

Invited

Photo-Epitaxial Growth of HgTe and Related Materials

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Photolytic decomposition of metal-organic precursors has been used for the first time to grow epitaxial layers of II-VI compounds. HgTe layers have been grown epitaxially at temperatures down to 200°C, which is 200° below the pyrolytic growth temperature. The process entails surface excitation of Hg atoms which are sufficiently energetic to dissociate the diethyltelluride molecules, yielding tellurium on the surface. Problems encountered with vapour phase nucleation are discussed for CdTe and $\text{Cd}_x\text{Hg}_{1-x}\text{Te}$ deposition and evidence presented for the suppression of these unwanted effects. The potential for growing multi-layer structures in $\text{Cd}_x\text{Hg}_{1-x}\text{Te}$ using this new growth technology will be speculated upon.

1. Introduction

This talk describes a new technique for low temperature epitaxy which relies on non-thermal decomposition of metal-organic molecules by UV photolysis. Low temperature epitaxial growth of HgTe and the important narrow band-gap semiconductor $\text{Cd}_x\text{Hg}_{1-x}\text{Te}$ (CMT) is important for the following reasons:-

1 To reduce the equilibrium vapour pressure of Hg during the growth process where for example, at the melting point ~ 790°C for a composition of $x = 0.2$ the equilibrium vapour pressure is ~35 atm (1). Such conditions create an explosive risk in a growth apparatus.

2 To minimise interdiffusion in the growth of heterojunctions where the graded composition region caused by the rapid Hg/Cd interdiffusion must be generally no greater than ~ 0.1 μm , and for a HgTe/CdTe superlattice it must be ~ 10 $\text{\AA}$ (2).

3 To control the electrically active Hg vacancy concentration which is only feasible at temperatures < 400°C (3).

The growth of abrupt structures such as a superlattice may require growth temperatures as low as 200°C (4). The current pyrolytic growth of CMT by MOVPE is constrained to a narrow band of temperatures around 410°C (5) and it is anticipated that using the photolytic route, not only will the growth temperatures be lower but a wider range of temperatures will be possible.

Although the prime motivation has been low temperature growth, other advantages such as selective area deposition and multi-step photo-processing are also very attractive possibilities.

2. Experimental

Epitaxial growth experiments were carried out in a horizontal flow system, operating at one atmosphere total pressure. The reactor cell is shown diagrammatically in Fig 1 for HgTe growth. The reactor cell diameter was 6 cm and the Hg reservoir zone divided into two so that a pure stream of carrier gas could flow over the section of wall illuminated with UV and prevent deposition. The metal-organics flowed over the Hg reservoir and mixed with the Hg vapour before passing over the substrate.

The substrates were either CdTe or InSb and heated by an infrared lamp controlled by a Eurotherm temperature controller with a reference thermocouple situated in the graphite holder. The CdTe substrates were prepared by polishing on a chemo-mechanical polisher with 2% Br/methanol solution followed by solvent rinses and a final rinse in deionised water. The InSb substrates were supplied as polished by Mining and Chemical Products and subsequently etched in 25:4:1, lactic acid, nitric acid, HF and finally rinsed in deionised water, before being loaded in the reactor.

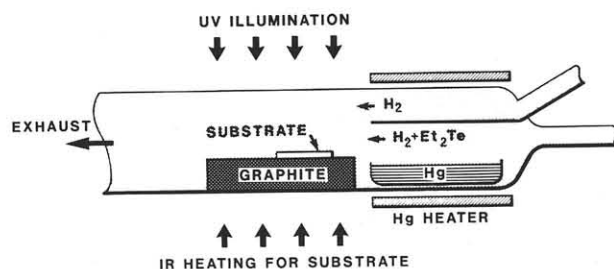


Fig 1. Reactor cell for UV photolytic deposition. The configuration shown here is for HgTe growth by Hg photosensitisation using H_2 carrier gas with Et_2Te and Hg vapour.

All gas flows were regulated by mass flow controllers. The hydrogen supply was purified by Pd/Ag membranes and the helium supply was passed through a molecular sieve which reduced the water vapour content to below 1 ppm. The metal-organics used were electronic grade diethyl-telluride (Et_2Te) and dimethyl-cadmium (Me_2Cd) supplied by Alfa Products.

