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INTERFACE EFFECTS IN METAL OXYNITRIDE CAPACITORS (PREPRINT)

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14. ABSTRACT

The evolution of electrical power systems to denser, higher power configurations calls for the continual improvement of robust component technologies. Capacitors are widely recognized as a limiting technology in these systems due to their low energy density, high loss, and limited life. Metal oxynitride thin films are a candidate dielectric material for developing thermally tolerant, compact, low loss capacitor structures due to their high energy density, high insulation resistance, and thermally stable dielectric properties. Pulsed DC reactive sputtering is utilized to deposit submicron thick films of aluminum oxynitride and hafnium oxynitride, which are then evaluated as single layer capacitors using different electrode schemes. Various electrode materials (e.g., aluminum, gold, etc.) and deposition methods appear to influence the electronic properties of the device due to modification of the electrode-dielectric interface. This effect is also demonstrated with controlled variation of the thicknesses for the dielectric, and appears to be apparent with similar modifications to the electrode layers as well. The interfacial capacitance in AlON is shown to go through a transition as the dielectric thickness increases above 2500 Å. Increasing the number of internal layers within the dielectric, obtained by sequential deposition of the same material, also appears to influence the electrical properties of the film.

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Interface Effects in Metal Oxynitride Capacitors

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Abstract

The evolution of electrical power systems to denser, higher power configurations calls for the continual improvement of robust component technologies. Capacitors are widely recognized as a limiting technology in these systems due to their low energy density, high loss, and limited life. Metal oxynitride thin films are a candidate dielectric material for developing thermally tolerant, compact, low loss capacitor structures due to their high energy density, high insulation resistance, and thermally stable dielectric properties. Pulsed DC reactive sputtering is utilized to deposit submicron thick films of aluminum oxynitride and hafnium oxynitride, which are then evaluated as single layer capacitors using different electrode schemes. Various electrode materials (e.g., aluminum, gold, etc.) and deposition methods appear to influence the electronic properties of the device due to modification of the electrode-dielectric interface. This effect is also demonstrated with controlled variation of the thicknesses for the dielectric, and appears to be apparent with similar modifications to the electrode layers as well. The interfacial capacitance in AlON is shown to go through a transition as the dielectric thickness increases above 2500 Å. Increasing the number of internal layers within the dielectric, obtained by sequential deposition of the same material, also appears to influence the electrical properties of the film.

Introduction

Weight and portability are critical issues to address for further improvement in performance of advanced power systems. Recent activity has focused on replacing mechanical systems with point-of-use electrical systems to reduce the size of mechanical components. Portability can be further increased by reducing weight and size of electronic components within point-of-use electrical power and control systems. Weight and size reductions are beneficial for space-based systems and airborne weapons to enable increased payloads or weapon lethality. For advanced directed-energy weapons such as airborne lasers and high-pulse microwaves, a weight and size reduction can concurrently create an increase in available power. These changes have resulted in aircraft electrical systems consistently evolving into higher power, more compact architectures.[1] Similar trends are occurring with the development of hybrid or all electric vehicles. Capacitors are widely recognized as a limiting technology in these systems due to their low energy density, high loss, and limited life.

Metal oxynitride thin films are a candidate dielectric material for developing thermally tolerant, compact, low loss capacitor structures due to their high energy density, high insulation resistance, and thermally stable dielectric properties. In general, films with a higher dielectric constant tend to have a corresponding lower insulation resistance.[2] The increased leakage current may be the result of the smaller bandgap in high-k materials[2] or the higher density of trap states introduced along grain boundaries due to crystallization in the dielectric film.[3,4] Although amorphous films frequently result in a decrease in the dielectric constant, the development of amorphous metal oxynitride dielectrics improves the insulation properties of these films by reducing the grain boundary conduits present in the polycrystalline configuration. Recent research activity in dielectric development has also indicated an improvement in voltage strength and voltage endurance of composite thin films possibly due to the orientation or increased volume percentage of the interfacial phase. These studies have suggested an improvement in breakdown strength and insulation resistance due to a change in charge trap density and depth, redistribution of space charge, local conductivity, or scattering of charge carriers at the interfaces between materials. Continued research activity may shed light on the ability to tailor interface architectures as a means to restrict the movement of charge carriers, thereby improving the performance and life of the dielectric under stressed conditions.

