CHEMISTRY LETTERS, pp. 1501-1502, 1985.

ELECTROCHROMISM OF GLASSES AND SPUTTERED AMORPHOUS FILMS IN THE SYSTEM $Li_2O-WO_3-Nb_2O_5$

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Electrochromic absorption spectra were measured for rapidly quenched glasses and RF-sputtered amorphous films in the system $Li_2O-WO_3-Nb_2O_5$. The absorption maximum was shifted to shorter wavelengths and the color varied from blue to brown with increasing Nb_2O_5 contents. The absorption maxima were broader in the sputtered films than in the rapidly quenched glasses, but no essential difference in absorption spectra was observed between the glasses and the sputtered films.

Since Deb[1)] published a paper on electrochromism in evaporated WO_3 films, much attention has been paid to the electrochromic coloration of WO_3 to form the blue tungsten bronze. Faughnan et al.[2)] reported that the electrochromic optical absorption of amorphous films in the mixed oxide system WO_3-MoO_3 occurred at higher energies than the absorption of either pure oxide alone. The absorption shift in the mixed oxides, however, was very small, and the color of the films was still blue. Thus the color of electrochromic materials ever reported has almost been restricted to blue. In previous papers[3,4)] we reported electrochromic properties of glasses in the systems R_2O-WO_3 (R=Li,Na,K) prepared by rapid quenching. The electrochromic coloration of those glasses was still blue. In the course of further investigation on electrochromism we have found that the addition of Nb_2O_5 to the R_2O-WO_3 glasses changed the color from blue to brown. The purpose of this letter is to present the absorption spectra of electrochromic coloration of the $Li_2O-WO_3-Nb_2O_5$ glasses (20-50 μm thick) prepared by rapid quenching. The RF sputtering is also useful for preparation of amorphous films, and the electrochromic absorption of such films (0.1-0.3 μm thick) is compared with that of the rapidly quenched glasses.

Table 1 lists the chemical composition of glasses and films investigated. If the compositions are plotted on the composition triangle of the ternary system $Li_2O-WO_3-Nb_2O_5$, these five compositions lie on the tie line between $30Li_2O{\cdot}70WO_3$ and $50Li_2O{\cdot}50Nb_2O_5$(mol%); $30Li_2O{\cdot}70WO_3$ was one of the best compositions in the electrochromic coloration in the R_2O-WO_3 systems and $50Li_2O{\cdot}50Nb_2O_5$ corresponds to the composition of lithium niobate $LiNbO_3$. The

Table 1. Chemical composition in the system $Li_2O-WO_3-Nb_2O_5$ investigated

	Composition	(mol%)	
No.	Li_2O	WO_3	Nb_2O_5
1	30	70	0
2	35	53	12
3	40	35	25
4	45	17	38
5	50	0	50

preparation technique of the rapidly quenched glasses were reported previously.[5)] The RF-sputtered films were prepared on a NESA coated glass substrate under 1.2×10^{-2} Torr of a 20% oxygen-80% argon gas mixture and 100W RF-power. The sintered plate (8 cm in diameter and 3 mm thick) of the compositions shown in Table 1 was used as the sputtering target. The glassy or amorphous state was confirmed by X-ray diffraction measurements.

Electrochromic coloration was made in different ways for glasses and sputtered films. In the sputtered films a NESA coated glass substrate acted as one electrode and another NESA coated glass was used as a counter electrode immersed in $LiClO_4$-dissolved CH_3CN solution; such a cell assembly would ensure the further analysis of coloration mechanism. In the rapidly quenched glasses the construction of such a cell was difficult and two parallel gold electrodes were evaporated onto the glass surface. The measurement of optical absorption has already been reported elsewhere in detail.[6)]

Figure 1 shows the absorption spectra of colored glasses. In the spectrum of glass $30Li_2O\cdot70WO_3$ a broad absorption band was observed at the near infrared region, similar to the case of colored WO_3 films.[1)] The absorption maximum was shifted to shorter wavelengths and the color varied from blue to brown with increasing Nb_2O_5 contents.

Figure 2 shows the absorption spectra of the sputtered films. In this case the absorption maximum was similarly shifted to shorter wavelengths with increasing Nb_2O_5 contents. The absorption band is slightly broader in the sputtered films than in the rapidly quenched glasses. The spectra, however, are very similar in sputtered films and quenched glasses. We can expect from these results that the multi-color electrochromic devices would be developed by the selection and combination of suitable transition metal oxides. The analysis of coloration mechanism is now under study and will be published elsewhere.

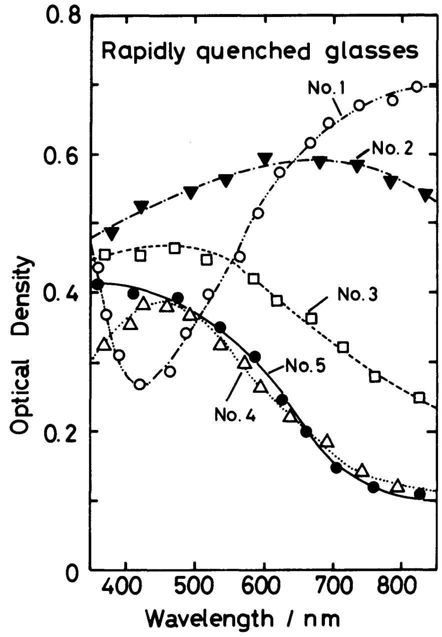

Fig.1. Absorption spectra of colored glasses prepared by rapid quenching in the system Li_2O-WO_3-Nb_2O_5.

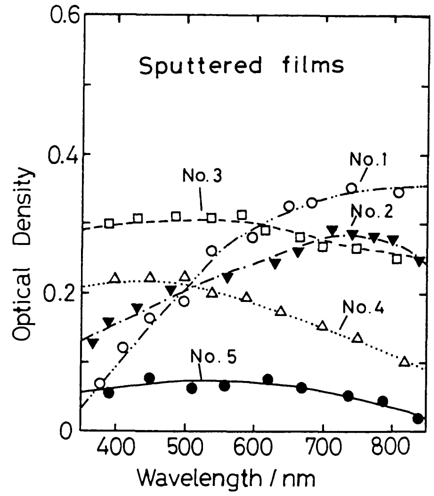

Fig.2. Absorption spectra of colored films in the system Li_2O-WO_3-Nb_2O_5.

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(Received July 11, 1985)