The UV source was a 3 kW mercury arc lamp with a water cooled, silica jacket, all supplied by Illumination Industries. The lamp was mounted in an elliptic reflector focussing to a 0.5 cm wide stripe on the substrate.

3 Growth of HgTe

It was found in preliminary experiments on UV photolysis of Et_2Te in H_2 that deposition onto silica would not occur in a region of high UV intensity but significant deposition would occur downstream in a region of low UV intensity (6,7). The first attempts at epitaxial growth in the present system using a Hg pressure of 1.7×10^{-3} and at $252^\circ C$ did not result in any deposit on a CdTe substrate or on the wall surrounding the substrate after half an hour exposure but some deposit was observed downstream. The minimum equilibrium Hg pressure required for growth of HgTe at $252^\circ C$ was estimated to be 4×10^{-5} atm, so the lack of deposition on the substrate could not be attributed to inadequate Hg pressure. The observed deposition downstream was consistent with the

preliminary experiments on Et_2Te photolysis described above. By further increasing the Hg pressure, deposition of HgTe was achieved on the reactor wall and on the substrate, leaving a specular surface to the layer.

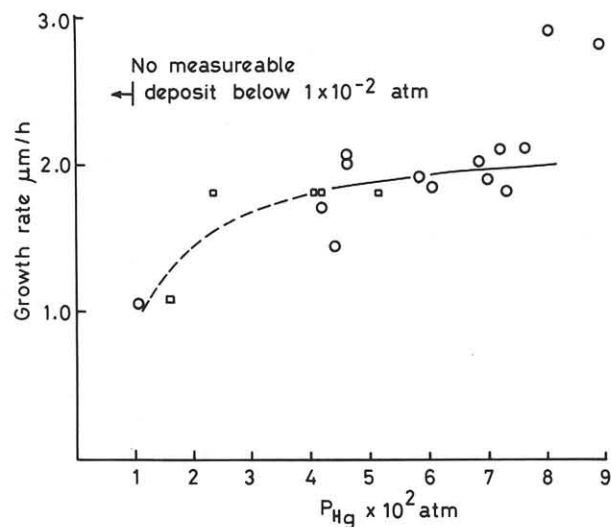


Fig 2. Growth rate vs mercury pressure for $240^\circ < T_s < 310^\circ C$ and $P_{Et_2Te} = 4.5$ Torr on (100) InSb substrates (O), and on (100) 2° towards (110) CdTe substrates (□).

Results on growth rate as a function of the Hg pressure are shown in Fig 2 for both InSb and CdTe substrates. No significant growth was observed below 1×10^{-2} atm and the growth rate rapidly increases with Hg pressures above this level to give growth rates in the region of $2 \mu\text{m/h}$. For the higher Hg pressure of 8×10^{-2} atm, some condensation was observed on the reactor wall in the region of the substrate and weight loss measurements on the Hg source may have given optimistically high values for P_{Hg} . Despite the scatter on these results it is clear that for P_{Hg} below $\sim 3 \times 10^{-2}$ atm the growth rate is strongly dependent on P_{Hg} but less dependent above this value. These results support a surface photosensitisation model for the surface dissociation of Et_2Te by reaction with excited $Hg(^3P_1)$ atoms (8).

Further growth rate studies were carried out to investigate the growth mechanisms under conditions of high P_{Hg} ($> 3 \times 10^{-2}$ atm). A plot of growth rate against substrate temperature, T_s , is shown in Fig 3. The lowest temperature was $198^\circ C$ and the electron channelling pattern for this

layer indicated that it was single crystal epitaxial HgTe. Although it was more difficult to maintain P_{Hg} at these lower substrate temperatures due to the condensation problem mentioned earlier, these values were all above 3×10^{-2} atm and from Fig 2 should have yielded growth rates in excess of 1 $\mu\text{m/h}$. In Fig 3 the growth rate increases with temperature, attaining a value of 2 $\mu\text{m/h}$ at 240°C, above which the growth rate appears to be independent of temperature.

