High temperature dielectric properties of ($B_xN_yO_z$) thin films deposited using ion source assisted physical vapor deposition

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The dielectric integrity has been one of the major obstacle in bringing out capacitor devices with suitable performance characteristics at high temperatures. In this paper, $B_xN_yO_z$ dielectric films for high temperature capacitors solutions are investigated. The films were grown on silicon substrate by using ion source assisted physical vapor deposition technique. The as-grown films were characterized by SEM, XRD, and XPS. The capacitor structures were fabricated using $B_xN_yO_z$ as a dielectric and titanium as metal electrodes. The elaborated devices were subjected to electrical and thermal characterization. They exhibited low electrical loss and very good stability when subjected to high temperature for a prolonged period of time.

Keywords: Boron oxynitride; dielectric; high temperature capacitor.

1. Introduction

Despite the attractiveness of oxynitrides in the electronic device industry as functional materials for integrated circuits, flash memories, and solar cells,^{1–3} very little work has been done on the ternary compounds made of boron, nitrogen, and oxygen. Thus, most of the boron oxynitride (BNO) properties remain unknown and its potential applications are unexplored. Milan *et al.*⁴ reported the presence of BNO, when they heated a mixture of boric acid and urea, in varying ratios. Gouin *et al.*⁵ thermally nitrated boric acid with ammonia at different temperatures to form BNO. Chen *et al.* first reported the synthesis of BNO as a compound by low frequency rf-plasma enhanced metal organic chemical vapor deposition technique in the year 2000.⁶

This paper reports on vacuum-deposited thin $B_xN_yO_z$ dielectric films using ion source assisted physical vapor deposition technique. This ensures higher quality films as compared to the techniques mentioned above where the growth of the film takes place under poor vacuum conditions. Deposition of thin dielectric films under high vacuum in the order of 10^{-6} Torr offers potential advantages because their structures can be controlled *in situ* at the near-atomic level. Although previous works have studied the physical and chemical properties of deposited BNO films, this study is mainly focused on the material applicability as a high temperature dielectric for energy storage solution. Silicon carbide- and gallium nitride-based power switches capable of

high temperature operation may operate safely at temperatures up to 350°C. At these temperatures, existing capacitor solutions have been shown to severely degrade. For high average power applications, capacitor failure is mainly due to thermal “runaway” resulting from internal friction and heat generated as a result of the polarization cycle during the charge and discharge of the capacitor under excessive pulse shots. Under these conditions, the temperature of the dielectric rises rapidly and produced localized heating, which reduces the dielectric strength. High temperature operating capacitors are needed to keep up with the high temperature demand in power conversion systems.^{7–9}

There are only very few thin film candidates “competitors” which were studied as high temperature dielectrics such as aluminum oxynitride (AlNO) capacitor,¹⁰ amorphous carbon nitride for high temperature capacitor dielectric,¹¹ and boron nitride capacitor which is patented by the author of this manuscript.¹² The BNO high temperature dielectric material presented in this work shows better thermal and frequency response characteristics than AlNO and diamond-like carbon counterparts.

2. Materials and Methods

The growth of the BNO thin films was carried out in a high vacuum chamber by using ion source assisted physical vapor deposition technique. Mark II gridless ion source with an End

hall configuration was used for the purpose (< 100 eV gas ions). Nitrous oxide N_2O is used as the feed gas to the ion source and solid boron is sublimated using an electron beam at a rate of $0.1\text{--}0.5$ Å/s. The nitrous oxide flux is $3\text{--}7$ sccm. The base pressure of the chamber is 10^{-8} Torr. The pressure during growth is 10^{-6} Torr and the silicon substrate temperature is maintained at 600°C during growth. The substrate is degreased with solvents (trichloroethylene, acetone, and methanol) and then etched with HF (1:10) to remove any native oxide. It is then loaded into the growth chamber and then preheated at 950°C for 1–2 min. The as-grown films were analyzed with SEM, XRD, and XPS. SEM imaging for BNO samples was made using a JEOL JVM 5470 machine. The acceleration voltage used is 20 kV and the BNO film thickness is from 200 to 250 nm. X-ray diffraction studies were performed to find the degree of crystallinity in the BNO films. It was performed using a Siemens D5000 Powder X-ray Diffractometer. The type of measurement was θ - 2θ scan and the target used was a Cu $K\alpha$ radiation that has a wavelength of 1.5418 Å. The elemental surface composition of the samples was determined by X-ray Photoelectron Spectroscopy (XPS). The XPS analyses were performed with PHI 5700 XPS instrument. Monochromatic Al $K\alpha$ (1486.6 eV) was used as X-ray source. The charging effect was reduced with the help of a neutralizer. The working pressure was 10^{-9} Torr. The sample's depth profile and also the high resolution B 1s, N 1s and O 1s spectra were obtained. The Gaussian-Lorentzian curve fitting was used to resolve the peaks. For capacitor fabrication, titanium is used as metal for both top and bottom electrodes. Elaborated capacitors were electrically and thermally characterized using an HP4275A LCR meter controlled by a LabVIEW-based program.

3. Results and Discussion

3.1. Material characterization

The surface morphology of the samples was examined with SEM. Figure 1 shows the surface morphology of a typical BNO film grown on Si at 550°C by using a boron rate of 0.2 Å/s and a nitrous oxide (N_2O) gas flow of 5 sccm. The analysis of BNO film reveals a smooth surface, continuous, and free of any pinholes.

