Use of Amorphous Oxides as High Temperature Dielectric Material in Wound Capacitors

Keith D. Jamison[1], Roger D. Wood[1], Byron G. Zollars[1], and Martin E. Kordesch[2]

[1]Nanohmics, Inc., 6201 East Oltorf St, Suite 400, Austin, TX 78741
Tel: 512-349-7987 Fax 512-389-9990
kjamison@nanohmics.com

[2]Department of Physics, Ohio University, Athens, Ohio, 45701

Abstract

Capacitors that perform well at temperatures exceeding 200ºC and have energy densities in excess of 5 J/cm^3 are an enabling technology for many applications in automotive, geophysical exploration, aerospace, and the military. To address this need Nanohmics has been examining the use of amorphous oxides as the dielectric material for high energy density, temperature-stable rolled film capacitors. Such capacitors can be fabricated by depositing ~0.3 -0.7 µm films on both sides of a thin metalized flexible substrate to form dielectric-coated electrodes. The two coated electrodes can then be rolled together into a cylindrical shape to produce a capacitor.

Capacitors fabricated using amorphous silicon dioxide as the dielectric have been shown to have stable capacitance, dissipation factor, and breakdown threshold over a wide temperature range. Nanohmics is evaluating other amorphous oxide dielectric materials that have a higher dielectric constant in order to improve the energy density. These materials include hafnium dioxide and zirconium dioxide. Initial results indicate that the capacitance for these other materials can be higher but breakdown voltage and dissipation factor is sacrificed.

Introduction

One of the most critical components for electronic systems is the capacitor. Even though a capacitor is generally thought of as an inexpensive passive component, its ubiquity in electrical energy storage, filtering, and power conversion roles, and its tendency to fail catastrophically, emphasize the need for more stable and reliable devices across the electronics spectrum. This is especially true for critical applications and operation at elevated temperatures. The key to producing highly reliable and stable capacitors is through improvements in the capacitor dielectric.

Previous studies have been made on diamond like carbon [1] and oxynitrides[2] to identify alternative dielectrics in film capacitors. In this paper we present the results from a study of the use of flexible high-k amorphous oxides as an alternative dielectric to polymer films for

fabrication of high energy density, non-polar, rolled film capacitors. Amorphous oxides have higher dielectric constant, improved breakdown strength, and are more temperature stable than their polymer counterparts, allowing capacitors fabricated from these materials to achieve high energy densities with consistent properties over a large temperature range and in harsh environments found in many electronic devices. By increasing the breakdown strength and dielectric constant compared to traditional polymer dielectrics, rolled film capacitors can be made smaller, thereby reducing the weight and size of many electrical systems. In addition to decreasing the size and improving performance, the temperature stability of amorphous oxide capacitors will make them compatible with the next generation of high temperature / high power electronic devices made using GaN and SiC.

Experimental

Nanohmics examined four standard oxide materials in this study. They are SiO_2, ZrO_2, TiO_2 and HfO_2. The oxide films were grown using reactive deposition in a CVC 601 sputter deposition tool. The growth properties were optimized in a set of designed experiments. Films were grown at a number of deposition parameters such as pressure and oxygen/argon composition in order to maximize the film growth for increased breakdown strength. The initial depositions took place on metalized glass substrates in order to characterize the oxide properties. The deposition was done on a cooled substrate to minimize re-crystallization of the sputtered material.

The standard deposition procedure followed for all growths was as follows:

1) Place nickel-coated 1”x 2” glass slide in CVC 601 vacuum chamber
2) Pump down to a pressure better than $2x10^{-6}$ Torr
3) Heat to 100°C for 10 minutes to degas sample
4) Deposit thin layer of titanium to aid in adhesion (2 minutes 200 Watts RF power)
5) Deposit amorphous oxide film (750 Watts RF for 90 minutes)
6) Vent system and measure thickness

All films were growth at a pressure between 3 mT and 10 mT at 10% to 50% oxygen in a balance of argon.

