in calix[6]arenediquinones seems to be larger than that of four carbonyl oxygens in calix[4]arenediquinones. The size of semiquinonecalix[6]arenes is comparble to the size of Cs^+ and their relatively strong complexation results in larger positive potential shift. The complexation of calix[6]arenediquinones with Cs^+ is found to more stable complex than with Ba^{2+}.

In pursuit of redox switchable receptors we prepared a series of tetraester calix[6]arenes and their corresponding quinones and investigated their cation binding properties. Tetraester benzyl derivative **3b** showed high extraction for potassium, rubidium, and cesium ion and complexed with potassium ion in 1 : 1 solution stoichiometry. The magnitude of shift in reduction potential depends on the size of metal cations and the complexation strength between reduced semiquinonecalix[6]arenes and cations. Generally, the larger the size of alkali metal ion, the larger the value of ΔE.

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Chemical Vapor Deposition of MgO Films Using a New Single Source

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The MgO single crystal is a preferred substrate for growing various thin film materials. The oxygen lattice of MgO crystal matches well with those of perovskite oxide crystals as well as those of Si and GaAs crystals. MgO buffer layers were employed to grow high T_c superconductors[1-4] and ferroelectrics[5-10] as well as a nitride.[11] Growing high quality superconductor films on GaAs using the MgO buffer layer received great attention for RF and microwave applications.[2,12,13]

There were several reports on chemical vapor deposition (CVD) of MgO although MgO films were more frequently prepared by physical vapor deposition methods such as electron beam evaporation,[12] pulsed laser deposition,[7,9-11] and

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sputter deposition.[5] Various magnesium compounds have been used as CVD sources. These are diethylmagnesium,[14] bis(2,2,6,6-tetramethyl-3,5-heptanedionato)magnesium,[15-18] bis(acetylacetonato)magnesium,[19-21] magnesium acetate,[22] magnesium 2-ethylhexanoate,[23] and bis(cyclopentadienyl) magnesium.[24] These compounds must be vaporized at high temperatures (higher than 100 °C except in the case of diethylmagnesium) and generally need an additional oxygen source such as H_2O and O_2.

Using a single CVD source provides a novel alternative to conventional CVD that employs separate sources for the constituent elements of compound materials.[25-28] Gas-phase mixing is not necessary and undesirable gas-phase reactions that can generate particles or impurity sources are much less likely to occur. Deposition usually proceeds at lower temperatures compared to conventional CVD.

Methylmagnesium alkoxides and methylzinc alkoxides were known to produce MgO and ZnO, respectively, upon thermal decomposition.[29] Methylzinc alkoxides were successfully used to prepare ZnO films at 250 °C.[30] We used methylmagnesium *tert*-butoxide as a single source for MgO CVD and found it to be a better source than other magnesium CVD sources previously reported.

Methylmagnesium *tert*-butoxide was synthesized from commercially available methylmagnesium bromide (CH_3MgBr) and potassium *tert*-butoxide (KO^tBu). In a typical synthesis, KO^tBu was slowly added to a diethyl ether solution of CH_3MgBr at 0 °C. After filtering KBr, the solvent was removed under reduced pressure. Only 36% of the as-obtained white solid was sublimed, whereas 73% was sublimed after refluxing in toluene for 24 hours. These results are in parallel with Ashby's report that the reaction product of $(CH_3)_2Mg$ with ^tBuOH at −70 °C was not sublimed, however, converted to sublimable form after refluxing in benzene for 4 days.[31]

A simple CVD apparatus was used, in which borosilicate glass tubing, quartz tubing, and stainless steel bodies were connected through O-ring joints. Si and GaAs substrates were degreased with trichloroethylene and rinsed with acetone, methanol, and deionized water. They were then treated with a 36% HCl solution, rinsed with deionized water, and immediately introduced into the CVD apparatus. The substrates were placed on a graphite heating block. Substrate temperature was monitored by a thermocouple inserted in the graphite block. The deposition temperature was maintained in the range 350-600 °C. No carrier gas was used and the source was vaporized at 80 °C. The base pressure of the CVD apparatus was 2-5 mPa and the pressure increased to 50-200 mPa after introducing the source into the CVD apparatus. Interference colors appeared on the substrate within 10 minutes and the deposition continued for several hours.

Figure 1 shows the X-ray photoelectron spectrum of a MgO film deposited on Si(100) at 350 °C. The spectrum clearly displays the photoelectron and Auger electron peaks for magnesium, oxygen and carbon only. The ratio of the areas under Mg 1s and O 1s peaks of this film was the same as that of a MgO single crystal. Photoelectron and Auger electron peaks for carbon are smaller than those of MgO films deposited from bis(2,2,6,6-tetramethyl-3,5-heptanedionato)magnesium.[18] Essentially the same photoelectron spectra were observed for all MgO films deposited under the experimental conditions.

