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Electroless deposition of Alpha-PbO_2 and Tl_2O_3

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Abstract. A chemical method for electroless deposition of thin film of α-PbO_2 and Tl_2O_3 has been developed. The deposition has been performed by ammonia, persulfate ion and metal ions at a higher temperature. The electrical resistance, mobility and carrier concentration have been measured with variation of thickness of the films. Optical absorption spectra reveal the band edges which are 1·7 eV and 1·95 eV of α-PbO_2 and Tl_2O_3 respectively.

Keywords. Lead oxide ; thallium oxide ; thin film ; chemical deposition.

1. Introduction

The anodic oxidation of some metal ions in aqueous solutions leads to the deposition of an oxide at the anode under certain conditions, according to the electrode reactions:

$$mM^{z+} + nH_2O \rightarrow M_mO_n + 2nH^+ + (2n - mZ)\,1. \qquad (1)$$

Some well-known examples are Pb^{++}/PbO_2, Mn^{++}/MnO_2, Ni^{++}/NiO_2, Tl/Tl_2O_3 and Ag^+/AgO. If the oxidation of the metal ion is carried out as a controlled heterogeneous reaction by a suitable oxidising agent instead of an external electric current, the deposition of the metal oxide can be called electroless in analogy to the corresponding process known for the metals.

These oxides are important as thin films, particularly of PbO_2, Tl_2O_3, for their high electrical conductivity and optical transparency and can be used as transparent electrical conductors like SnO_2. Capacitors with PbO_2 coating show self-healing properties (Robinson 1962). In an earlier work, Mindt (1970, 1971) deposited thin film of PbO_2 and Tl_2O_3 with $S_2O_8^{2-}$ as oxidising agent and Ag^+ as catalyst from a solution containing Pb^{2+} or Tl^{1+} in presence of acetate buffer. He produced α-PbO_2 films by electroless deposition on the substrate in which an initial PbO_2 layer of a few hundred angstroms was precipitated; the same procedure was adopted to get the film of appropriate thickness. The initial deposited layer acted as catalytic surface for further deposition. In all cases Ag^+ was used as the catalyst.

A new method is developed where a film of PbO_2 or Tl_2O_3 can be deposited on any substrate without Ag^+ catalyst. It is found that the presence of NH_3 in solution at pH 8 can fulfil the desired condition to deposit the film of Tl_2O_3 or PbO_2 with appreciable thickness.

2. Experimental

Lead acetate (12 ml of 0·8 (M/10)) solution was heated and to this solution 15 ml of 3 (M) ammonium acetate and 9–10 ml of 0·2 (M) $K_2S_2O_8$ solution were added. Concentrated NH_3 solution was then added to control the pH (8–10) and a glass substrate or ceramic substrate was placed in the solution, heated at 80° C when an initial thin film of α-PbO_2 was obtained. This was followed by another deposition to get a uniform thin film of α-PbO_2. Thickness of the film varied between 1–5 × 10^{-4} cm.

For the deposition of Tl_2O_3, 15 ml of 1·5 (M/10) $TlNO_3$ solution was mixed with 5 ml of 0·9 (M/10) $K_2S_2O_8$ solution and 15 ml ammonia liquor. The substrate was placed in the solution and heated to 60–80° C. A uniform thin film to Tl_2O_3 was obtained. In both cases, the borosilicate glasses were found to be the best substrates for uniform deposition.

3. Discussion

The structure of the films was studied using x-ray diffraction and scanning electron microscopic techniques. X-ray diffraction pattern of PbO_2 film confirmed the polycrystalline nature of α-PbO_2. Scanning electron-micrograph showed the random orientation of fine crystallites (figure 1). Specific resistance and Hall-effect measurements indicated the carrier density of the order of 7–9 × 10^{19} carriers/cm^3. Specific resistance was found to be 1·304 × 10^{-3} ohm–cm. The calculated mobility was about 50 cm^2/v/sec. The electronic absorption spectra revealed that optical band gap was 1·7 eV (figure 2). Variation of resistivity, mobility