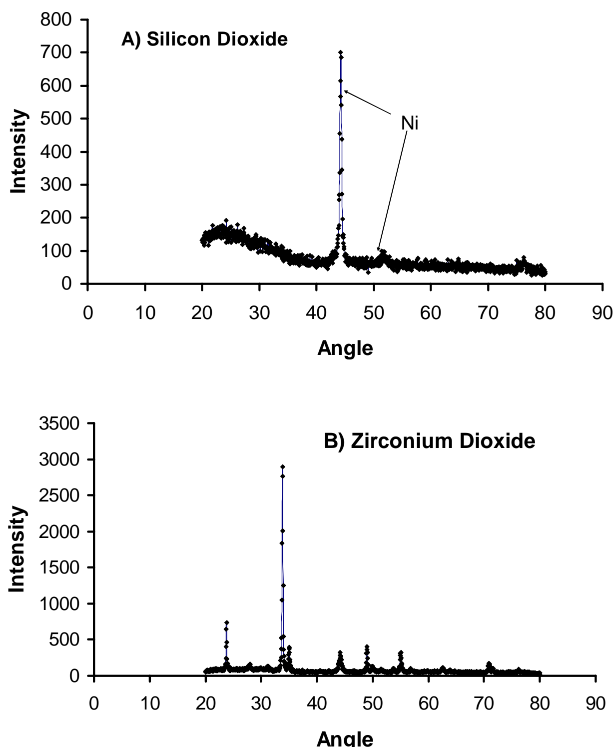
Between 10 - 20 samples of each material, TiO_2, ZrO_2, HfO_2 and SiO_2 were grown at thicknesses ranging from 0.2 microns to 5 microns. After deposition, the thickness was measured optically and 2 mm diameter nickel dots were deposited on the surface to allow characterization of the dielectric properties between the nickel dot and the backing nickel electrode. Representative samples of the dielectric materials were also characterized by X-ray diffraction to determine their crystalline properties. The capacitance of the dielectric material under the nickel test dot test structure was measured to determine the dielectric constant. For small capacitances (<2 nF), measurements were made at 100kHz and 1 MHz with a DC bias between –20 and 20 VDC using a Keithley 590 CV measurement system.

Larger capacitances were measured with either a simple capacitance meter or an HP 4274A LCR meter operating at 1 KHz. The breakdown voltage of the dielectric material was determined by measuring current vs voltage (I-V) curves of a ~ 25 micron diameter probe touching the bare dielectric surface. Breakdown measurements were made using a Bertan 10KVDC power supply to apply an adjustable voltage to the probe and an ammeter to measure the current through the dielectric.

Characterization of the amorphous oxide films

The TiO_2 films deposited under all growth conditions for this study were highly stressed and did not adhere well to the substrate. In addition, the breakdown strength was poor and the dielectric constant varied across the deposition area. These results indicate that isotropic amorphous films of TiO_2 were not grown using the deposition conditions studied. Instead different polytypes of titanium oxide were most likely formed during deposition with the various TiOx polytypes having different dielectric constants. Because of the problems in forming TiO_2 by reactive sputtering and the difficulty with adhesion, it was decided to abandon growths of TiO_2 films and remove this film from consideration.

Figure 1 shows the x-ray theta-2 theta rocking curves from selected samples of the three remaining dielectric films. The results indicate that SiO_2 was the only material that formed truly amorphous films. The HfO_2 formed nanocrystalline films as indicated by the broad peaks found in the films. The ZrO_2 formed polycrystalline films under the deposition conditions used in this study. For the SiO_2 film, one of the nickel dots was inadvertently placed in the x-ray beam during measurement.



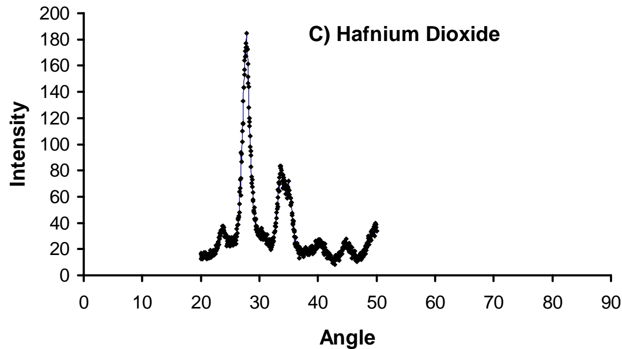


Figure 1. X-ray theta-2 theta scan from (a) SiO_2, (b) ZrO_2, and (c) HfO_2. The peaks at 44 and 52 degrees are from the Ni dots deposited on the surface after the oxide film growth.

Optical micrographs of the surface are shown in Figure 2. All films were smooth, adhered well and showed no indications of cracking.

