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Physical Vapor Deposition of Low-Cost Ceramic Armor Device for US Army Low-Dielectric Application

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14. ABSTRACT

In this report, boron carbide nitride (BCN) thin film is explored for its structural and electrical properties as an alternative to, and potential replacement for, silicon dioxide as interlayer dielectric (ILD) materials. Physical vapor deposition (PVD) of BCN films were prepared by RF sputtering from a stoichiometric boron carbide target and deposited on blank and metallized electrode sapphire to create parallel capacitance structures. Two different gas mixture ratios of argon:nitrogen (Ar:N_2) were used for deposition. Discussed in this report are the electrical characterization of BCN, including dielectric constant, current versus voltage curves, and dielectric breakdown voltage characteristics extracted from the semiconductor system. A gas mixture of Ar:N_2 80:20 produced films with a surface roughness of 5.6 nm and a dielectric constant of 3.7 at 1.0 MHz. The dielectric constant decreased by 30% as the nitrogen concentration was reduced from 80:20 to 90:10 ratio of Ar:N_2, respectively. Additionally, the BCN 80:20 film achieved a resistivity of 1.33×10^8 ohm-cm while the dielectric breakdown voltage exceeded 25 MV/m, showing that BCN is suitable for low-κ-dielectric ILD applications.

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1. Introduction

Semiconductor devices continue to demand higher processing speeds; however, the space constraint in an integrated circuit (IC) is the major cause of increasing crosstalk interference, power mismatch, resistive–capacitive (τ = RC) delay between the interconnect structure and thus diminishes the speed of the IC. A typical I7-core control processing unit now has, and insulation material to be processed in an extreme environment, upward of 2 billion transistors per processor and this is expected to rise to 10 billion for a Xeon core.[1] Increasing speed requires each electrical component, interface, metallization including material deposition, photolithography, and etching, to produce a functional and reliable circuitry device.

Two possible methods to compensate space constraint and enhance signal processing are 1) optimizing conductivity of the transmitting wire, such as replacing aluminum with copper wiring and/or 2) replacing the interlayer dielectric (ILD) with a lower-dielectric, higher-breakdown material, which will consequently reduce the fringing capacitance. The ILD is the insulating material layer between transmission lines and a significant factor affecting the speed and the reliability of the device.[2,3] The actual performance of the devices depends on the speed of signal propagation, fringing, and cross-interference to and from the device through the metal interconnects. It has been theorized that ILDs made up of smaller atoms/ions, such as carbon (C) and boron (B), will have lower dielectric constants.[4,5] The research presented in this report explores boron carbide nitride (BCN) thin-film materials as a proposed low-dielectric, high-breakdown material to replace dense silicon dioxide (ε_r = 3.9) as the ILD for future microelectronic devices.

Currently, the US Army Research Laboratory is among the leaders in research exploring improved strengthening mechanisms in bulk ceramics, such as boron carbide (B_4C).[6,7] B_4C is known for useful characteristics, including extreme hardness, excellent chemical resistance, and good nuclear absorption properties, which are well suited for Army armor application, wear resistance, and the nuclear industry. However, B_4C can also be explored for other alternative applications that could meet the increasing technological and industrial demands for more-complex and advanced material properties. Materials within the BCN ternary system are known to have a high refractive index and a large band gap. They can also be tuned by changing the atomic composition and structure. These exceptional properties have attracted much attention from mechanical, optical, and electronic perspectives.[8–11] Numerous approaches to deposit BCN films have been reported, such as plasma-assisted chemical vapor deposition,[10,12] ion beam deposition,[13] and pulsed laser deposition.[14,15] Thin films are deposited by bombarding material from a source target, which then deposits a thin layer of material onto a receiving substrate. RF sputtering (Fig. 1) offers a wide range of advantages including large-area deposition, which offers better adhesion. Adhesion is essential for integration of IC processing and is an industry manufacturing standard suitable for scaling-up to large area processes for ultra-large-scale semiconductor-insulated device semiconductors.

