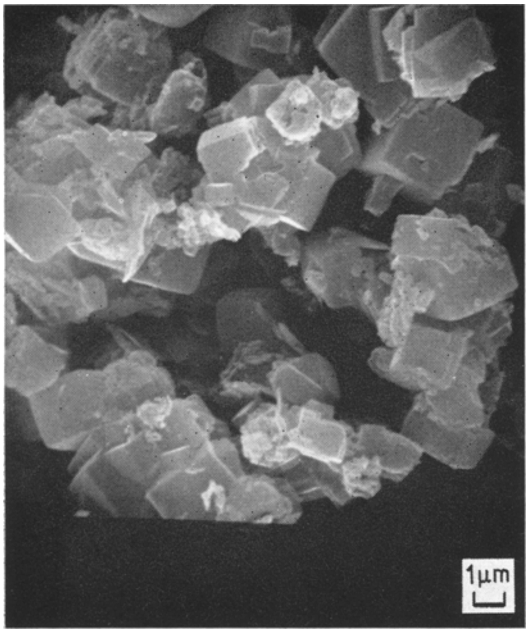

Figure 4 Solids – unsatisfactory conversion (× 5000).

electron micrographs were made, using a Cambridge Mk 2A Stereoscan. Another portion was analysed by X-ray diffraction to determine crystallinity.

Acknowledgements

The samples were prepared by Mr Ray Lambert and the micrographs were made by Mr Richard Roberts.

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The Annealing of ZnS Films on Silicon

Although epitaxial films of ZnS have been grown successfully by electron beam sublimation of the powder in UHV [1, 2] there are circumstances when it is not feasible to adjust growth conditions such that good quality single crystal films are produced. Consequently the possibility of using annealing to produce epitaxy or substantially to improve the crystal structure of films deposited under various conditions was examined.

Previous heat treatment work with films of II-VI compounds has mainly been concerned with recrystallisation and activation for luminescence purposes using various impurities [3]. However, it has been shown possible to produce epitaxy by periodic annealing of thin GaAs films deposited on GaAs [4]. In the work [4] on GaAs, deposition and examination were carried out in the same system, the films (up to 30 nm in thickness) were examined by glancing angle electron diffraction.

In this work films were deposited on to silicon substrates by electron beam sublimation in UHV [1], and by RF triode sputtering under ordinary vacuum conditions in a special "clean" sputtering system. The material used for sublimation was ZnS powder of the highest purity available commercially from various sources, mass spectrographic analysis showed that the purity was about 100 ppm. The sputtering target was an Eastman Kodak Irtran 2 disc and analysis of deposited films showed that the target must have a similar purity to the powders. Samples were examined after deposition using the high resolution diffraction stage of an AEI EM6G electron microscope by glancing angle electron diffraction. Annealing of the films was done in the microscope (a vacuum of 1 to 10 mNm^{-2}, 10^{-4} to 10^{-5} torr) by means of electron bombardment of the silicon substrate on the opposite face to that of the film. Thermocouple readings were calibrated so that surface temperature could be quoted to an accuracy of ± 10%. Diffraction photographs of the hot sample were taken after equilibrium had been reached, which took between 1 and 3 min, and the sample was then heated up to the next temperature. Longer annealing periods similar to those which Cho [4] has found to be necessary to produce complete structural transformations were tried. Samples were annealed for periods up to 15 min (after reaching equilibrium); generally no observable effects occurred provided the temperature was less than that at which significant evaporation occurs. As a further check on time effects some samples were annealed for 24 h periods in a tube furnace under vacuum (~ 1 Nm^{-2}, 10^{-2} torr), in steps of 50°C.

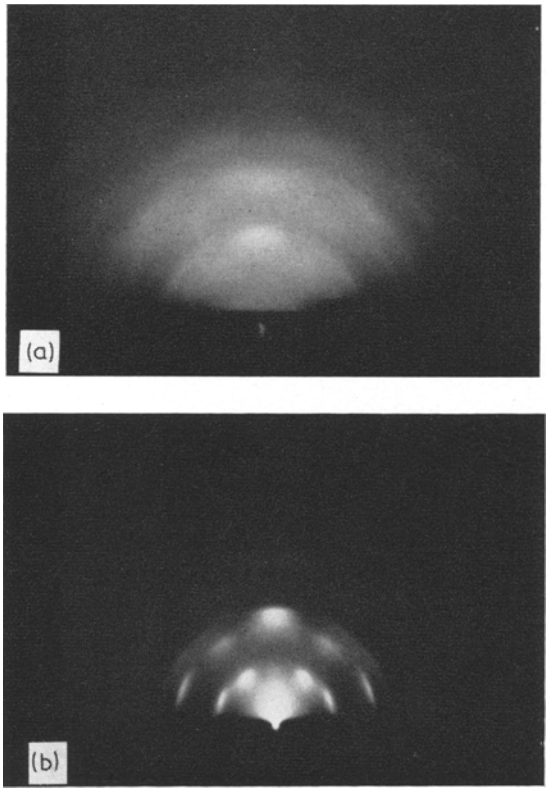

Figure 1 (a) Sputtered ZnS layer on (111) silicon prior to heating. (b) After heating to 195°C ± 10% for ~ 3 min, original thickness 1.2 μm.