Measurements were made of the breakdown strength of the oxides by touching the probe tip to the surface of the dielectric and measuring the leakage current as a function of voltage. Figure 3 shows a representative example of the current vs voltage measurement. The breakdown strength varied somewhat for different areas tested. The results are summarized in Table I showing the properties of the tested dielectric films when grown under optimal deposition conditions. The results reported are the average breakdown for a number of measurements made on each film and normalized for the thickness of the film.

SiO_2 ZrO_2 HfO_2

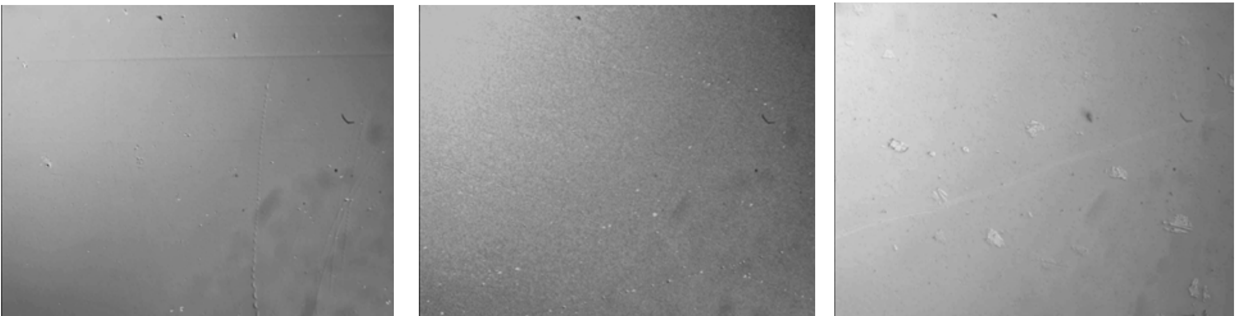


Figure 2. Optical micrographs of (a)SiO_2, (b)ZrO_2 and (c)HfO_2 films. All micrographs were taken in DIC mode with magnification of 200x.

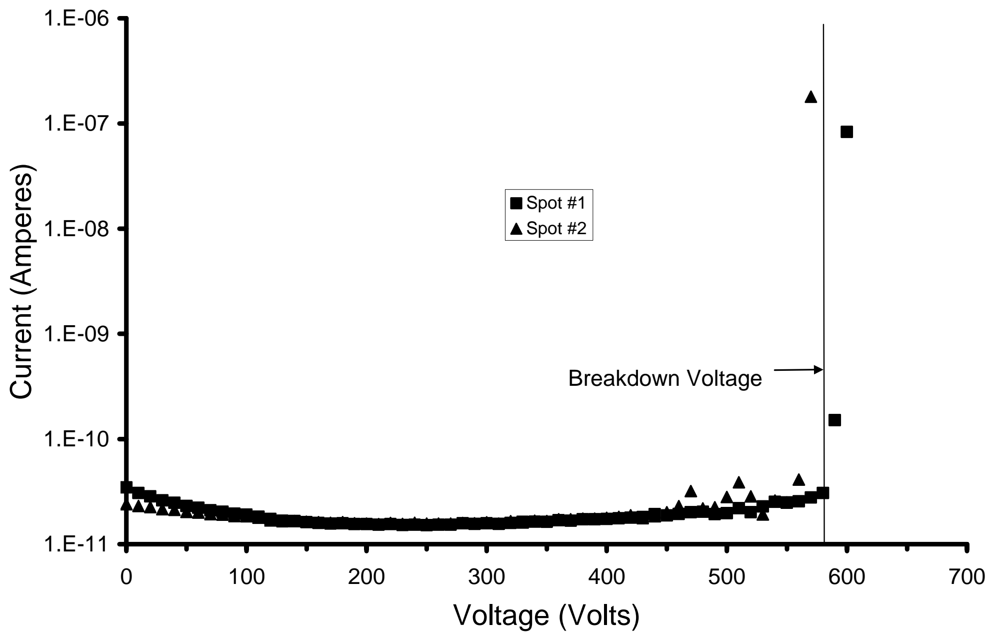


Figure 3. Current vs voltage of typical film showing the breakdown voltage of the dielectric. The breakdown field was calculated by dividing the breakdown voltage by the film thickness

In addition to the breakdown voltage, the capacitance of the nickel dot test structures SiO_2, and HfO_2 dielectric films were measured. Capacitance measurements were made at 100kHz and 1 MHz with DC bias between –20 and 20 VDC using a Keithley 590 CV measurement system. In all cases the capacitance did not significantly change when changing frequency between 100 kHz and 1MHz. The measured capacitance, and thus the dielectric constant of both the SiO_2 and HfO_2 films were very consistent over all deposition parameters and corresponded to what has been previously reported in the literature [3].

