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Control of the Surface Composition of Isothermal Vapor Phase Epitaxial Mercury Cadmium Telluride.

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A memod is described for controlling the surface composition of mercury cadmium telluride during isothermal vapor phase epitaxy (ISOVPE) of mercury cadmium telluride. The method employs a three phase solid-liquid-vapor source in equilibrium with the desired composition. The thermodynamic and kinetic basis of the method is outlined.

I. Introduction

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Isothermal vapor phase epitaxy of mercury cadmium telluride $(Hg_{1-x}Cd_xTe)$ has been studied since the 1960's.¹⁻¹⁶ Since the band gap of the material is governed by the composition, ranging from 1.6 eV. for CdTe to -0.3 eV. for HgTe, the control of composition is a major practical concern. The isothermal growth technique produces relatively flat composition profiles near the surface due to the way the interdiffusion coefficient varies with composition.¹⁷ The composition of this plateau region is determined by that of the surface of the layer; thus, controlling the surface composition is critical. The desired surface composition may be obtained by either equilibrium or non-equilibrium methods. In non-equilibrium techniques, the surface composition of the layers changes

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continuously with time, requiring that the process be terminated after a fixed time. These methods rely on the fact that the surface composition changes relatively slowly with time through the composition range of interest, 0.3-0.2 mole fraction CdTe. However, using equilibrium methods, the surface composition remains at the desired value after an initial transient. In practice, equilibrium techniques rely on controlling the mercury partial pressure⁹ or the composition of the source.^{3,16} In this paper, only the latter method will be considered, along with a description of the thermodynamic basis for this approach.

II. Experimental.

The general experimental geometry used is shown in Fig. 1. The sources consisted of ~90% solid mercury cadmium telluride of the desired composition and ~10% of a liquid tellurium-rich liquid which is in equilibrium with that solid at the growth temperature. The liquid composition was determined from the LPE data of Harman.¹⁸ Batches of source material were made by reacting the components in a sealed quartz ampoule at 650°C for 16 hours and then quenching the ampoule in water. The source material was then powdered and sintered for 30 minutes at 500°C in order to ensure homogeneity. After growth, the layers were mounted in epoxy, cross-sectioned, polished, coated, and analysed by electron probe microanalysis.

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III. Results and Discussion.

The results of growths performed under the same conditions, (550°C and 24 hours) but with different source compositions are

given in Fig. 2. For sources with fractions of CdTe greater than 0.2, the surface of the sample is the same as that of the mercury cadmium telluride in the source. The thermodynamic basis of this behavior is illustrated by the Hg-Cd-Te Gibbs triangle, shown schematically in Fig. 3. Initially, the overall composition of the source is at point A, which is in equilibrium with mercury cadmium telluride of composition C and a tellurium rich liquid. If we add a piece of CdTe to the system, the overall composition of the entire system is moved towards CdTe to point B, which is in equilibrium with a solid of composition D and a tellurium-rich liquid. When the source is much greater than the substrate, or if the kinetics of growth are such that the source is only in communication with a small fraction of the substrate, the system essentially remains at point A, thereby fixing the surface composition of the layer.

The system approaches its equilibrium composition through the growth of the mercury cadmium telluride layer on the substrate. Growth proceeds by the deposition of HgTe, which is limited by Te₂ vapor transport from source to substrate and interdiffusion between Hg and Cd in the growing layer.¹⁶ It is this interdiffusion which maintains a gradient in the tellurium chemical potential between the source and the substrate surface. Initially the layer is thin so that interdiffusion quickly changes the surface composition so that growth is limited by tellurium transport and the fraction of CdTe at the surface of the growing layer is greater than that of the solid Hg_{1-X}Cd_XTe in the source. However, as the layer thickens the interdiffusion process becomes rate limiting. Once this has occured, the source and substrate surface are essentially in equilibrium so that the composition at the surface of the layer is the same as that of the solid in the source.

Factors which increase the rate at which HgTe is deposited relative to the amount of interdiffusion between Hg and Cd allow the surface to approach equilibrium more rapidly. Since growth of material with lower fractions of CdTe requires relatively more HgTe deposition per Cd diffusing to the surface, and since the interdiffusion coefficient at the surface of these layers is greater, (the interdiffusion coefficient increases over three orders of magnitude in going from CdTe to HgTe^{17,19,20}), the non-equilibrium transient time is longer in this composition range. With material grown from higher X value sources, the layers have thickened sufficiently relative to the interdiffusion coefficient of the material at the surface, so that the surface of the layer is essentially in equilibrium with the source, and the surface composition will be constant with time. Thus the composition of the source sets a lower limit on the composition of the mercury cadmium telluride formed.

The present method has the advantage that the desired surface composition does not change with time once it has been established and is easy to implement. Another method for fixing the surface composition is by control of the mercury partial pressure to sufficiently low levels so that only material with the desired, or higher, fractions of CdTe are stable. Evidence for this can be seen in the work of Becla.⁹ However, this method is somewhat more complicated since it requires the use of a two zone system to control the mercury overpressure.

IV. Summary.

A solid-liquid-vapor source is described which allows accurate control of the component chemical potentials, the theoretical basis for this being the Gibbs Phase Rule. There exists an initial transient during growth in which the composition of the sample surface is not in equilibrium with the source due to interdiffusion within the growing layer. This transient period is longer for layers grown with lower X values, greater source to substrate spacings, and higher temperatures.

Acknowledgements.

We thank Dr. Margaret Brown of Rockwell International for helpful discussions and for supplying some of the CdTe substrates used in this work. This project was sponsored by DARPA through the Office of Naval Research, contract no. N00014-84K-0423. One of the authors, J.G.Fleming, gratefully acknowledges the support of an Office of Naval Research Fellowship.

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Fig. 1. The experimental geometry used to investigate the effect of the source composition. Just after the substrate was etched, the ampoule was assembled, evacuated to $\sim 10^{-5}$ torr and sealed. The source to substrate spacing was 3cm. Growth was performed in the isothermal zone of a sodium heat pipe.

Fig. 2. Composition profiles of samples grown under the same conditions, (550°C and 24 hours) but with different source compositions (shown on top). Notice that for material grown from sources with fractions of CdTe greater than 0.2, the surface compositions are the same as the solid in the source.

Fig. 3. A schematic of the Hg-Cd-Te phase diagram at the growth temperature. Initially the source is at position A, in equilibrium with mercury cadmium telluride of composition C. If the source is in communication with a piece of CdTe (the substrate), the overall composition of the system is moved to point B. Since the source is large compared to the film which is grown, the overall composition of the system is only perturbed slightly by the presence of the substrate.



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