Aluminum Oxynitride Dielectrics

Aluminum oxide (Al_2O_3) is a promising material for use in microelectronics, optical coatings, and corrosion barriers[5]. Its chemical stability, relatively high dielectric constant, and thermal stability also identify it as a potential dielectric for high power capacitor applications. Film structures from amorphous to epitaxial crystals have been obtained by varying deposition parameters and substrates.[6] Crystallization usually occurs above 600 °C,[7] but is also dependent on the substrate, film composition, and thickness.[8] Al_2O_3 can be deposited using many different techniques including atomic layer deposition,[9] reactive sputtering,[10,11] and chemical vapor deposition (CVD).[5,12] Magnetron sputtering offers large area uniformity and good step coverage. Sputtering also avoids many of the hazardous precursors and byproducts associated with CVD processes and results in less thermal stressing of the films[13]. Pulsed DC sputtering has been shown to produce faster deposition rates than RF sputtering. The DC pulsing helps discharge the target to reduce charging and arcing, increasing the deposition rate and reducing particulates. The incorporation of nitrogen to form an oxynitride film has been suggested to inhibit crystallization, suppress impurity diffusion, avoid charge traps and reduce movement of charge carriers through dielectric thin films to include Al_2O_3, SiO_2, HfO_2, and Ta_2O_5.[14-16] Nitrogen is not gettered on the aluminum target surface like oxygen, therefore the presence of nitrogen during sputtering reduces the target poisoning that occurs during Al_2O_3 sputtering, making the AlON process easier to control and reproduce.[10] Nitrogen can be introduced into the film during deposition by the inclusion of a nitrogen species, such as N_2 or N_2O, into the reactive gas mixture or through post deposition processing, such as annealing in N_2 or NH_3.

Hafnium Oxynitride Dielectrics

Hafnium oxide (HfO_2) began receiving attention in the 1990s as a possible high-k replacement material for SiO_2 in integrated circuit devices.[17] More recently, it has been evaluated as a high temperature dielectric for high energy density capacitors.[18] Many deposition techniques, including reactive sputtering,[17-20] have been documented for HfO_2 deposition. As mentioned above with AlON, pulsed DC sputtering of HfO_2 has the advantage of high deposition rate with minimal substrate heating and thermal stressing. A fundamental concern with the use of hafnium oxide as

a dielectric is the crystallization of the material during film growth or post-deposition annealing. The addition of nitrogen to the HfO_2 films to form an oxynitride material has been shown to improve the thermal stability of the amorphous state.[21-24] It is believed the nitrogen suppresses crystallization in the film by disrupting the crystal network formation. The amorphous films result in lower leakage current, which could be due to a decrease in the trap state density with a lower crystalline fraction.[23] Nitrogen also inhibits the diffusion of reactive species present after deposition. Layered architectures may inhibit crystallization and/or inhibit formation of percolation paths between traps centers.

In this paper we discuss the development of amorphous or nanocrystalline AlON and HfON dielectrics and the impact of the material interfaces within the device with respect to the dielectric properties of the capacitors at room temperature. Various electrode materials (e.g., aluminum, gold) and deposition methods appear to influence the electronic properties of the device due to modification of the electrode-dielectric interface. Preliminary data is also reported to examine the role of internal interfaces within the dielectric layer, which is formed by sequential deposition of the dielectric material.

Experimental

Film Synthesis
The metal oxynitride films were deposited using pulsed DC magnetron sputtering. The chamber was pumped to a base pressure less than 5×10^{-6} Torr before deposition. DC power was varied from 100 – 2000 W with pulse frequencies from 25 – 250 kHz. Films were deposited using nitrous oxide (N_2O) gas with 99.9995% pure aluminum or 99.9% pure hafnium sputter targets. Gas pressures ranged from 3 mTorr to 20 mTorr. Internal layers were created by stopping deposition, allowing the sample and chamber to cool, and then continuing the deposition until the desired number of layers was achieved. X-ray diffraction (XRD) was performed using a Rigaku DMAX B instrument operating at 40 kV, 150 mA, with continuous 2θ scanning from 10° – 100° at $12^{o}\,min^{-1}$ and a step size of 0.05^{o}. XRD confirmed the amorphous structure of the aluminum oxynitride films while the hafnium oxynitride films showed partial crystallinity. Profilometry measurements were used to determine the film thickness using a Dektak[3] ST Surface Profiler. The composition of the films was investigated using a Jeol JSM6060 Scanning Electron Microscope equipped with a Noran System SIX X-ray Imaging System. The nitrogen content of the AlON films was determined to be ~5%, while the HfON films contained ~1% nitrogen. This was confirmed with x-ray photoelectron spectroscopy. Parallel plate capacitors were constructed by depositing 3 mm diameter dots on the top surface of the deposited films through a shadow mask for initial film characterization.

