

Short Communication

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

I. Studies with alternating-current (a.c.) impedance

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Abstract

The semiconducting properties of the anodic plumbous oxide films formed on lead and lead-antimony alloys in 4.5 M H₂SO₄ (20 °C) at 0.9 V (versus Hg/Hg₂SO₄) for 2 h have been studied using the a.c. method. From the Mott-Schottky plots, the films are demonstrated to be n-type semiconductors. The flat-band potentials of the films on Pb, Pb-1at.%Sb, Pb-3at.%Sb and Pb-9at.%Sb are -0.95, -1.0, -0.69 and -0.70 V (versus Hg/Hg₂SO₄), respectively; while the corresponding donor densities are 0.82×10^{16} , 1.2×10^{17} , 5.5×10^{17} and 6.3×10^{17} cm⁻³. The shift of the flat-band potential to more positive values with increase in the antimony content is probably due to the occlusion of a Sb₂O₃ phase in the film. The effect of antimony on the donor density and the lattice-defect density of the n-type semiconductor oxide both conform to the Hauffe Rules.

Introduction

It is well known that the deep-discharge cycle life of lead/acid batteries is enhanced by using positive grid alloys containing antimony [1]. The mechanism of this antimony effect is, however, still not fully understood. Bojinov and Monahov [2] have studied the characteristics of the anodic PbO films formed on lead and Pb-6wt.%Sb alloy in 1 M Na₂SO₄ using a.c. impedance method. The films were treated as solid electrolytes, and it was concluded that the PbO film on Pb-Sb alloys has a higher stability and less ionic conductivity than that produced on pure lead. As the films are mixed conductors, a study was undertaken on the electronic properties of the anodic plumbous oxide film on pure lead in 4.5 M H₂SO₄ using a.c. impedance techniques. It was found that the film is an n-type semiconductor with a donor density of 1×10^{16} cm⁻³ and

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a flat-band potential of -0.9 V (versus $\text{Hg}/\text{Hg}_2\text{SO}_4$) [3]. It was suggested that antimony may become incorporated in the plumbous oxide film and thereby modify the electronic properties. As a consequence, a change occurs in the corrosion rate of the substrate.

In the present work, the behaviour of three Pb-Sb alloys is examined by the a.c. impedance technique in order to demonstrate the influence of antimony on the semiconducting properties of the plumbous oxide film, and to verify the above findings. Related work exploring photoelectrochemical-current phenomena will be reported in a subsequent paper.

Experimental

Details of the electrochemical cell, electrode holder, solution and linear potential sweep method are the same as those described in ref. 4.

Pure lead (99.999%), Pb-1at.%Sb, Pb-3at.%Sb and Pb-9at.%Sb alloys were used as working electrodes; all had an apparent surface area of 0.28 cm². Potentials are reported with respect to a $\text{Hg}/\text{Hg}_2\text{SO}_4$ reference electrode that contains the same solution as that in the electrochemical cell. The electrochemical cell was maintained at 20 °C.

Alternating current impedance measurements were conducted with a PAR 5208 lock-in amplifier, a PAR 273 potentiostat, and a sine-wave signal of 5 mV (rms). The impedance is represented by an equivalent circuit composed of a resistance (R_p) and a capacitance (C_p) in parallel, or a resistance (R_s) and a capacitance (C_s) in series.

Results and discussion

Phase composition of the anodic film

As PbO_2 and PbSO_4 are not of interest in the present work, 0.9 V was chosen as the anodizing condition for the growth of Pb(II) oxides as the main constituents of the films under examination. A method described previously [4] was applied to analyse the phase composition of the anodic films. The experimental results show that when pure lead or Pb-1at.%Sb is anodized in 4.5 M H_2SO_4 at 0.9 V for 2 h at 20 °C, an anodic film consisting of $\text{PbO} \cdot \text{PbSO}_4$ and a comparatively small amount of PbO_x ($2 > x \geq 1$) is formed. Moreover, with Pb-3at.%Sb or Pb-9at.%Sb substrates, a new phase of Sb_2O_3 occurs in the film. The yield of PbSO_4 does not change after anodizing for 15 min.