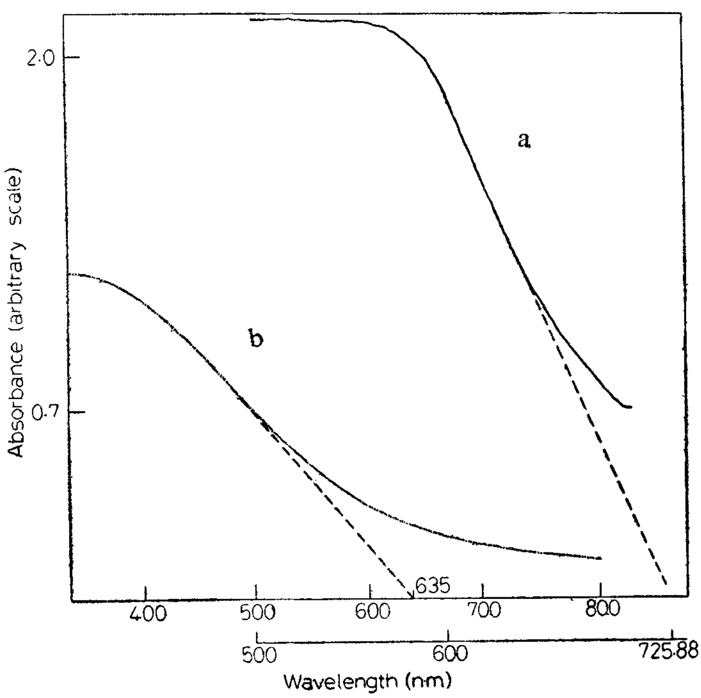
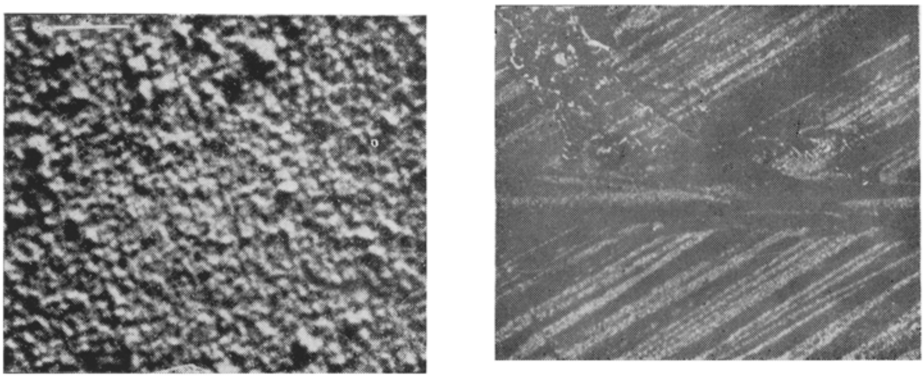


Figure 2. Electronic spectra of (a) α-PbO_2 and (b) Tl_2O_3.



(a) (b)

Figure 1. Scanning electron micrograph of (a) α-PbO_2 and (b) Tl_2O_3.

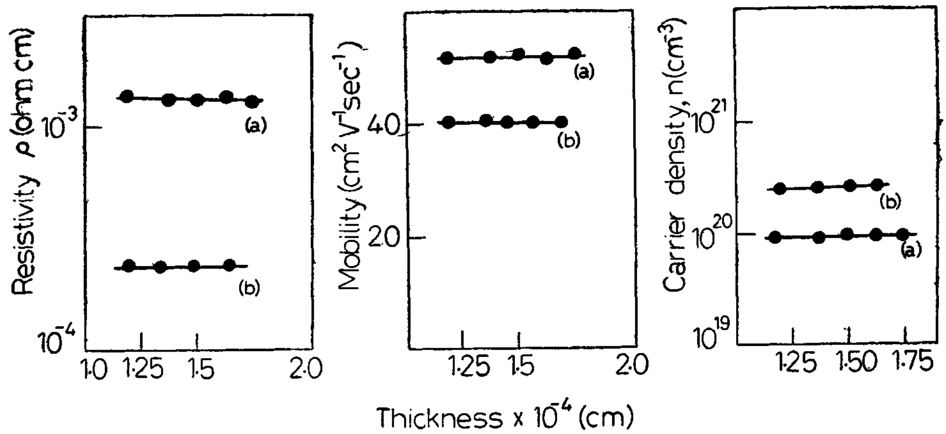


Figure 3. Variation of resistivity, mobility and carrier-density with thickness of (a) α-PbO_2 and (b) Tl_2O_3.

and carrier density with thickness of the film is presented in figure 3.

X-ray studies showed that the Tl_2O_3 film was polycrystalline cubic while the scanning electron micrograph showed that the films had a unique deposition pattern (figure 1). The specific resistance and calculated mobility from Hall effect were $3 \cdot 7 \times 10^{-4}$ ohm-cm and $40 \cdot 54\ cm^2/v/sec$ respectively. Carrier density was of the order of $4 \cdot 16 \times 10^{20}$ carriers/cm^3. The electronic absorption spectra revealed that optical band gap was $1 \cdot 95$ eV (figure 2). Variation of resistivity, mobility and carrier density with thickness of Tl_2O_3 film are presented in figure 3.

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