Dielectric Property Evaluation
Capacitance and dissipation factors were measured as a function of frequency using a Hewlett Packard 4284A LCR meter. Multiple measurements were taken at a variety of frequencies (20 Hz to 1 MHz) and DC bias values (0, 10, 20, 30 and 40V) and averaged for the capacitor. Several capacitors were tested on each film to confirm uniformity across the material.

Results and Discussion

Film Composition
Deposition conditions impact the composition, structure and dielectric properties of the sputtered films. Previous work has shown that the reactive gas mixture during sputtering strongly impacts the dielectric properties of AlON thin films.[25] High nitrogen content in the dielectric film resulted in greater frequency dependence in the capacitance and a higher dissipation factor. This may be the result of partially bonded nitrogen in the film. The addition of oxygen reduced the nitrogen concentration and improved the dielectric properties. Reactive sputtering using N_2O instead of N_2 and O_2 improved the deposition rate while maintaining the desirable dielectric properties.

Another potential candidate dielectric for reactive sputtering with N_2O is hafnium oxynitride. Building on our experience with AlON deposition, HfON was sputtered using N_2O as the reactive gas. Hafnium is five times denser than aluminum, and different deposition parameters were needed to deposit HfON films. DC power was varied from 100 W to 1500 W and deposition pressure was investigated from 3 mTorr to 20 mTorr. Optimal deposition

parameters were identified by the frequency stability of the dielectric constant and the value of the dissipation factor. Figure 1 shows the dielectric constant and dissipation factor for both AlON and HfON. At 1 kHz, HfON has a dielectric constant of 11.7 while the AlON dielectric constant is 8.5. The dielectric constant changes by less than 4% from 20 Hz to 1 MHz. The dissipation factor at 1 kHz is 0.005 and 0.004 for HfON and AlON, respectfully. It remains below 1 % for both materials to frequencies greater than 100 kHz.

Figure 1. Dielectric constant and dissipation factor for HfON deposited from N_2O.

X-ray diffraction was employed to evaluate the crystallinity of the oxynitride films. The spectra for the AlON films confirmed the amorphous structure of the films, indicated by the absence of peaks in the spectra. The hafnium samples displayed small peaks in the spectra, corresponding to both HfO_2 and HfN crystal structures in the films. These peaks had significantly lower peak intensity than our reference peaks and several of the corresponding peaks for a purely crystalline material were not present, both of which suggest only partial crystallization of the dielectric. This is further supported by our measured dielectric constant of 12-13 for HfON, which is much lower than reported values of 25 for crystalline HfO_2. Examination of the composition revealed that the nitrogen content in the HfON films was lower than in the AlON materials. The nitrogen content in our HfON films was ~1 at%. Greater than 5 at% nitrogen was present in the AlON. Modifying our deposition to increase the nitrogen incorporation should help maintain the amorphous structure desired by inhibiting crystallization. Heating the films to 400 °C in air or under vacuum does not increase the degree of crystallization. Further investigation of the crystallinity and composition of the films is underway using I-V measurements and microscopy techniques.

Interface Characterization

Characterization of these dielectric films suggested that the electrode/dielectric interface impacted the properties of the capacitor. A common technique to evaluate the electrode/dielectric interface in capacitors is to examine the ratios of area/capacitance vs. the dielectric thickness. A non-zero intercept indicates the presence of an interfacial layer in series with the bulk film. Figure 2 shows area/capacitance data for three different thickness series of AlON films. Two series were deposited on evaporated aluminum electrodes and the third was deposited on sputtered aluminum electrodes. The inset in Fig. 2 magnifies the data for thicknesses less than 1 µm for the evaporated aluminum series. Close examination reveals that there is a break in the data between 2500 Å and 3500 Å. Fitting

