

ELECTROCHROMIC EFFECT IN VANADIUM PENTOXIDE THIN FILMS

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Introduction

Electrochromic devices can be applied in practice in special devices such as information displays, mirrors with regulated light reflectance and surfaces with regulated radiation “Smart windows“. Electrochromic materials can change their optical properties upon charge insertion/extraction. Material is created by insertion of ions from the electrolyte (ion conductor) into the structure of the host material (electrochromic film) in the present of electric voltage. Electrochromic layers have composition of special thin films coated on glass substrates. The following figure shows the composition of electrochromic device.

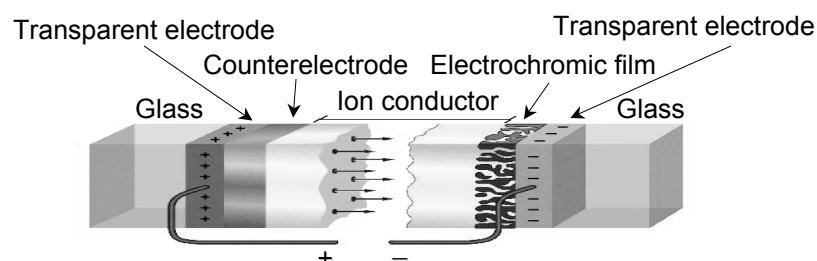


Fig. 1 Basic design of an electrochromic device, indicating transport of positive ions under the action of an electric field [1].

The transparent layers must have the following features: high light transmission for visible range of solar radiation, high electric conductivity and chemical and electrochemical neutrality. These layers are connected with electric voltage. *Electrochromic film* is electrochromically active layer in the whole system. In the presence of electric field the electrochromic process occurs within the layer - the insertion of ions and electrons from the electrolyte. During this process the change of chemical composition of layer and change of its optical properties does not cause any change to the material crystalline lattice structure. Hence, the reversible reaction can be activated by change of electric field of reversible polarity and the material will return into the initial phase. *Ion conductor layer* is represented by the central electrolyte in the system. It must be relatively highly conductive at the room temperature. High light transmission of the electrolyte is also required. Central electrolyte serves as the source of ions for the active electrochromic layer. Electrolyte layer serves for the fluent transport of ions between electrochromic layer (host layer) and layer of reversible electrode (ion storage layer). *Reversible layer* is a layer that can collect

ions. Ions from the electrochromic layer are transported in the reversible direction into the ion storage layer in the presence of electric voltage of the reversible polarity [2].

Experimental

Solution of dissolved $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ in H_2O_2 and ethylalcohol were deposited by a stream of air from an all-glass atomizer. For addition of NH_4F as dopant the ingredient was dissolved in small quantity of water and then added to ethanol. SbCl_3 was added directly to ethanol solution. The FTO and the ATO transparent electrodes were prepared with different dopant ratio. Solution of dissolved V_2O_5 powder in H_2O_2 was deposited by dip-coating method onto glass substrate covered by FTO. In this way, the V_2O_5 electrochromic layers were obtained. Microscopic glass slides were used as substrates. The size of the glass support was 20 x 20 mm.

Preparation of conductive layers: 10 g $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ was dissolved in 4 ml of 15% H_2O_2 under agitation. This solution was heated at 80°C and 50 ml ethanol was added. The $[\text{NH}_4\text{F}/\text{SnCl}_2]$ ratio by weight percentage in the spray liquid is kept at values of 0, 4, 7, 10 and 13, the $[\text{SbCl}_3/\text{SnCl}_2]$ ratio at 0, 0,1, 0,25, 0,4, 0,7 and 1. Higher SbCl_3 concentration has negative influence on film structure and the optical transmission is lowered [3]. The respective deposition temperature was 420 °C.

Preparation of vanadium layers: 0.5 g V_2O_5 was dissolved in 30 ml of 15% H_2O_2 . This red-brownish solution was very unstable and it had to be placed into a water-bath at 80 °C for 0.5 h [4]. It was obtained very viscid solution. This solution was diluted with distilled water in the ratio 2:1, 1:1, 1:2, 1:3 and one part was kept neat. The glass substrates with FTO (7% wt.) were dipped into these solutions and covered with different thickness of vanadium layers. These samples were heat-treated in an oven at 150 °C for 1 h and homogenous greenish films were obtained.

