Electrochromic Effect in Amorphous α-WO_3 as a Outcome of the Occupation of the Bottom of Conduction Band by Electrons

G. Ya. Kolbasov, Yu. S. Krasnov
Institute of General & Inorganic Chemistry of the Ukrainian National Academy of Sciences, 32-34 prosp. Palladina, 03680 Kiev 142, Ukraine
Fax: +(38044) 444-3070, e-mail: kolbasov@ionc.kar.net

Electrochromic films of amorphous α-WO_3 produced by the electrochemical deposition of tungsten-containing compounds were studied with simultaneous determination, during deposition, of current values of thickness and optical refractive index by an interferometric method. The disorder of the structure of these films as numerous terminal double W=O bonds instead of W-O-W bridge bonds is caused by the presence in them of fine pores filled with water molecules (water content up to 15 %). The potential of films was cycled in 1M H_2SO_4 over a range of +0.4 V to -0.4 V (SCE). Two "waves" were distinguished in cathode region ; reversible coloration of films with light absorption peak, whose position depended on potential and varied from 1.3 μm to 0.5 μm , corresponded to these waves. The fundamental absorption edge ε_α of WO_3 shifted by 0.5 V, which corresponded to a change of 0.6 V in the quasi-equilibrium potential E_0 of WO_3. A shift in E_0 which is observed in this case is caused by a change in the electrochemical potential of electrons ε_f .

The comparable changes in E_0, ε_α and ε_f indicate that the injected electrons occupy sequentially the vacant energy levels of the bottom of conduction band. This lead to an increase on several orders of magnitude in film conductivity and to decrease in refractive index from n=1.68 up to n=1.45 due to a high electron concentration in a film. In this case, despite of degeneration of an electronic subsystem as a result of pairing electrons at d levels, the coloration of films corresponds to electronic intracentre d-d transitions in W. The W ions are in a ligand field, which differs from octahedral one. The higher the degree of ligand field disturbance, the lower the W centre energy and the lower the quantum energy needed for the optical excitation of the corresponding d-d transition.