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Coverage of rough substrates by ZnS using vacuum evaporation and atomic layer epitaxy

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The effects of various deposition techniques on the growth of ZnS thin films on a sintered $BaTiO_3$-based complex perovskite substrate, using the scanning electron microscope have been studied. The results clearly show a non-uniform and incomplete coverage of the substrate in the case of films grown by electron-beam evaporation and resistance-heated evaporation. A shadowing effect is observed in these films. Increase in the thickness of the films tends to decrease the shadowing effect. On the contrary, films grown by the atomic layer epitaxy method, exhibit a complete and uniform coverage of the substrate, even for thin (< 100 nm) ZnS films.

1. Introduction

Since the introduction of Inoguchi *et al's* [1] ZnS: Mn a.c.-driven thin-film electroluminescent device (ACTFEL), numerous efforts have been made to improve its performance [2, 3]. The device consists of a ZnS: Mn active layer sandwiched between two insulating layers and two electrodes. This unique structure avoids breakdown by preventing steady current flow through the device.

Recent investigations have focused on the modification of this device in order to improve its appearance and reliability using ceramic substrates. Traditionally, the insulating layers of an ACTFEL device have been sputter deposited or vacuum evaporated. It is also known that the dielectric constant and breakdown field is governed by preparation conditions of the dielectric films [4]. Sano *et al.* [5], proposed and investigated, an ACTFEL device using a ZnS: Mn film grown on a multilayer ceramic substrate. As anticipated, their device had a better breakdown resistance and a lower driving voltage than that of the traditional one. The ceramic substrate in this device poses a unique problem for the growth of the ZnS: Mn film – namely that of surface roughness, on the order of several micrometres. This paper suggests and investigates the use of atomic layer epitaxy (ALE), for the first time, on a substrate of this type. Note that ALE here refers to the growth technique of Suntola *et al.* [6]. We do not claim to achieve epitaxial growth in a strict sense.

The thin films, constituting the device, may be deposited by various techniques – vacuum deposition, sputtering, metal-organic chemical vapour deposition (MOCVD) [7], atomic layer epitaxy [6, 8, 9] etc. It has been shown that the quality and crystallinity of the thin film is superior when it is grown by ALE [10]. We present here, the results of the investigations carried out in our laboratory, comparing the growth pattern of ZnS thin films deposited by three different methods – vacuum deposition, electron beam deposition and atomic layer epitaxy. In all the samples investigated, the ZnS thin films were grown on a multilayer ceramic substrate.

2. Experimental techniques

Thin films, of various thicknesses, of zinc sulphide were deposited on polycrystalline ceramic substrates. The substrates were made from a sintered, $BaTiO_3$-based complex perovskite. The average surface roughness was about 5 μm and the grain size $\leqslant 6\,\mu$m, (see Fig. 1). Deposition was carried out by three different techniques, under identical conditions. The appropriate details of the deposition are shown in Table I.

The vacuum deposition system, for the electron-beam assisted deposition is a diffusion-pumped, bell-jar type one, capable of attaining high vacuum (10^{-6} to 10^{-7} torr). The electron gun has source–substrate distance of 250 mm and the normal to the plane of the substrate was at 30° to the source. An accelerating potential of 2 kV was maintained during the deposition. The resistance-heated deposition utilized a

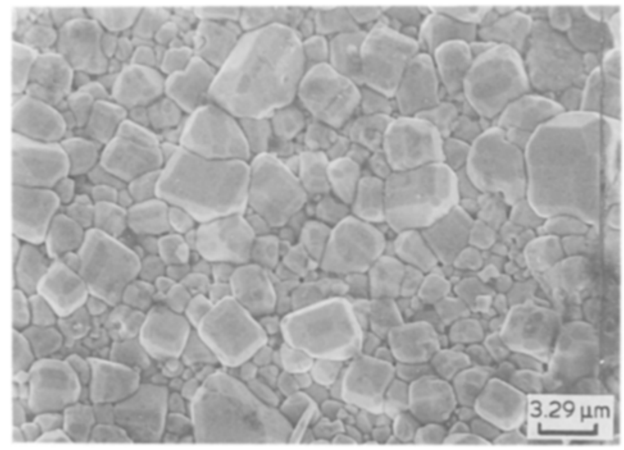

Figure 1 Typical SEM image of the ceramic substrate used in this study.

