

## MOCVD Deposition of MgAl<sub>2</sub>O<sub>4</sub> Films Using Metal Alkoxide Precursors

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Amorphous thin films of MgAl<sub>2</sub>O<sub>4</sub> have been deposited onto crystalline silicon and glass substrates from the metal alkoxide source, Mg[Al(OPr<sup>i</sup>)<sub>4</sub>]<sub>2</sub>, at temperatures between 250 and 500 °C. The growth rate, which was negligible at 250 °C, increased with substrate temperature between 300 and 425 °C, consistent with a surface reaction limited process. Above 425 °C, the growth was limited by the availability of reactant, and no further increases in the conversion efficiency or the growth rate were observed. The volatility of the alkoxide source allowed vaporization at modest source temperatures, between 120 and 170 °C. The liquidity of the alkoxide at temperatures below 100 °C offers the possibility of low-cost, high-rate spray pyrolysis as a means of film deposition. Infrared adsorption by CH<sub>3</sub> groups, clearly evident in films deposited at a substrate temperature of 350 °C, decreased with substrate temperature becoming undetectable at 500 °C. However, physical and electrical properties of the transparent, dense films showed little temperature dependence. Mg/Al ratios of 1:2 and high breakdown field strength were exhibited by nearly all films. Dielectric constants varied from 5 to 11 for films thicker than 1000 Å as expected for a metal oxide film, but very thin films (<1000 Å) frequently exhibited dielectric constants less than 2, independent of growth temperature.

### Introduction

Metal oxide films are useful for a variety of applications including high-*T<sub>c</sub>* superconductors, ion conductors, catalysts, IR windows, mechanical/thermal protective layers, and as passivation layers in microelectronic devices. While many systems rely on high-temperature reactions with carrier gases to form volatile metal species, the volatility and low-temperature decomposition of many metal alkoxides make them excellent candidates for direct deposition using metal-organic chemical vapor deposition (MOCVD). Examples of materials deposited from metal alkoxides include Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, Ta<sub>2</sub>O<sub>5</sub>, Nb<sub>2</sub>O<sub>5</sub>, PbTiO<sub>3</sub>, and BaTiO<sub>3</sub>.<sup>1–8</sup> In the MOCVD processes, bimetallic oxide films are normally deposited using multiple sources to achieve the desired composition.

Bulk single and polycrystalline magnesium aluminum spinel, MgAl<sub>2</sub>O<sub>4</sub> is widely recognized for its infrared transmission characteristics, excellent mechanical and thermal shock resistance, and chemical durability. Epitaxial films have been prepared from the vapor phase using the Al–HCl–MgCl<sub>2</sub>–CO<sub>2</sub>–H<sub>2</sub> system for fabrication of silicon-on-insulator (SOI) integrated circuits<sup>9</sup> and as a buffer layer on which to deposit superconductor films.<sup>10</sup> This process requires temperatures between 600 and 800 °C for formation of the volatile metal compounds and growth temperatures around 900 °C. More recently, it was reported<sup>11</sup> that stoichiometric spinel films had been achieved at growth temperatures from 500 to 1000 °C using magnesium dialuminum isopropoxide, a bimetallic precursor with the same 1:2 Mg/Al ratio as the film. This latter process used flash vaporization of a precision metered liquid source composed of 10% {Mg[Al(OPr<sup>i</sup>)<sub>4</sub>]<sub>2</sub>}<sub>2</sub> dissolved in a 9:1 mix of isopropyl alcohol:tetraglyme. A 3:1 oxygen/argon carrier gas was used. The focus of this work was synthesis of an epitaxial buffer layer on which to deposit ferroelectric-based infrared detectors and so focused on the properties at growth temperatures, around 900 °C. Thicker spinel films have also been used as protective layers for zirconia electrolytes in devices such as solid-

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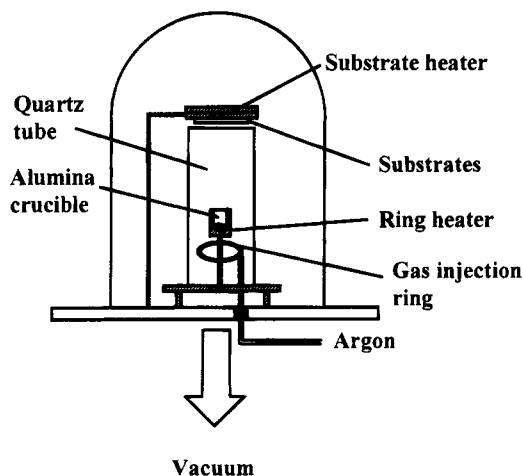
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**Figure 1.** Schematic of metal-organic chemical vapor deposition system.