The crystalline quality of the HgTe layers was studied using electron channelling patterns in a Cambridge 150 SEM and single crystal x-ray diffractometer traces using $\text{Cu K}\alpha$ radiation. Single crystal behaviour was observed in layers covering the complete range of growth temperatures (200–300°C) indicating good quality epitaxial growth.

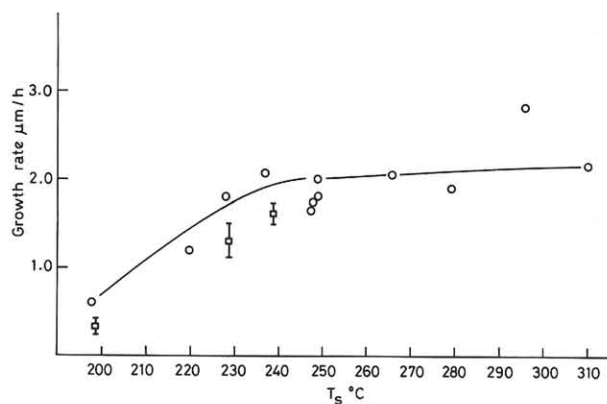


Fig 3. Plot of HgTe growth rate vs substrate temperature T_s °C for H_2 carrier gas (O), and He carrier gas ($\square$). The other growth conditions were $P_{\text{Hg}} > 3 \times 10^{-2}$ atm, $P_{\text{Et}_2\text{Te}} = 5.9 \times 10^{-3}$ atm and substrates were InSb oriented (100).

4 Growth of CMT and CdTe

The method of surface photosensitisation cannot be simply extended to the growth of CdTe and CMT because of the problem of vapour phase reactions. This problem is more severe than when only cadmium is being deposited. The probability of the occurrence of homogeneous nucleation depends on the supersaturation of Cd and Te which in turn depends on the difference between the actual vapour phase concentration and the equilibrium vapour pressure. At 250°C equilibrium vapour pressure over Cd is $\sim 10^{-5}$ atm but over

CdTe (under congruent evaporation conditions) it is $\sim 10^{-12}$ atm.

It can be seen that a given Cd pressure, resulting from photo-dissociation of Me_2Cd , will provide a much larger supersaturation for nucleation of CdTe than for Cd. Implicit in this argument is the corresponding dissociation of Et_2Te to yield Te and combine with the Cd. This effect is observed experimentally and results in the formation of a CdTe dust which covers the surface. Similarly for CMT with Hg vapour present, premature nucleation will occur forming a dust of CMT.

The vapour phase chemistry can be changed by replacing the reactive H_2 carrier gas with an inert gas such as He (9, 10).

It would be expected that the absence of H_2 will give rise to a higher free alkyl radical concentration as the collision probability between alkyl radicals will be much lower than with H_2 , both reactions yielding stable alkanes. In turn, the higher free radical concentration could give the reverse reaction thus reducing the vapour concentrations of Cd and Te. For example, in the case of Me_2Cd the reaction could be written:



Results for HgTe growth using He carrier gas are shown in Fig 3. The growth rates are similar to those when H_2 was used which suggests that the higher free radical concentration is not inhibiting the surface photo-dissociation of Et_2Te . Higher alkanes are probably formed on the surface by reaction between alkyl radicals.

For the growth of CMT two similar deposition experiments were carried out at 250°C with Me_2Cd added to the reactant gas stream but one experiment used H_2 and the other He carrier gases. The two micrographs in Fig 4 show the difference in deposition using the two carrier gases. For H_2 carrier gas, the surface appears black and consists of a fragile network of submicron sized particles of CMT which have formed in the vapour and fallen to the surface, as can be seen in Fig 4a. By contrast, Fig 4b shows a flat surface with very slight ripple, although to the eye it appears as a mirror surface. This layer was 1.3 μm thick and was grown onto a (110) oriented

CdTe substrate. An X-ray diffraction trace for the (220) reflections is shown in Fig 5 and shows that this layer is epitaxial. The $k_{\alpha 1}$ and $k_{\alpha 2}$ reflections from CMT are clearly resolved and a weaker $k_{\alpha 1}$ reflection from the CdTe substrate can also be seen. Using a lattice parameter for CdTe of $6.4829 \text{ \AA}$, the lattice parameter of the CMT layer can be calculated and gives a value of $6.466 \text{ \AA}$ which is reasonable for CMT $x \sim 0.3$.

