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Aluminum oxynitride dielectrics for multilayer capacitors with higher energy density and wide temperature properties

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ABSTRACT

Amorphous aluminum oxynitride (AlON) possesses unique properties of high dielectric strength, high resistivity, low loss, high decomposition temperature, chemical inertness, and high thermal conductivity. These properties make it a candidate for a next generation capacitor dielectric. DC pulsed magnetron reactive sputtering is used to produce amorphous AlON films on various substrates. Dielectric properties are optimized by adjusting DC power, pulse frequency, total pressure, substrate temperature, and gas ratio. Simple parallel plate structures are utilized to characterize the dielectric properties. Clearable electrodes are evaluated in device performance. Defects cleared without significant loss of capacitance. Temperature dependent dielectric properties were evaluated from −200 °C to +400 °C. Stacked multilayer capacitor device is developed for high energy density and wide temperature applications.

1. Introduction

1.1. High power density capacitors

Capacitors are key components in all forms of electrical devices. Numerous applications utilize millions of capacitors and consider them key components due to their susceptibility for failure. Military requires wide temperature capacitors capable of operating from −55 °C to 300 °C with tens of microfarads capacitance at up to 300 V. Future applications require the development of compact, high energy density capacitors for high power and extreme environment applications. Current applications are dominated by polymer film capacitors. Available state-of-the-art dielectric materials include polymer films such as polypropylene, polyester and polyvinylidene fluoride (PVdF) [1]. Polypropylene is commonly used for many AC applications because of its non-polar nature and low dielectric losses. Key drawbacks to polymer films include their low operating temperature, typically ~100 °C [1], and their large volume-to-weight ratio, which compromises energy storage density.

Most polymers also have a dielectric constant (k) in the range of 2–4, although k for PVdF is from 10 to 12 [1]. These low k values make it difficult to obtain the high energy density required for future military applications. Polymer breakdown voltage is typically ~550 V/μm [1]. Energy density (u_v) depends linearly on dielectric constant (k) and on the square of the breakdown strength (E_B) of a capacitor as shown in Eq. (1),

$$u_v = {}^1/_2\, k\varepsilon_o E_B{}^2 \tag{1}$$

where ε_o is the permittivity of free space. Increasing the breakdown field increases the energy density more rapidly than increasing the dielectric constant. Current state-of-the-art polymer dielectrics achieve material energy densities between 3 and 10 J/cm^3. Improved dielectric materials for capacitors are needed to meet the military's future power applications. Materials with a higher dielectric constant, greater dielectric breakdown strength and superior thermal stability are needed to improve capacitor performance to meet emerging needs.

1.2. Aluminum oxynitride dielectrics

Crystalline aluminum nitride (AlN) is a semiconductor with a large bandgap (6.2 eV) [2,3] high dielectric strength (between 400 and 550 V/μm [4]) and thermal conductivity above 320 W/mK [3]. Amorphous AlN improves breakdown strength over the polycrystalline formulation by reducing grain boundary induced defects while maintaining good thermal conductivity and electrical insulation. Thin AlN films have been deposited using a wide range of processes including chemical vapor deposition [5,6], RF and DC magnetron sputtering [4,7–10], and pulsed laser deposition [3,10]. Film structures from amorphous to epitaxial crystals have been obtained by varying deposition parameters and substrates [11]. Pulsed DC sputter

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deposition produces faster deposition rates than other deposition methods and also results in less substrate heating and thermal stressing of the films [9]. The aluminum target does not experience the same target poisoning that occurs during Al_2O_3 sputtering, making the AlN process easier to control and reproduce [8]. Thin amorphous Al_2O_3 films have shown breakdown strength ~500 V/μm [12]. Aluminum oxynitride deposition utilizing DC pulsed magnetron sputtering is a stable, repeatable process. Thin films deposited from this method show breakdown strengths ~600 V/μm [13,14].

1.3. Stacked multilayer capacitors

Stacked multilayer capacitors are a well established technology for commercial ceramic capacitor construction by connecting several single layer capacitors in parallel. The capacitance value is increased as the number of layers increases. Fig. 1 shows a schematic cross-section of a multilayer capacitor construction. This method consists of depositing alternating layers of dielectric and metal on a rigid substrate.