oxide gas sensors.<sup>12</sup>

We have developed a MOCVD process which allows direct vaporization and film growth from a variety of volatile alkoxides, one of which was the magnesium dialuminum isopropoxide. Given the interesting optical and robust mechanical and chemical properties of spinel, we were interested in exploring the possibility of depositing stoichiometric films at reduced temperatures. In this paper, we report the deposition and characterization of  $\text{MgAl}_2\text{O}_4$  films grown at temperatures between 300 and 500 °C using solid  $\{\text{Mg}[\text{Al}(\text{OPr}^i)_4]_2\}_n$  as the source. Stoichiometric, transparent films were achieved using a pure argon carrier without the introduction of additional oxidant into the system.

## Experimental Section

**Preparation of  $\{\text{Mg}[\text{Al}(\text{OPr}^i)_4]_2\}_n$ .** The moisture sensitive  $\{\text{Mg}[\text{Al}(\text{OPr}^i)_4]_2\}_n$  was prepared, as described in the literature,<sup>13</sup> by the reaction of Mg with 2 equiv of  $\text{Al}(\text{OPr}^i)_3$  in isopropyl alcohol. All reactions and manipulations were carried out under dinitrogen using standard Schlenk and dry box techniques. Although pure  $\text{Mg}[\text{Al}(\text{OPr}^i)_4]_2$  is a volatile liquid, experiments show<sup>13</sup> that freshly distilled  $\text{Mg}[\text{Al}(\text{OPr}^i)_4]_2$  becomes solid over several minutes. The solidification is believed to result from dimerization of the  $\text{Mg}[\text{Al}(\text{OPr}^i)_4]_2$  to  $\{\text{Mg}[\text{Al}(\text{OPr}^i)_4]_2\}_2$ . At room temperature the polymeric form is favored and the material is solid. However, by about 100 °C, the equilibrium is shifted toward the liquid monomer which distills at about 105–109 °C at a pressure of 0.1–0.2 Torr. In the MOCVD experiments, samples of solid  $\{\text{Mg}[\text{Al}(\text{OPr}^i)_4]_2\}_n$  were weighed in a dry box and transferred to the MOCVD apparatus under high-purity dinitrogen. The sample was loaded into the apparatus under a stream of argon gas. Films were then deposited via the procedures described below.

**Film Deposition by MOCVD.** Glassy  $\text{MgAl}_2\text{O}_4$  films were deposited using a modified bell-jar type evaporation system shown schematically in Figure 1. The substrates were mounted about 20 cm above the alkoxide source. A radiant heater fabricated from a serpentine strip of NiKovar sandwiched between two sheets of Vycor was used to heat the substrates to as high as 500 °C. The substrate area was typically 25 cm<sup>2</sup> while the total heated area subject to film growth was 80 cm<sup>2</sup>. The metal alkoxide precursor was loaded into a 2.5 cm diameter alumina crucible which was inserted into a resistance ring heater for vaporization. A 0.64 cm diameter stainless

steel line with 1.0 mm perforations, shaped into a circular gas injection ring, was located just below the crucible, providing a uniform flow of gas past the crucible toward the substrates during evaporation of the alkoxide. The entire crucible and gas feed assembly were enclosed in a 10 cm diameter quartz tube which was helpful in controlling the vapor flow path. The system was pumped with a Leybold WSU151 Roots pump backed by a mechanical pump.

The substrate and metal alkoxide source temperatures were controlled using OMEGA temperature controllers. Substrate temperature was measured using a small-diameter K-type thermocouple affixed to the substrate surface. The alkoxide source temperature was measured with a shielded thermocouple inserted into the heater assembly wall. The pressure within the reaction chamber was controlled automatically by a MKS Baratron pressure control system with an exhaust throttle valve located near the inlet of the pump. The argon flow rate was fixed at 200 standard cubic centimeters per minute (sccm) using an in-line rotameter.