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TABLE I Details of sample preparation

Sample no.	Method of deposition	Pressure (torr)	Substrate temp. (° C)	Estimated thickness	Growth rate (nm sec^{-1})	Reference
1	vacuum deposition	$\sim 7 \times 10^{-6}$	200	~ 450 nm	0.49	
2	electron-beam deposition	$\sim 2 \times 10^{-6}$	200	~ 150 nm	1.0	
3	electron-beam deposition	$\sim 2 \times 10^{-6}$	200	~ 1.5 nm	1.0	
4	ALE	Atmospheric	200	~ 138 nm		[9]
5	ALE	Atmospheric	200	~ 69 nm		[9]

similar vacuum system. The source, in this case, was a tantalum baffle boat and the angle between the substrate normal and vapour source was ~ 10°.

The ALE system, operating at atmospheric pressure, uses dimethylzinc (DMZ) and hydrogen sulphide (H_2S) as reactants. This system has been described in detail elsewhere [9].

It is known that the substrate temperature is extremely critical in thin-film growth of ZnS [11]. For the sake of comparison, the substrate temperature was identical (200° C) for all the samples investigated. Post-deposition anneal was not carried out on any of the samples.

3. Results and discussion

Fig. 2a is a scanning electron micrograph of a ZnS thin film (sample 1) deposited on the ceramic substrate. The film, which was grown by vacuum deposition, is about 450 nm thick. It can be clearly seen that the thin film is not very uniform on the substrate. Fig. 2b shows the detail of the same film, revealing directionally favoured growth due to shadowing. To understand the physical basis behind this phenomenon, consider Fig. 3 which shows an idealized view of the rough substrate. During thermal deposition (resistive and electron-beam heating), the source evaporates and these vapours condense on the substrate to form the thin film. Owing to the surface roughness, some parts of the substrate do not see the vapour stream. Consequently, film growth does not occur in these regions. Figs 4a and b show micrographs, taken at different magnifications, of an electron-beam deposited ZnS film (sample 2). Here again, the phenomenon of shadowing is obvious. As seen from Table I, this film is approximately 150 nm thick. It may be pointed out that Fig. 4a proves that this effect is not localized, but is observed throughout the substrate.

To see the effect of thickness on the growth pattern of the ZnS thin films, a thicker film (sample 3), measuring approximately 1.5 μm, was grown and then observed under the scanning electron microscope (SEM). The results are now different. The film did not show any evidence of shadowing. Figs 5a and b confirm this idea. This observation may be explained as follows: the films were grown with the substrate heated to 200° C. Hence, surface diffusion might influence the thin film growth after a certain film thickness, leading to a more uniform coverage of the substrate. This agrees well with the observations reported by Theis [10] wherein transmission electron microscope (TEM) analysis of electron-beam deposited film showed that increasing film thickness leads to larger columnar grains and an increase in mean grain diameter. The small pit-like defects (Figs 5a and b) could be a result of outgassing of the sintered ceramic substrate. It is not seen in any other samples because they are comparatively thin.

The third method of deposition used was atmospheric pressure atomic layer epitaxy. Use is made of the reaction between the two gaseous reactants [9], DMZ and H_2S, to give ZnS; the unreacted components are removed by flushing the reaction chamber with nitrogen gas. When the substrate is exposed to the DMZ vapour, these molecules are chemisorbed on to the substrate. A pulse of H_2S is then injected, following a nitrogen purge, which leads to the formation of ZnS on the substrate. It may, then, be seen that there is no possibility of any sort of shadowing occurring, in the case of ALE, and one would expect a uniform and complete coverage of the rough