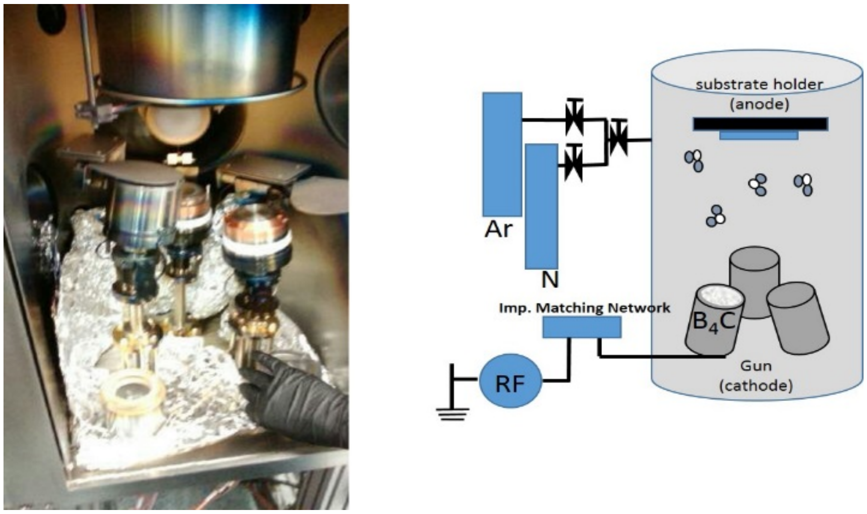


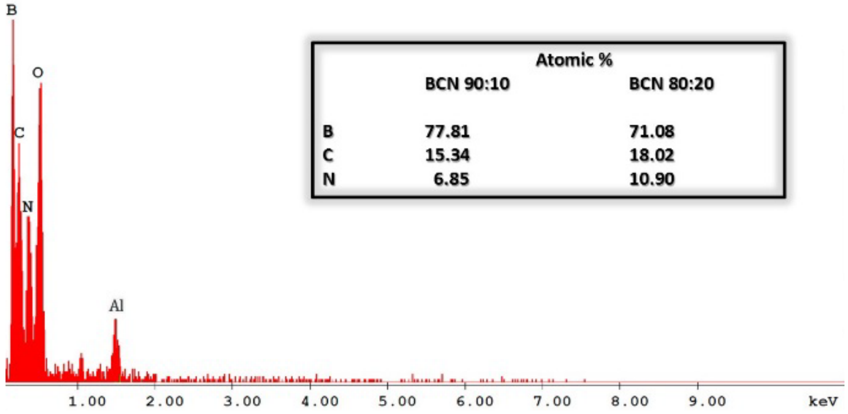
Fig. 1 Photo (left) and schematic (right) of the PVD-75 RF sputter system with multi-target configuration and argon (Ar):nitrogen (N_2) mixed-gas setup

This research involves precisely controlled thin-film deposition for investigating the electrical and structural properties of BCN. This enhances local research efforts of nanoscale and interfacial effects in the development and performance characteristics of B_4C for ILD applications. At the same time, the understanding of these property interrelationships for other BCN ceramic applications, including ultra-hard and lightweight armor, will be expanded.

2. Experiment Setup

BCN thin films were deposited by physical vapor deposition (PVD) using reactive RF magnetron sputtering operated at 13.56 MHz. A B_4C (99.5% purity; KJ Lesker, Inc.) source was used as the target, which deposited thin layers of B_4C and BCN onto 2-inch, single-crystal, (111)-orientation, c-plane sapphire wafers. These wafers were coated on the top and bottom with platinum to provide electrodes for electrical characterization. Bare substrates were plasma cleaned inside the deposition chamber using a 50-W RF plasma in Ar for 10 min prior to deposition. The target–substrate distance was approximately 10.0 cm, and the substrate holder was held at 1000 °C, which yielded 800–850 °C on the substrate (based on an in-house calibration curve). The substrate was also rotated at 10 rpm for uniform heating and deposition. The base system vacuum was less than 1.0×10^{-7} torr. Ultra-high-purity Ar (99.999%) and N_2 (99.99% purity) gas mixtures were introduced at the partial pressure ratios of 90%–10% and 80%–20% volume. Deposition pressure was set at 5.0 mTorr with a total flow rate of 20 sccm. A forward power of 150-W RF was used in conjunction with an automatic impedance matching network. The applied power was ramped at less than 2 W/min to prevent cracking of the target. Deposition time was 5 h, and the samples were cooled to room temperature at 10 °C/min before removing the samples from the vacuum chamber.

