Anodic processing of submicron grained PbS thin films

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The performance of infrared sensing galena thin films is critically[1] dependent on small uniform grain size. Electrochemical processing is promising for this purpose, although it has so far proved difficult to promote adequate adherence

Lead thin films were deposited by magnetron sputtering, at 20 mA, to 70 nm thickness, over 12.5 x 12.5 x 1 mm polycarbonate substrates, which were subsequently anodised, in stirred 0.2 M thioacetamide aqueous solutions, with a pH range of 4 to 5, under a voltage clamp controlled potential ($-0.910\ V < V_A < -0.800\ V$), with reference to a standard Ag/AgCl electrode. A 1 M KNO_3 salt bridge connected the half cell to the $Cu/CuSO_4$ (saturated aqueous) counter electrode. Chrono-amperometric monitoring indicated a 3 mA maximum current.

The hydrolysis of thioacetamide[2] yields:

$$CH_3CSNH_2 + H_2O \leftrightarrow CH_3CONH_2 + SH_2$$

The dissociation constants for SH_2, $pK_1=6.99$ and $pK_2=13.9$, are consistent with H_2S, as the dominant species in the pH range of this work, hence the proposed[3] anodic reaction is:

$$Pb^o + SH_2 \leftrightarrow SPb + 2H^+ + 2e^-$$

Examination with ambient scanning electron microscopy (Fig. 1) and atomic force microscopy (Fig. 2) revealed that solution and reprecipitation phenomena compete with direct electrochemical anodization, to produce filling and occlusion of micron sized chemical deposits in film discontinuities, produced by release of tensile stress in the Pb deposit, which serve as nucleation centers. This coarser grained precipitate is strongly inhibited by face down configuration of the work electrode.

Direct anodization is dependent on the presence of light, to promote carriers to the conduction band of the PbS semiconductor. In darkness, the indirect solution and precipitation mechanism is dominant.

Cu Kα glancing x-ray diffraction, with a 1º angle of incidence is consistent with a dominant cubic ($Fm\bar{3}m$) galena phase[3]. Subsidiary PbS_2[4] peaks are present for $V_A \geq -0.800$ V. Average grain size, which is below the resolution of the available direct space microscopic techniques, can be estimated with the Scherrer equation, by the broadening of low angle peaks, to be in the order of 7 nm.

The deposition and anodization process can be reiterated to overcome the widely acknowledged limited thickness of anodic thin films, to obtain a multiple fold increase, without detriment to film quality.

References

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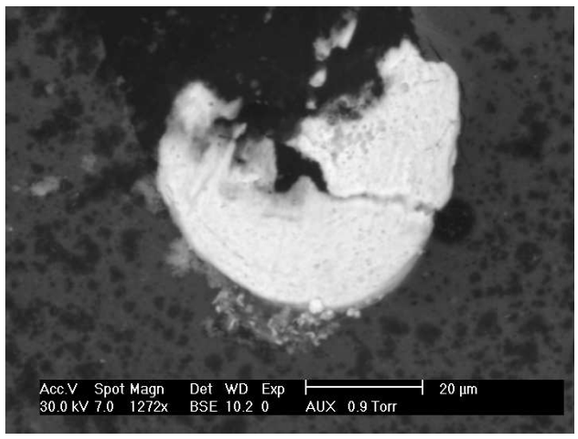

Figure 1. Ambient scanning back scattered electron image of anodized lead thin film reveals coarse grained filling of discontinuities by chemically precipitated PbS, with face up electrode configuration.

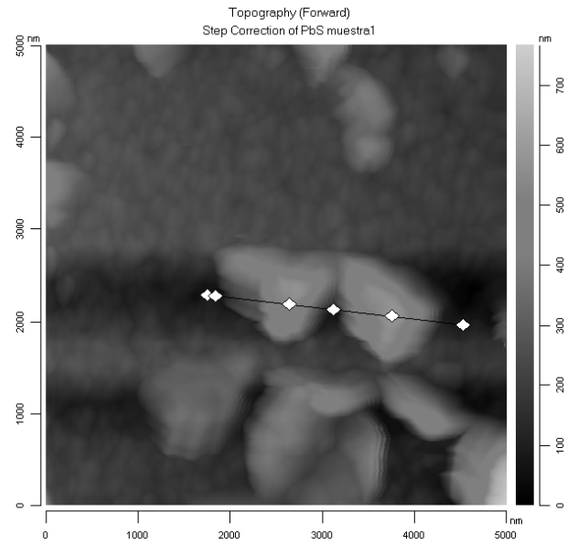

Figure 2. Scanning force microscopy image of anodized lead thin film reveals coarse grained filling of discontinuities by chemically precipitated PbS, with face up electrode configuration.