under open-circuit conditions should be caused by the oxidation of H\(_2\)NbO\(_4\). The reason for its dependence on the preceding cathodic potential is unknown at present. However, it is possible to assume that difference in distribution, i.e., depth profile of reduced moiety (H\(_2\)NbO\(_4\)), depending on the cathodic potential, gives considerable influence on the oxidation of H\(_2\)NbO\(_4\). Research along this line is now in progress.

**Conclusion**

Thin film of NbO\(_2\) was prepared on NESAA glass substrates by the sol–gel process. The optimum EC properties were obtained for the film consisting of crystalline NbO\(_2\). Its stability in repeated polarization cycles depended on the cathodic polarization time. The NbO\(_2\) films prepared by the sol–gel process in this work have higher coulombic efficiency than the other NbO\(_2\) films in previous reports. However, the spontaneous bleaching proceeds under open-circuit conditions. Clarification of the reason for this poor memory characteristic and improvements are necessary for the practical use of this NbO\(_2\) film as the electrochromic material.

**Acknowledgment**

The authors indebted to Mr. Masaya Chigane (Osaka Mun-

cipal Technical Research Institute) for his cooperation in XRD measurements. Dr. Hiroaki Tada (Nippon Sheet Glass Co. Ltd.) is greatly acknowledged for the supply of NESAA glass substrates.

Manuscript submitted Nov. 29, 1993; revised manuscript received May 2, 1994.

Kyoto University assisted in meeting the publication costs of this article.

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Fig. 8. Memory characteristics of 30/733 film immersed in (a) 1.0 mol dm\(^{-3}\) aqueous formic acid and (b) 0.1 mol dm\(^{-3}\) acetonitrile solution of lithium fluoroborate. In the experiment in acetonitrile electrolyte (a), the film was cathodically polarized (solid lines) to attain ΔOD 0.4, and the circuit was opened (dashed lines).