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Influence of vacuum Pressure on Electrochromic Properties of WO₃ Films

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Abstract

The electrochromic WO₃ thin films were prepared by using the electron beam deposition technique. The influences of vacuum pressure were examined in terms of the surface morphology and the electrochromic properties of films. From the results, the electrochromic behavior of electron beam deposited films strongly depends on the vacuum pressure during deposition. The film prepared under a vacuum pressure of 5×10^{-4} mbar was found to be rather stable when subjected to the repeated coloring and bleaching cycles in an aqueous acid electrolyte of 1M H₂SO₄. It was also found that the degraded film by repeated cycling in the aqueous acid solution changed the grain shape of film surface.

I. INTRODUCTION

In recent years, considerable attention has been given to both the theoretical and experimental investigations of the physical and physicochemical properties of electrochromic thin films due to their favourable and promising applications such as electrochromic devices, energy-efficient smart windows, automobile mirrors, and building glazings [1-6]. Electrochromic films are characterized by a reversible and persistent change of the optical properties under the action of an applied electric field.

Among the electrochromic materials WO₃ films have been investigated widely due to their applicability in smart windows which allow the dynamic control of the solar energy transmission. Smart windows are constituted by multilayers comprising a glass, a transparent conductor, an electrochromic material, an ion conductor, an ion storage and a (transparent) conductor. The most important element of smart windows is an electrochromic material. Although electrochromic materials show particular advantages including a low energy consumption due to an open circuit memory, an excellent contrast and a high coloration efficient enough to be used as a window, they still have problems such as a layer degradation and slow switching time. Accordingly, various processes for producing electrochromic WO₃ thin films have been proposed and the properties have been studied in order to improve the performance and chemical stability of the electrochromic films and devices [7-9]. However, the vacuum pressure effect on the electrochromic properties has not been investigated yet.

The present study is intended to analyze the electrochromic properties and the degradation of the WO₃ film for the purpose of improving the preparation condition of the film under different vacuum pressures .

II. EXPERIMENTAL

WO₃ thin films were prepared by reactive electron beam deposition method. For the deposition of the films, pellets of WO₃ powder with 99.99% purity were put into carbon crucible in a stainless steel chamber, and then deposition of WO₃ film was conducted on ITO-coated glass (thickness: 2000 Å, sheet resistance: 10 Ω/cm²) by irradiating of an electron beam (Leybold L560) The substrate was placed 20 cm above the crucible, and the substrate temperature was maintained at room temperature. An electron beam of 1.7 KeV energy was irradiated on the WO₃ pellet. The film thickness and the deposition rate were monitored by the quartz - crystal thickness monitor. Their values were about 4000 Å and 10 Å/s, respectively. The color of deposited film was almost transparent. The structure of films was identified in amorphous state by X-ray diffraction. The base pressure of the vacuum chamber was controlled to 9 x 10⁻⁶ mbar before conducting the deposition. Then oxygen gas was injected into the chamber to change the pressure from 4 x 10⁻³ to 6 x 10⁻⁵ mbar. All samples after deposition were stored in a desiccator before the electrochemical and surface morphology measurements.