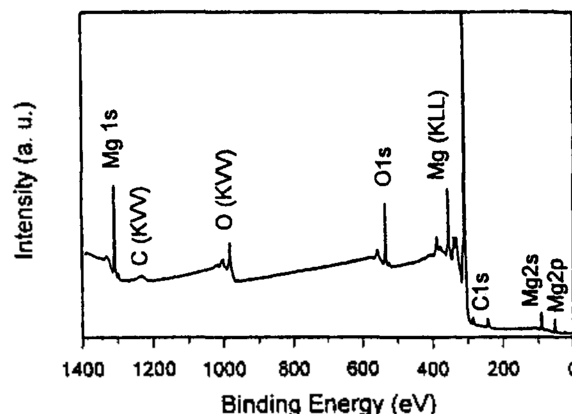

Figure 1. X-ray photoelectron spectrum of a MgO film grown on Si(100) at 350 °C.

Figure 2a shows the X-ray diffraction pattern of a MgO film deposited on Si(100) at 500 °C. A characteristic peak of cubic MgO at $2\theta = 42.91°$ diffracted from the (200) plane is visible in the pattern as well as a smaller peak at $2\theta = 62.31°$ diffracted from the (220) plane. This indicates that the film is polycrystalline and preferentially oriented to the [100] direction. However, MgO films deposited on Si(111) at 500 °C and deposited on GaAs(100) at 350 °C are less oriented and display characteristic peaks diffracted from the (111), (200), (220), (311), and (222) planes of cubic MgO (Figures 2b and 2c).

The MgO films were also examined by scanning electron

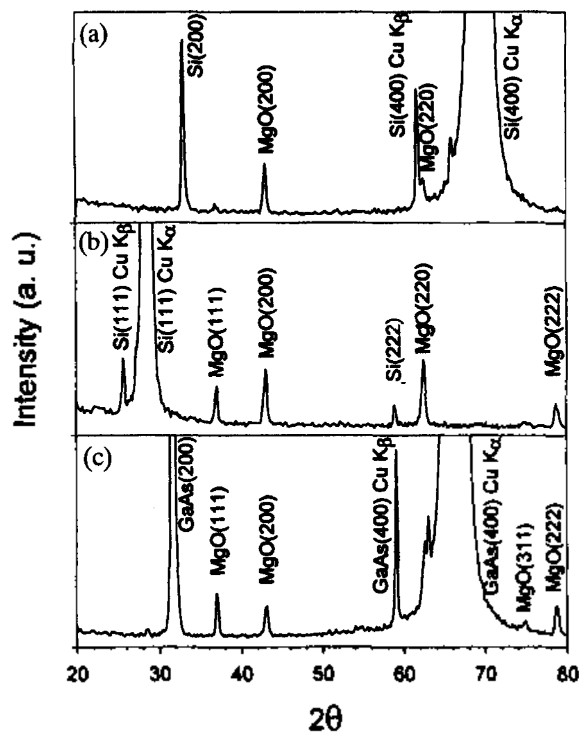

Figure 2. X-ray diffraction patterns of MgO films grown (a) on Si(100) at 500 °C, (b) on Si(111) at 500 °C, and (c) on GaAs (100) at 350 °C.

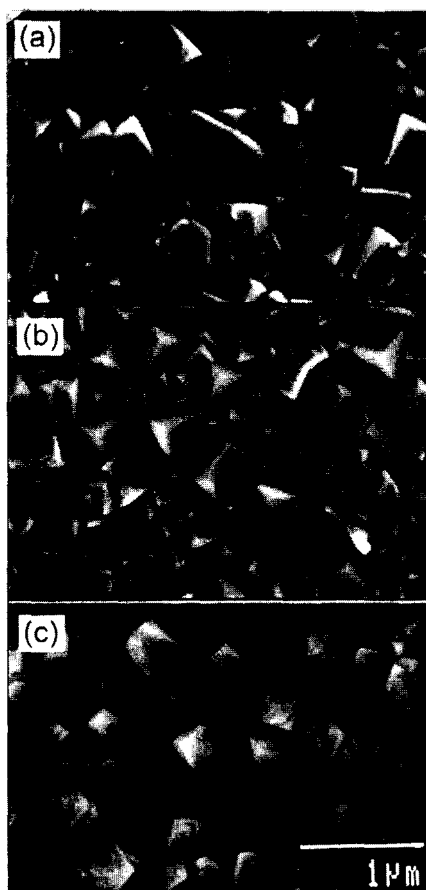

Figure 3. SEM images of MgO films grown (a) on Si(100) at 500 °C, (b) on Si(111) at 500 °C, and (c) on GaAs(100) at 350 °C.

microscopy (SEM). Figure 3 shows SEM images of the films the diffraction patterns of which are shown in Figure 2. All the films show rough surfaces. Well-shaped facets of cubic MgO crystallites are observed on the films deposited at 500 °C (Figures 3a and 3b), however, less well-shaped crystallites are observed on the film deposited at 350 °C (Figure 3c). A MgO film deposited on Si(100) at 350 °C displays diffraction pattern and SEM image very similar to those of the film deposited on GaAs(100) at the same temperature.

In summary, methylmagnesium *tert*-butoxide was synthesized and successfully employed as a single CVD source to grow polycrystalline MgO films on Si and GaAs substrates at temperatures as low as 350 °C.

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