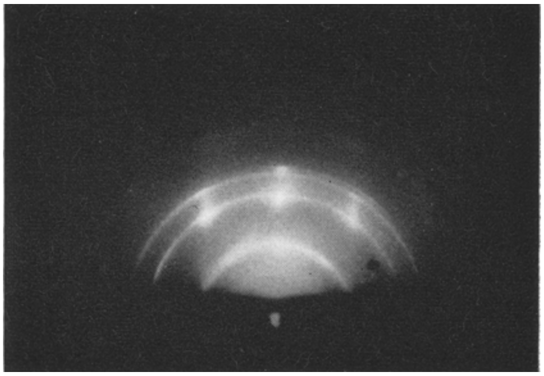

Figure 2 Sputtered ZnS layer on (111) silicon after heating to 480°C ± 10% for ~ 3 min, same samples as fig. 1.

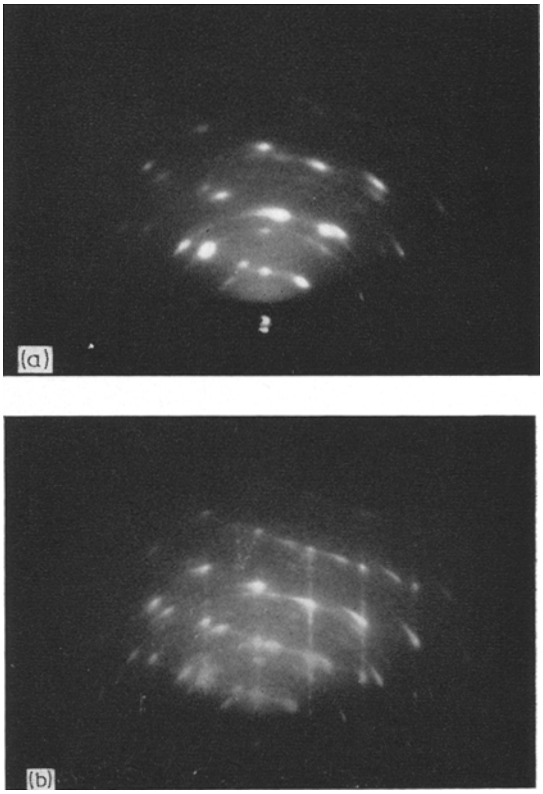

Figure 3 (a) UHV evaporated ZnS layer on (111) silicon prior to heating. (b) After heating to 620°C ± 10% for ~ 3 min, original thickness 250 nm.

All films examined were deposited on (111) silicon of about 10 Ω cm *N*-type and ranged initially from almost amorphous to single crystals with high defect densities. Originally all samples were deposited on silicon cleaned by a standard process [2] which resulted in a relatively flat, clean, and work damage-free surface, though surface cleanliness and topography affected the initial structure there is no indication that it had any effect on the annealed structure. In general, samples that were most disordered showed improvement at the lowest temperatures. Fig. 1 shows an amorphous sample prior to and after annealing at 195°C ± 10% for 3 min, it is evident that substantial improvement occurred though the sample is not monocrystalline. Samples of better initial structure show on significant improvement at this temperature. At evaporation occurs (a few monolayers only being removed). Equally there is a more pronounced improvement in structure when temperature and time are such that considerable evaporation occurs. The difference between short and long higher temperatures ~ 500° C (fig. 2) amorphous samples improve still further though calculations using extrapolated vapour pressure [5] show that evaporation is beginning to occur (two monolayers in 5 min). At this order of temperature better samples begin to show definite sharpening of spots, though this is less noticeable the better the initial structure. At temperatures in the vicinity of 600° C little further improvement occurs for the poorer initial structure layers, but the better layers are more obviously improved (fig. 3) though considerable amounts of evaporation must occur (200 monolayers in 5 min). Above these temperatures (though the layers must be almost completely removed) the structure is either improved further (fig. 4) to single crystal for the better layers, or a ring pattern due to an unidentified compound is formed. Annealing for 24 h periods seems to have little effect except in the range 400 to 600° C when some improvement generally occurs, above 600° C the complex compound is formed.