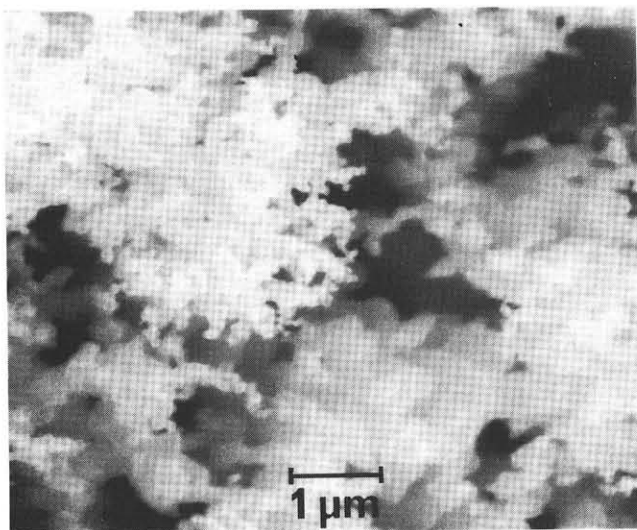


Fig 4a. SEM micrograph of CMT deposited using H_2 carrier gas, $x \sim 0.5$ showing a porous polycrystalline structure.

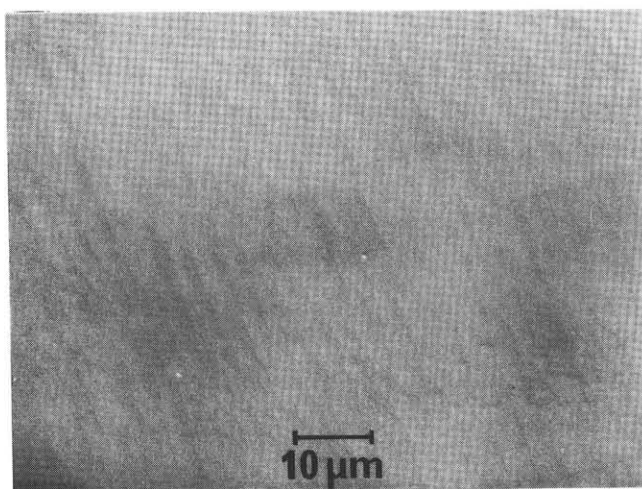


Fig 4b. SEM micrograph of a CMT epitaxial layer, $x = 0.33$ after using He carrier gas.

Secondary ion mass spectrometry (SIMS) analysis of the major elements, Cd, Hg and Te, confirm the quality of this layer with uniform composition and a sharp interface width of $\sim 300 \text{ \AA}$. The sharpness of this interface is a factor of ten smaller than equivalent interfaces grown by thermal-MOVPE at 410°C (11). This shows the potential for the growth of heterostructures in

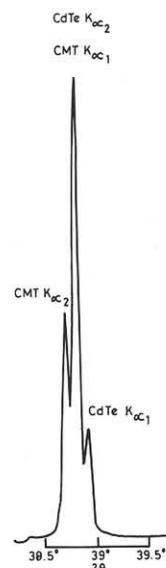


Fig 5. X-ray diffraction peaks for the (220) reflections from $1.3 \mu\text{m}$ thick CMT layer on a CdTe substrate. Cu K_α radiation was used and the positions of the $\text{K}_{\alpha 1}$ and $\text{K}_{\alpha 2}$ reflections for CMT and CdTe are indicated.

CMT at low temperatures while maintaining the crystalline quality.

5 Conclusions

Results have been presented on the low temperature photo-epitaxial growth of HgTe where a surface photolytic reaction is promoted by Hg photosensitisation. The problems encountered in vapour phase nucleation when using Me_2Cd , have been overcome by using an inert carrier gas to enable a higher free alkyl radical concentration in the vapour. High quality epitaxial layers have been grown at substrate temperatures as low as 200°C which opens new possibilities for device technologies in CMT.

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