2. Experimental details

2.1. Film synthesis

Amorphous aluminum nitride films were deposited using a pulsed DC magnetron sputtering technique. The chamber was pumped to a base pressure less than 6.66×10^{-4} Pa before deposition. DC power was varied from 500 to 2000 W with pulse frequencies from 25 to 250 kHz. Films were deposited using pure nitrogen, nitrogen/oxygen and nitrogen/nitrous oxide gas mixtures with 99.999 % pure aluminum sputter targets. Gas pressures ranged from 0.4 Pa to 2.6 Pa. Deposition conditions strongly influence the crystallinity of the films [15], but optical observations and scanning electron microscopy (SEM) using a Jeol JSM 6060 confirmed the films were amorphous under the deposition conditions examined. The target-to-substrate spacing was adjusted to influence substrate heating and film uniformity with an optimal distance of 4 in. used for the majority of the runs. Deposition times were adjusted to achieve ~500 nm films. Thicknesses were verified using profilometry and optical spectroscopy. Parallel plate capacitors were constructed by evaporating 3 mm diameter dots on the top surface of the deposited films through a shadow mask for initial film characterization. Larger area (1 cm × 1 cm) single and multilayer capacitors were formed for more in-depth evaluation.

2.2. Multilayer capacitor fabrication

Multilayer capacitor structures were deposited using in-situ processing. A wafer transfer manipulator was used to precisely position the substrate behind shadow masks. The pulsed magnetron system was employed to deposit metal contacts from an argon plasma and oxynitride dielectric layers from a nitrous oxide gas mixture in the same chamber. Separate targets were employed for the metal and dielectric deposition. Targets were presputtered before deposition to remove contamination from the surface.

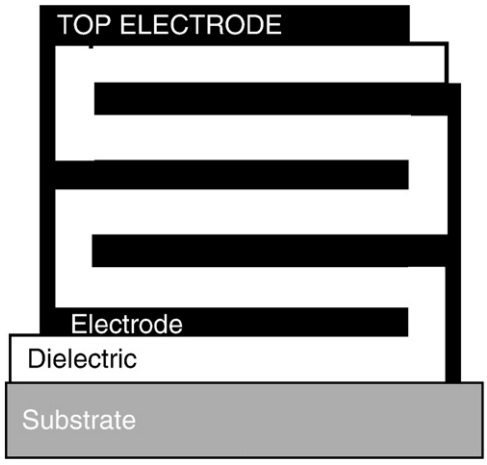

Fig. 1. Schematic cross-section of a multilayer capacitor.

2.3. Dielectric property evaluation

Capacitance and dissipation factor (DF) were measured as a function of frequency using an Hewlett Packard 4284A LCR meter. Multiple measurements were taken at each frequency and averaged for the capacitor. Several capacitors were tested on each film to confirm uniformity across the material. The dielectric constant was calculated using the average capacitance value at 1 kHz and the measured thickness for each film. The capacitance and dissipation factor were also measured at elevated and cryogenic temperatures. The dielectric breakdown strength was measured using an electrometer. Breakdown voltage was determined by incrementally stepping an applied voltage five or ten volts across a capacitor for five second durations, and measuring the resulting leakage current until film failure occurred. Over three hundred films were deposited and evaluated using simple parallel plate capacitors with 3 mm diameter electrodes. Multilayer capacitors were constructed for an additional one hundred samples, with 1 cm × 1 cm active areas and up to ten capacitor layers.

3. Results and discussion

3.1. Film composition

Optical surface observations and SEM reveal amorphous AlN films under the deposition conditions utilized. Energy dispersive X-ray analysis (EDS) and Rutherford backscattering spectroscopy (RBS) were utilized to examine the chemical composition of the films. Assessment of films deposited from a pure nitrogen plasma clearly showed oxygen in the spectrum. Both techniques determine ~30% oxygen in the deposited film. The composition is constant through the entire film thickness. This oxygen may result from adsorbed gases on the deposition chamber walls. The Al:N ratio in these films is ~1:1. Increasing the DC power increases the Al concentration in the films.

The composition changes dramatically when oxygen is intentionally introduced into the process. The oxygen almost completely replaces the nitrogen in the film and an AlO compound is formed. RBS and EDS confirm the film is primarily AlO with a small amount of nitrogen, with an Al:O ratio of ~1:2, and ~5% N present. The standard heats of formation for crystalline AlN and Al_2O_3 are −318 kJ/mol and −1675.7 kJ/mol, respectively. The formation of aluminum oxide is ~5X more thermodynamically favorable than aluminum nitride. Although reactive sputtering does not operate at thermodynamic equilibrium, the heats of formation indicate any excess oxygen will displace nitrogen in the films. Formation of a stable AlON film requires tight control of the oxygen content. In this article, films deposited from pure nitrogen feed gas are referred to as AlN, while those with additional oxygen intentionally added are called AlON. AlON films

Table 1
Film composition for N_2, N_2:O_2, and N_2O reactive gases.

Feed Gas	Measurement	Composition (%)		
		N	O	Al
N_2	RBS	32 ± 5	32 ± 4	36 ± 1
	EDS	35 ± 2	23 ± 2	40 ± 2
N_2+O_2	RBS	7 ± 5	60 ± 4	30 ± 1
	EDS	1 ± 2	56 ± 2	25 ± 2
N_2O	EDS	2 ± 2	58 ± 2	23 ± 2