

Figure 3. Visible region spectra of a Langmuir-Blodgett film of **2**. Line 1 at 25 °C; line 2 at 130 °C.

of 41 Å in the unheated film is about twice this value, suggesting that the molecules are standing essentially perpendicular to the substrate surface.

The spectrum of the heated LB film of **2**, λ_{max} 672, 710, 732 (s) nm, shows a close similarity to the spectrum of the D_1 mesophase of **1**. This implies that when the film is heated the columnar packing is reorganized, the herringbone packing being replaced by one that mimics the hexagonal packing shown in Figure 1. We postulate, therefore, that on heating the film the molecules within a column become fully cofacial and that a cross section of the columnar packing within a bilayer can be broadly represented by the lower two rows of circles in Figure 1. On this basis and because of the shorter distance from the carboxylic acid residues to the other side of the molecule, the bilayer spacing in the heated film should be somewhat lower than the distance $a = 39.3$ Å, as is indeed the case.

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Growth of Polycrystalline CaF_2 via Low-Temperature Organometallic Chemical Vapor Deposition

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Silicon-on-insulator (SOI) material structures are of considerable interest in integrated circuit technology. This

type of structure, if successfully developed, allows the fabrication of three-dimensional integrated circuits. It also allows the fabrication of memory and logic circuits that are immune to both soft errors due to α particles and single-particle upset events caused by high-energy particles.¹ Almost all of the current research and development activity in SOI is focused on the use of a layer of amorphous SiO_2 of thickness 1500–5000 Å as the insulator. The 1000–5000-Å single-crystal overlying silicon layer is then formed by various approaches involving the recrystallization of amorphous or polycrystalline silicon from seed locations in the underlying silicon substrate or the use of very high dose ($\sim 10^{18}$ ions/cm²) ion implantation of oxygen to form an amorphous SiO_2 layer below the surface of silicon substrate. These approaches all have numerous obstacles to overcome due to the difficulty in obtaining low-defect density, high-quality single-crystal silicon on the amorphous SiO_2 layer.

An alternative approach to the formation of the SOI structure is the use of a single-crystal, lattice-matched insulator. This then allows the possibility for the growth of the single-crystal overlying silicon layer directly on the insulator. Calcium fluoride (CaF_2) is an excellent candidate for SOI because it has a wide bandgap and a cubic structure similar to that of silicon, and it is lattice matched to silicon to within 0.6% at room temperature. SOI insulator based on CaF_2 has been demonstrated by using molecular beam epitaxy (MBE).² The source of CaF_2 for this growth process is CaF_2 itself, evaporated from tungsten or graphite crucibles at very high temperatures (1200–1400 °C) onto silicon substrates at temperatures of 550–700 °C.^{3,4} However, much work remains to be done to achieve high electrical quality SOI structures and interfaces and topographically smooth layers of uniform thickness.

We have initiated a program aimed at achieving high-quality CaF_2 on silicon at lower temperatures (200–400 °C) since this should prevent layer mixing, wafer warpage, and film stresses, which are problems associated with high-temperature depositions. The new approach is based on the combination of an organometallic chemical vapor deposition (OMCVD) reaction to form CaF_2 and a remote plasma-enhanced chemical vapor deposition (RPCVD) materials growth technique.

One key requirement for the success of this approach has been to identify and develop appropriate volatile precursors and CVD reactions that will produce CaF_2 . Unlike other well-documented OMCVD processes such as those employed for the fabrication of thin films of III/V compound semiconductors,⁵ there appears to be no previous reports of CVD growth on CaF_2 . This may be due to the lack of suitable volatile calcium compounds.⁶ Earlier work on organocalcium chemistry tended to focus on the use of small ligands such as methyl and ethyl. This lack of steric saturation often resulted in intractable oligomeric materials or decomposition products (typically via hydrogen abstraction). The use of bulkier groups has resulted in the isolation of stable organocalcium deriva-

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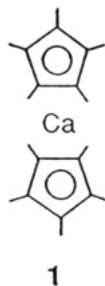


Figure 1. Bis(pentamethylcyclopentadienyl)calcium (Cp^*_2Ca).

tives. Thus, while bis(cyclopentadienyl)calcium is polymeric in the solid phase, the volatile organometallic derivative bis(pentamethylcyclopentadienyl)calcium ($(\text{C}_5\text{Me}_5)_2\text{Ca}$ or Cp^*_2Ca (I)) is monomeric (Figure 1). This compound was recently reported by Andersen and co-workers⁷ and may be sublimed at 75 °C and 10^{-3} Torr of pressure.