the two regions independently reveals a difference in the interfacial layer thickness, evidenced by the different intercept values calculated. These intercept values suggest the thinner films have an interfacial thickness near zero. Figure 3 shows the dielectric constant vs. the film thickness for the films less than 5000 Å thick. Above 3500 Å the dielectric is approximately 8.5. There is transition between 2500 Å and 3500 Å, where below 2500 Å the dielectric constant is close to 11. This suggests that the films may reach a critical thickness in this transition region causing an interfacial layer to form in order to reduce the stress in the films.
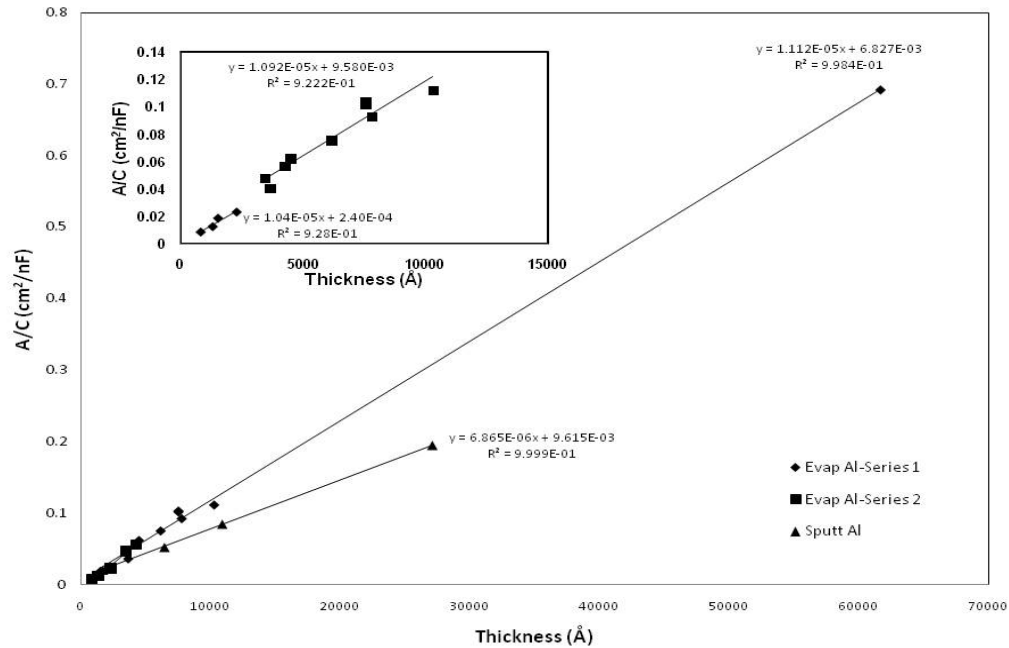

Figure 2. A/C vs. thickness reveals the interfacial capacitance in AlON capacitors.
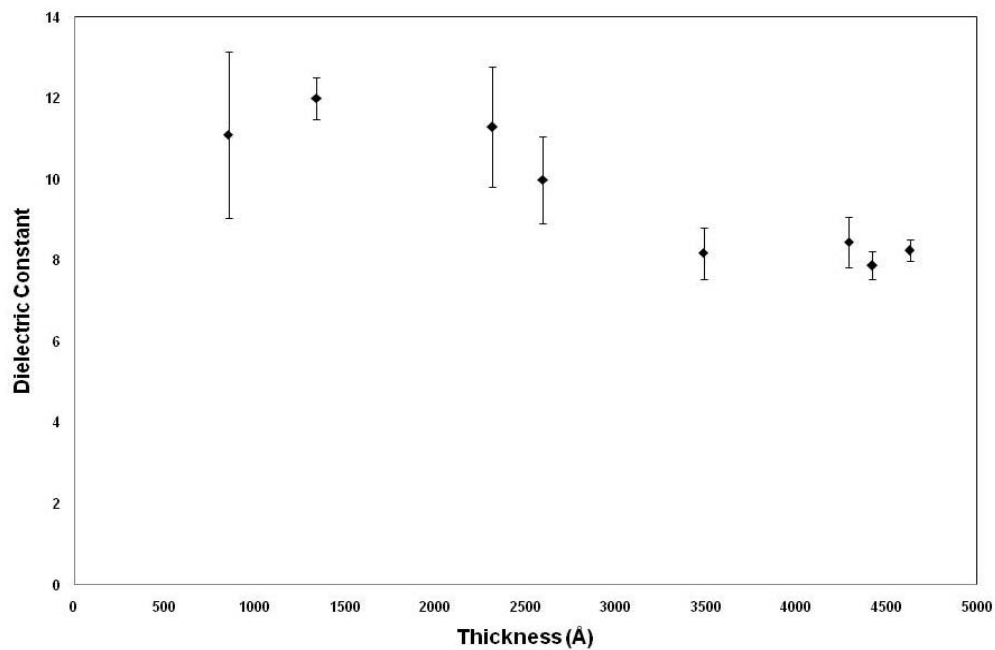

Figure 3. Dielectric constant vs. thickness for AlON on evaporated Al electrodes.