Surface characterization, including morphology and roughness, is a vital part of the thin film analysis determining the grain structure and quality of the BCN films. Likewise, film roughness and morphology are important considerations that affect electrical characteristics and possible integration into any multilayered thin-film processes. Ideally, films should retain minimal roughness and be free of hillock or pinhole-type defects that could produce electrical shorts through the dielectric. The surface characteristics of the films were characterized using an atomic force microscope (AFM). The samples were also cleaved for cross-sectional evaluation and characterized using a Hitachi SM-4700 field-emission scanning electron microscope (SEM). Film thicknesses of 450 nm were determined from the cross-sectional images. The sample cross section has been analyzed with electron diffraction X-ray spectroscopy (EDXS) (Fig. 2).



Atomic %

	BCN 90:10	BCN 80:20
B	77.81	71.08
C	15.34	18.02
N	6.85	10.90

Fig. 2 Typical element normalized EDXS quantification of elements including B, C, and N of atomic percentage of BCN. Inset shows atomic percentage chart of 90:10 and 80:20, respectively.

BCN films deposited onto the platinized sapphire were used for electrical characterization. Circular top-electrodes with a 200-µm diameter were fabricated by sputtering nominally 100 nm of platinum through a stainless steel shadow mask to produce an array of BCN parallel-plate capacitors. Electrical characterization, including current–voltage (I-V) curves and breakdown voltage, was conducted using a Janis cryogenic probe station with a Keithley 4200-SCS Semiconductor Analyses System (Fig. 3). Dielectric constant versus frequency response sweeps were acquired using an Agilent ENA-E5061B network analyzer with Signatone DC probes up to 1 MHz. To ensure appropriate on-wafer measurement accuracy and safeguard proper current flow through the correct path, a standard calibration of Short-Open and guarding triaxle cables was used to consider stray capacitance of the cable lengths and validate that the signal and the inner shield guard were kept at approximately the same electrical potential. This step is used to eliminate leakage current between the inner and outer shield, which might affect the true measurements, and enhance precision of low-current readings.