The capacitance of the ZrO_2 samples were too large to measure using the Keithley 590 CV measurement system (>2 nF) so the capacitance was measured using a HP 4274 LCR meter operating at 1 KHz.. The capacitance of the ZrO_2 samples for identical dot size varied considerably depending on deposition conditions and position of the 2 mm nickel test dot on the sample. This indicates a growth-parameter dependence of the dielectric constant and the formation of distinct domains during growth that have different dielectric constants. For the ZrO_2 films, the dielectric constant (computed using the known capacitor area and thickness of the dielectric film) yielded a dielectric constant that was well in excess of 25 which is the most commonly reported dielectric constant in the literature[3]. The measured dissipation factor was also quite large (~0.2-0.5). We attribute the variation in our measurements to the polycrystalline and anisotropic nature of the film.

Table I. Summary of the dielectric characterization measurements.

	SiO_2	TiO_2	ZrO_2	HfO_2
Growth Rate (750 W)	1μm/hr	0.2μm/hr	0.5μm/hr	0.72 μm/hr
Breakdown Strength	800V/μm	Poor	220V/μm	400V/μm
Temperature Stability	Good	Not Tested	Not Tested	Good
Adhesion	Good	Poor	Good	Good
Film Type	Amorphous	Polycrystalline	Polycrystalline	Nanocrystalline
Dielectric Constant	4.9	>80	>25	25

A few items are immediately apparent when examining the results from Table I. First SiO_2 looks like it has the best dielectric breakdown properties, The HfO_2 breakdown strength is acceptable and would be a good choice for applications requiring high capacitance. TiO_2, as explained earlier, is probably not the best choice for use as a capacitor dielectric. ZrO_2 may also be a good dielectric material if truly amorphous films can be produced. This may be accomplished by depositing the films at lower substrate temperature.[4]

Film Flexibility

After characterization of the dielectric films on metal-coated glass substrates, amorphous SiO_2 films were deposited on metalized polymer substrates provided by SteinerFilm to determine the flexibility of the dielectric films. Flexibility is critical in order to wind the capacitor into a cylindrical shape without compromising the dielectric strength. For these tests, ~0.5 μm of amorphous SiO_2 films were deposited on both sides of a 5 cm square sample of metalized polymer. Deposition was done on a cooled substrate holder. This insured that the polymer substrate remained near room temperature during deposition.

In order to examine the flexibility/ bendability of the amorphous SiO_2 dielectric films, a strip of the flexible metalized polymer substrate coated with a 0.7 micron thick amorphous SiO_2 film on each side of the substrate was wrapped around a 3/8" diameter mandrel then placed into a JEOL 820 scanning electron microscope SEM. For this test, the coated substrate extended past the end of the mandrel in order to examine the dielectric film-substrate interface. SEM micrographs of the SiO_2 film are shown in Figure 4 at a number of magnifications. The SiO_2 film is continuous and shows no cracking except in the areas that were damaged during cutting of the film and in unsupported areas that were inadvertently damaged during placement onto the SEM mount.