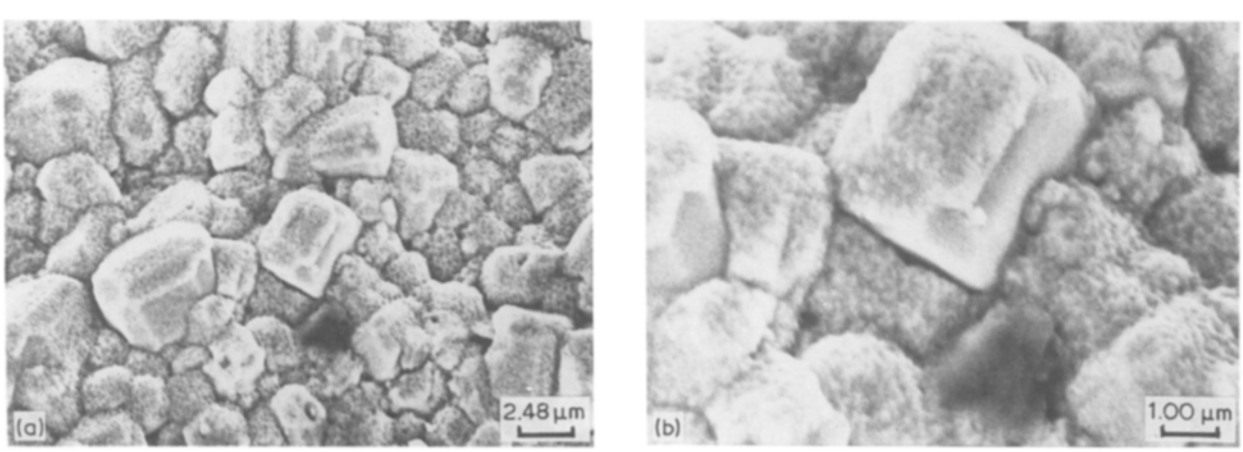

Figure 2 SEM image of a vacuum-deposited ZnS thin film showing shadowing.

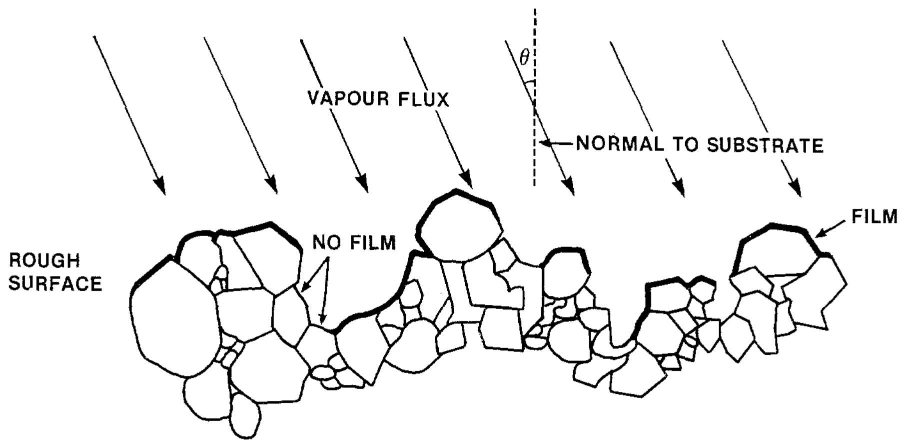

Figure 3 Schematic diagram showing the shadowing effect observed for thin ZnS films, deposited on a rough substrate. The shadowing effect is directional due to the angle of vapour flux, θ.

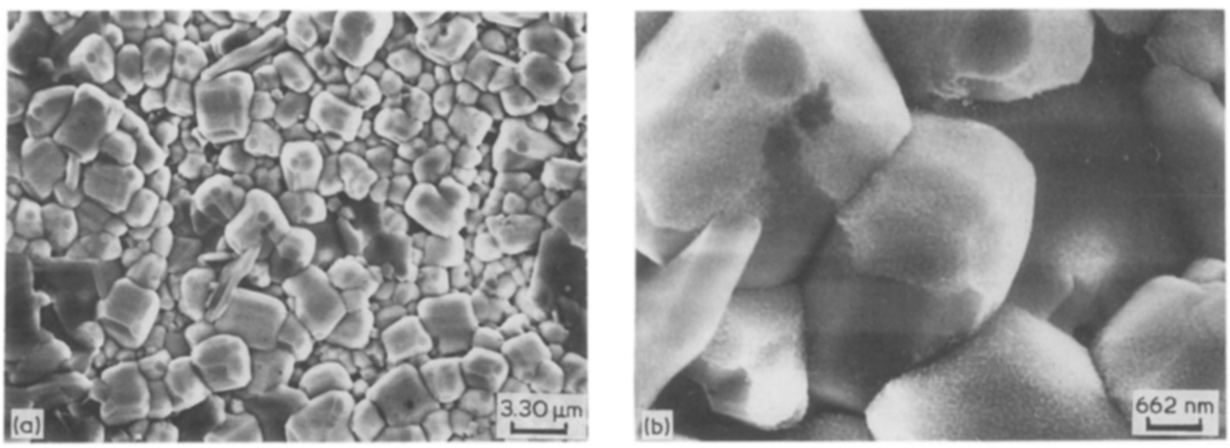

Figure 4 Scanning electron micrograph of a ZnS film (~ 150 nm) deposited by electron-beam evaporation showing shadowing.