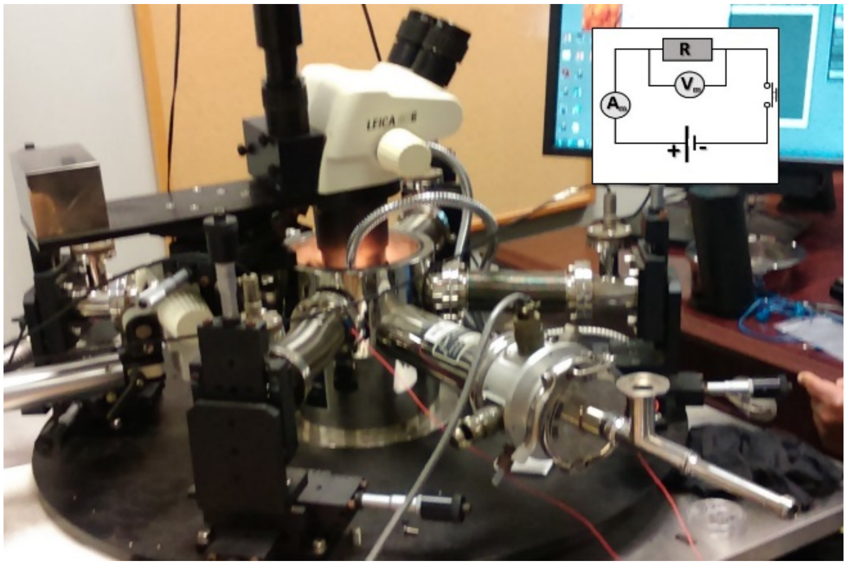
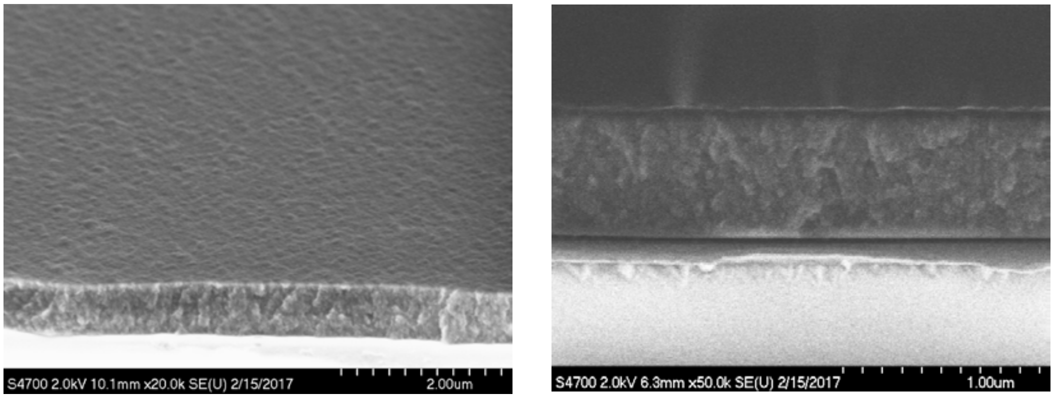


Fig. 3 Electrical characterization of BCN setup using the Janis cryogenic probe station with Keithly 4200-SCS Semiconductor Analyses System and Agilent ENA-E5061B network analyzer with Signatone DC probing up to 1 MHz

3. Results and Discussion

EDXS analysis of the samples revealed the presence of B, C, N, oxygen, and aluminum. Aluminum and oxygen signals are presumed to be due to the underlying oxidation and substrate holder. Figure 2 shows a typical EDXS spectra from a BCN film on sapphire (without platinum metallization). The composition of the BCN 90:10 and BCN 80:20 films are also given in the inset table in Fig. 2. The EDXS peaks show the percentage concentrations with respect to the elements. The ratio of B:C yielded approximately 5:1 and 4:1, respectively, for the 90%:10% and 80%:20% films. The stoichiometric bulk target ratio of is in the reasonable to the range of makeup chemistry. The results quantitatively showed that higher C atomic percentage and confirmed the makeup chemistry of BCN thin films.

The reproducibility and reliability of ICs depend on their dielectric properties, which are influenced by the quality of the surface between interfaces. High surface roughness can cause high leakage currents and become the major cause of premature breakdown failure and cross-reference interference between components. SEM images (Fig. 4) of BCN 90:10 shows uniform and smooth features in 3-D, and the cross section is dense and crack-free. The surface morphology of BCN was also assessed via tapping-mode AFM over 1- × 1-µm and 5.0- × 5.0-µm ranges. AFM images (Fig. 5) displayed a dense microstructure with no obvious cracks, pinholes, or other surface defects on both films (80:20 and 90:10). Smaller grain sizes and larger amorphous regions indicate that the lower B:C ratio seen in the BCN 80:20 sample yielded nearly a 50% smoother surface than the BCN 90:10 sample with the higher B:C ratio. Additional Fourier transmission-Raman and X-ray diffraction analyses are needed to verify the deposited phase. At the time of experiment a determination of the extent of amorphous and crystalline phases was not possible due to equipment limitations and the thicknesses of the films. The faded features of grain size and larger amorphous regions could be strongly related to the dielectric constant of the BCN film.