The 0,5M LiClO_4/PC polymer gel electrolyte was applied like the ion conductor.

Resistance was measured on glass slices of dimensions 20 x 20 mm (approx.) in a four-point arrangement. The current leads were created as stripes of silver paint on opposite sides and the voltage probes as small dots between them. The transmission spectra were measured on the PU 8720 UV – VIS spectrometer. The morphology and elemental composition were monitored by the X-ray spectrometer SIEMENS D5000. Observations of the layer morphology were performed also by the optical microscope.

Results and Discussion

It seems probable that the droplets of the tin compound solution evaporate immediately when they touch the substrate. The surface of the conductive layer consists of small particles formed probably by rapid evaporation of the droplets. It is due to used method.

The XRD measurements approved the inherency of the vanadium oxide film. This film was found crystalline with orthorhombic structure. The water in the crystalline structure was found.

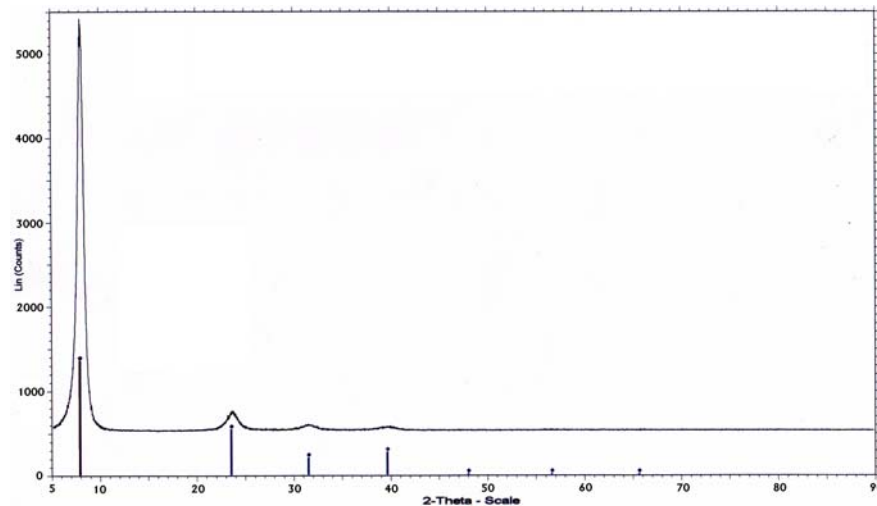


Fig. 2. XRD patterns of sol-gel dip-coated $V_2O_5 \cdot 1,6H_2O$ film

In the fluorine doped tin oxide films, the F^- anion substitutes for an O^{2-} anion in the lattice, creates more free electrons and decreases the value of R_{sh} . Increasing the value of R_{sh} after a specific level of F content probably represents a solubility limit of F in the tin oxide lattice. The excess F atoms do not occupy the proper lattice positions to contribute to the free carrier concentration and at the same time the increasing disorder leads to the increase of the sheet resistance [5].

When Sb is added to SnO_2 , Sb is incorporated into the Sn^{4+} sites of the SnO_2 lattice substitutionally. In ATO samples, Sb is in two different oxidation states namely, Sb^{5+} and Sb^{3+} . During the initial addition of Sb in tin oxide film, the Sb^{5+} substituted on the Sn^{4+} site act as donors and creates excess electrons. So the free carrier concentration is higher and consequently the sheet resistance decreases with the addition of Sb up to a certain level. Further addition of Sb introduces the Sb^{3+} sites, which act as acceptors. The Sb species would compensate the donor levels, which were created by the Sb species, leading to an increase in the R_{sh} [5].

