Electrochromic properties of niobium oxide thin films prepared by radio-frequency magnetron sputtering method

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Electrochromic niobium oxide thin films were prepared by a radio-frequency magnetron sputtering method. Amorphous Nb_2O_5 thin films deposited at radio-frequency power 100 W showed the electrochromic behavior: Reduction and oxidation of the films in 0.1 M Na_2CO_3+0.1 M $NaHCO_3$ buffer solution resulted in coloration and bleaching, respectively. Coulometry indicated that the coloration efficiency was 10 cm^2/C.

One of the group *V-B* oxide, niobium oxide (Nb_2O_5), exhibits electrochromism like that of tungsten oxide WO_3. The electrochromic niobium oxide films were electrochemically formed by an anodic oxide growth on a niobium electrode.[1] However, little work has been performed on this system to qualify it for thin film use in optical shutters.

This letter shows the electrochemical and optical properties of the Nb_2O_5 thin films prepared by the radio-frequency (rf) magnetron sputtering method.[2] The optical properties are studied under electrochemical polarization *in situ* in spectroelectrochemical cells.

The Nb_2O_5 film was deposited on a transparent electrode. The electrode substrates were 0.9×5 cm^2 pieces of glass with a conductive coating of a fluorine-doped tin oxide (SnO_2:F, FTO) on one side (Nippon Sheet Glass Co. Ltd).

In preparing Nb_2O_5 films, rf magnetron sputtering equipment (Osaka Vacuum Co. Ltd.) was used with a Nb_2O_5 powder (Taki Chemical Co., Ltd.) target. The sputtering gas was an argon-oxygen mixture (Ar/O_2 =4/1). The flow rate of the sputtering gas was 30 sccm. Before sputtering, the chamber was evacuated to 2×10^{-6} Torr. The target was presputtered for 10 min. During sputtering, the substrate was water cooled, and the chamber pressure was kept at 3.0×10^{-3} Torr. The deposited film thickness was adjusted to about 50–200 nm by selecting an appropriate sputtering time.

The crystallinity of the film was analyzed by x-ray diffraction with Cu $K\alpha$ radiation. The electrochromic behavior was evaluated using a sample cell that was installed in the sample compartment of a spectrophotometer. The sample cell was made of a standard quartz cuvette with a 1-cm pathlength. An electrode active area of 0.5 cm^2 was used in these experiments. The counterelectrode was SnO_2:F film coated on the glass plates. The electrolyte used was a 0.1 M Na_2CO_3+0.1 M $NaHCO_3$ buffer solution.[1] The reference compartment contained a cuvette filled with electrolyte and a pair of electrodes of SnO_2:F film coated onto the glass plates. Thus, the transmittance measurements of the Nb_2O_5 electrode included contributions from only the Nb_2O_5 film. A voltage of ±3.0 V was applied between the electrodes. Cyclic voltammetry was done by using a potentiostat and a function generator at a potential sweep rate of 70 mV/s from −1900 mV to +500 mV vs SCE (standard calomel electrode). A saturated calomel reference electrode with extended Luggin capillary was used. The amount of moving charge was measured with a Coulometer.

The Nb_2O_5 films deposited under the deposition condition of this study (rf power⩽300 W) were confirmed by x-ray diffraction usually in the amorphous state. Figure 1 shows the x-ray diffraction pattern of the 200 nm thick Nb_2O_5 film on a FTO-coated glass substrate for rf power 300 W. No trace of peaks for Nb_2O_5 is observed.

The Nb_2O_5 films were transparent. The optical energy gap of the Nb_2O_5 film was estimated from the optical absorption measurements for 50 nm thick amorphous films, which were deposited at two different rf powers. Figure 2 shows the absorption coefficients as a function of photon energy. The extrapolations to abscissa show an optical energy gap E_g of about 3.8 eV.

Figure 3 shows the cyclic voltammogram of the 157

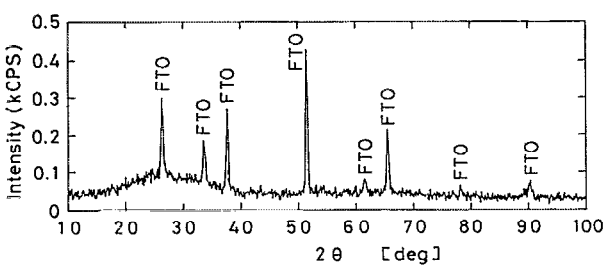

FIG. 1. X-ray diffraction pattern of the 200 nm thick Nb_2O_5 film deposited at rf power 300 W on a FTO-coated borosilicate glass substrate.