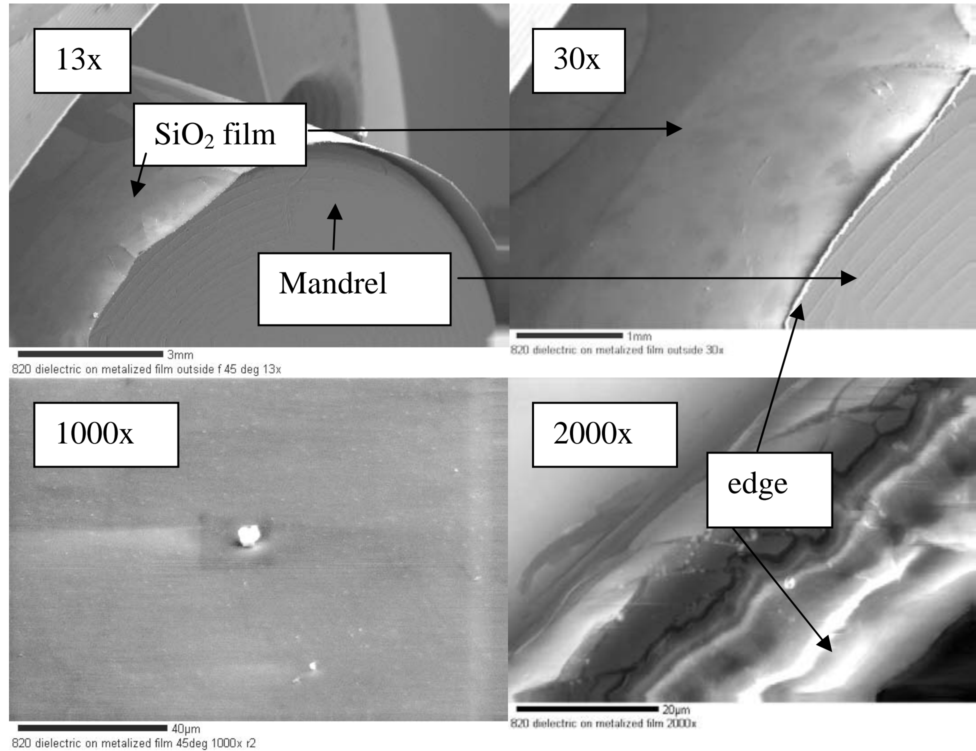


Figure 4. SEM micrographs of a metalized polymer substrate coated with ~0.7 microns of amorphous SiO_2 on each side then wrapped around a 3/8" mandrel. The 13x micrograph shows the mandrel and the SiO_2 coated substrate wound around the mandrel. The 30x micrograph shows that the film is not cracked during winding. The 1000x micrograph shows the smooth SiO_2 film on the mandrel and the 2000x micrograph shows the damage to the edge of the film during cutting.

The data from the initial flex test indicate that amorphous SiO_2 films can be rolled into a cylindrical shape without damage. To further characterize the flexibility of amorphous SiO_2 dielectric films, a study was made of how small of a diameter mandrel the dielectric film could be wrapped around without damaging the dielectric. For this study we used a metalized polymer film substrate coated with 0.7 microns of amorphous SiO_2 on both sides of the substrate. The film was inspected then wound around mandrels of varying diameters ranging from 1/8" to 1/2" in diameter. After winding, the film was unwound then re-inspected. The larger diameter samples did not show any indications of cracking when wound around the mandrel. Only samples wound around the 1/8" mandrel were cracked when unwound and inspected. The cracking was primarily on the outside of the films indicating that tensile stress was excessive during winding onto such a small diameter mandrel.

Thermal testing of dielectric films

To examine the temperature stability of the amorphous dielectric films we made capacitance measurements as a function of temperature for the SiO_2 and HfO_2 dielectric films. The test capacitors were fabricated using the metal dots on the dielectric films as the capacitor. We also tested two SiO_2 coated metalized polymer films placed on top of each other to form a ~1" x1" capacitor to better simulate a film capacitor. The capacitance measurements were made using a HP 4274 LCR meter operating at 1 KHz. Figure 5 shows the capacitance and dissipation factor of a metal dot capacitor made using HfO_2 as a function of temperature. In both cases the dissipation factor increases as a function of temperature with SiO_2 having significantly better dissipation factor than HfO_2.