(a) **(b)**

Fig. 4 SEM images of a) BCN show uniform and dense feature in 3-D and b) crack-free cross section of BCN 90:10

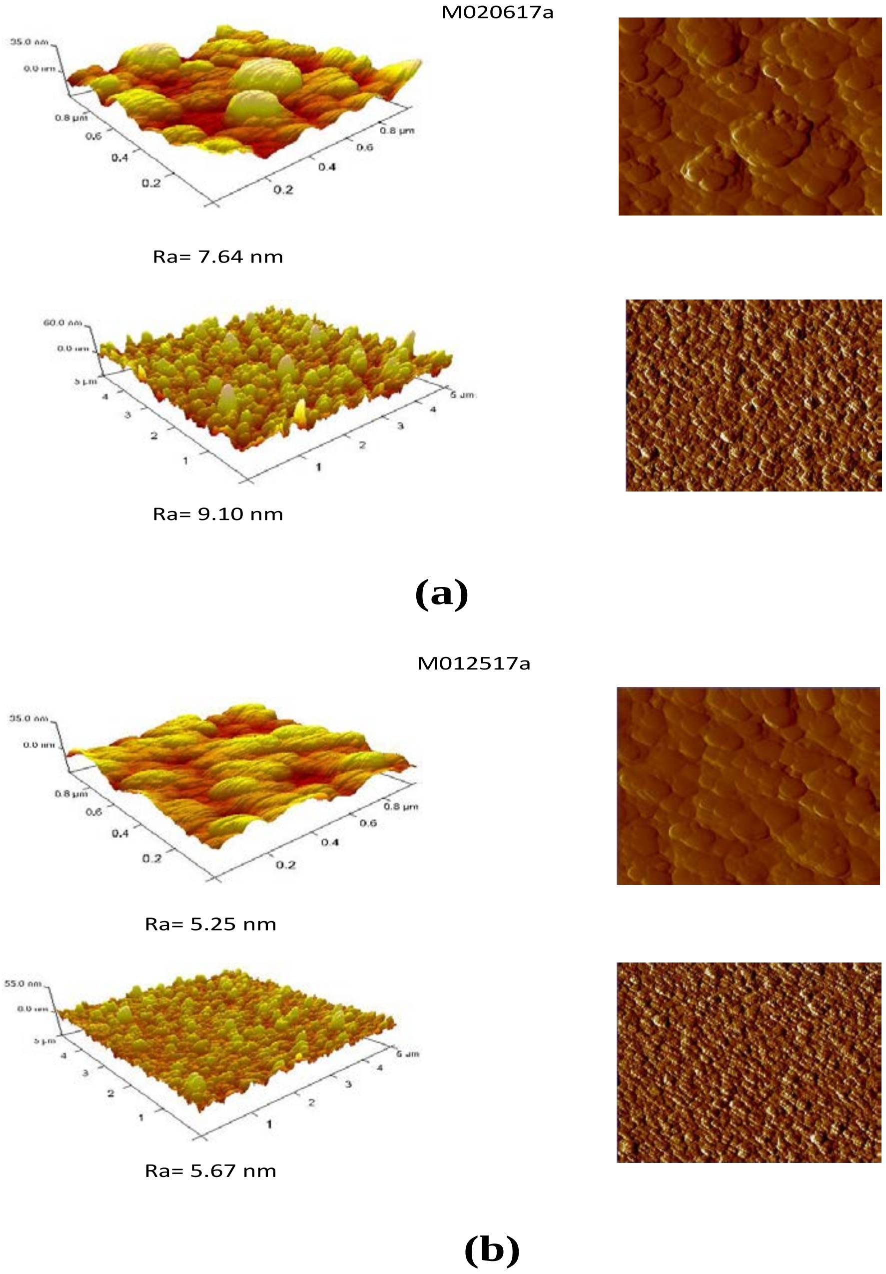


Fig. 5 Morphology of surface in 2-D and 3-D of a) BCN 90:10 Ar:N_2 gas flow ratio and b) BCN 80:20 Ar:N_2 gas flow ratio