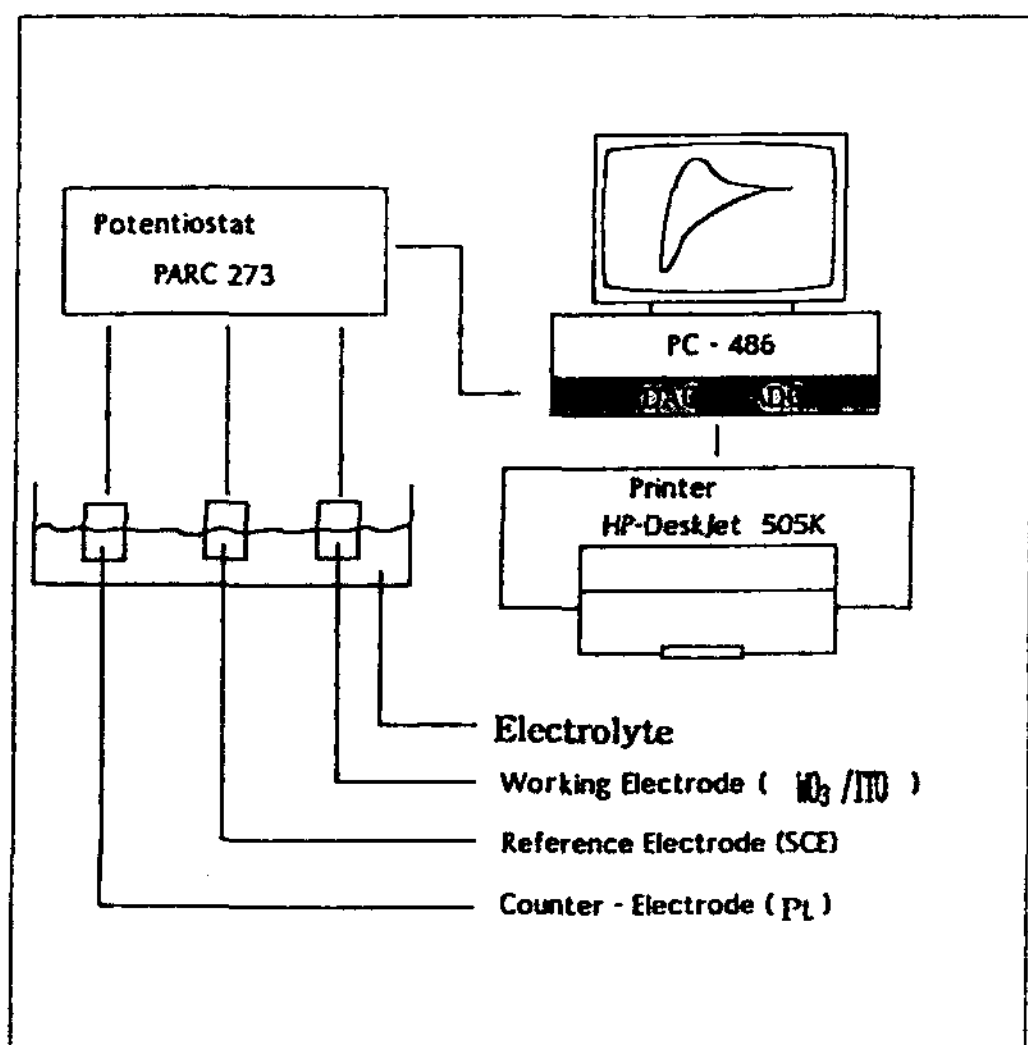


Fig.1. Experimental set up for voltammetry measurement on a WO_3 thin film in the electrochromic cell.

Figure 1 shows the apparatus of the electrochromic (EC) cell to monitor the ion insertion (extraction) reaction in WO_3 film. WO_3 film was used for the working electrode in the EC cell. A platinum wire was used for the counterelectrode. One mole of H_2SO_4 solution was used for the electrolyte. The coloration area of WO_3 was about 2.5cm^2 . Each potential was measured relative to the saturated calomel electrode (SCE). For coloration and bleaching, the voltage was applied between WO_3 film and Pt electrode under the potentiostat condition (PARC, Model 273). After repeated cycles of the coloration and bleaching, about 10 nm thickness of gold was deposited on the degraded film to observe the surface using a scanning electron microscopy (SEM). In order to characterize the electrochromic behavior of deposition film, cyclic voltammetry (CV) was performed using a potentiostat.

III. RESULTS AND DISCUSSION

In a cyclic voltammetry experiment, the potentiostat applies a potential ramp to the working electrode to gradually change the potential and then reverses the scan, returning to the initial potential. During the potential sweep, the potentiostat measures the current resulting from the applied potential. These values are then used to plot the cyclic voltammetry graph of current versus the applied potential. Electrochemical properties of the deposited WO_3 films were studied by cyclic voltammetry.

