ADVANCED MATERIALS

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Low Temperature Deposition of a CaF_2 Insulator Layer on GaAs*

Over recent years there has been widespread interest in the development of alternative insulators for silicon and GaAs, especially where these might be obtained in epitaxial layer form to permit the production of multilayer semiconductor-insulator structures.[1-3] Several workers have reported the growth of epitaxial CaF_2 on silicon[4-6] and GaAs.[7-9] The major problems in obtaining good quality films lie in the lattice mismatch between the layer and substrate (0.6% for Si; 3% for GaAs) and the thermal conductivity mismatch (α $CaF_2 = 1.9 \times 10^{-5}\ K^{-1}$; α Si $= 4 \times 10^{-6}\ K^{-1}$; α GaAs $= 6.9 \times 10^{-6}\ K^{-1}$). For GaAs applications the former has been overcome, partially at least, by the use of solid solutions of CaF_2–SrF_2, the composition $Ca_{0.44}Sr_{0.56}F_2$ being perfectly lattice-matched to GaAs at 25 °C.[10] The thermal expansion coefficient differences between GaAs, CaF_2, and SrF_2 produce strain at the film/substrate interface during cooling from the growth temperature. In the case of high elastic modulus material such as CaF_2 and CaF_2-rich alloys this leads to cracking, whilst the more plastic SrF_2 and SrF_2-rich alloys deform by dislocation generation, so that the layer becomes a poor substrate for subsequent semiconductor overgrowth. The best solution to this problem lies in a reduction of a growth temperature to minimize cooling strains. This demands a growth system which permits transport and low temperature decomposition of a suitable precursor, which must nevertheless remain sufficiently stable to withstand premature thermal decomposition.

Benac et al.[11] have recently reported polycrystalline growth by pyrolytic decomposition of bis(pentamethylcyclopentadienyl)calcium $(C_5Me_5)_2Ca$ in either SiF_4 or NF_3 at 150 °C. This low decomposition temperature may, however, lead to handling problems. At the observed growth rates of 10–100 μm/hr the product is polycrystalline CaF_2 with a grain size of 20–50 μm but X-ray photoelectron (XPS) studies show relatively high impurity levels (approximately 18% carbon and 7% oxygen) in these films.

Recent work at RSRE Malvern and Queen Mary College London has led to the development of a new approach to the deposition of CaF_2 on GaAs at low temperatures, which combines the advantages of the organometallic approach with those of photochemically-induced precursor decomposition. This permits the use of thermally stable precursors, thus reducing the risk of premature reaction outside the required deposition zone, and of gas phase reactions which generally result in poor epitaxy. Careful design of the photochemical reactor and the use of suitable projection masking in the incident photon beam can then be used to promote selected-area deposition.

The process is based on the photochemical decomposition of bis(1,1,1,5,5,5-hexafluoro-2,4-pentanedionato)calcium(II), $Ca(hfac)_2$, (Fig. 1) using xenon lamp radiation in the 180–300 nm waveband. The precursor compound was developed and synthesized at Queen Mary College, London.[12]

The material is obtained in the form of a pale yellow powder which sublimes at approximately 100 °C. It is impor-

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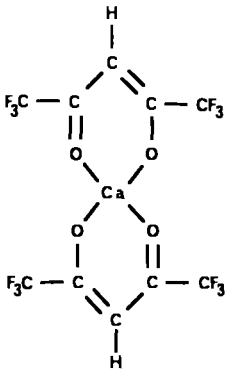

Fig. 1. Bis(1,1,1,5,5,5-hexafluoro-2,4-pentadionato)calcium(II) precursor for low temperature deposition of CaF_2.

tant to obtain the material in its anhydrous state as the hydrated or even partially hydrated compound does not appear to yield CaF_2 under the experimental conditions described here.[13] The material is thermally stable to approximately 300 °C, above which it can be pyrolytically decomposed to give CaF_2. In the photo-assisted decomposition process the precursor is transported from a bubbler held at 100 °C into a MOVPE reactor containing one or more substrates of GaAs heated to 100 °C (Fig. 2). The reactor pressure is approximately 10^{-1} Torr.

Radiation from a 450 watt xenon lamp is broad-band filtered (180–300 nm) and illuminates the substrate at normal incidence through an aperture in the furnace wall.

A deposited CaF_2 layer approximately 4000 Å thick is obtained at a deposition rate of around 30 Å min^{-1}. XPS analysis of the layer shows Ca and F peaks together with *small* carbon and oxygen (< 10%) peaks. X-Ray diffraction data indicate a polycrystalline CaF_2 layer with a high degree of preferred orientation. At this stage no attempt has been made to clean up the reactor or substrate prior to deposition and the polycrystallinity and impurity results are not unexpected. Work is now in progress to improve the layer structure. Further details of the photochemical process are awaiting publication.[14]

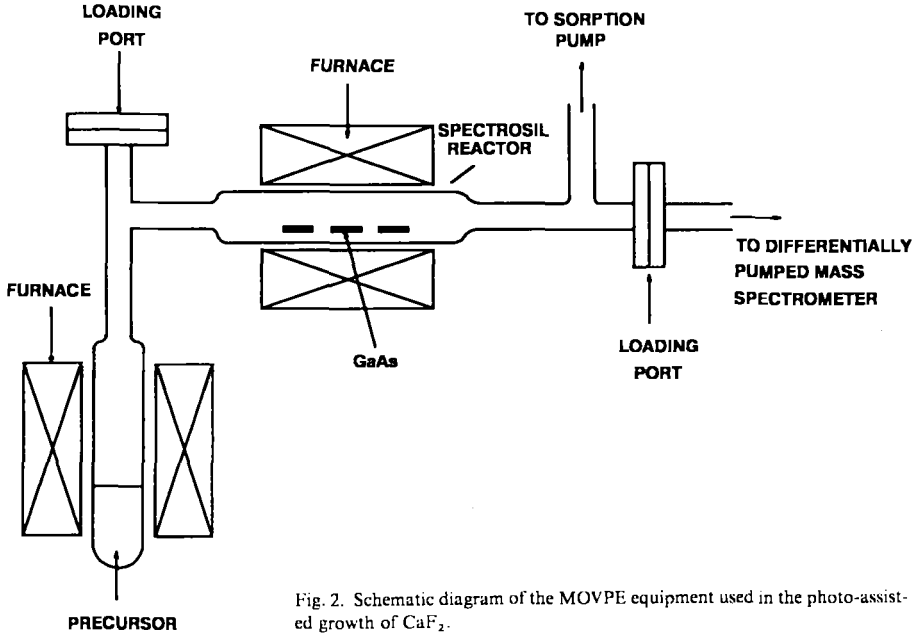

Fig. 2. Schematic diagram of the MOVPE equipment used in the photo-assisted growth of CaF_2.

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