The dielectric properties measurements were conducted in the metal–insulator–metal (MIM) parallel capacitor configuration at room temperature.[16,17] MIM capacitors were formed by the DC Denton sputter depositing platinum circle electrodes with 0.5-mm spacing through a shadow mask covering approximately 2.54 cm^2 area. Dielectric properties were measured with an E5061B ENA Vector Network Analyzer and a high-performance on-wafer Cascade Microtech Summit

9000 DC probing station. Figure 6 shows the dielectric constant of BCN samples plotted as a function of frequency. The dielectric versus frequency measurements were conducted by applying a small AC signal of 10-mV amplitude and sweep frequency from up to 1.0 MHz across the sample. The dielectric properties did not show any considerable dispersion within the frequency range, indicating good film–electrode electrical contact and interfacial characteristics. The dielectric constant was approximately 3.7 for the 80:20 film and decreased to as low as 2.4 for the 90:10 film at 1 MHz. Because both films exhibit equal or lower dielectric constants than typical B_4C (5 to 8) and also have a similar dielectric constant to existing semiconductor insulating dielectrics of silicon dioxide (3.9), BCN is attractive for use in low dielectric applications. Lowering the N_2 mixture appears to further reduce the dielectric constant.[18,19] However, additional refinement of the other processing parameters should be investigated to tailor and correlate the grain structure with dielectric properties.

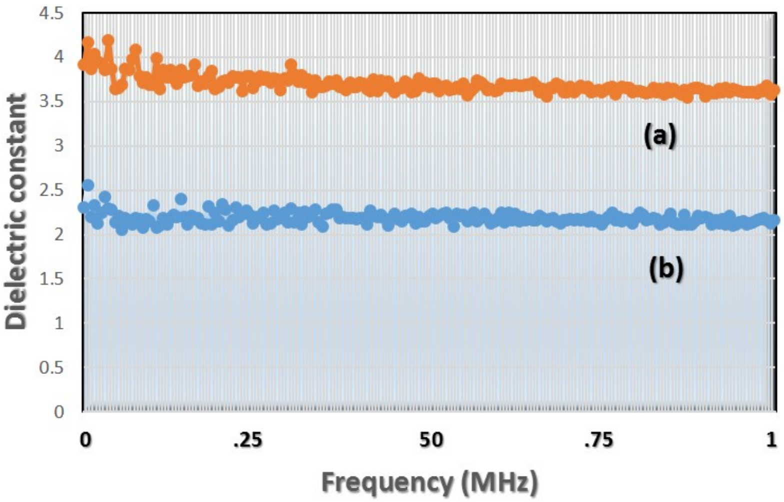


Fig. 6 Dielectric constant sweep of a) BCN 80:20 and b) BCN 90:10 vs. frequency

The I-V characteristic was recorded using a 2-point method by sweeping an applied voltage across the electrodes and measuring the resulting current through the capacitor structure. Figure 7a shows that a B_4C film (grown in Ar with no N_2) has nonlinear behavior with Schottky contact characteristics showing non-ohmic contacts to the material. Conversely, both BCN 90:10 and 80:20 films exhibit a linear, ohmic contact with very high resistance. Resistivity ($R = \rho L/A$), where R is the resistance, ρ is resistivity, L is length (film thickness), and A is the area of the platinum top electrode, was 1.33×10^8 ohm-cm for the 80:20 BCN. The I-V characteristic validated that BCN has ohmic characteristic that reduces parasitic capacitance and potentially enables faster switching speeds and lower heat dissipation. Furthermore, DC bias was applied to observe the dielectric breakdown capacity. The dielectric breakdown of thin films is often expressed terms of the electric field at which the insulator is electrically conductive and the material is damaged and loses its insulating properties (in volts per meter [V/m]). Depending on the manner in which the stress voltage or stress current is applied, several test methods for measuring the breakdown parameters can be used. A DC bias up to 10 V was applied to the thin film using the most commonly known procedure, the voltage ramp, with linear ramp rate versus time (dV/dt). At the ramp rate of 1 V/min, both BCN films survived an equivalent of 25 MV/m and showed no indication of electrical breakdown. Thus, these BCN thin films have many characteristic of an ILD properties, including low dielectric constant, good resistivity, and high dielectric breakdown, which suggests BCN as an attractive alternative in ILD applications.