substrate. This, indeed, is the case in practice, as can be seen in Figs 6a and b. These micrographs are of a ~ 138 nm thick ZnS film grown by ALE (sample 4). The film is very uniform and covers the entire substrate. A scan throughout the surface showed no discontinuities or even the slightest evidence of shadowing. It may be worthwhile to note that films of comparable thickness grown by the other two methods were non-uniform and discontinuous. Even a 450 nm thick film (sample 1) exhibited shadowing. This makes the film undesirable for ACTFEL devices. Of course, an increase in the thickness tends to make the vacuum deposited and electron-beam deposited film more continuous, but it should be remembered that the optimum thickness of the ZnS: Mn layer in an ACTFEL device is often just 300 nm [1]. The above discussion clearly shows that atomic layer epitaxy has distinct advantages for thin film fabrication aimed at making thin film electroluminescent devices on rough substrates. As reported by Theis [10], the crystallinity and homogeneity of these films is also very good.

The growth pattern of a thinner (~ 69 nm) ALE-grown (sample 5) ZnS film was also investigated. The electron photomicrographs of the same are shown in Figs 7a and b. It can be seen that the film is not continuous, but rather a combination of minute "droplets" or islands. It is interesting to note that

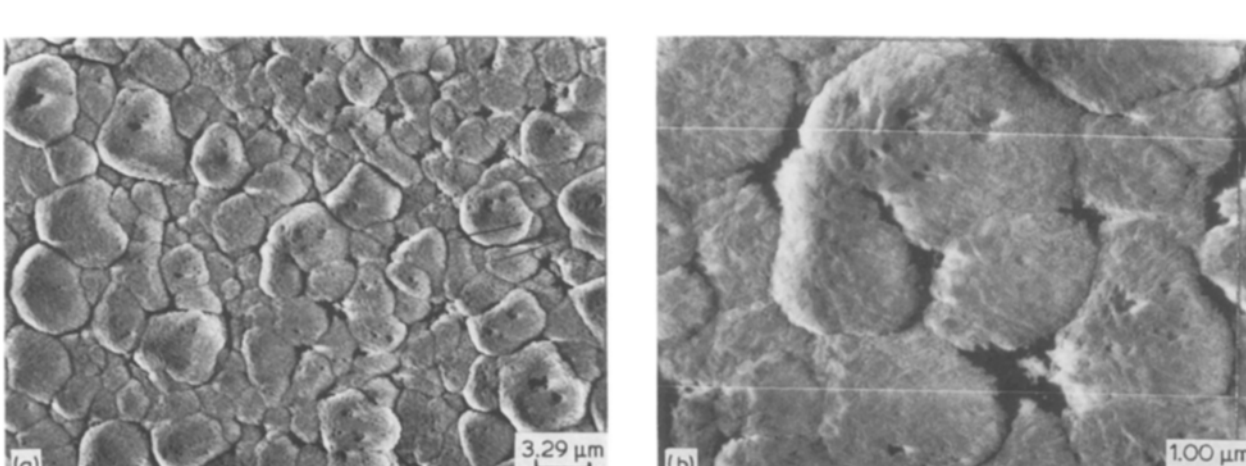

Figure 5 SEM images of a ZnS film ($\sim 1.5\,\mu$m) deposited by electron-beam evaporation showing a more complete coverage of the substrate.

