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Formation of Pb during epitaxial growth of PbS on KCl in a vitreous silica hot wall system

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Thin monocrystalline films of PbS grown epitaxially from the vapour on KCl in a vitreous silica hot wall system, present lower specular reflectivity than expected. Electron micrography shows that the surfaces of the films are studded with a multitude of small blobs. They scatter partially the incident light. By electron probe microanalysis and Bragg diffractometry it was found that the blobs are made up of elemental Pb and PbS. As basic lead sulphates were also found on the films the presence of elemental Pb is attributed to the roast reduction reaction. We believe that the silica of the apparatus provides the major part of the oxygen involved in this reaction.

1. Introduction

In a previous paper [1] a method of quasi equilibrium epitaxial growth of PbS films on KCl, in a vitreous SiO_2 demontable system, shown in Fig. 1, was reported in detail. The films thus obtained in spite of the fact that they were monocrystalline, did not show the high specular reflectivity that could be expected. We report here our investigations concerning this "bloom" on the films as well as some other aspects of the growth of PbS films.

2. Experimental

2.1. Electron micrography

Scanning electron micrographs have shown that the surface of the films 10, 11 and 12 [1] (temperature of the substrate, 400 $\pm$ 2°C; temperatures of the PbS source, 605, 562 and 517°C; time of growth, 10, 50 and 300 min; rates of growth, 0.33, 0.09 and 0.027 μm min^{-1}; thicknesses, 3.3, 4.5 and 8.1 μm respectively) were covered with a multitude of solidified blobs (Figs. 2 and 3). The transmission electron micrographs of carbon replicas of the surface revealed, under high magnification (Fig. 4), that the surface between big blobs (diameter of the order of 100 μm) was studded with small blobs (diameter of the order of 10^{-1} μm) which may coalesce into bigger droplets. One of the big blobs is shown in Fig. 5 under high magnification. It has rudimentary facets, disposed in a threefold symmetry, the ⟨111⟩ axis being perpendicular to the (100) plane of the films. The facets are granulated, indicating that the blobs are not a single phase. On the surface of some of the blobs small crystals can be found (Fig. 5).

2.2. Electron probe microanalysis

Directing the electron beam (diameter ~ 15 nm) of the scanning electron microscope on a given spot of the sample, the emitted X-rays can be analysed. This procedure revealed that the blobs contain S and Pb, but that they are richer in Pb than corresponds to PbS. In fact, the ratio of the intensities of PbL_α and S$K_{\alpha,\beta}$ lines emitted by the material of the blobs is always greater than the ratio corresponding to the PbS film. For example, $I_{PbL_\alpha}/I_{SK_{\alpha,\beta}}$ was 0.36 for a blob on film no. 12 and only 0.16 for the cleaved surface of the film itself.

2.3. Diffractometry

Diffractometric measurements of the surface of the films, using CuK_α radiation, showed (Fig. 6) the presence of PbS, Pb and basic lead sulphates $PbSO_4 \cdot PbO$ and $PbSO_4 \cdot 2PbO$, the latter identified by means of spacings given by Lander [2]. Formation of these basic lead sulphates by

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oxidization of thin PbS films is already reported in the literature [3]. On the diffractograms appear only the 111 line of Pb and its higher orders. This indicates that Pb grows epitaxially on PbS from the liquid state, with the (111) plane parallel to the (100) plane of PbS, itself parallel to the (100) plane of KCl. It means also that all threefold symmetry axes of the blobs are parallel.