The  $\{\text{Mg}[\text{Al}(\text{OPr}^i)_4]_2\}_n$  source liquefied at about 60 °C at a vacuum below  $10^{-4}$  Torr. Bubbles were observed in the liquid around 115 °C, indicating the onset of boiling. Early experiments were often complicated by frothing in the liquid which resulted in variability of the evaporation rate and in extreme cases to loss of precursor due to splashing. The splashing was more apparent during depositions conducted at low substrate temperature with the larger initial alkoxide loadings. In the most severe cases, bubbling in the liquid was not observed until the source temperature was as high as 130 °C at which time violent boiling was initiated with the loss of a significant fraction of the alkoxide. The problem was attributed to uneven heating and poor heat transfer in the melted alkoxide. The problem was somewhat alleviated at the higher substrate temperatures due to the increased heat input to the surface of the melted alkoxide. The splashing was eliminated completely by the addition of boiling chips and an adjustment of the heat-up rate. Under these latter more controlled conditions it was possible to get an accurate determination of the overall conversion of the alkoxide to film. Although experiments were continued until vaporization of the alkoxide was complete, difficulty ascertaining the endpoint resulted in considerable uncertainty in the calculated growth rate. The conditions used for deposition of  $\text{MgAl}_2\text{O}_4$  films in this study were

weight of metal alkoxide	0.2–4.0 g
substrate temperature	250–500 °C
chamber pressure	0.5 torr
argon flow rate	200 sccm
alkoxide source temperature	120–175 °C
nominal deposition time	5–40 min

## Film Characterization

The  $\text{MgAl}_2\text{O}_4$  films were deposited on silicon wafers, metallized Corning 7059 glass slides and quartz slides for use in a variety of characterizations. Films deposited from the  $\{\text{Mg}[\text{Al}(\text{OPr}^i)_4]_2\}_n$  generally appeared dense and transparent as deposited. They adhered well to all substrates and were resistant to scratching. Film thickness was measured using a Tencor Alpha 200 profilometer across small sections of substrate masked during deposition to prevent film growth. Measurements taken at several locations indicated less than 2% variation in film thickness across the 5 cm diameter substrate zone.

X-ray energy dispersion microanalysis (EDAX) carried out with an ISI-SS40 energy dispersion spectrometer by International Scientific Instrument was used to

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determine the Mg/Al atomic ratio in selected films. Sensitivities for the Mg and Al signals were determined from [110] and [100] oriented crystalline spinel samples. Sensitivity did not depend on crystal orientation. The Mg/Al atomic ratio in films deposited at the temperatures ranging from 350 to 500 °C, was 1:2; the same as in the  $\{Mg[Al(OPr^i)_4]_2\}_n$  precursor and the crystalline spinel samples. The stoichiometry of the films did not change with substrate temperature or film growth rate, a strong indicator of the absence of disproportionation reactions during either the vaporization or film growth. Stauff et al.<sup>11</sup> reported similar success, albeit at a higher growth temperature, using  $\{Mg[Al(OPr^i)_4]_2\}_2$  in his liquid flash vaporization system. However, Huang and Kitai<sup>14</sup> reported considerably difficulty achieving stoichiometric films using separate sources, bis(cyclopentadienyl)magnesium and triethylaluminum, even though they used a well-controlled atomic layer deposition system. It is likely that a bimetallic molecule similar to the initial alkoxide source is the film precursor in our experiments. These results indicate that bimetallic alkoxides such as  $\{Mg[Al(OPr^i)_4]_2\}_n$  may also be a very convenient starting material for the synthesis of stoichiometric powders for use in bulk processing.

X-ray diffraction using a Scintag PAC V diffractometer with a Cu  $K_\alpha$  source showed no evidence of crystallinity in the as-deposited films. Other physical and electrical properties including refractive index, dielectric constant, and breakdown voltage were routinely measured to characterize the amorphous films. Fourier transform infrared spectroscopy (FTIR) and scanning electron microscopy (SEM) were applied selectively to provide a more detailed characterization of the chemical bonding and morphology of films grown at different temperatures.

