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The Structure of Willemite Films on Silicon

G. S. EDWARDS*, A. N. RUSHBY
Department of Applied Physics and Electronics, University of Durham, UK

Thin films have been prepared on silicon substrates by reacting manganese doped zinc fluoride with silicon oxide. A structural analysis has shown that the films consist of small crystallites of alpha-zinc orthosilicate (willemite) embedded in a matrix of silicon oxide.

1. Introduction
Thin films of willemite have been prepared on silicon single crystals by a chemical reaction on the oxidised substrate. The films have potential applications for display devices based on silicon technology. They show bright green cathodoluminescence and weak electroluminescence. The purpose of this paper is to describe an investigation into the structural properties of the thin films.

2. Experimental
The structure of the films has been investigated using X-ray powder methods and electron microscope transmission and reflection techniques. The instrument employed was a JEM-120 microscope operating at 120 kV. An AD-3 attachment provided the reflection electron diffraction (RED) facility. The X-ray powder photographs were taken with a Philips PW 1009 X-ray generator.

3. Film Preparation
The method of preparing the thin films will be described fully in a future publication [1]. The basic procedure is as follows:
(*a*) The surface of a slice of silicon single crystal is oxidised.
(*b*) A film of zinc fluoride activated with 1% manganese by weight is then evaporated from a platinum crucible at 825°C on to the silicon oxide.
(*c*) The reaction between ZnF_2:Mn and SiO_2 is subsequently achieved by baking the slice for 10 min at 1100°C in an atmosphere of oxygen.

4. Results
4.1. X-ray Analysis
The product of the reaction between zinc fluoride and silica was identified from X-ray powder photographs. A powdered mixture of ZnF_2:Mn and SiO_2 in the correct molar proportions was baked in an oxygen atmosphere at 1100°C for 10 min. Powder photographs taken before and after baking were compared with that of a commercial willemite phosphor (Derby Luminescents Ltd, Phosphor P1). The baked mixture was thus identified as willemite. Further confirmation was obtained by checking that the inter-planar spacings corresponded with those given in the ASTM index for alpha-zinc orthosilicate.

4.2. Electron Microscopy
Electron microscopy was employed to observe the structure of the thin films. Difficulty was encountered in preparing samples for transmission by etching away the silicon since the films were attacked rapidly as the silicon perforated. The method which was adopted was to remove a film of silicon oxide from its substrate with hot chlorine gas. The gas does not attack the unconverted oxide. ZnF_2:Mn was then evaporated on to the oxide and the reaction completed by baking as previously described. The resultant films showed bright green cathodoluminescence as did their silicon based counterparts.

Fig. 1 shows an electron micrograph of one of the films. Randomly oriented crystallites can be seen. The dimensions of the crystallites lie in the range 0.1 to 1 μm. The diffraction pattern from the area marked on the micrograph is

*Present address: Oxley Developments Ltd., Priory Park, Ulverston, N. Lancs.

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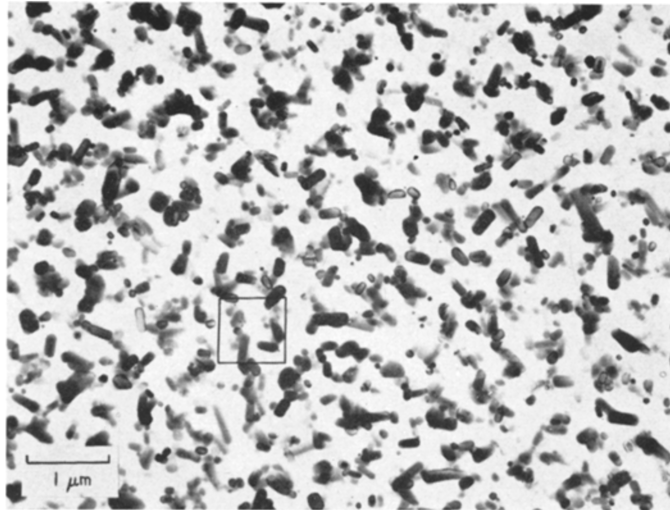

Figure 1 Transmission electron micrograph of willemite film.

shown in fig. 2. Random spots occur at large distances from the central spot which is masked by the contribution from the amorphous matrix.

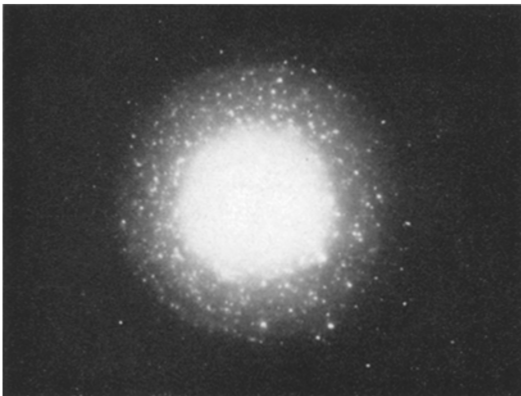

Figure 2 Electron diffraction pattern from area marked on fig. 1.

A RED pattern from a film prepared on silicon is shown in fig. 3. The area of the film contributing to this diffraction pattern is several orders of magnitude greater than that of fig. 2. Microdensitometer traces of a number of such patterns were taken and good agreement was found between the inter-planar spacings calculated from the camera constant and the trace, and those tabulated in the ASTM index for willemite.

5. Discussion

The films evidently consist of small willemite crystallites in an amorphous matrix. This can be explained in terms of a reaction mechanism which involves firstly the melting of the zinc fluoride, since the baking temperature of 1100° C is well above 870° C, the m.p. of ZnF_2. Surface tension effects are such that the molten film does not wet the underlying oxide, but forms into globules. Where the molten ZnF_2 is in contact with the silicon oxide a chemical reaction takes place. As willemite melts at 1785° C, a solid crystalline layer is formed at the interface. Further growth occurs by zinc ions diffusing through the willemite layer and replacing some of the silicon ions in the oxide. The excess silicon diffuses out through the solid and reacts with the molten layer to form the gas silicon tetrafluoride which escapes through the liquid.

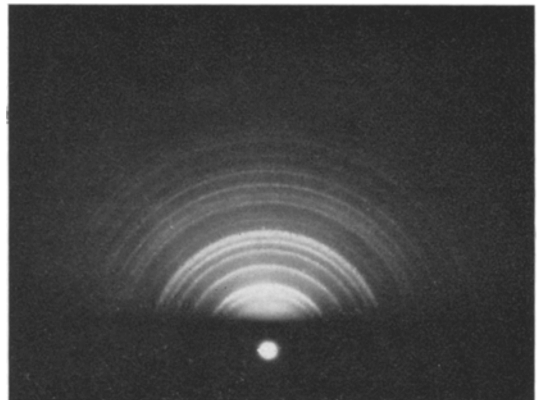

Figure 3 Typical RED pattern from willemite film on silicon.

The reaction is completed when all the ZnF_2

has vaporised. In practice, the process was found to take about 10 min at a temperature of 1100°C when a film of zinc fluoride 1000 Å thick was employed. As the thickness of the zinc fluoride is increased, the reaction conditions favour the growth of non-stoichiometric willemite with an excess of zinc at the surface. Such conditions are undesirable since they lead to a marked decrease in the luminescent efficiency of the films.

6. Conclusions

The thin films prepared by the method described above consist of microcrystallites of willemite distributed randomly throughout a glassy matrix of silicon oxide. The films have excellent adhesion to the silicon substrate. A device based on this technique for producing luminescent thin films on silicon may have applications for displays if the electroluminescent efficiency can be improved.

Acknowledgements

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Reference

1. In preparation.

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