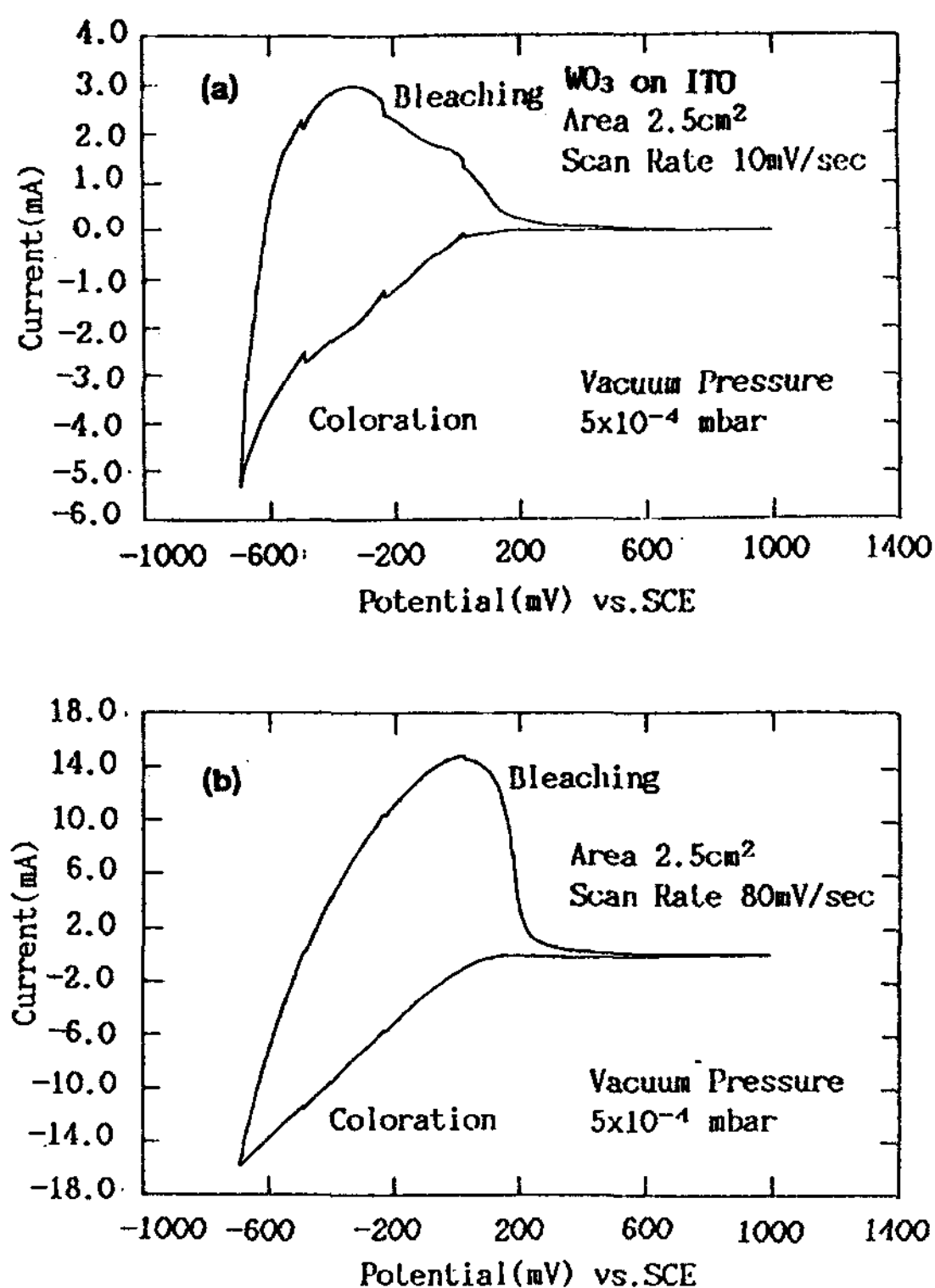


Fig. 2. Cyclic voltammogram of a WO_3 / ITO / glass electrode in 1 M H_2SO_4 electrolyte (The vacuum pressure was 5×10^{-4} mbar). (a) scanning rate of 10 mV/s, (b) scanning rate of 80 mV/s.

Figure 2 shows the cyclic voltammetry curves of WO₃ film at different scanning rate in sulfuric acid. Films were prepared under the vacuum pressure of 5×10^{-4} mbar. It can be seen that H⁺ ion is reversibly injected and extracted into and from the film. The cathodic peak for coloration was 700mV and the anodic peak for bleach was 400mV at the scanning rate of 10mV/s. But, at the scanning rate of 80mV/s, the cathodic peak for coloration showed about 700mV and the anodic peak for bleaching was revealed 0mV. This result explains that ions are diffused into the film to be trapped in the interior of the material even at the low scanning rate sample (a) but the coloration current density was lowered than sample (b). It further demonstrates that the coloration peak might be occurred at such a low voltage as 0.7 mV or below.

In the electrochemical cell, water is contained not only in the electrolyte but also in the WO₃ film. At first, we examined the effect of water molecules on the film behavior by applying different pressures.

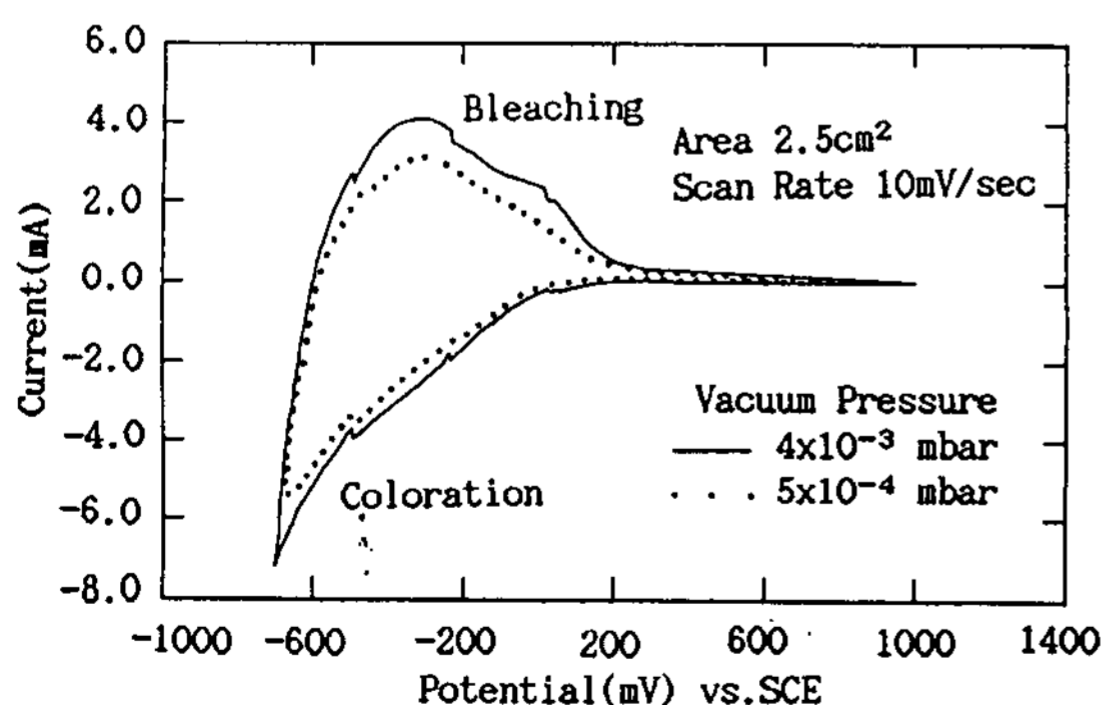


Fig.3. Cyclic voltammograms of an as-deposited WO₃ / ITO / glass electrode prepared under different pressures.

Figure 3 shows CV spectra of films prepared under different vacuum pressures. It is assumed that water could be contained in the film during the deposition process. But although the water content in the film is not possible to measure directly, it is increased as vacuum pressure increased. Accordingly, the coloration reaction was examined for WO₃ films which were prepared under the different vacuum pressures. It is shown that the cathodic and anodic peaks of the film produced at the vacuum pressure of 4×10^{-3} mbar are higher than those of the film prepared at the vacuum pressure of 5×10^{-4} . This result explained that the film prepared at vacuum pressure of 4×10^{-3} mbar had higher porosity and ionic conductivity [10]. Accordingly, the reason is inferred mainly because the oxidation and reduction reactions can be occurred well because the hydrogen ions can be easily transported via H₃O⁺ by exchange between adjacent water molecules [7]. However, it is also known that excess water in the film gradually dissolves the film through hydrolysis reaction [11]. This reaction deteriorates the performance of the film. From the results, it was found that the rate of coloration and bleaching were controlled by the diffusion of ions in the film. Accordingly, it is also inferred that a diffusion coefficient of the porous film increases due to a lowered diffusion energy barrier [10].