Figure 2 also compares AlON with sputtered aluminum electrodes to the films with evaporated electrodes. A distinct reduction in the slope is evident with the sputtered electrodes. The slope is inversely proportional to the dielectric constant, suggesting that the dielectric constant is dependent on the electrode deposition process. Figure 4 examines the dielectric constant for different electrode materials and thicknesses deposited by evaporation and sputtering. For films with evaporated aluminum electrodes, the dielectric constant was independent of the electrode thickness. For sputtered electrodes, both the electrode material and thickness appear to influence the dielectric constant. As suggested from Fig. 2 and 3, the dielectric constant is influenced by the formation of an interfacial layer. Sputtering is a more energetic deposition process than evaporation and may result in increased heating of the dielectric, which can promote interfacial mixing or diffusion of mobile species. This may result in the formation of a thicker, more metal-rich interface. Differences in the density of the metal also influence the energy with which the metal arrives at the surface during deposition which could increase the interface thickness or alter the composition. The dielectric constants are based on the observed capacitance. Changes in the composition or thickness of the interface would change the apparent dielectric constant, while the bulk dielectric constant may be independent of the electrodes. Additional characterization and microscopy are underway to further define the thickness and composition of the interfacial layers with different electrode processes. The bulk dielectric film properties can then be evaluated from a series capacitor model.
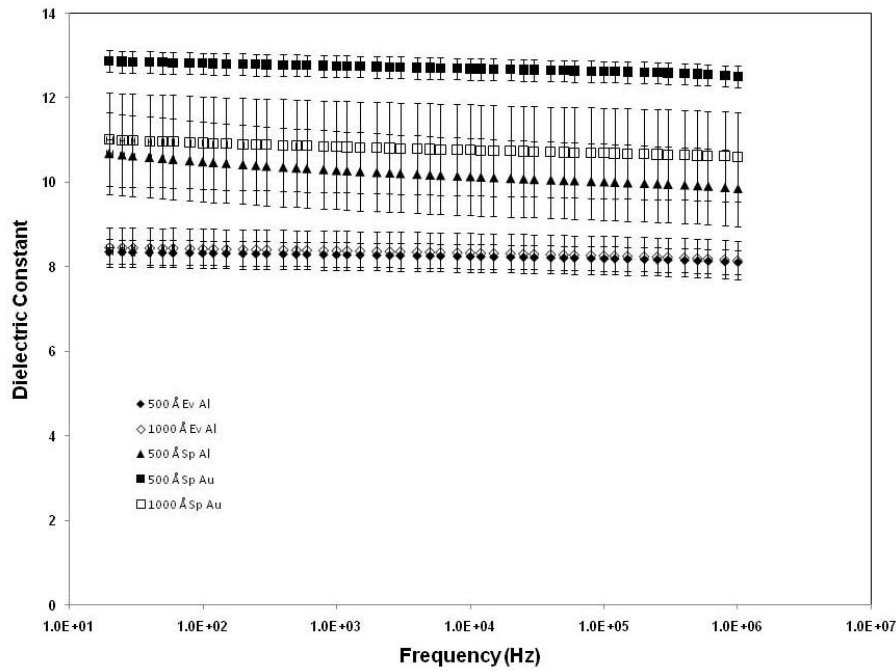

Figure 4. Dielectric constant vs. frequency for AlON films with various electrode metals and deposition methods.

Internal Dielectric Layers
The formation of homogeneous internal interfaces within the dielectric layer by the sequential deposition of the dielectric may enhance the ability to tailor the properties of the film. HfON and AlON films were deposited with one to twenty layers. The total thickness of the stack remained constant, so as the number of layers increased, the thickness of the individual layers decreased. Films were allowed to cool before depositing the subsequent layer. As can be seen in Fig. 5, increasing the number of internal layers appears to lower the dielectric constant of the HfON films. For only a few layers (1-6), the dielectric constant is approximately constant with a value near 12-13. It then decreases as the number of layers is increased to 20, with a dielectric constant close to 9.5. A similar trend is seen with the AlON films as well, although the decrease in the dielectric constant is not as pronounced. As the number of