Pu [5] obtained a good linear relationship between the quantity of electricity (Q) required to form the anodic films under the above conditions and the square root of formation time ($t^{1/2}$). It was concluded that the growth rate of the films is controlled by a diffusion mechanism. The values of $(dQ/dt^{1/2})$ thus obtained for Pb, Pb-1at.%Sb, Pb-3at.%Sb and Pb-9at.%Sb electrodes are 7.9 , 3.5 , 1.9 and 2.5 mC cm⁻² s^{-1/2}, respectively [5]. Hence, the presence of antimony inhibits the diffusion process of film growth. This finding is in agreement with the results of Bojinov and Monahov [2].

Equivalent circuit of the electrodes

Figure 1 shows the equivalent circuit that is generally used to represent semiconductor electrodes [6], and is adopted here for the analysis of the a.c. impedance data of the anodic films.

The R_s measured at 100 kHz is at least three orders of magnitude less than the resistance of the space-charge layer of the films (R_{sc}), hence, the resistances of the

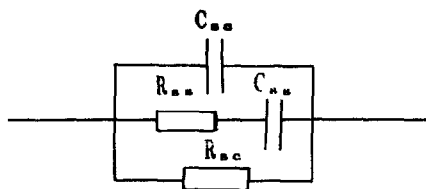


Fig. 1. Equivalent circuit for analysis of impedance data for anodic Pb(II) oxides films in 4.5 M H₂SO₄ (20 °C). C_{sc} : space charge layer capacitance; C_{ss} : surface state capacitance; R_{sc} : space charge layer resistance; R_{ss} : surface state resistance.

bulk film, the solution and the contact between lead and the film may be neglected. The last conforms to the consideration of Schmickler and Schultze [7] that the metal–film interface is permeable to the metal cations, and that there exists only a small space-charge region.

The impedance of the PbSO₄ film formed on lead at -0.96 V within 7 to 52 min is nearly constant and has a value of 2 Ω cm² (measured at 410 Hz). If it is assumed that the exchange current density of the Pb²⁺/Pb couple in 5 M H₂SO₄ is 5 × 10⁻⁶ A cm⁻² [8], then the capacitance of the Helmholtz layer adjacent to the PbSO₄ film is >1.9 × 10⁻⁴ F cm⁻², and the resistance of the PbSO₄ film is <2 Ω cm². The former may attributed to adsorption effects, while the latter may be due to the fact that the PbSO₄ film is very thin. Therefore, the Helmholtz-layer capacitance and the resistance of the PbSO₄ film (which is the outermost part of the anodic film) are both omitted in Fig. 1.

C_{ss} and R_{ss} in Fig. 1 represent, respectively, the capacitance and resistance of the surface state. These parameters may be calculated through the following equation:

$$(R_p^{-1} - R_{sc}^{-1})^{-1} = R_{ss} + C_{ss}^{-2} R_{ss}^{-1} \omega^{-2} \quad (1)$$

where ω is the angular frequency. R_{sc} may be obtained at low frequencies by rearranging eqn. (1), i.e.:

$$R_p^{-1} = R_{sc}^{-1} + C_{ss}^2 R_{ss} \omega^2 [1 + (C_{ss} R_{ss} \omega)^2]^{-1} \quad (2)$$

When $(C_{ss} R_{ss} \omega) \ll 1$, eqn. (2) can be simplified to:

$$R_p^{-1} = R_{sc}^{-1} + C_{ss}^2 R_{ss} \omega^2 \quad (3)$$

Thus, R_{sc} can be obtained from the R_p^{-1} versus ω^2 relation. The space-charge capacitance (C_{sc}) of the film can be obtained from the following equation:

$$C_p = C_{sc} + C_{ss} [1 + (C_{ss} R_{ss} \omega)^2]^{-1} \quad (4)$$

In the present work, R_p is at least 25 times less than R_{sc} thus, eqn. (1) may be simplified to:

$$R_p = R_{ss} + C_{ss}^{-2} R_{ss}^{-1} \omega^{-2} \quad (5)$$

Relation between C_p and time for film development

Figure 2 presents the dependence of C_p on the reciprocal of the square root of time for anodizing lead and lead–antimony alloys at 0.9 V in 4.5 M H₂SO₄ (20 °C), measured at 2500 Hz. If the space-charge region in the film is a depletion layer, the thickness of the film is less than the Debye length and the film is planar, then C_{sc} can be written as [9]:

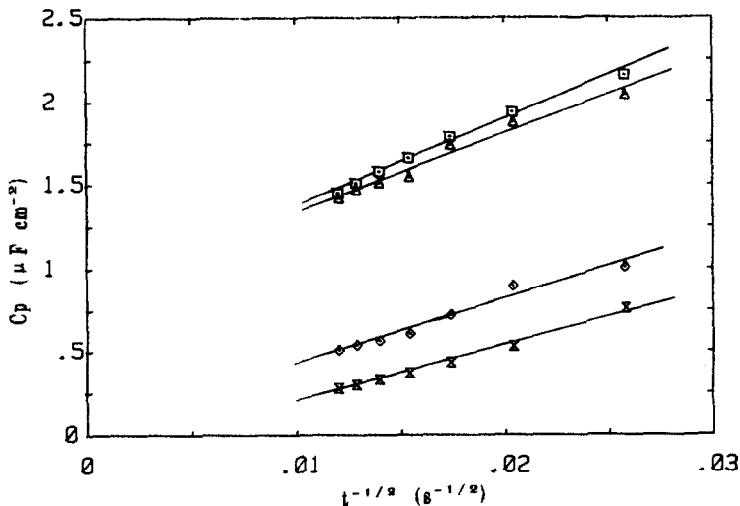


Fig. 2. C_p vs. $t^{-1/2}$ for electrodes at 0.9 V (vs. Hg/Hg₂SO₄) in 4.5 M H₂SO₄ (20 °C), measured at 2500 Hz. (X) Pb; (◇) Pb-1at.%Sb; (□) Pb-3at.%Sb; (△) Pb-9at.%Sb.

$$C_{sc} = \epsilon \epsilon_0 / L \quad (6)$$

where: ϵ_0 is the permittivity of vacuum; ϵ is the dielectric constant of the film; L is the thickness of the film. Clearly, C_p decreases with increase of the anodizing time (Fig. 2), so it is reasonable to assume that the film is dense. Thus, the thickness of the film can be given as:

$$L = QV_m / (zF) \quad (7)$$

where V_m is the molar volume of PbO·PbSO₄, z is the number of electrons required to form a PbO·PbSO₄ molecule from lead, and F is the Faraday constant.

Thus:

$$dL^{-1}/dt^{-1/2} = (zF/V_m)(dQ/dt^{1/2})^{-1} \quad (8)$$

From eqns. (6) and (8):

$$dC_{sc}/dt^{-1/2} = (\epsilon \epsilon_0 zF/V_m)(dQ/dt^{1/2})^{-1} \quad (9)$$

If C_{ss} and R_{ss} are both independent on time, then from eqns. (4) and (9), the following relation is obtained:

$$dC_p/dt^{-1/2} = (\epsilon \epsilon_0 zF/V_m)(dQ/dt^{1/2})^{-1} \quad (10)$$

From the data given in Fig. 2 and the values of $dQ/dt^{1/2}$, the dielectric constants at 2500 Hz of the PbO·PbSO₄ films grown on lead, Pb-1at.%Sb, Pb-3at.%Sb and Pb-9at.%Sb can be calculated, using eqn. (10), to be 6.2×10^2 , 3.0×10^2 , 2.1×10^2 and 2.6×10^2 , respectively. In an electric field, the vacancies of oxygen anions in the film preferentially increase the migration rate of the oxygen anions, so that an electric double-layer forms and the dielectric constant increases [10]. Hence, the smaller dielectric constants of the films grown on antimonial lead are probably due to the smaller density of oxygen anion vacancies in the films. The latter is also the cause of