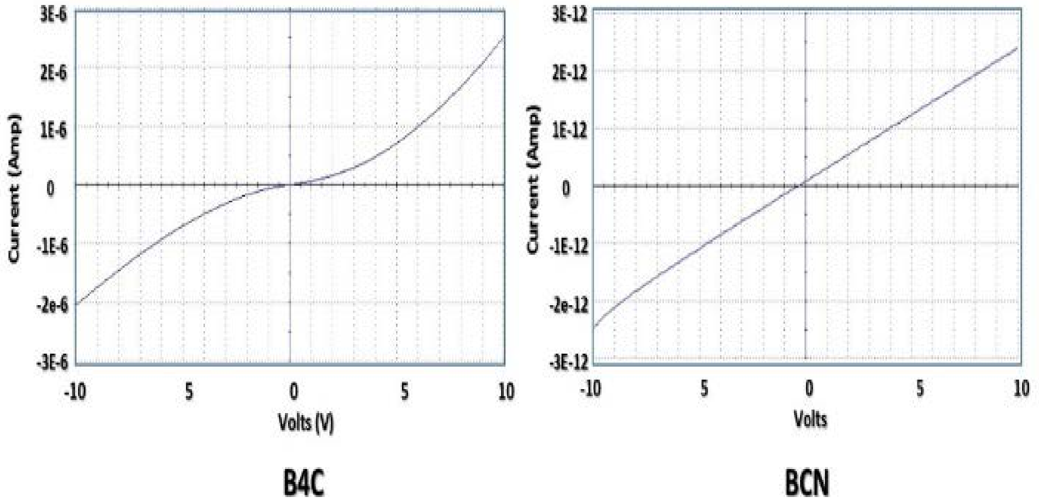


Fig. 7 Thin films current vs. voltage characteristic of (left) B_4C and (right) BCN 90:10 Ar : N_2 gas mix ratio

4. Conclusion

BCN thin films were deposited using RF PVD at high vacuum conditions. The electrical and the structural morphology properties of thin films produced with dielectric materials from both fundamental and practical application points of view were examined. Surface images exhibited a dense microstructure and no obvious cracks, pinholes, or other surface defects. Energy dispersive spectroscopy confirmed, quantitatively, the makeup chemistry of BCN thin films. Dielectric constant as low as 2.4 for BCN 90:10 was obtained. Dielectric breakdown reached beyond 25 MV/m and yielded resistivity of 1.33×10^8 ohm-cm.

Future validation and research interests in BCN include 1) exploring interface mechanical fracture toughness between crystalline and amorphous films to enhance mechanism response by using 4-point bend configuration, ultraviolet–visible spectroscopy properties for transparent ILDs, 2) extreme temperature dependency for high dielectric breakdown, 3) low thermal conductivity for high-power electronics, 4) neutron absorption for radiation protection, and 5) ultra-high-electromagnetic spectrum response for imaging and photonics technology. In addition, at the microscale level, the electrical properties have a direct correlation to the structural mechanics of bulk armor ceramic. These properties can potentially reduce cost and increase effectiveness of ceramic armor and generatlly increase applications for B_4C.

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List of Symbols, Abbreviations, and Acronyms

2-D	2-dimensional
3-D	3-dimensional
AC	alternating current
AFM	atomic force microscope
Ar	argon
sccm	standard cubic centimeters per minute
B	boron
B_4C	boron carbide
BCN	boron carbide nitride
C	carbon
DC	direct current
EDXS	electron diffraction X-ray spectroscopy
IC	integrated circuit
ILD	interlayer dielectric
I-V	current–voltage
MIM	metal–insulator–metal
N/N_2	nitrogen
PVD	physical vapor deposition
RF	radio frequency
SEM	scanning electron microscope
V/m	volts per meter

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