Dielectric constant and breakdown field strength were determined using metal-insulator-metal (MIM) capacitor structures. The  $MgAl_2O_4$  films were deposited on Cr coated (5000 Å thick) Corning glass slides onto which 1 mm diameter aluminum dots were deposited by thermal evaporation to form the top contact of the MIM capacitors. Dielectric constants were calculated from the capacitance measured at 100 kHz. Reported dielectric values represent an average of at least three determinations whose dispersion was less than 4% of the reported value. The breakdown voltages were recorded as the applied voltage required to produce a leakage current of 1  $\mu A$  in the MIM capacitor. Breakdown field strengths were then obtained as the quotient of the breakdown voltage and film thickness. Refractive indices were determined from films deposited on p-type silicon wafers using a Rudolph AutoIII ellipsometer. FTIR spectra of select films deposited on the same p-type wafers were taken using a Perkin-Elmer 1600 FTIR spectrometer.

### Results and Discussion

Figure 2 shows the conversion efficiency of  $\{Mg[Al(OPr^i)_4]_2\}_n$  to film, characterized as the ratio of measured film thickness to the initial mass of alkoxide in the crucible, as a function of substrate temperature in an Arrhenius type plot. The data shown were obtained in a series of depositions carried out with initial alkoxide

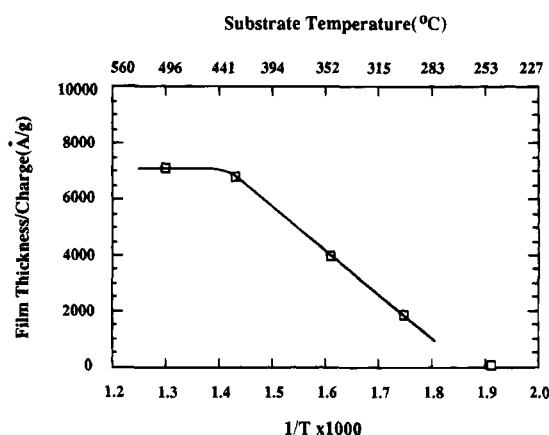


Figure 2. Effect of substrate temperature on the conversion of  $\{Mg[Al(OPr^i)_4]_2\}_n$  to film.

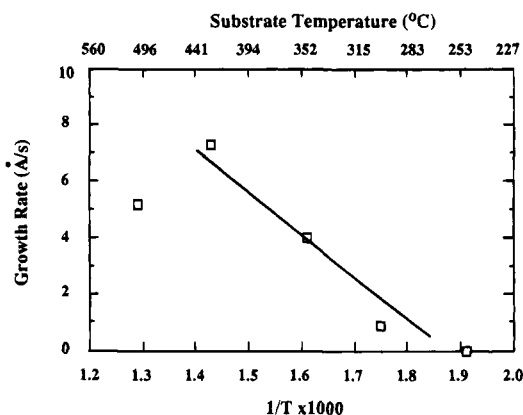


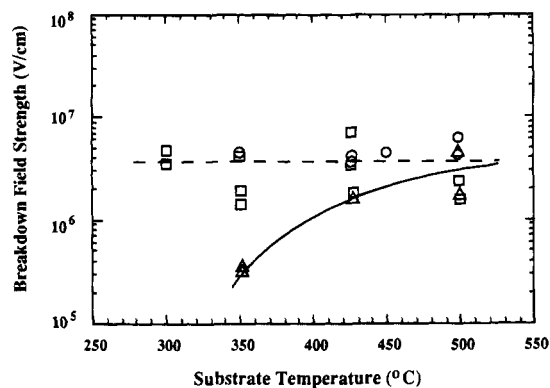
Figure 3. Effect of substrate temperature on film growth rate with fixed rate of vaporization of  $\{Mg[Al(OPr^i)_4]_2\}_n$ .

charges between 0.9 and 2.0 g with boiling chips added to prevent spillover. Initial boiling was observed at a crucible temperature around 115 °C as expected. Source heat-up rates were the same from run to run with a final source temperature of 170–175 °C. With similar source temperature profiles and alkoxide loads, the vaporization rates can be assumed similar as well. Under these conditions, the conversion efficiency, i.e., the film thickness per weight of alkoxide vaporized, is a good indicator of relative growth rate. The Arrhenius plot shows linear behavior for substrate temperatures between 250 and 425 °C which we interpret as indicative of a surface reaction limited process. At temperatures higher than 425 °C, the conversion efficiency remained constant, indicating that the rate of film formation is limited by the availability of alkoxide from the vapor phase.