TABLE 1

Calculated values for C_{sc} at 2500 Hz for films on lead and lead-antimony alloys, in 4.5 M H_2SO_4 (20 °C) at 0.9 V for 2 h

| Electrode | E^a (V) | f (kHz) | R_p ($k\Omega\text{ cm}^2$) | C_p ($\mu\text{F cm}^{-2}$) | C_{sc} ($\mu\text{F cm}^{-2}$) | R^b | |
|------------|--------------|--------------|------------------------------------|------------------------------------|---------------------------------------|--------|--------|
| Pb | -0.40 | 1.8 | 0.408 | | | | |
| | | 2.0 | 0.379 | | | | |
| | | 2.2 | 0.354 | | | | |
| | | 2.5 | 0.321 | | 0.390 | 0.265 | 0.9963 |
| | -0.50 | 1.8 | 0.393 | | | | |
| | | 2.0 | 0.370 | | | | |
| | | 2.2 | 0.345 | | | | |
| | | 2.5 | 0.313 | | 0.409 | 0.286 | 0.9913 |
| | -0.55 | 1.8 | 0.369 | | | | |
| | | 2.0 | 0.354 | | | | |
| | | 2.2 | 0.333 | | | | |
| | | 2.5 | 0.302 | | 0.426 | 0.312 | 0.9769 |
| | -0.60 | 1.8 | 0.353 | | | | |
| | | 2.0 | 0.326 | | | | |
| | | 2.2 | 0.309 | | | | |
| | | 2.5 | 0.280 | | 0.458 | 0.320 | 0.9958 |
| | -0.65 | 1.8 | 0.324 | | | | |
| | | 2.0 | 0.306 | | | | |
| | | 2.2 | 0.293 | | | | |
| | | 2.5 | 0.264 | | 0.490 | 0.359 | 0.9812 |
| -0.70 | 1.8 | 0.276 | | | | | |
| | 2.0 | 0.265 | | | | | |
| | 2.2 | 0.244 | | | | | |
| | 2.5 | 0.230 | | 0.565 | 0.417 | 0.9850 | |
| Pb-1at.%Sb | 0.00 | 1.8 | 0.648 | | | | |
| | | 2.0 | 0.598 | | | | |
| | | 2.2 | 0.561 | | | | |
| | | 2.5 | 0.524 | | 0.593 | 0.522 | 0.9999 |
| | -0.10 | 1.8 | 0.613 | | | | |
| | | 2.0 | 0.563 | | | | |
| | | 2.2 | 0.538 | | | | |
| | | 2.5 | 0.488 | | 0.625 | 0.547 | 0.9948 |
| | -0.20 | 1.8 | 0.581 | | | | |
| | | 2.0 | 0.531 | | | | |
| | | 2.2 | 0.492 | | | | |
| | | 2.5 | 0.462 | | 0.655 | 0.568 | 0.9978 |
| | -0.30 | 1.8 | 0.512 | | | | |
| | | 2.0 | 0.486 | | | | |
| | | 2.2 | 0.463 | | | | |
| | | 2.5 | 0.418 | | 0.701 | 0.613 | 0.9905 |
| | -0.40 | 1.8 | 0.470 | | | | |
| | | 2.0 | 0.440 | | | | |
| | | 2.2 | 0.397 | | | | |
| | | 2.5 | 0.371 | | 0.771 | 0.659 | 0.9917 |
| -0.45 | 1.8 | 0.423 | | | | | |
| | 2.0 | 0.391 | | | | | |
| | 2.2 | 0.365 | | | | | |
| | 2.5 | 0.338 | | 0.823 | 0.708 | 0.9998 | |
| -0.50 | 1.8 | 0.366 | | | | | |
| | 2.0 | 0.339 | | | | | |
| | 2.2 | 0.322 | | | | | |
| | 2.5 | 0.295 | | 0.885 | 0.760 | 0.9973 | |
| Pb-3at.%Sb | 0.00 | 1.8 | 0.287 | | | | |
| | | 2.0 | 0.266 | | | | |
| | | 2.2 | 0.247 | | | | |
| | | 2.5 | 0.222 | | 1.32 | 1.13 | 0.9953 |

(continued)

