ANODIC SULPHURATION OF SUBMICRON-GRAINED THIN FILMS FOR IR SENSING

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Abstract

Equilibrium and kinetic properties of the anodic sulphuration of magnetron sputtered lead thin films at room temperature are reviewed. Tafel plots and cyclic voltametry data demonstrate the existence of competing two electron reactions. Direct anodization produces PbS of 8 nm average grain size (Scherrer), whereas a solution-reprecipitation mechanism induces coarser deposits. PbS_2 contamination can be minimized by controlling pH and the anodic potential. Optimized working conditions were found for 0.2 M thioacetamide solutions, at a buffered pH of 4.6 and a working potential of 0.600 V, with respect to the Ag/AgCl reference electrode.

Resumen

Se examinaron aspectos cinéticos y de equilibrio para la reacción de sulfuración anódica de una película de plomo obtenida por deposición por plasma magnéticamente confinado. Los gráficos de Tafel y voltametría cíclica indican la existencia de reacciones bielectrónicas competitivas. La anodización directa produce PbS de un tamaño de grano promedio de 8 nm por la ecuación de Scherrer. Mientras que la solución-reprecipitación induce granulometría más gruesa. La contaminación con PbS_2, puede minimizarse por control del pH y potencial. Las condiciones operativas óptimas se obtienen para soluciónes de tioacetamida 0,2 M, a pH = 4,6 y potencial anódico de 0,600 V, con respecto al electrodo de referencia Ag/AgCl.

Introduction

Nanocrystalline (1-20 nm) PbS thin films find numerous opto-electronic applications. The onset of strong quantum confinement, when grain size becomes commensurate with the Bohr exciton, can be used to modify the semiconducting band gap. Consequently, a wide variety of appropriate synthesis techniques [1-3] have received recent attention. Electrochemical methods [4-6] offer the intrinsic advantages of room temperature operation,

phase selectivity by controlling the working potential and current density to determine grain size, which are surveyed in this investigation of anodic processes [7].

Experimental

Lead was magnetron sputtered onto 12.5 x 12.5 x 1mm plastic PTG (polyethylene terephthalate polyester) substrates, to a piezogravimetric thickness of 80 nm. The lead thin films were anodised in a stirred 0.2 M thioacetamide solution, buffered to pH = 4.6 by an acetic acid-sodium acetate buffer and PbS saturated by Pb° electrolysis, a fretted glass separated stainless steel counter-electrode, in 1M potassium nitrate. A voltage clamp circuit controlled the working potential, referred to a standard Ag°/AgCl electrode placed in the sample half cell compartment. Cyclic voltametries were undertaken upon completion of electrolysis, at 50 mV/s, initially anodic, between 0.1 and 1.0 V.

Results and discussion

The use of thioacetamide in metallic sulphide precipitation is well established. Its hydrolysis [8] in acid media, namely:

$$
\begin{array}{ccc}
\text{SH} & & \text{H-S}^+\text{-H} \\
| & \xrightarrow{\text{H}^+} & | \\
\text{CH}_3\text{- C = NH} & & \text{CH}_3\text{- C = NH}
\end{array}
$$
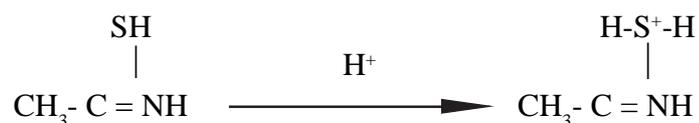
leads to the formation of hydrogen sulphide by the dissociation:

$$
\begin{array}{ccc}
\text{H-S}^+\text{-H} & & \\
| & \longrightarrow & \text{CH}_3\text{- C} \equiv \text{NH}^+ + \text{H}_2\text{S} \\
\text{CH}_3\text{- C = NH} & &
\end{array}
$$

The kinetics of these reactions are pH dependent, which promote different precipitation mechanisms. For instance, at pH = 4.6, the PbS rate of precipitation [9] can exceed the rate of hydrolysis by six orders of magnitude. Further constraints arise from complexing reactions, which are absent in the acetic–acetate buffer. Continuous stirring was implemented for removal of soluble reaction products from the anode surface.