Assuming stoichiometric composition, uniform coverage across the heated substrate platen, and a film density equal to that of crystalline spinel (3.58 g/cm<sup>3</sup>), up to 8% of the total metals from the alkoxide source was incorporated into film. The remaining material deposited as a powdery coating on the sides of the quartz tube or passed through unreacted. Although some light interference was observed, indicating the presence of a film, the film grown at 250 °C was too thin to characterize. From a practical standpoint, 300–350 °C is the minimum temperature at which the film growth occurs.

Figure 3 shows the estimated film growth rate from the same experiments used to construct Figure 2, also plotted in an Arrhenius type plot. These growth rates were calculated based on final film thickness and the

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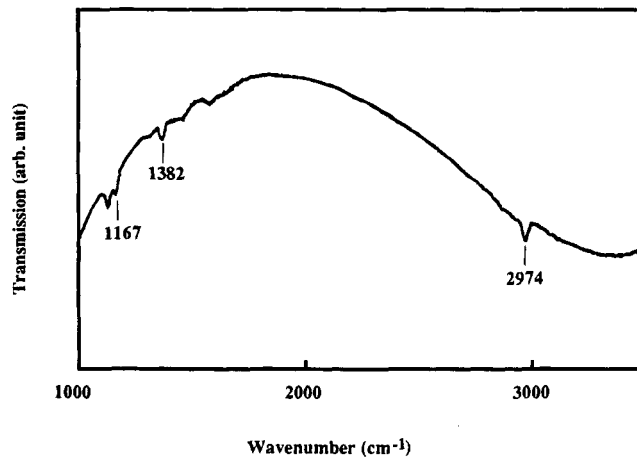


**Figure 4.** Effect of substrate temperature and film thickness on the breakdown field strength in metal-oxide-metal capacitor structures ( $\Delta$ , less than 800 Å thick;  $\square$ , 1000–5000 Å thick;  $\circ$ , greater than 5000 Å thick).

deposition time, defined as the time between the onset of boiling in the alkoxide source and its complete vaporization. Uncertainty in the deposition time was introduced by the vaporization of material during the transient period between the onset of boiling and when the source reached its final temperature as well as difficulty identifying the end of the run (a dry crucible) in some runs. Despite these difficulties, the activation energy from the calculated film growth rate shows excellent agreement with that estimated from the more reliable measure of conversion of alkoxide to film. We attribute the lower than expected growth rate for the 500 °C substrate temperature to difficulty identifying the endpoint of the experiment in these particular runs. The average growth rate increased from less than 1 Å/s at a substrate temperature of 300 °C to approximately 7 Å/s at 425 °C. We are confident that much higher growth rates could be achieved with a well-designed closed source operating at a temperature around 150 °C. The liquidity of the source at temperatures below 100 °C also offers to possibility of using high rate techniques such as spray pyrolysis for deposition of stoichiometric films.

The refractive indices of the films ranged from 1.52 to 1.61, somewhat lower than the values of 1.68 to 1.71 reported for crystalline spinel,<sup>15,16</sup> consistent with a lower density amorphous film. The refractive index showed no dependence on substrate temperature or film thickness.

Figure 4 shows the breakdown field strength as a function of substrate temperature for films ranging in thickness from 580 to over 11 000 Å. The breakdown field strength of the thinner films (less than 800 Å) showed a significant temperature dependence as indicated by the solid line in Figure 4, from around  $3.3 \times 10^5$  V/cm for the two films deposited at 350 °C to as high as  $4.3 \times 10^6$  for a 750 Å thick film deposited at 500 °C. Breakdown field strengths for the films thicker than 1000 Å were between  $1.0$  and  $7.0 \times 10^6$  V/cm, independent of thickness or growth temperature. These values compare favorably with the 450 V breakdown voltage reported<sup>9</sup> for epi-Si wells isolated by one-micron thick walls of epitaxial spinel grown at 900 °C.



**Figure 5.** Infrared spectra of 8000 Å thick  $\text{MgAl}_2\text{O}_4$  film grown at 350 °C from magnesium dialuminum isopropoxide.