dielectric layers increases, the deposition time per layer is reduced, which corresponds to less heating of the material during the deposition and less time for the impinging species to diffuse to an optimal configuration. The reduced heating and diffusion during deposition could lead to nonhomogeneous film composition. Variations in the film structure and composition could cause the observed decrease in the dielectric constant as the number of layers increase. Crystallization has also been shown to be dependent on film thickness and decreasing the individual layer thickness as the number of layers increase may result in a lower crystal fraction in the films. The amorphous dielectric constant is commonly lower than the crystalline dielectric constant. The onset of deposition may also initiate some damage to the surface of the underlying layer before steady state growth is reached, creating an interfacial layer with different properties than the bulk film. As the number of layers increases, the volume of this interfacial composition would increase and the interfacial properties may begin to impact the overall film properties. The change in properties with the formation of internal interfaces may also be caused by a space charge effect or the disruption of conductive conduits and the redistribution of charge along the interfaces. Further characterization and evaluation are needed to fully explain this phenomenon.
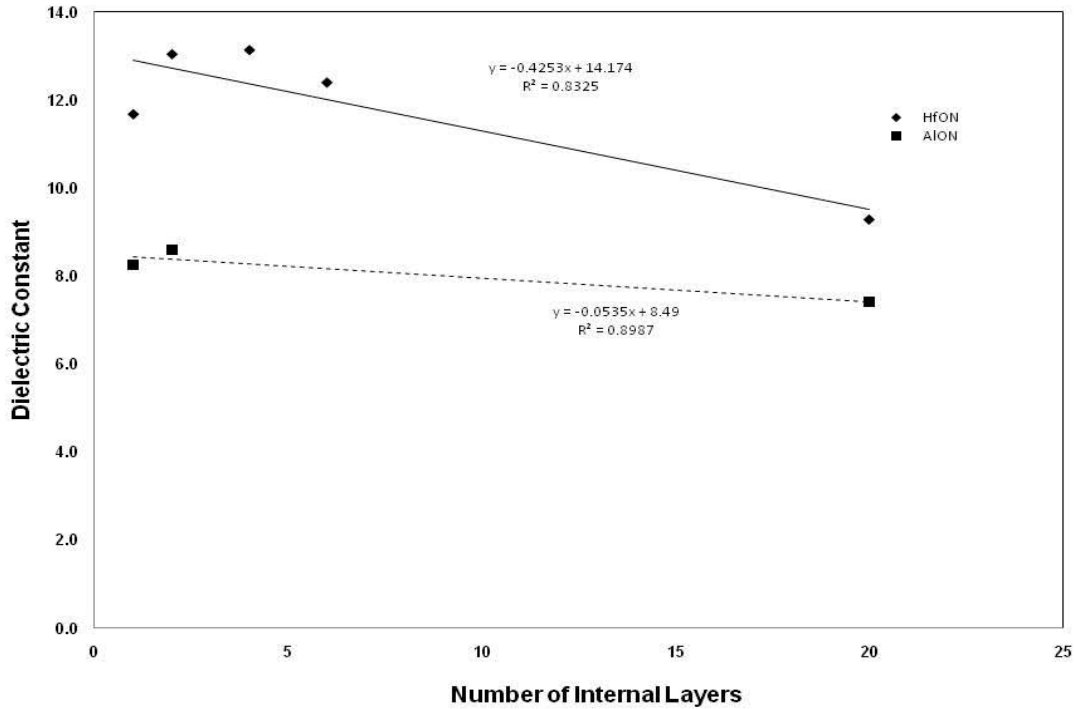

Figure 5. Dielectric constant vs internal layers for AlON and HfON.

Conclusions

Pulsed DC reactive sputtering has been utilized to deposit AlON and HfON thin films. The AlON films are amorphous while the HfON films appear nanocrystalline. The dielectric constants at 1 kHz are 8.5 and 12, respectively, with less than 4 % variation between 20 Hz and 1 MHz. An interfacial layer is observed to form in AlON at film thickness between 2500 Å and 3500 Å when using evaporated aluminum electrodes. The electrode material and deposition method appear to influence the thickness and/or composition of the interfacial layer. The deposition of sequential dielectric layers also influences the dielectric properties of both HfON and AlON. The dielectric constant remained approximately constant for up to six layers, but decreased for the twenty layer structure. These observations may possibly be due to decreased film heating and diffusion as the deposition time decreases, formation of interfacial layers, or suppressed crystallization with decreasing layer thickness. Investigation is still underway to improve our understanding of these events.

7

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