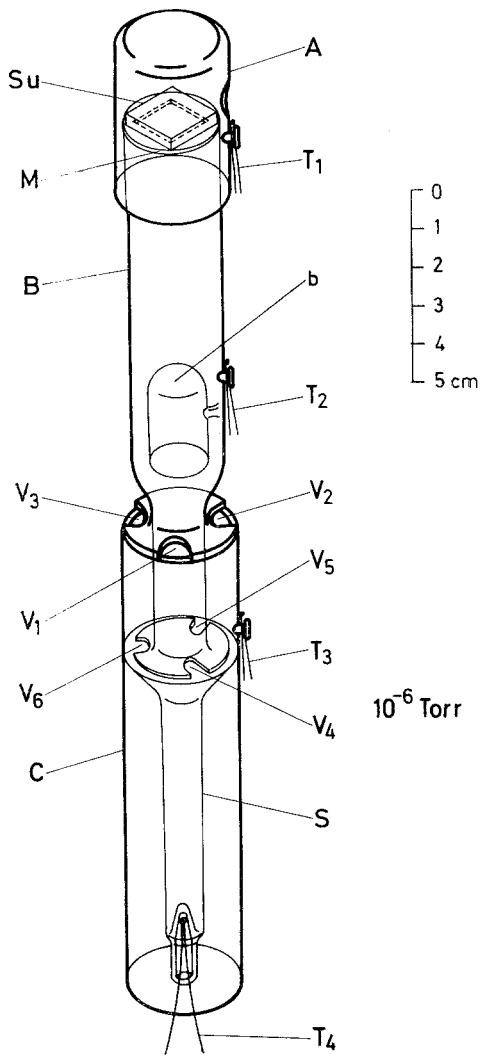

Figure 1 Vitreous silica hot wall apparatus for quasi equilibrium epitaxial growth of PbS films. A, B and C, coaxial, separate parts; S, PbS beam source, independently heated with a resistance coil (not represented); b, baffle; T_1, T_2, T_3 and T_4, thermocouples; Su, KCl substrate; M, stainless steel mask; V_1 to V_6, vents for pumping out of the system (outside pressure $\sim 10^{-6}$ torr). A convenient temperature profile is obtained by means of a radiation furnace (not represented).

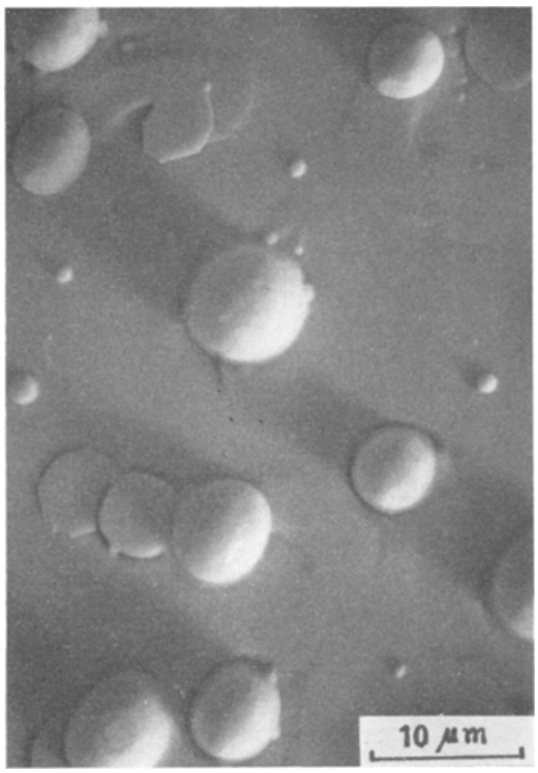

Figure 2 Scanning electron micrograph of the surface of film no. 12. The flat crystals are of tetrafold symmetry and belong to epitaxially grown PbS from the liquid droplets. Some of the droplets have changed their original position. The reasons for it may be: (i) not quite horizontal substrate; (ii) vibrations of the apparatus originated from the mechanical vacuum pump; (iii) shift to a position of smaller surface free energy.

3. Discussion

(a) At 400°C the blobs are droplets of Pb in which ~ 0.02 at. % of PbS is dissolved [4]. They are exposed to an incessant influx of PbS vapour that is absorbed in the droplets, supersaturating the liquid in PbS. From the liquid phase PbS can grow epitaxially on the PbS monocrystalline film (Fig. 2). During cooling the content of dissolved PbS falls to the eutectic amount of 0.0017 at. %. The eutectic, practically pure Pb, crystallizes epitaxially on the PbS film, squeezing out microcrystals of PbS formed during the relatively rapid cooling, which gives the granulated aspect to the surface of the blobs (Fig. 5).

(b) Products of oxidization of PbS are present in

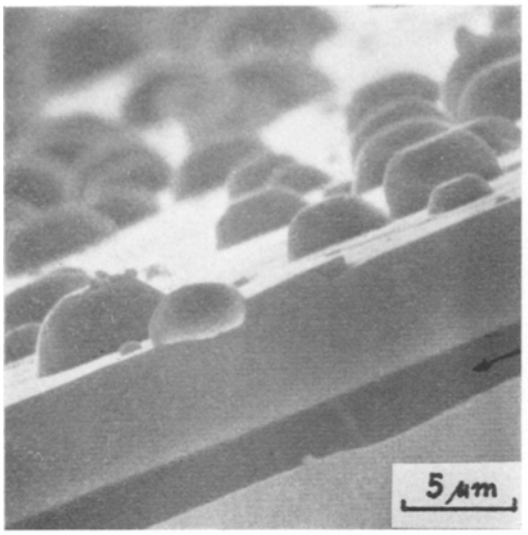

Figure 3 Scanning electron micrograph of cleaved section of film and substrate (no. 10). In the KCl substrate, adjacent to the PbS film, appears a dark region, marked by an arrow, the nature of which is not clear. This phenomenon was observed in connection with all films we have grown were they monocrystalline or polycrystalline.