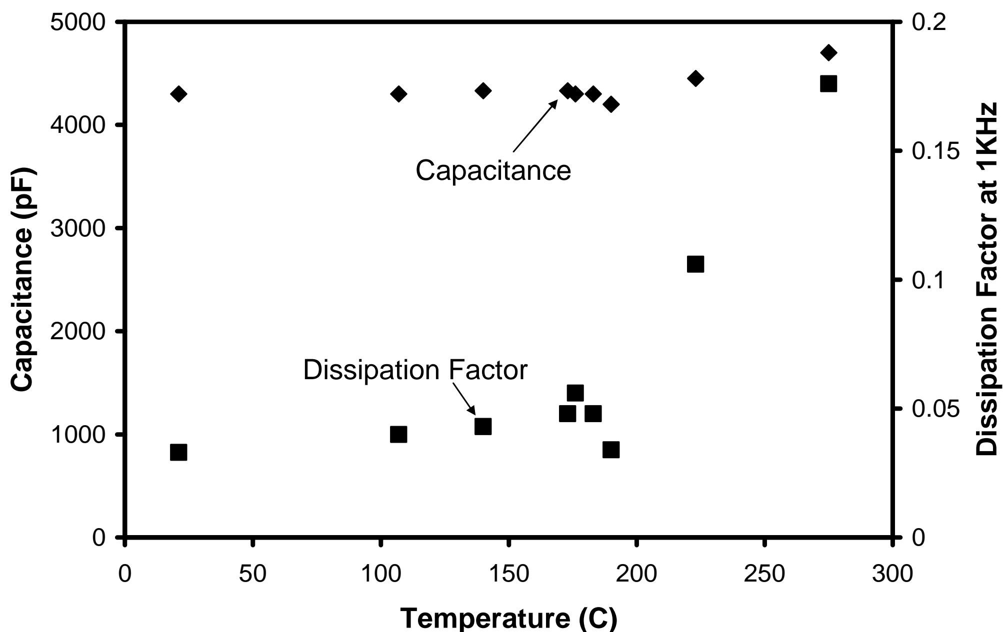


Figure 5. Plot of the capacitance and dissipation factor of HfO_2 dielectric measured as a function of temperature.

Measurements of a capacitor made from two metalized polymer films coated with SiO_2 placed on top of each other are shown in Figure 6.

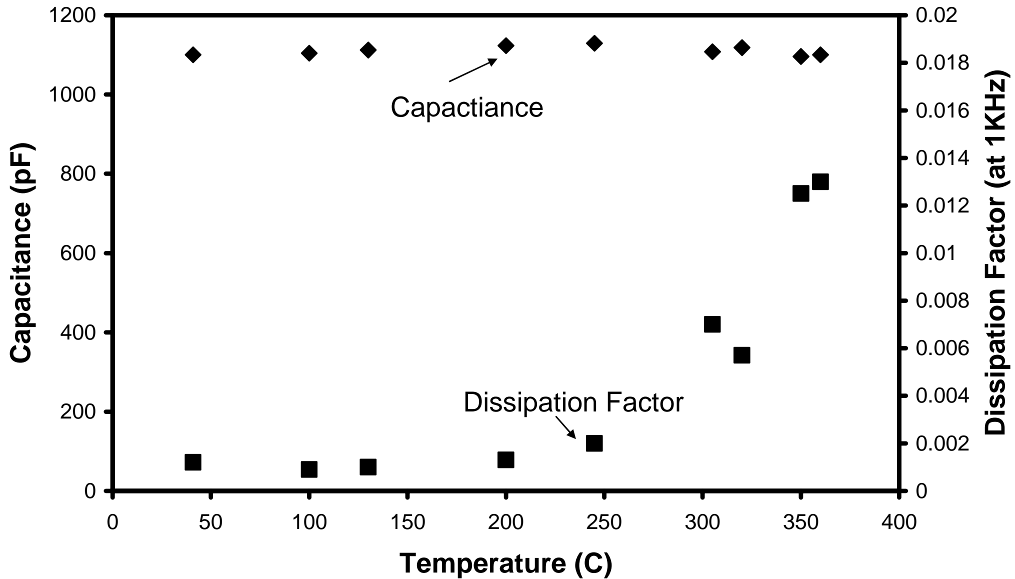


Figure 6. Plot of the capacitance and dissipation factor of SiO_2 dielectric measured as a function of temperatures.

Conclusions

Of the oxide dielectric materials examined, SiO_2 and HfO_2 appear to be the best films for use as the dielectric material to fabricate high energy density, temperatures stable rolled film capacitors. Both the HfO_2 and SiO_2 films show stable dielectric properties at temperature exceeding 300C. SiO_2, because of its superior dielectric strength may be better for applications that require high energy density and HfO_2 better for applications that require large capacitance.

Acknowledgements

This works was supported by Air Force contract FA8650-05-C-2628.

References

1.) S. Fries Carr, J.A. Weimer, B. Tsao, and R.L.C. Wu, “High Temperature Diamond Thin Film for Capacitor Applications” Proceedings of 1995 International Conference on Power Electronics and Drive Systems, (1995) 271.

2.) K.R. Bray, R.L.C. Wu, J. Weimer, and S. Fries-Carr, "Aluminum Oxynitride Dielectrics for High Power, Wide Temperature Capacitor Applications" Proceedings of CARTS USA April 2006, 161.

3.) J.W. McPherson, J. Kim, A. Shanware, H. Mogul, and J. Rodriguez, "Trends in the Ultimate Breakdown Strength of High Dielectric Constant Materials", IEEE Transactions on Electron Devices, **50** (2003) 1771.

4.) F. Jones, "High-rate Reactive Sputter Deposition of Zirconium Dioxide" J. Vac. Sci. Technol **A**6 (1988) 3088.