Cyclic voltametries of partially sulphured lead thin films (Fig.1) are consistent with two competing reactions. The EMF measurements of the Pb°/work solution//Ag°/AgCl cell, on the initial solution, correspond to a Pb^{2+} activity of 4.14×10^{-5}, which suggests the reaction

$$Pb° + SH_2 \Leftrightarrow PbS + 2H^+ + 2e^- \qquad E = 0.3142 \text{ V vs. SHE}$$
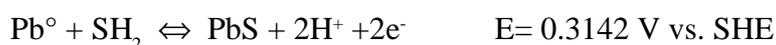
for direct anodisation, given $pK_1 = 6.99$ and $pK_2 = 13.99$, for the dissociation constants of SH_2 [10] and Kps = 9.04×10^{-9} for PbS [10]. Lead oxidation according to

$$Pb^\circ \iff Pb^{2+} + 2e^- \qquad\qquad E = 0.2558 \text{ V vs SHE}$$

and subsequent chemical precipitation is also present, leading to micron grain deposits of PbS, filling cracks and discontinuities produced by the release of tensile stress in the films, which serve as nucleation centres, as revealed by ambient scanning electron microscopy (Fig 2). This coarser grained precipitate is strongly inhibited by the face down configuration of the working electrode. Direct anodisation is dependent on the presence of light, to promote carriers to the conduction band of the PbS semiconductor. In darkness, the indirect solution and reprecipitation mechanism is dominant.
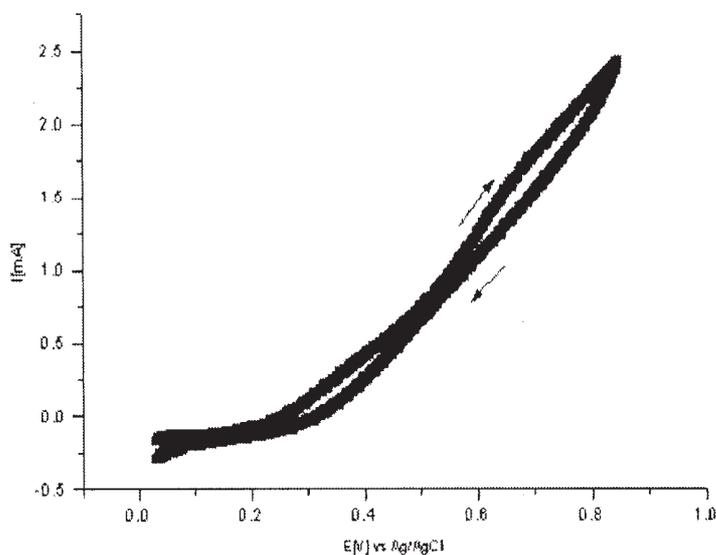
Fig.1. *Cyclic voltametry of partially anodised lead film, from 0.1 to 1 V, at 50 mV/s.*
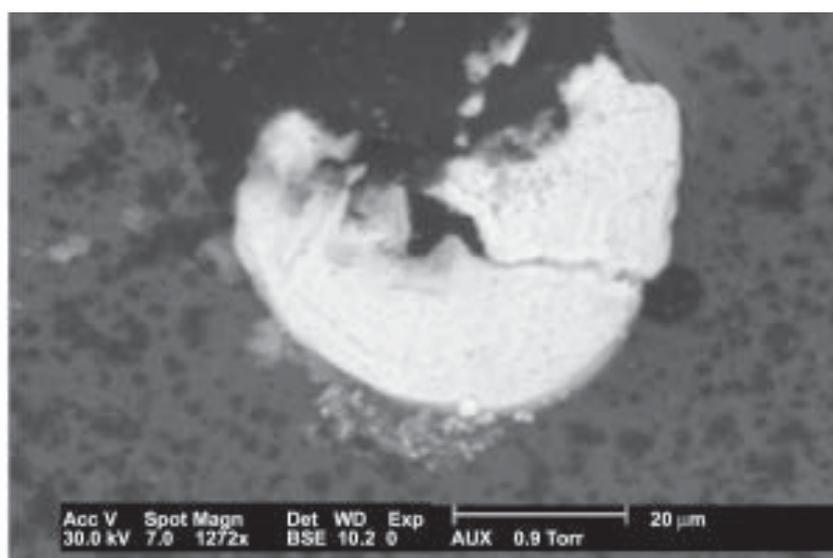
Fig. 2. *Ambient SEM micrograph of PbS thin film.*