The dielectric constants ranged from less than 2.0 for several of the films thinner than 800 Å to greater than 10 for films between 1800 and 11 000 Å thick. The dielectric constant for the sixteen films thicker than 1000 Å ranged from 5.3 to 11 with a median value of 7.5, consistent with dielectric constants reported for high-temperature epitaxial films (7.5–8.0).<sup>9</sup> Although the considerable scatter in the measured dielectric constants makes it difficult to discern trends, there are indications that the dielectric constant is slightly higher for films grown at 500 °C. In particular, the average dielectric for films grown at 500 °C is 9.2 compared to less than 8 at all other temperatures (excluding films thinner than 1000 Å); and the two highest values, 10.6 and 11.3, were both measured on films grown at 500 °C.

Five films were produced in which the final thickness was less than 800 Å. Of these, four had remarkably low dielectric constants, between 1.5 and 2, while the fifth was slightly below 5. Values below 2 were measured on films grown at both 350 and 500 °C. As previously stated, the low dielectric values were accompanied by a low breakdown field strength for the two thin films grown at 350 °C, but those grown at 425 and 500 °C had the same high breakdown field strengths as the thicker films indicating high-quality in these very thin films.

SEM and Fourier transform infrared (FTIR) spectroscopy were used to explore structural changes with growth temperature. Films deposited at 500 °C had very smooth surfaces with no distinguishable features or defects visible at magnifications up to 10000 $\times$ . In contrast, films deposited at 400 °C and below were found to have numerous surface defects, many with the appearance of round pits up to 20  $\mu\text{m}$  in diameter which were visible at magnifications as low as 250 $\times$ .

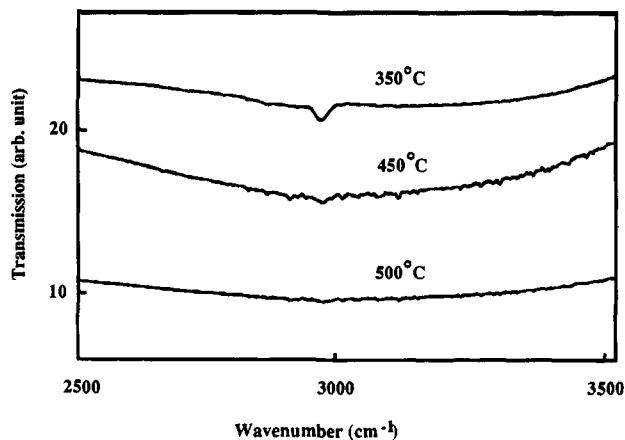
The FTIR spectra of one of the low temperature films (8000 Å thick at 350 °C) with easily detected defects is shown in Figure 5. Adsorption peaks which we attribute to  $\text{CH}_3$  or  $\text{CH}$  adsorption<sup>17,18</sup> are identified on the scan. The  $\text{CH}_3$  stretch at 2974, used to follow changes in residual hydrocarbons with substrate temperature, was evident in all films deposited at substrate

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**Figure 6.** Infrared spectra of  $MgAl_2O_4$  showing  $CH_3$  stretch adsorption for films grown at different temperatures.

temperatures of 450 °C or lower. Figure 6 shows the FTIR scans from 2500 to 3500  $cm^{-1}$  for films deposited at 350, 450, and 500 °C. The adsorption from  $CH_3$  is clearly evident in the low temperature film, barely visible at 450 °C and not detectable in the film grown at 500 °C. The decrease of the C-H bond density with increasing substrate temperature is consistent with volatilization and evaporation of residual organic group

at the higher substrate temperatures.

It is our belief based on the infrared spectra and SEM observations that at 500 °C residual organic groups are fully volatilized during film growth, yielding a dense, defect-free film and surface. At lower temperature, these groups can be partially incorporated into the film as it grows. Subsequent removal during later stages of growth results in the more porous, defective films. In spite of the residual hydrocarbons in the low-temperature films, electrical properties were found to be nearly invariant with growth temperature over the range studied. Selected films were also annealed for several hours in air at 700 °C with no evidence of any change in electrical properties. The low deposition temperature of these films combined with inherent electrical stability up to at least 700 °C could make them of interest as barrier layers on temperature sensitive surfaces or as dielectrics for integrated circuits.

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