Figure 4 shows the peak currents with regard to various scanning rates of films prepared at the vacuum pressure of 5×10^{-4} mbar. The diffusion coefficient can be determined from this results. The heights of peaks tend to increase linearly with square root proportion to scanning

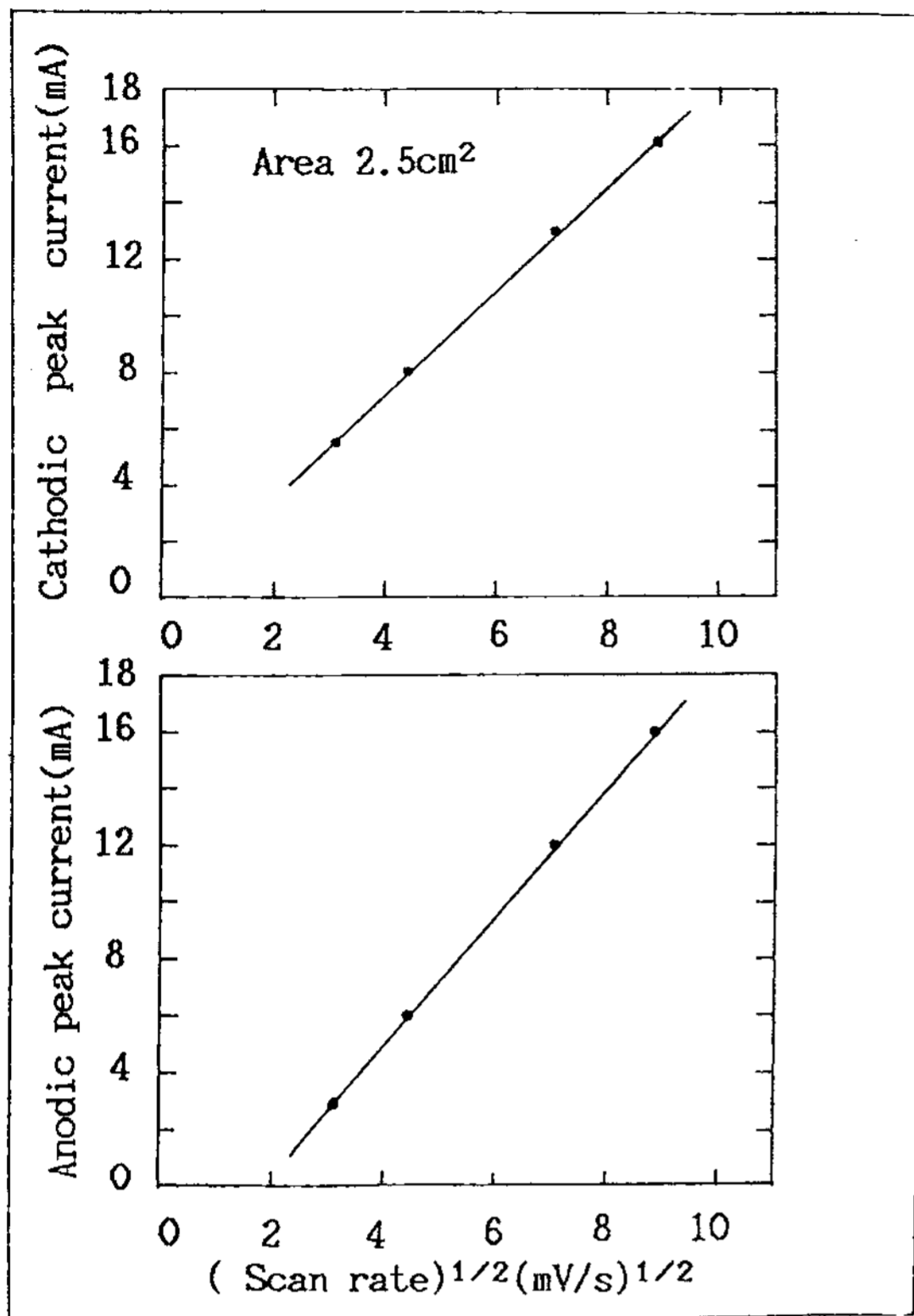


Fig. 4. Peak currents of a WO₃ / ITO / glass electrode at various scan rates.

rates. That is, they are reversible. The slope of line is in proportion to the diffusion coefficient as shown in Randles-Sevcik equation [12]. From these results, the coloration is exclusively controlled by the diffusion of H⁺ ion. It is believed that H⁺ ion diffusion process occurred not in the electrolyte but in the film. Accordingly, H⁺ ion diffusion plays an important role in determining the reaction rate of coloring and bleaching processes.

Figure 5 shows CV spectra of films before and after 30 cycles in sulfuric electrolyte at a scanning rate of 20 mV/s. Films were prepared at the vacuum pressure of 4×10^{-3} mbar. A phase change was not found in the film conducted the