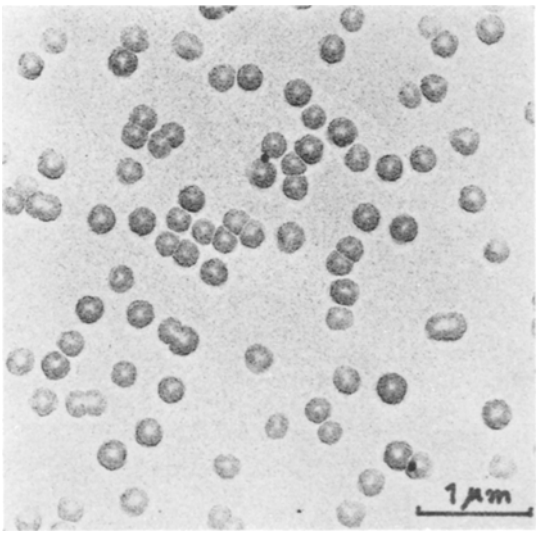

Figure 4 Carbon replica electron micrograph of the surface between big blobs of film no. 10, under high magnification.

the system. This may account for the occurrence of the small crystals on the blobs, visible in Fig. 5.

Elemental Pb on films may be due to excess Pb in the initial source material or to its formation during film growing. The source material, in spite of being heavily Pb doped*, gives a Debye-

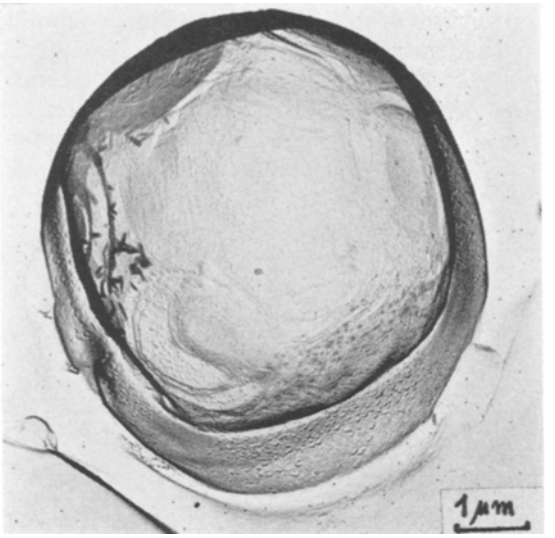

Figure 5 Carbon replica electron micrograph of a big blob on the surface of film no. 10 with small foreign crystals (black), presumably basic lead sulphates.

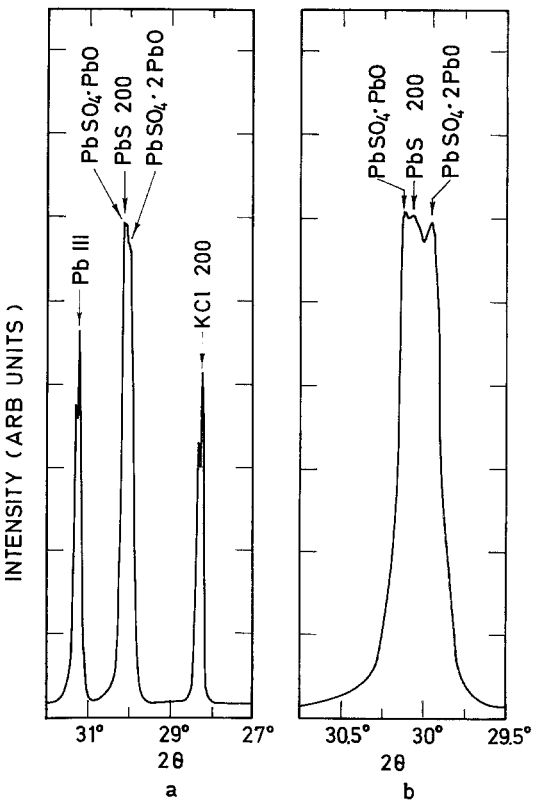

Figure 6 Diffractograms of surfaces of films near the 200 CuK_α reflection of PbS. (a) Film no. 12, (b) Film no. 10. Four times greater resolution than in the former case.

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Scherrer diffractogram showing only PbS lines. Thus it seems most probable that the appearance of elemental Pb is due to S removing reactions inside the SiO_2 apparatus, diminishing the available amount of S that can be combined to Pb as PbS. The presence of basic lead sulphates indicates that these reactions are oxidization of PbS.

