

## Short Communication

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# Effect of antimony on the semiconducting properties of the anodic plumbous oxide film formed in sulfuric acid solution

## II. Studies of photoelectrochemical current

Cong Pu\*, Zhuo-Li He and Wei-Fang Zhou

*Department of Chemistry, Fudan University, Shanghai 200433 (China)*

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### Abstract

The semiconducting properties of t-PbO (also known as tet-PbO or  $\alpha$ -PbO) in the anodic plumbous oxide films formed on lead and lead-antimony alloys in 4.5 M H<sub>2</sub>SO<sub>4</sub> (22±2 °C) at 0.9 V (versus Hg/Hg<sub>2</sub>SO<sub>4</sub>) have been studied using measurements of photoelectrochemical current. Antimony has little effect on the value of the bandgap energy of t-PbO in the films. From the relation between quantum yield and electrode potential, the values of the donor density of the t-PbO in the films formed on Pb, Pb-1at.%Sb, Pb-3at.%Sb, and Pb-9at.%Sb are  $9.3 \times 10^{15}$ ,  $3.1 \times 10^{16}$ ,  $4.5 \times 10^{17}$  and  $5.8 \times 10^{17}$  cm<sup>-3</sup>. Meanwhile, the flat-band potential of the t-PbO in the various films ranges from -0.07 to -0.28 V (versus Hg/Hg<sub>2</sub>SO<sub>4</sub>). By comparing the effect of antimony of the growth rate of the t-PbO with that on donor density, it is concluded that these experimental results conform to the Hauffe Rules.

### Introduction

According to the Hauffe Rules [1], for an n-type semiconductor oxide, if the valency of the alloying metal is higher than that of the basic metal, then the free-electron density will increase, but the density of lattice defects (i.e. oxygen anion vacancies in the work discussed here) will decrease. In previous work, an a.c. impedance method has been used for studying the semiconducting properties of the anodic Pb(II) oxide films formed on pure lead and lead-antimony alloys. The experimental results conform to the Hauffe Rules [2]. The a.c. impedance method can, however, only detect the response from the outer part of a semiconducting film. As the phase composition of the aforementioned films is rather complex [2], the outer parts of the films are not well-defined systems. Fortunately, certain semiconducting species can be detected via an ability to generate photoelectrochemical current [3]. This approach is adopted in the present work to examine the semiconducting properties of t-PbO (also known as tet-PbO or  $\alpha$ -PbO) in the oxide films formed on lead and lead-antimony alloys in sulfuric acid.

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\*Author to whom correspondence should be addressed.

## Experimental

The experimental set-up for measuring the photoelectrochemical currents consisted of the following units: stabilized 250 W halogen-tungsten lamp, Suzhou WDG05-III monochromator, EG&G PARC 197 chopper, EG&G PARC 5209 lock-in analyser, Shanghai JH2C potentiostat, and photoelectrochemical cell (PEC). The light beam was chopped at a frequency of 24 Hz. The intensity of the monochromatic light at the position of the quartz window of the PEC was measured by a Hamamatsu R955 photomultiplier tube (spectral response range 160–900 nm), which was connected to a Hamamatsu DP type socket assembly C956-06 (output voltage range –200 to –1250 V), and the above-mentioned lock-in analyser. Corrections were made [4] for reflection losses at both the window of the PEC and the working electrode, as well as for absorption losses in the electrolyte. The incident photon fluxes were controlled to be less than  $4 \times 10^{12} \text{ cm}^{-2} \text{ s}^{-1}$  in order to avoid changes of the growth rate of the given film. The photoelectrochemical current, measured by the lock-in analyser, was converted into quantum yield with respect to the incident radiation.

The electrode under investigation was a section of either lead rod (99.999%) or antimonial lead rod. This was sealed with epoxy resin at the lower part of an L-shaped glass tube, exposing a circular area of  $0.28 \text{ cm}^2$  to the electrolyte. A flat-working electrodes surface was obtained by mechanical polishing with emery paper of successively decreasing grain size down to about  $10 \mu\text{m}$ . Afterwards, the working electrode was rinsed with distilled water, and then placed in the PEC behind an optically flat quartz window. The electrode surface was vertical to that of the electrolyte. The counter electrode was a platinum wire that surrounded concentrically the working electrode. An Hg/Hg<sub>2</sub>SO<sub>4</sub> electrode containing the same solution as that in the PEC served as a reference electrode. All potentials are reported with respect to this electrode.

The electrolyte was a 4.5 M H<sub>2</sub>SO<sub>4</sub> solution prepared from AR H<sub>2</sub>SO<sub>4</sub> and distilled water. All the measurements were performed in a shielded room at a temperature of  $22 \pm 2 \text{ }^\circ\text{C}$ .

As the PbO layer in the anodic film was the subject of study in this work, 0.9 V was chosen as the anodizing condition for forming the film.

