INFLUENCE OF SUBSTOICHIOMETRY, HYDROGEN CONTENT AND
CRYSTALLINITY ON THE OPTICAL AND ELECTRICAL PROPERTIES
OF HxWOy THIN FILMS

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(Received October 28, 1977; revised April 10, 1978)

We have prepared HxWOy amorphous thin films both by evaporation of tungsten trioxide powder and by cathodic sputtering of a tungsten target in an argon/oxygen/hydrogen reactive gas mixture. The evaporated layers have the composition HxWO2.7 (0.2 < x < 0.5). Their oxygen content seems rather insensitive to the evaporation parameters. We do not observe any correlation between x and these parameters. Evaporated virgin layers are nearly transparent. Annealing, under vacuum leaves y unchanged, under oxygen increases y to 3. Annealing of the virgin layer under vacuum induces the growth of the 1.38 eV absorption band (giving blue coloration) and a decrease of the activation energy for conduction. Annealing the blue layers in oxygen destroys the 1.38 eV band and increases the activation energy for conduction. In both cases annealing at high temperature induces a microcrystalline phase with an absorption band centered about 0.72 eV (giving also a blue coloration) and a jump in electronic conductivity. As in the case of the 1.38 eV band, an increase of the intensity of the 0.72 eV band induces a decrease of the activation energy for conduction. The two bands are interpreted as polaronic like. They can be induced in transparent layers without any change in global composition by excitation of the hydrogen atoms from a "passive" state to an "active" state. In addition to the hydrogen content, the existence of the 1.38 eV band requires so-
me substoichiometry. The study of the optical and electrical properties of amorphous H\textsubscript{x}WO\textsubscript{y} sputtered layers, supports our previous conclusions about the composition range (C) for the coloration capability of transparent thin films. In addition there is a composition range (B) where the virgin layers are blue, and a composition range (M) where they have a metallic like behavior. On the other side of (C), there is a range (C') where uv illumination only induces a decrease in the activation energy for conduction, then a range (T) where the layers are completely nonresponsive. One can pass from (T) to (B) through (C') and (C) either at constant hydrogen content by increasing the departure from stochiometry, or at constant substoichiometry by increasing the hydrogen content.

Key words : electrochromic and photochromic material, amorphous hydrogenated tungsten trioxide, optical and electrical measurements.

* A part of this work was presented at EMC Cornell, New York July 1, 1977.

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Introduction

Deb (1) has shown that thin films obtained by evaporation of tungsten trioxide powder exhibit two passive stable states. The first one is transparent and highly resistive, the second one is blue and less resistive. These layers have a blue color when observed by reflection of ambient light due to the existence of a broad absorption band in the red and near infrared centered around 0.9\textmu (1.38 eV). Figure 1 shows the variation of the optical absorption coefficient versus photon energy for a 6000 Å thick evaporated thin film before (T) and after (B) coloration. The coloration occurs with an increase of the conductivity and a decrease of the activation energy for electrical conduction. Figure 2 shows the variation of conductance 1/R versus the reciprocal temperature 10^3/T for the layer of Fig. 1 before (T) and after (B) coloration. The films transmit about three times more light and are a thousand time more resistive in the transparent state than in blue state. The reproducibility of the evaporated thin films is commonly poor and Figs. 1 and 2 also show, for example, the optical absorption bands and the corresponding conductivity for