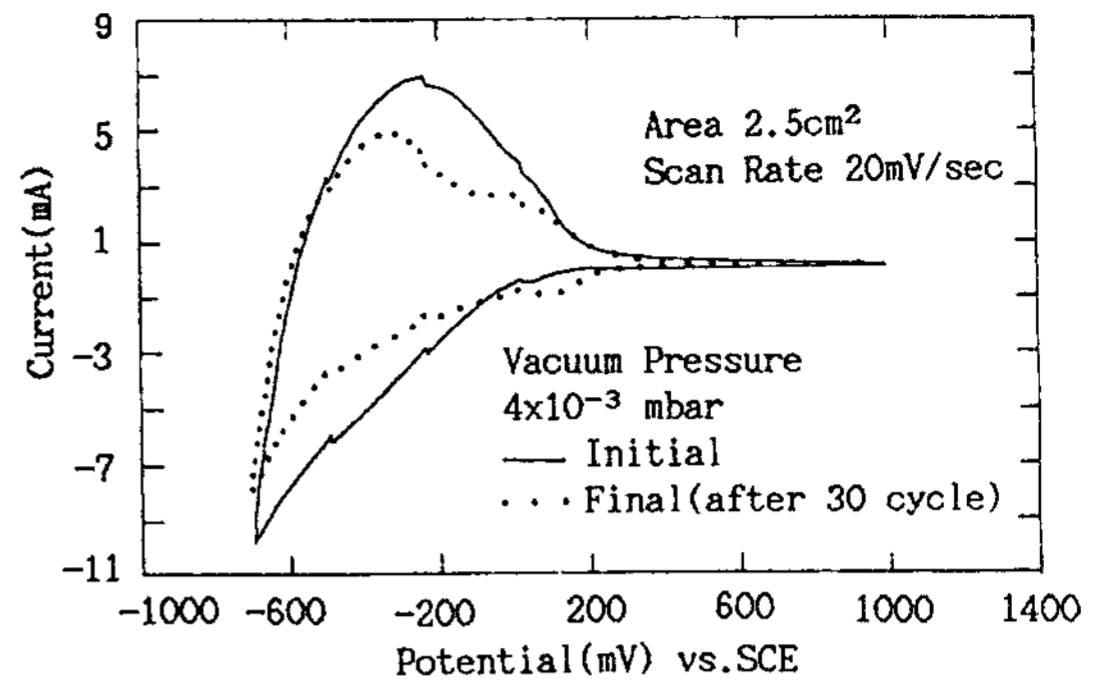


Fig.5. Cyclic voltammograms of WO₃ / ITO / glass electrode before and after 30 electrochromic switching cycles in 1 M H₂SO₄ electrolyte. The vacuum pressure was 4×10^{-3} mbar.

cycles of coloring and bleaching. After 30 cycles, the coloration and bleaching peaks were decreased, and the coloration peak was shifted from 700 mV to 710 mV and the bleaching peak was shifted from 200 mV to 400 mV. The results explain that surface morphology of the film during the bleaching process was changed. Furthermore, a considerable amount of water is contained in as-prepared film (WO₃ · nH₂O), and an amount of H⁺ ion injected into the hydrated film was accumulated by repeated the electrochromic switching cycles [11]. This result showed that electric current was decreased because electrochromic reactions were not taken place completely. This is due to the degradation of film. It may be also understood that since the capacity of charge needed for coloration is dependent upon the thickness of the film, the repeated cycles of coloration and bleaching caused the film to be dissolved. Due to the dissolved thickness of the film, the capacity of charge is reduced to lower the electric current.

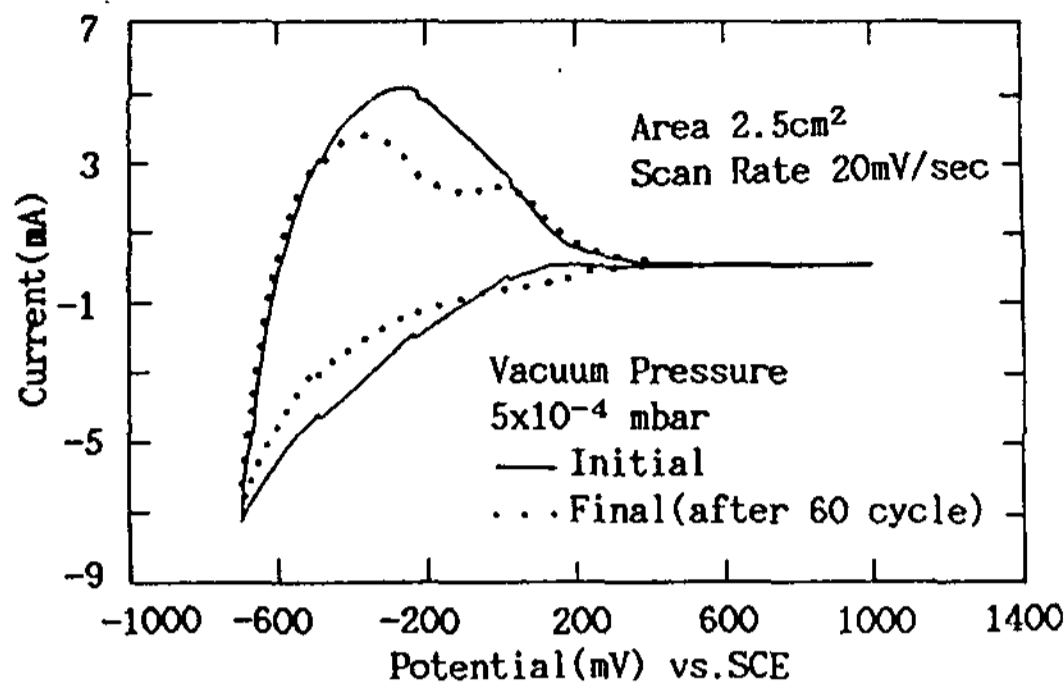


Fig.6. Cyclic voltammograms of WO₃ / ITO / glass electrode before and after 60 electrochromic switching cycles in 1 M H₂SO₄ electrolyte. The vacuum pressure was 5×10^{-4} mbar.

Figure 6 shows CV spectra of WO₃ film before and after 60 cycles of coloration and bleaching reactions in the sulfuric electrolyte. Films were prepared at vacuum pressure of 5×10^{-4} mbar. As can be seen, no more changes in CV spectra were observed during repeating the cycles from 30-60 cycles.