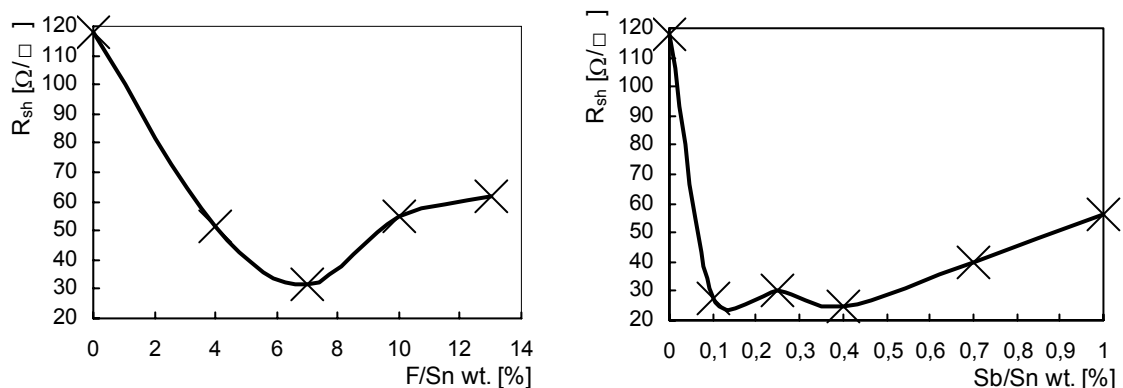


Fig. 3. Minimum sheet resistance of fluorine (left) and antimony (right) doped SnO_2 thin films

The optical transmission of the electrochromic device samples was measured between 300 and 900 nm for all. The results for sample diluted in the ratio 1:2 and for pure solution are shown in figure 4.

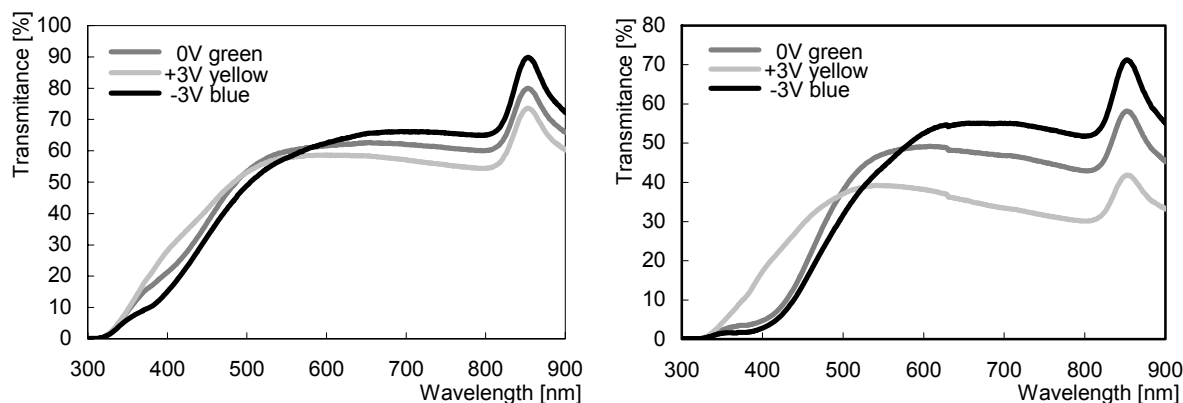


Fig. 4. Electrochromic device with diluted (left) and pure (right) V_2O_5 film

Conclusions

The preparation of SnO_2 based layers by spray method seems interesting for the technology as no vacuum is necessary for it. The fluorine and antimony dopant ratio were varied and the lowest values of resistivity were founded. For FTO is the best value $30 \Omega/\square$ (F/Sn = 0.7 wt.%) and $20 \Omega/\square$ (Sb/Sn = 0.25 wt.%) for ATO. The films have moderate optical transmission. Vanadium oxide films were dip-coated on FTO (0.7 wt. %) layers. Coating solution was prepared by dissolving V_2O_5 powder in H_2O_2 solution. The vanadium oxide films showed a reversible multichromism (yellow $\leftrightarrow$ green $\leftrightarrow$ blue) upon Li^+ ion insertion/extraction. The transmittance modulation range can be varied by adjusting the film thickness. The vanadium oxide films with a proper thickness could be used in a realization of multicolored electrochromic devices.

Acknowledgements

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