We have now discovered a novel low-temperature chemical vapor deposition process for the production of CaF_2 . At present the process does not require the use of a remote plasma. However, the RPCVD technique may of course be ultimately necessary for the growth of ultrahigh purity epitaxial CaF_2 . We report here initial results of the low-temperature CVD of CaF_2 using Cp^*_2Ca with either SiF_4 or NF_3 as the source of fluorine.

The experimental procedure employed involves a vertical hot-wall glass reactor connected to a vacuum manifold which permits the introduction of SiF_4 or NF_3 . The organometallic calcium source Cp^*_2Ca is placed in the lower portion of the tube, which is heated to 150 °C in an oil bath. The system is evacuated to 10^{-2} Torr, and SiF_4 or NF_3 admitted until the total pressure in the system reaches 10 Torr. The system is then sealed, and the temperature of the oil bath is maintained at 150 °C. After 1 h, white polycrystalline deposits are observed on the walls of the vessel in the region immediately above the oil level. It seems unlikely that a stable volatile intermediate between Cp^*_2Ca and SiF_4 or NF_3 would exist at 150 °C in the gas phase due to the very large heat of formation of CaF_2 . Our observations indicate that under the reaction condition employed Cp^*_2Ca reacts directly with NF_3 or SiF_4 to give CaF_2 . The reaction may well occur in the gas phase with subsequent nucleation of CaF_2 occurring on the walls of the reaction vessel and substrate surfaces. In the absence of solvent, Cp^*_2Ca and SiF_4 or NF_3 do not appear to react below 150 °C. We are currently investigating the possibility of an intermediate formation in solution—although this may not be particularly relevant to a CVD process. An alternative setup involves the use of a horizontal hot-wall glass reactor in a sealed system. We have obtained polycrystalline deposition under similar conditions on glass and $\text{Si}(100)$. Growth rates and film thicknesses appear to be influenced by the distance of the Cp^*_2Ca from the reaction regime in the reactor. Thus, thickness varying from 10 to 100 μm can be observed. These correspond to very approximate growth rates of 10–100 $\mu\text{m h}^{-1}$. We have, so far, not investigated the adhesion properties to $\text{Si}(100)$, although preliminary studies suggest that this is not particularly high. There appears to be little difference in the film properties when grown on glass or silicon substrates or with SiF_4 vs NF_3 . X-ray powder diffraction patterns matched the JCPDS data and confirm that they are polycrystalline CaF_2 .⁸ Normarsky optical microscopy

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Figure 2. Nomarsky optical microscopic view of polycrystalline CaF_2 on $\text{Si}(100)$ (magnification $\times 400$).

confirmed the polycrystalline nature of the product (Figure 2). The size of the crystallites appears to range from 20 to 50 μm . XPS data were obtained on various samples that were etched twice with ionized argon at 5-min intervals. The corrected Ca 2p and F 1s signals at 347.7 and 684.6 eV, respectively, compare well with the literature values (347–348, 689.6 eV)⁹ and confirm the Ca:F stoichiometry of 1:2. XPS analysis also revealed the presence of considerable quantities of carbon (18%) and oxygen (7%) in the films. We do not feel that this is altogether unexpected since no particular precautions were taken in handling the samples. The high carbon levels may also be due to organic fragments that remain in the deposited material. We are currently investigating the volatile byproducts of the reaction to gain further insight into the process of CaF_2 formation.

Although the CaF_2 produced by this method is polycrystalline in nature, we believe that this is a major step toward the goal of low-temperature growth of epitaxial CaF_2 on silicon using our alternative approach. There is clearly scope for the optimization of the reaction conditions and to adapt the process to a RPCVD one. Future studies will be focused on the incorporation of the RPCVD technique to achieve films of ultrahigh quality.

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(8) Joint Committee for Powder Diffraction Standards (JCPDS), International Center for Diffraction Data, 1601 Park Lane, Swarthmore, PA 19081, Card No. 35-816, 1988.

(9) XPS data were obtained on a VG Scientific Escalab Mark II with a Mg $K\alpha$ X-ray anode. The observed binding energies (Ca 2p (354.1 eV), F 1s (691.0 eV)) were corrected for electrostatic charging. Literature values were obtained from: *The Handbook of X-ray Photoelectron Spectroscopy*; Wagner, C. D., Riggs, W. M., Davis, L. E., Moulder, J. F., Muilenberg, G. E. G. E., Eds.; Perkin-Elmer, Physical Electronics Division, 1976.