Comparing Fig. 6 with Fig. 5, it may be seen that the coloration density of the film prepared at vacuum pressure of 4×10^{-3} mbar is a little higher than that of the film prepared at vacuum pressure of 5×10^{-4} mbar. This fact also means that the film produced at vacuum pressure of 4×10^{-3} mbar contained more water during the deposition process than the film under vacuum pressure of 5×10^{-4} mbar. However, in comparing the film degradations, the coloration charge is more decreased in the sample prepared at vacuum pressure of 4×10^{-3} mbar. On the other hand, as shown in Figure 7 the film was peeled off and corroded in some places of the sample produced under 6×10^{-5} mbar, and the

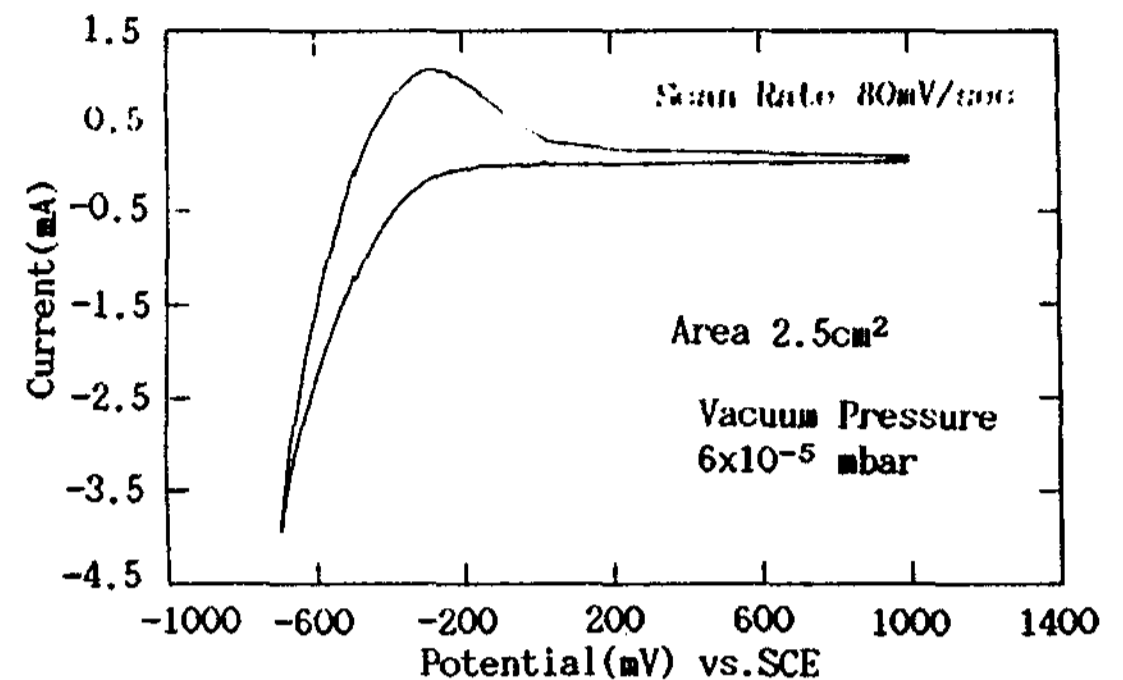
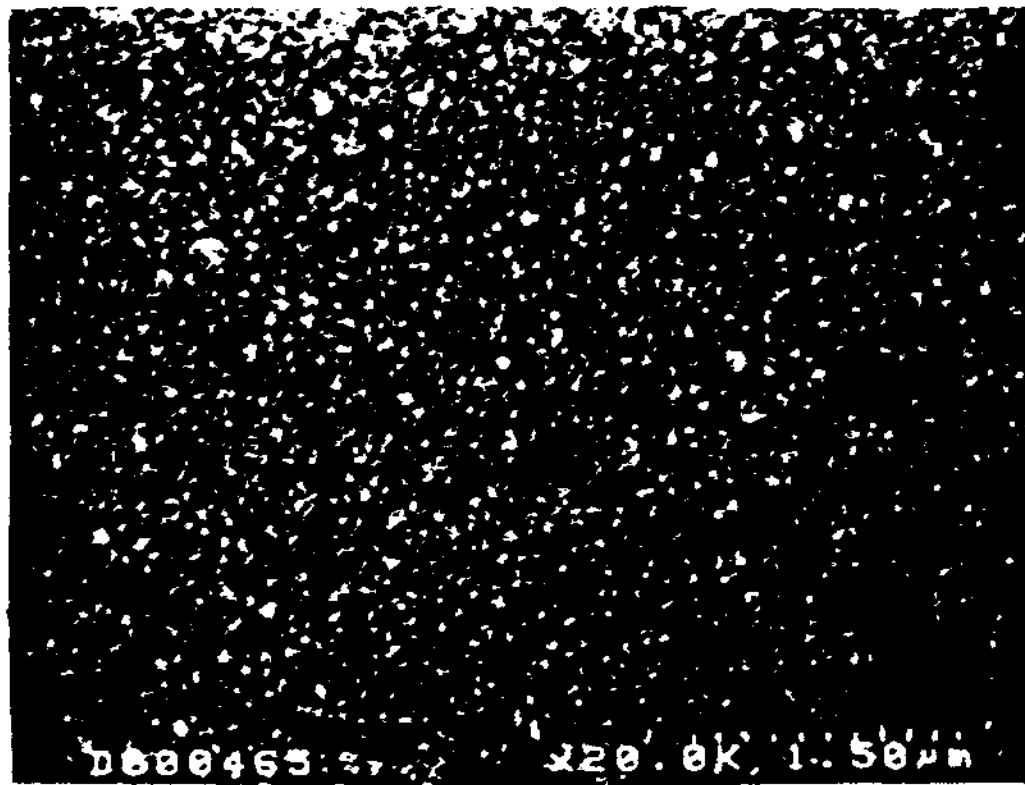