The question arises where does the oxygen come from? There are three possibilities:
(1) Residual air at the pressure of $\sim 10^{-6}$ torr contains, obviously, oxygen. Indubitably it contributes to the oxidation of PbS but its quantity, considering even the big volume of the outer vessel ($\sim$ 30 litres) in which the SiO_2 apparatus was placed, would produce only about 1 μg of Pb, in our case undetectable by diffractometry. Moreover, if oxygen, diffusing from the outer vessel to the interior of the SiO_2 system, was solely responsible for the formation of Pb, its total quantity having penetrated inside, should increase with time. However, although the time of growth varied as 1 to 30 the number of blobs per unit area did not change significantly.
(2) The source material might have contained products of oxidization of PbS that could sublimate and react with gaseous or solid PbS to give, finally, by the roast reduction process [5], elemental Pb. Such products were not detected by diffractometry in the source material however.
(3) The oxygen could have come from the fused SiO_2 tubes of the apparatus. This assumption should not be discarded since the mass of oxygen present is large, although it is bound to silicon. There are many mechanisms that may account for binding of sulphur to oxygen of the silica, at temperatures involved in our experiments [6]. Once the oxidization products formed, the reduction process could also take place. The assumption that the reacting oxygen is present inside the apparatus is supported by the following experiment.

The vents V_1, V_2 and V_3 (Fig. 1) of the silica apparatus were covered with a stainless steel foil. The pumping resistance of the system was thus increased. After prolonged pumping (3 h, temperature of the substrate 397°C) to ensure as well as possible the evacuation of the interior of the apparatus (external pressure $\sim 10^{-6}$ torr), the evaporation process was started. (Temperature of the source, 518°C; time of evaporation 50 min.) As the penetration of O_2 from the outer vessel was hindered a smaller amount of blobs should have been expected – if this O_2 is the reason for their formation. Comparison of the scanning electron micrograph of the surface of the film thus obtained, with the corresponding images of films 10, 11 and 12, shows that the number of blobs per unit area is at least the same if not greater than with open vents. Moreover, the film was not stable: kept over Silicagel it expanded and detached itself from the substrate (Fig. 7). This behaviour is attributed to the presence of an increased amount of products of oxidization and reduction which cannot escape as easily as when the vents are open and condense on the substrate with PbS vapours. In the desiccator they undergo chemical transformations resulting in an increase of volume which destroys the film.

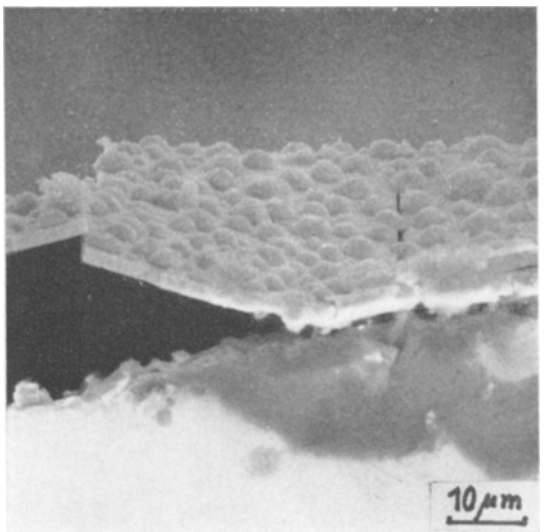

Figure 7 Scanning electron micrograph of the cleaved section of KCl substrate and PbS film no. 13.

4. Conclusions

In our opinion the results of our experiments indicate that the oxygen responsible for the oxidization of PbS is inside the apparatus. We believe that it comes from the silica. The use of vitreous Al_2O_3 instead of SiO_2 may decide the question and trace the way for improvement of the promising hot wall technique.

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References

1. M. PAIĆ, V. PAIĆ, K. DUH, and J. N. ZEMEL, International Conference on Thin Films, 15-19 May 1972, Venice, Italy.
2. J. J. LANDER, *Trans. Electrochem. Soc.* **95** (1949) 174.
3. "Gmelins Handbuch der Anorganischen Chemie", (Verlag Chemie GMBH, Weinheim, Bergstrasse, 1969) Pb, C, 584 and 588.
4. M. HANSEN and K. ANDERKO, "Constitution of binary alloys" (McGraw Hill Book Co, Inc, New York, 1958) p. 1099. P. ELLIOTT, "Constitution of binary alloys, First Supplement" (McGraw Hill Book Co, New York, 1961) 721.
5. Ref. 3, pp. 3, 427, 486-503, 512 and 592.
6. *Ibid*, 1959, Si(B), pp. 743, 747 and 752.

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