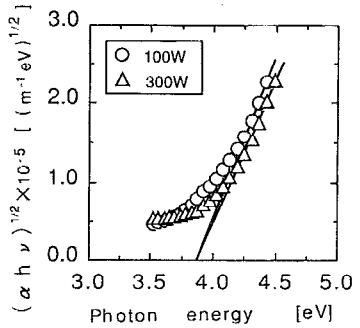

FIG. 2. Relation between absorption coefficient and energy of incident photon.

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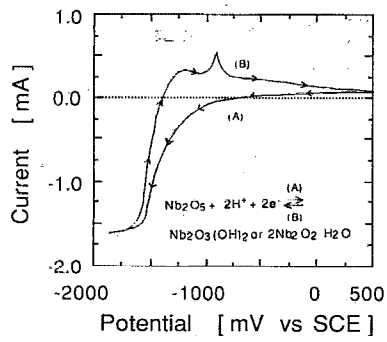

FIG. 3. Cyclic voltammogram of the Nb_2O_5 film in 0.1 M Na_2CO_3+0.1 M $NaHCO_3$ buffer solution at a sweep rate of 70 mV/s.

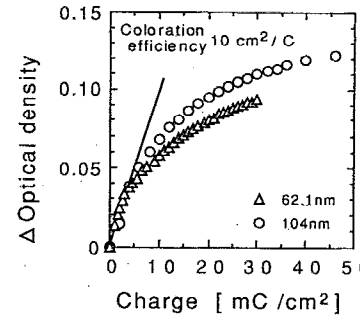

FIG. 5. Change in optical density at a wavelength of 550 nm as a function of charge density.

nm thick Nb_2O_5 film. The anodic peak appears at approximately -900 mV (SCE), while the cathodic peak appears at about -1500 mV (SCE), respectively. Coloration (upon reduction) and bleaching (upon oxidation) are associated with redox peaks at potentials in the range observed for the Nb_2O_5 redox couple. In an electrolyte, the following reaction[1] is postulated to describe the film conversion process:

$$Nb_2O_5+2H^+ +2e^- \rightleftarrows Nb_2O_3(OH)_2 \quad \text{or} \quad 2NbO_2\cdot H_2O.$$
$$\text{(bleached)} \qquad \text{(colored)} \qquad (1)$$

Figure 4 shows the optical transmittance spectra of the as-deposited, reduced (colored), and oxidized (bleached) niobium oxide films sputtered at rf power 100 W on FTO-coated glass substrates. In the as-deposited state, the film is

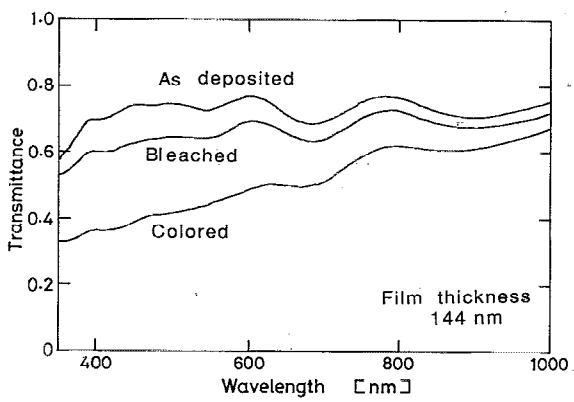

FIG. 4. Optical transmittance spectra of a Nb_2O_5 film in the as-deposited, reduced (colored), and oxidized (bleached) states.

essentially transparent, but upon reduction (on application of -3.0 V) it produced a marked change in light absorption throughout the visible wavelength region of the spectrum. The change can be removed on oxidation (on application of $+3.0$ V). The transmittance of the bleached film is lower than that of the as-deposited film.

Thus, the Nb_2O_5 film sputtered at 100 W exhibited clear electrochromism. However, the films sputtered at 200 and 300 W showed no change in transmittance by applying voltage. This is postulated to be caused by the substrate temperature rise due to the high rf power during sputtering. In order to observe electrochromism in WO_3, it has been reported that the substrate temperature must be kept lower than 100 °C when preparing films by the sputtering method.[3]

The change in optical density for $\lambda=550$ nm as a function of injected charge density is shown in Fig. 5. The slope of the linear part, i.e., change in optical density divided by the injected charge density, gives the value of the coloration efficiency. The coloration efficiency of the sputtered Nb_2O_5 film is 10 cm^2/C.

In conclusion, electrochromic niobium oxide thin films were prepared in air by a rf magnetron sputtering method. Amorphous thin films deposited at rf power 100 W showed the electrochromic behavior: Reduction and oxidation of the films in 0.1 M Na_2CO_3+0.1 M $NaHCO_3$ buffer solution resulted in coloration and bleaching, respectively. Coulometry indicated that the coloration efficiency was 10 cm^2/C.

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