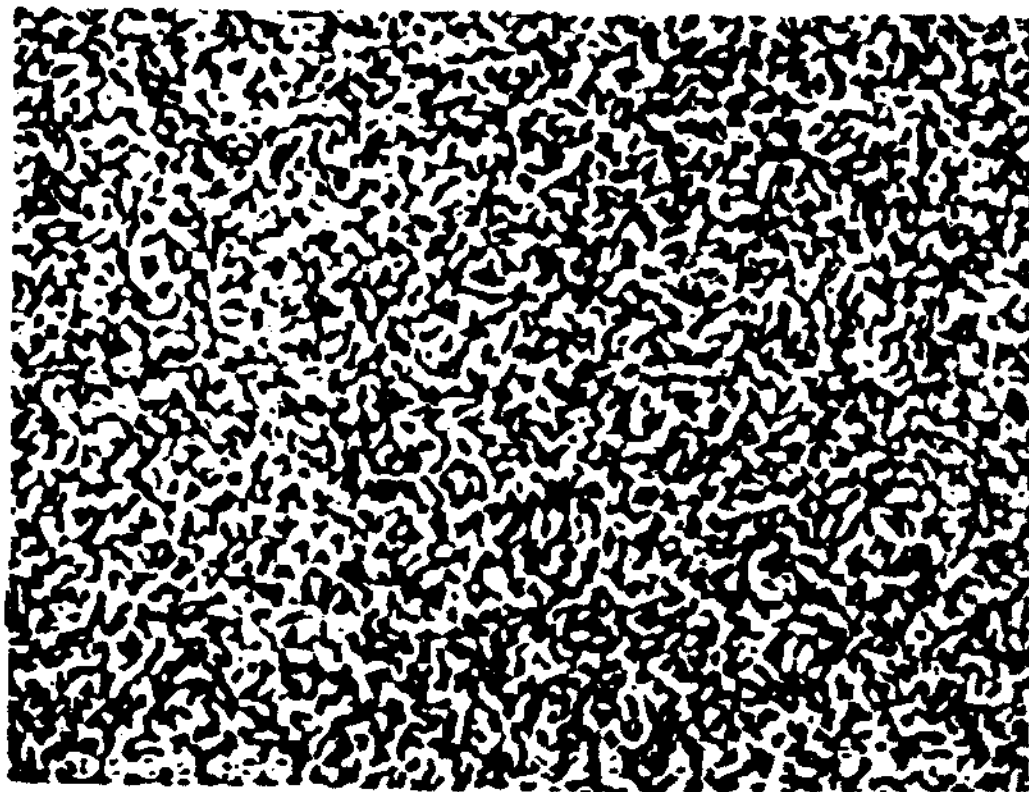
Fig. 7. Cyclic voltammogram of a WO₃ / ITO / glass electrode in 1 M H₂SO₄ electrolyte at 80 mV/s scan rate. The vacuum pressure was 6×10^{-5} mbar.

injected charges were not completely extracted from the film.

Film remains light blue color. From these experimental observations, it may be readily understood that the films prepared at vacuum pressure of 4×10^{-3} mbar and 5×10^{-4} mbar are superior to the film prepared at vacuum pressure of 6×10^{-5} mbar. The degradation of the film prepared at vacuum pressure of 5×10^{-4} mbar was rather small compared with others. This result will be caused by the differences in the water content and the porosities of the films during the deposition process.



(a) as-prepared film

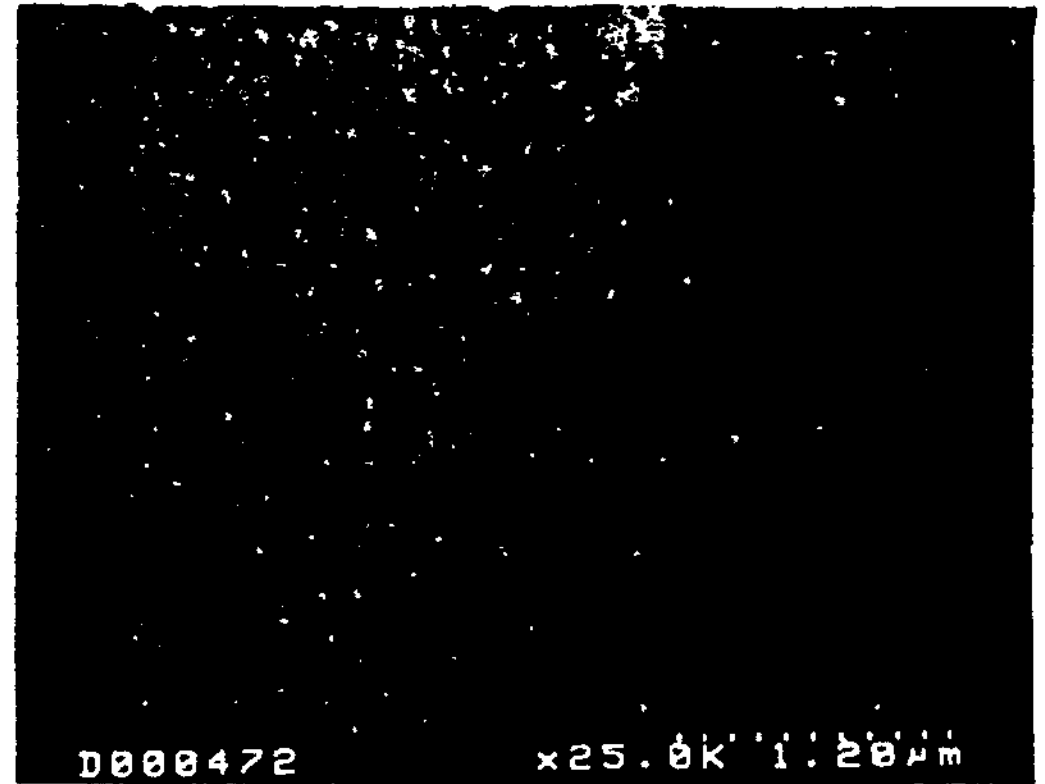


(b) degraded film
(after 30 cycles)