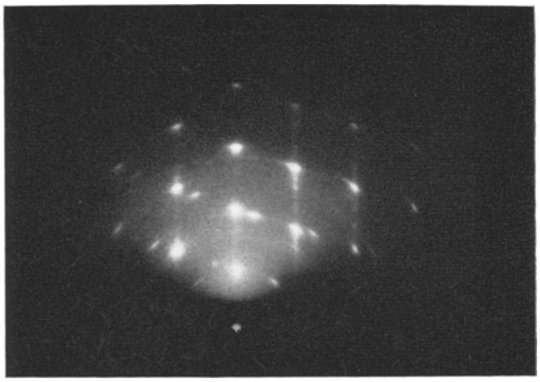

Figure 4 UHV evaporated ZnS layer on (111) silicon after heating to 745° C ± 10% for ~1 min. Same sample as fig. 3.

Table I is an attempt to summarise these results. It seems evident that for films in this thickness range there is in general a definite improvement in crystal structure at annealing temperatures which are considerably below temperatures and times for which significant times suggests that two different annealing modes occur, surface and bulk. The most obvious short term effects occur at temperatures at which significant evaporation begins, when the surface atoms must be extremely mobile, surface rearrangement occurs rapidly and is immediately detected by the glancing angle technique. This does not necessarily mean that the whole thickness of the layer has been affected, as it is likely that at these temperatures the diffusion coefficient of vacancies in the bulk is much less than that of atoms on the surface. This is borne out by studies of the sintering of ZnS powders in vacuum [6] in which it is shown that up to ~ 600° C surface diffusion is the predominant

TABLE

Initial structure	Time	200° C	400 to 600° C	> 600° C
Amorphous	Short	Highly ordered polycrystal	Single crystal (single twins) + polycrystal	Complex compound
	Long	Small improvement	Highly ordered polycrystal	Complex compound
Near single crystal (multi twins) + small grain polycrystal	Short	Small improvement	Single crystal (multi twins) + polycrystal	More perfect single crystal (multi twins) + polycrystal
	Long	Small improvement	Single crystal (multi twins) + polycrystal	Complex compound
Single crystal (multi twins) + polycrystal	Short	Small improvement	More perfect single crystal (multi twins) + polycrystal	Single crystal (single twin), single crystal, or complex compound
	Long	Small improvement	More perfect single crystal (multi twins) + polycrystal	Complex compound

N.B. There is some overlap in the higher temperature ranges. Thicknesses lie between 1 and 0.1 μm.

mechanism for sintering. It also seems to be borne out by the fact that long periods of annealing at temperatures similar to those which give significant changes in surface structure for short periods do not improve the surface structure further. Assuming that the bulk has an effect on the surface layers, either volume diffusion is so small that the bulk changes very little and consequently the surface is constrained so that it cannot improve any further; or alternatively volume diffusion is significant, in which case the change is only comparable with the initial surface improvement which nucleates and grows on the bulk as a substrate These results do not seem inconsistent with the results of Cho [4] on GaAs, for in the work reported here ZnS evaporated to such an extent that eventual layers were of similar thickness to those examined by Cho. It seems evident therefore that in both instances significant improvement in crystal structure only occurred when the layers were so thin and the temperature such that surface diffusion could be significant, and when the structure some tens of monolayers below the surface was of good quality and did not constrain the surface layers, but allowed them to nucleate and grow. It seems likely that this may be generally the case and annealing results which give epitaxy can only occur where surface mobility effects have a dominant role as in very thin films.

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The Thermal Conductivity of Porous Copper

Increasing use is being made of powder metallurgical techniques to fabricate components, but information on the thermal conductivity of porous metals is still sparse. Grootenhuis *et al* [1] demonstrated that the thermal and electrical conductivities of porous bronze compacts both decrease linearly with increasing porosity, reaching notionally zero values at a porosity of 47.64%; this is the theoretical porosity $[100(1 - \pi/6)]$ of a simple cubic array of touching uniform spheres, and is independent of radius. Literature data for the electrical conductivity of porous copper, iron and nickel compacts are found to lie on the same linear plot. Recently, Taubenblat [2] has measured the electrical conductivity of copper sintered at 1000°C and obtained results near this line. The same trend is shown in several Russian papers on sintered iron, nickel and steel [3-6], although porosities up to 55% are quoted, presumably because of the presence of large pores. Similar results have been reported also for porous tungsten compacts [7]. Mitoff [8] in a recent treatment of the properties of heterogeneous systems states that to a first approximation the conductivity of a metal with fraction of pores x is $[1 - (3/2)x]$ times the conductivity of dense metal. Euler [9] has produced a theoretical model which closely resembles the empirical Grootenhuis relationship and considers factors which can lead to a departure from linear behaviour. The Grootenhuis relationship applies to uniform spheres, sintered together in good metallurgical contact, but this is possibly not the situation prevailing for unsintered porous metal layers prepared by flame or plasma-spraying of powders.

In the present letter we report thermal conductivity data for porous copper compacts prepared by these techniques, as well as for dense electroplated copper. Methods employed to prepare sprayed copper have been described in the literature [10]. The thermal conductivities were derived from thermal diffusivity measurements over the temperature range 40 to 600°C according to the relation

$$k = \alpha\rho\, C_p$$