## Results and discussion

### Bandgap energy

For thin films:

$$W_{sc} \ll 1/\alpha \quad (1)$$

$$L \ll 1/\alpha \quad (2)$$

and the dependence of the quantum yield of the photoelectrochemical current ( $Y$ ) on the photon energy ( $h\nu$ ) can be given by [5]:

$$[-\ln(1-Y) h\nu]^n = A(h\nu - E_g) \quad (3)$$

where:  $W_{sc}$  is the thickness of the space-charge region;  $L$  is the minority carrier diffusion length;  $\alpha$  is the optical absorption coefficient of the semiconductor for photons of energy  $h\nu$ ;  $A$  is a constant;  $E_g$  is the bandgap energy. The exponent  $n$  is 1/2, 2/3 or 2 when the transition is indirect, forbidden direct or allowed direct, respectively.

Figure 1 presents the  $[-\ln(1-Y)h\nu]^{0.5}$  versus  $h\nu$  plots for the anodic films formed at 0.9 V in 4.5 M H<sub>2</sub>SO<sub>4</sub> for 7 h on both lead and lead-antimony alloys. Using

eqn. (3), the values of  $E_g$  for films formed on Pb, Pb-1at.%Sb, Pb-3at.%Sb, and Pb-9at.%Sb are found to be 1.92, 1.91, 1.85 and 1.87 eV, respectively. It is interesting that antimony has little effect on the bandgap energy. The individual values are virtually the same as that for a single crystal of t-PbO, i.e.,  $1.936 \pm 0.01$  eV [6].

#### Film growth

When the thickness of the t-PbO film ( $L_t$ ) is much smaller than  $1/\alpha$ , the Gärtner equation can be simplified to [3]:

$$Y = \alpha L_t \quad (4)$$

If the t-PbO film is dense, then

$$L_t = QV_m / (zF) \quad (5)$$

where:  $Q$  is the quantity of electricity required for forming the t-PbO;  $V_m$  is the molar volume of t-PbO;  $F$  is the Faraday constant;  $z$  is the number of electrons required for producing t-PbO molecule from lead. Assuming that the growth rate of the t-PbO film is controlled by an oxygen anion diffusion process, then [7]:

$$Q = (4zF^2Dc/V_m)^{1/2} t^{1/2} \quad (6)$$

where:  $c$  is the concentration of the oxygen anion at the surface of the t-PbO film;  $D$  is the diffusion coefficient of the oxygen anion;  $t$  is the time for forming the t-PbO film. From eqns. (4) to (6), the increase of  $Y$  with  $t^{1/2}$  can be expressed by:

$$dY/dt^{1/2} = 2\alpha(V_m Dc/z)^{1/2} = k \quad (7)$$

Figure 2 shows the  $Y$  versus  $t^{1/2}$  plots ( $\lambda = 510$  nm) for the anodic films formed at 0.9 V in 4.5 M  $H_2SO_4$  on both lead and lead-antimony alloys. The curves agree well with eqn. (7). By differentiating of eqn. (7) with respect to  $t^{1/2}$ :

$$dY/dt^{1/2} = \alpha dL_t/dt^{1/2} \quad (8)$$

and hence:

$$dL_t/dt^{1/2} = k/\alpha \quad (9)$$

As the values of  $E_g$  for the t-PbO film on lead and lead-antimony alloys are nearly the same, it can be assumed that the corresponding values of  $\alpha$  are also virtually the

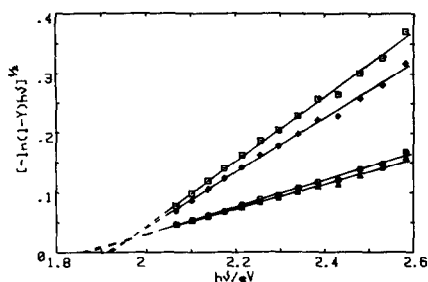


Fig. 1.  $[-\ln(1-Y)h\nu]^{1/2}$  vs.  $h\nu$  plots for electrodes at 0.9 V in 4.5 M  $H_2SO_4$  ( $22 \pm 2$  °C) for 7 h. ( $\square$ ) Pb; ( $\diamond$ ) Pb-1at.%Sb; ( $\triangle$ ) Pb-3at.%Sb; ( $\circ$ ) Pb-9at.%Sb.

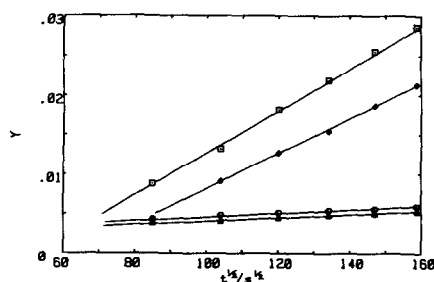


Fig. 2.  $Y$  vs.  $t^{1/2}$  plots ( $\lambda = 510$  nm) for electrodes at 0.9 V in 4.5 M  $H_2SO_4$  ( $22 \pm 2$  °C). ( $\square$ ) Pb; ( $\diamond$ ) Pb-1at.%Sb; ( $\triangle$ ) Pb-3at.%Sb; ( $\circ$ ) Pb-9at.%Sb.

same. Thus, the values of  $k$  for the t-PbO films can be used to compare their growth rates.