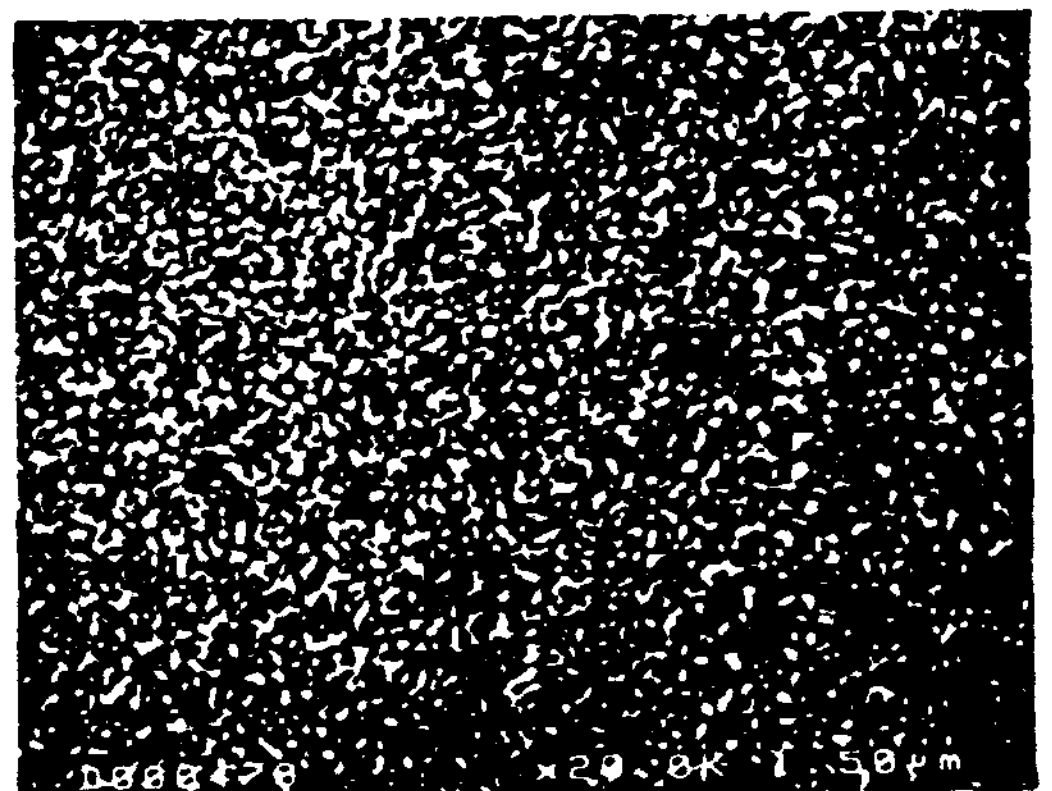
Fig. 8. SEM micrographs of as-prepared (a) and degraded (b) films.

The vacuum pressure was 4×10^3 mbar.

Figure 8 shows a SEM micrographs of WO_3 film which was prepared under vacuum pressure of 4×10^3 mbar and then repeated the 30cycles of coloration and bleaching. It is shown that the surface morphology of the films produced at vacuum pressure of 4×10^3 mbar and 5×10^4 mbar respectively didn't show critical differences. However, after the degradation, it was found that a grain shape of surface was changed from a big



(a) as-prepared film



(b) degraded film

Fig. 9. SEM micrographs of as-prepared(a) and degraded (b) films.

The vacuum pressure was 5×10^4 mbar.

round form to a little longish form. As a result of film degradation, the surface of film was rather porous form and the change of grain shape of surface also affected a transmittance of film.

Figure 9 shows a SEM micrograph for the sample of Fig. 6. It may be readily seen that the sample repeated to the 60cycles of coloring and bleaching was more porous than the as-prepared sample, and surface morphology of the film became a granular type by corrosion.

Accordingly, in order to improve stability of film, it is necessary to change the microstructure of film or to use a organic electrolyte excluded from water. But, it has been known that the response time for coloration with organic electrolyte is very slow [7]. It was also observed that peak current in CV spectra was decreased by the change of the shape of surface as compared with Fig. 6.

IV. CONCLUSION

This study tried to clarify electrochromic properties of WO₃ films prepared under different vacuum pressures. The results are summarized as follows:

The electrochromic behavior of electron-beam deposited films strongly depended on the vacuum pressure during deposition. Degradation of films prepared under the vacuum pressure of 4×10^{-3} mbar, 5×10^{-4} mbar and 6×10^{-5} mbar respectively is mainly due to water contained in the films and sulfuric acid electrolyte. Film prepared at vacuum pressure of 5×10^{-4} mbar was found to be rather stable by cyclic durability test.

It was found that the shape of surface of the film was changed from a round form to a little longish form, and finally to a granular type by cyclic degradation. It was also observed that peak current in CV spectra was decreased by the change of the shape of film surface.

ACKNOWLEDGMENT

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