TABLE 1 (continued)

| Electrode | E^a (V) | f (kHz) | R_p ($k\Omega\text{ cm}^2$) | C_p ($\mu\text{F cm}^{-2}$) | C_{sc} ($\mu\text{F cm}^{-2}$) | R^b |
|------------|--------------|--------------|------------------------------------|------------------------------------|---------------------------------------|--------|
| | -0.10 | 1.8 | 0.264 | | | |
| | | 2.0 | 0.244 | | | |
| | | 2.2 | 0.226 | | | |
| | | 2.5 | 0.204 | 1.40 | 1.19 | 0.9970 |
| | -0.20 | 1.8 | 0.227 | | | |
| | | 2.0 | 0.211 | | | |
| | | 2.2 | 0.195 | | | |
| | | 2.5 | 0.174 | 1.55 | 1.30 | 0.9929 |
| | -0.30 | 1.8 | 0.189 | | | |
| | | 2.0 | 0.175 | | | |
| | | 2.2 | 0.163 | | | |
| | | 2.5 | 0.152 | 1.73 | 1.48 | 0.9996 |
| | -0.40 | 1.8 | 0.154 | | | |
| | | 2.0 | 0.143 | | | |
| | | 2.2 | 0.132 | | | |
| | | 2.5 | 0.121 | 2.11 | 1.77 | 0.9977 |
| | -0.45 | 1.8 | 0.147 | | | |
| | | 2.0 | 0.135 | | | |
| | | 2.2 | 0.124 | | | |
| | | 2.5 | 0.110 | 2.46 | 2.03 | 0.9958 |
| | -0.50 | 1.8 | 0.140 | | | |
| | | 2.0 | 0.127 | | | |
| | | 2.2 | 0.116 | | | |
| | | 2.5 | 0.103 | 2.72 | 2.24 | 0.9985 |
| Pb-9at.%Sb | 0.00 | 1.8 | 0.173 | | | |
| | | 2.0 | 0.162 | | | |
| | | 2.2 | 0.151 | | | |
| | | 2.5 | 0.139 | 1.60 | 1.33 | 0.9968 |
| | -0.10 | 1.8 | 0.160 | | | |
| | | 2.0 | 0.148 | | | |
| | | 2.2 | 0.138 | | | |
| | | 2.5 | 0.125 | 1.73 | 1.40 | 0.9972 |
| | -0.20 | 1.8 | 0.140 | | | |
| | | 2.0 | 0.130 | | | |
| | | 2.2 | 0.120 | | | |
| | | 2.5 | 0.109 | 1.93 | 1.55 | 0.9967 |
| | -0.30 | 1.8 | 0.120 | | | |
| | | 2.0 | 0.111 | | | |
| | | 2.2 | 0.103 | | | |
| | | 2.5 | 0.0953 | 2.18 | 1.76 | 0.9994 |
| | -0.35 | 1.8 | 0.109 | | | |
| | | 2.0 | 0.101 | | | |
| | | 2.2 | 0.0960 | | | |
| | | 2.5 | 0.0918 | 2.40 | 2.05 | 0.9956 |
| | -0.40 | 1.8 | 0.106 | | | |
| | | 2.0 | 0.0967 | | | |
| | | 2.2 | 0.0900 | | | |
| | | 2.5 | 0.0810 | 2.65 | 2.11 | 0.9987 |
| | -0.45 | 1.8 | 0.103 | | | |
| | | 2.0 | 0.0942 | | | |
| | | 2.2 | 0.0856 | | | |
| | | 2.5 | 0.0778 | 2.87 | 2.27 | 0.9986 |
| | -0.50 | 1.8 | 0.102 | | | |
| | | 2.0 | 0.0923 | | | |
| | | 2.2 | 0.0849 | | | |
| | | 2.5 | 0.0752 | 3.08 | 2.43 | 0.9984 |

^a E is the potential at which the impedance of the anodic film is measured.

^bCorrelation coefficient between ω^{-2} and R_p .

