ZrO$_2$ and Ta$_2$O$_5$ films were used as solid electrolyte layers in electrochromic cells of WO$_3$. Measurement of the weight changes of those cells during coloration and bleaching suggested that water contained in the cells played an important role for the coloration. Another kind of cell showed that it is not the water in WO$_3$ layer but that in a solid electrolyte layer that is essential. Reasons of deterioration of the electrochromic cells are not only a peeling Au electrode off from the cells but also a kind of morphologic changes of films.

Key words: electrochromic cell, WO$_3$, solid electrolyte, water in the film layer, deterioration of cell.

Introduction

The coloration of evaporated WO$_3$ films has been studied by many workers.(1)-(14) It is reported that the coloration is induced by forming HxWO$_3$ when a WO$_3$ film is in contact with liquid electrolyte.(13) When a solid electrolyte is used, several origins of coloration are proposed as follows;

1) color center (1)
2) metal-tungsten bronze (8)
3) hydrogen tungsten bronze (14).

We have already reported that the absorbed water in a solid cell plays an important role in the coloration of a solid state electrochromic cell when ZrO$_2$ or Ta$_2$O$_5$ is used as a solid electrolyte (14). In this paper, we report further evidence of the role and two feasible deterioration causes of a cell.

Sample preparation

We fabricated three kinds of cells for four different experiments. First one (A) consisted of a Cr coated quartz crystal and four kinds of thin film layers, i.e., Au electrode, WO$_3$, ZrO$_2$, and another Au electrode. The quartz crystal is a sensor of film thickness controller. The Au electrodes were deposited from electrically heated tungsten boat. An Au electrode thickness is 500A and another 120A. Cr, WO$_3$, and ZrO$_2$ (or Ta$_2$O$_5$) films were deposited by electron beam gun at the rate of about 1A/sec., 20A/sec. and 6A/sec., respectively. Their film thicknesses are 10A, 5000A and 3000A, respectively.

Second cell (B) constructed on a slide glass instead of a quartz crystal. Third cell (C) consisted of six layers, where all the layers have similar configuration to the second cell except that the other monitor Au electrode (400A thickness) was inserted into a part of the boundary between a WO$_3$ layer and a solid electrolyte layer.

The schematic design structures of the first and third cells are shown in Fig.1 and Fig.2, respectively, where only ZrO$_2$ is mentioned as a solid electrolyte because the Ta$_2$O$_5$ showed almost the same behavior as ZrO$_2$.

Experiments and results

a) When a constant charge was injected into a cell (A) constructed on a quartz crystal, the cell turned blue. A reverse current made the cell's color return back to the original state. It is important that the color change corresponded to the reversible and simultaneous weight change of the cell, placed in air. However, in vacuum of about 10$^{-2}$