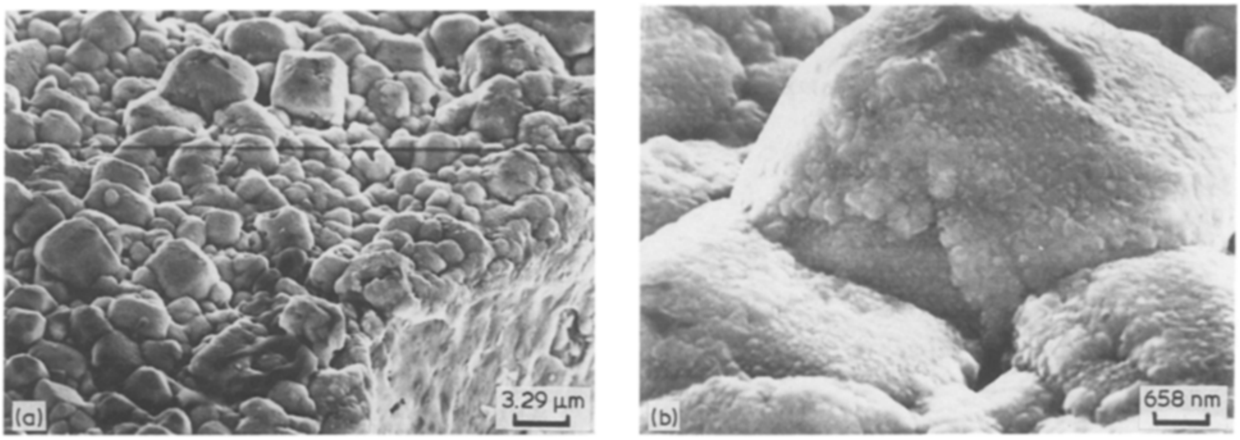

Figure 6 SEM images of ALE grown ZnS film (~ 138 nm) showing no evidence of shadowing.

these tiny "droplets" are formed randomly on the substrate, i.e. shadowing or preferential deposition is not observed. Thus, it may be concluded that, even at a lesser thickness, a spatially preferential thin film growth does not occur, when the film is deposited by ALE.

4. Conclusion

We have studied the growth pattern of ZnS thin films on a rough ceramic substrate. The sintered ceramic substrate was chosen because it forms one of the insulating layers for an ACTFEL device. Three different techniques for the thin film growth were employed: vacuum deposition, electron-beam deposition, and atomic layer epitaxy. It was observed in the case of the first two techniques that the ZnS film formed was discontinuous and non-uniform. A shadowing phenomenon is thought to take place in thinner films ($\lesssim 1\ \mu m$). This is attributed to a shadowing effect of the rough surface which prevents all surfaces being in a direct line of sight of the vapour stream. Consequently, no condensation of vapours takes place in these areas and no film growth occurs. On the other hand, thin films, grown at the same substrate temperature by the ALE technique show a very uniform coverage and no evidence of shadowing. This is explained by the fundamental difference between the physics of film growth in case of ALE and thermal evaporation (both resistive and electron-beam heated). We are, at present, not able to explain the presence of "droplets" observed on the thin ALE films.

The results clearly show the advantages of the ALE grown films. We expect to report on complete ACTFEL devices grown on ceramic substrates using the ALE technique in the near future.

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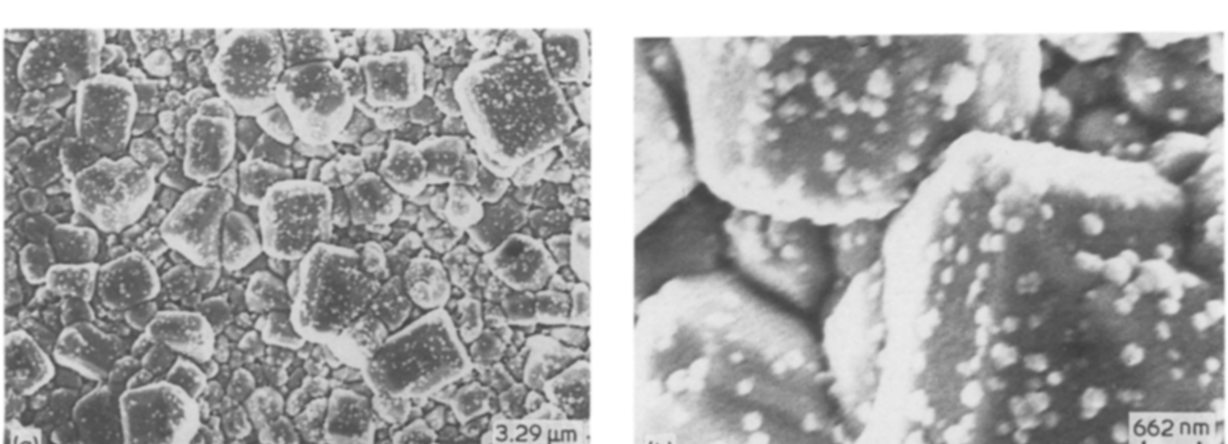

Figure 7 SEM images of a thinner (~ 69 nm) ZnS film deposited by ALE.

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