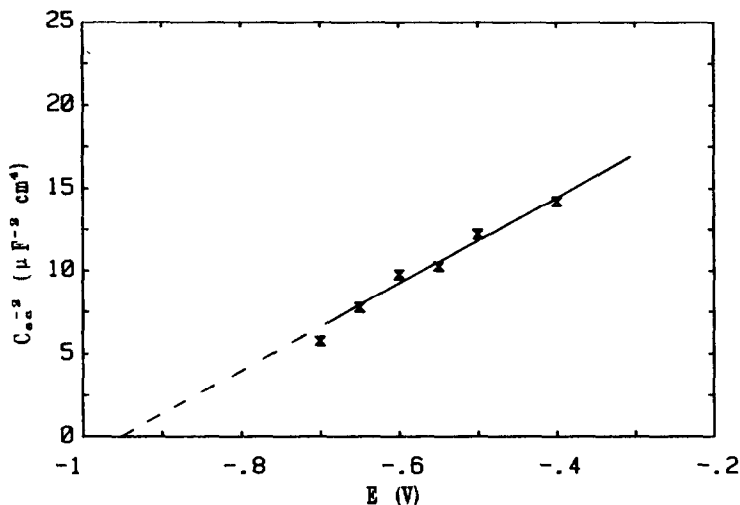


Fig. 3. Mott-Schottky plot for lead electrode at 0.9 V (vs. $\text{Hg}/\text{Hg}_2\text{SO}_4$) in 4.5 M H_2SO_4 (20 °C) for 2 h, measured at 2500 Hz.

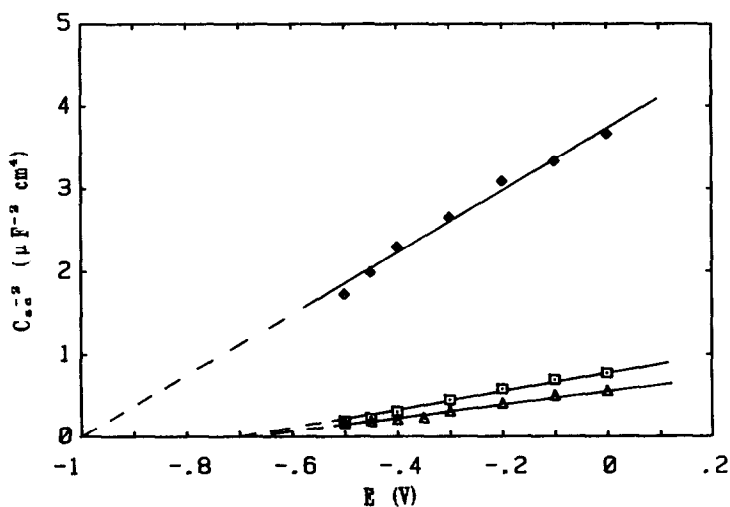


Fig. 4. Mott-Schottky plots for Pb-Sb alloy electrodes at 0.9 V (vs. $\text{Hg}/\text{Hg}_2\text{SO}_4$), in 4.5 M H_2SO_4 (20 °C) for 2 h, measured at 2500 Hz. (\diamond) Pb-1at.%Sb; (\square) Pb-3at.%Sb; (\triangle) Pb-9at.%Sb.

the smaller diffusion rates of the oxygen anion in the films grown on lead-antimonial electrodes and this, in term, gives rise to the slower growth rates.

Mott-Schottky plots

The Mott-Schottky equation for an n-type semiconductor is given by [11]:

$$C_{sc}^{-2} = \frac{2}{\epsilon\epsilon_0 e N_D} \left(E - E_{fb} - \frac{kT}{e} \right) \quad (11)$$

where: E is the potential of the electrode; E_{fb} is the flat-band potential; k is the Boltzmann constant; T is the absolute temperature; e is the elementary charge; N_D is the donor density.

The values of C_{sc} used for the Mott-Schottky plots are calculated by R_p and C_p from eqns. (4) and (5) and listed in Table 1. Figures 3 and 4 give the C_{sc}^{-2} versus E curves of the anodic films measured at 2500 Hz. The results show that the films are n-type semiconductors. The values of E_{fb} for the films on lead, Pb-1at.%Sb, Pb-3at.%Sb and Pb-9at.%Sb are -0.95 , -1.0 , -0.69 and -0.70 V, respectively. The corresponding values of N_D are 0.82×10^{16} , 1.2×10^{17} , 5.5×10^{17} and 6.3×10^{17} cm^{-3} .

According to Hauffe's Valency Rules [12], 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 (oxygen anion vacancies in the present case) will decrease. The experimental results obtained here conform to the Hauffe Rules.

The shift in E_{fb} for films on Pb-3at.%Sb and Pb-9at.%Sb about 0.3 V relative to that for pure lead is probably due to the occlusion of an Sb_2O_3 phase in the films.

Acknowledgements

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