The oxidation reaction:

$$2\,S^{2-} \Leftrightarrow S_2^{2-} + 2\,e^- \qquad\qquad E° = 0.5241\ V\ vs.\ SHE$$
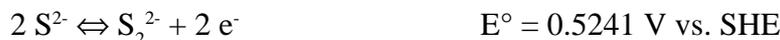
constitutes a more serious interference, because the tetragonal PbS_2 [11] phase is not a direct gap semiconductor and consequently does not contribute to the electro-optic sensitivity. X-ray diffraction patterns obtained at a glancing angle of 1°, with Cu Kα radiation, demonstrate that the presence of this contaminant, prevalent at high working potentials (Fig 3,b), is minimised by operation at 0.600 V, with respect to Ag°/AgCl (Fig. 3,a), consistent with E = 0.3778V vs. SHE.
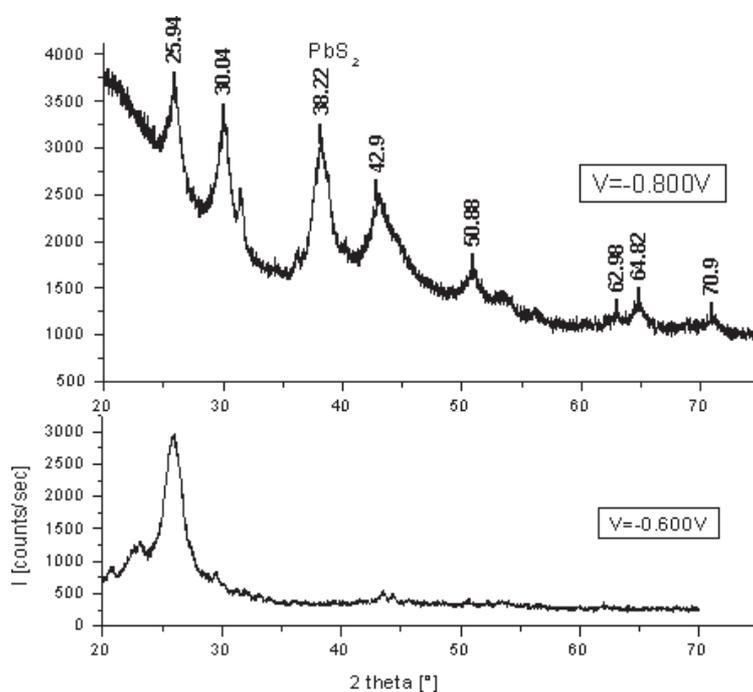
Fig. 3. *XRD with a 1° glancing angle of: a) thin film anodised at 0.600 V b) thin film anodised at 0.800 V*

The strong linear character of the Tafel plot for the voltametric data (Fig. 4) corroborates that the active processes are charge transfer controlled, consistently with their dependence on adequate illumination. The logarithmic current / voltage slope of 2.57 V and intercept $i_0 = 1.41$ mA correspond to a transfer coefficient $\alpha = 0.1$.

The grain size resulting from direct anodic sulphuration may be estimated from the Scherrer equation [12], with a width at half height of the low angle X-ray diffraction peaks, as 8 nm, for the data in Fig 3, a.
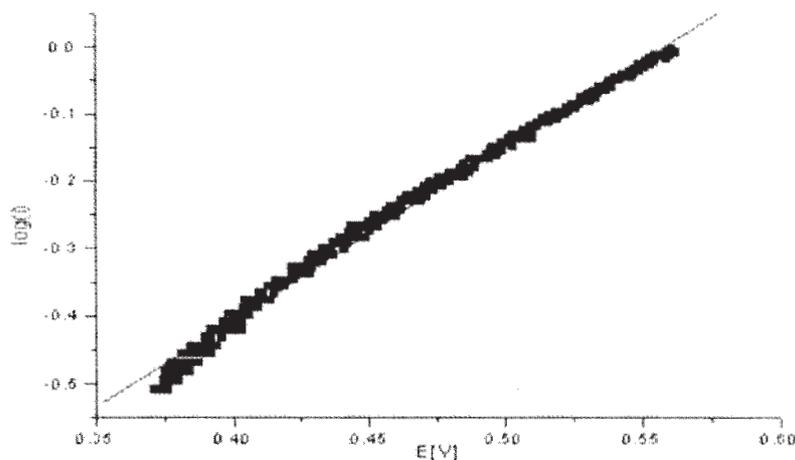
Fig. 4. *Tafel plot of cyclic voltametry data*

Conclusions

Anodic sulphuration of lead thin films, at a working potential of 0.600 V with respect to Ag/AgCl, in PbS saturated thioacetamide solutions, buffered at pH = 4.6, produces single phase, nanometric PbS thin films, suitable for electro-optic IR detectors. Unlike cathodic deposition techniques, anodic potential control can be implemented to create essentially single phase galena, without resorting to post deposition treatments. Grain size is one or two orders of magnitude finer than that obtained from chemical deposition.

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