The experimental results reveal that the t-PbO films develop via a diffusion-controlled process, and that the values of  $k$  for the t-PbO films on Pb, Pb-1at.%Sb, Pb-3at.%Sb, and Pb-9at.%Sb are  $2.72 \times 10^{-4}$ ,  $2.22 \times 10^{-4}$ ,  $2.06 \times 10^{-5}$  and  $2.12 \times 10^{-5} \text{ s}^{-1/2}$ , respectively. It is concluded that antimony can inhibit the growth of t-PbO film, especially when the antimony content of the substrate is greater than 1 at.%.

#### Relation between quantum yield and electrode potential

From the sign of the photoelectrochemical current, t-PbO in the film is found to be an n-type semiconductor. The  $W_{sc}$  of the semiconductor can be expressed by [5]:

$$W_{sc} = [2\epsilon\epsilon_0(E - E_{fb})/(eN_D)]^{1/2} \quad (10)$$

where:  $\epsilon_0$  is the permittivity of vacuum;  $\epsilon$  is the dielectric constant;  $E_{fb}$  is the flat-band potential;  $E$  is the electrode potential;  $e$  is the elementary charge;  $N_D$  is the density of the donor. Substituting eqn. (10) in the Gärtner equation yields:

$$-\ln(1-Y) = \ln(1 + \alpha L) + \alpha[2\epsilon\epsilon_0(E - E_{fb})/(eN_D)]^{1/2} \quad (11)$$

Again, for thin films,  $L \ll 1/\alpha$ , and eqn. (11) can be expressed as:

$$[-\ln(1-Y)]^2 = \alpha^2[2\epsilon\epsilon_0/(eN_D)](E - E_{fb}) \quad (12)$$

Figures 3(a) and (b) provides  $[-\ln(1-Y)]^2$  versus  $E$  plots ( $\lambda = 500 \text{ nm}$ ) for t-PbO in the anodic films formed at 0.9 V in 4.5 M  $\text{H}_2\text{SO}_4$  for 7 h on lead and lead-antimony alloys. From the intercepts of these lines the value of  $E_{fb}$  for t-PbO films on Pb, Pb-1at.%Sb, Pb-3at.%Sb, and Pb-9at.%Sb is found to be  $-0.20$ ,  $-0.28$ ,  $-0.07$  and  $-0.12 \text{ V}$ , respectively. The corresponding values of  $N_D$ , obtained from the slopes of the plots, are  $9.3 \times 10^{15}$ ,  $3.1 \times 10^{16}$ ,  $4.5 \times 10^{17}$  and  $5.8 \times 10^{17} \text{ cm}^{-3}$ , on the assumption that the value of  $\alpha$  is  $1.03 \times 10^3 \text{ cm}^{-1}$  [6], and  $\epsilon_0$  is 25.9 [8]. The values of  $N_D$  are close to those determined by the a.c. impedance method, as previously reported [2]. Comparing the effect of antimony on  $N_D$  (and, thereafter, free-electron density) with that on the growth rate of t-PbO in the films, it is found that the t-PbO in the anodic film obeys the Hauffe Rules.

The values of  $E_{fb}$  differ appreciably from those obtained by the a.c. impedance measurements [2]. This may be a consequence of the a.c. impedance method and the photoelectrochemical current method each detecting different parts of the film with different composition.

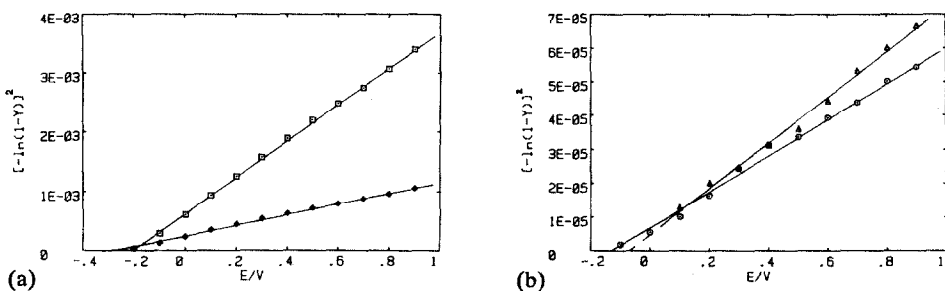


Fig. 3.  $[-\ln(1-Y)]^2$  vs.  $E$  plots ( $\lambda = 500 \text{ nm}$ ) for electrodes at 0.9 V in 4.5 M  $\text{H}_2\text{SO}_4$  ( $22 \pm 2 \text{ }^\circ\text{C}$ ) for 7 h. (a): ( $\square$ ) Pb; ( $\diamond$ ) Pb-1at.%Sb, (b): ( $\triangle$ ) Pb-3at.%Sb; ( $\circ$ ) Pb-9at.%Sb.

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