The XRD analysis was performed to find the degree of crystallinity in the BNO film. The XRD plot is shown in Fig. 2. Apart from the signals for silicon and titanium, a peak at 29.5° (Ref. 4) can be seen and it corresponds to BNO compound. Although the peak is present, its intensity is very small and weak. There are other broad and very weak peaks present from 35° to 39° . These results suggest that the film is amorphous with a very little crystalline content. The formation of an amorphous film is easier than formation of a polycrystalline film because of the uniform stoichiometry required for a polycrystalline film. Also, by having amorphous dielectrics, which have dense microstructures, allows

Fig. 1. SEM micrographs of BNO thin films deposited under nitrogen and nitrous oxide beam energies of 45 eV.

us to avoid many of the problems associated with grain boundaries in polycrystalline dielectrics.

The XPS studies were performed to analyze the elemental and chemical composition of the film. To trim the research efforts and expenses, a graded sample with alternate layers of metal (spacer layer) and dielectric (BNO layer) was made. The BNO layer was grown at different temperatures (500°C , 550°C , and 600°C) and the titanium (Ti) metal was deposited at room temperature. The top layer was duplicated to check the deposition reproducibility. The metal layers were 10 nm thick. Figures 3(a) and 3(b) show the typical structure and XPS depth profile of the sample.

The binding energies of the constituent elements (boron, nitrogen, and oxygen) at different growth temperatures were determined. There is a very little variation in the oxygen and nitrogen 1s peaks at different growth temperatures. The binding spectrum is not presented but it is shown in Table 1. B1s on the other hand shows peaks at 188.3, 190.3, and 192.5 eV (Fig. 3(c)). The peak at 188 eV corresponds to B1s peak of the metallic boron (supported by XPS analysis of pure B

Fig. 2. XRD plot of the analyzed sample.

Fig. 3. (a) Graded sample for XPS analysis, (b) XPS depth profile of the graded sample and (c) High resolution XPS spectra of B1s.

Table 1. The binding energies of BNO films at different growth temperatures.

	500°C	550°C	600°C
Boron	189.2 192.1	188.46 190.4	188.31 190.31
Nitrogen	398.4	398.82 192.42	398.77 192.52
Oxygen	532.92	533.14	533.04

Table 2. The chemical composition of BNO films at different growth temperatures.

Growth temperature	Boron	Nitrogen	Oxygen	Titanium
500°C	52.13	22.57	24.96	0.33
550°C	56.54	19.88	17.61	5.95
600°C	49.88	17.54	21.21	11.35

sample). The peak at 190.4 eV confirms the presence of BN.¹³ Pure boron oxide (B_2O_3) peak is at 193.7 eV.¹⁴ The peak at 192.5 eV is in the intermediate range of pure BN and pure B_2O_3 .¹⁵ It also falls within the binding range B1s (191–193 eV) as reported by Chen *et al.*⁶

The chemical composition of each layer was analyzed and it is shown in Table 2. The film stoichiometry at different temperatures is also shown in Table 3.

3.2. Device characterization

The capacitor devices were made by deposition of Ti metal through a stencil mask with different sizes for electrode openings. The capacitance versus frequency and temperature measurements were recorded using a 4275A HP LCR meter. Figure 4(a) indicates a very small variation ($\sim 1\%$) of capacitance over a range of frequencies (10 kHz–2 MHz) and exhibits a good uniformity and linearity in terms of electrode area. The measurements were performed for a

Table 3. The stoichiometry of BNO films at different growth temperatures.

Growth temperature	Composition
500°C	B _{0.52} N _{0.23} O _{0.25}
550°C	B _{0.61} N _{0.61} O _{0.18}
600°C	B _{0.56} N _{0.62} O _{0.24}

typical 250 nm thick B_{0.52}N_{0.23}O_{0.25} layer and a 100 nm thick Ti electrode. The dielectric permittivity of deposited BNO films is found to be 5.5. The variation in capacitance over a range of temperatures 25–400°C is about 10% for BNO film with similar composition, footprint, and metal electrodes (Fig. 4(b)).

Figure 4(c) shows the variation in dissipation factor (dielectric loss) of the same capacitor structure with temperature and frequency. It is about 0.5% at 10 kHz and increases to 5% with increasing temperature up to 390°C.

The capacitors devices with B_{0.52}N_{0.23}O_{0.25} dielectric thickness of 200 nm and Ti metal electrodes of 100 nm were also subjected to thermal stress experiments to determine the temperature degradation of the capacitance and dielectric integrity at high temperatures. The samples were heated under vacuum conditions for up to 400 h. The capacitance measurements were taken during the annealing period. Two different capacitor areas were tested for thermal stability. Figure 4(d) shows the variation of capacitance with time under high temperatures up to 400°C. The capacitor devices under tests were practically very stable for the duration of the experiments.

Fig. 4. (a) Variation of capacitance of BNO capacitor as a function of frequency for different electrode sizes. (b) Variation of capacitance of BNO capacitor as a function of temperature. (c) Variation in dissipation factor of BNO capacitor as a function of temperature and frequency and (d) Variation of capacitance with time as a function of temperature (400°C).

4. Conclusions

BNO thin films were grown with ion source assisted physical vapor deposition technique and prototype capacitors with BNO as dielectric have been fabricated. BNO material was characterized by SEM, XRD, and XPS. The dielectric constant of the material was found out to be 5.5. The film is mostly amorphous and the composition of the film has been determined. Capacitor devices with BNO as dielectric were subjected to electrical and thermal characterization. Experimental results indicate a very small variation ($\sim 1\%$) of capacitance over a range of frequencies (10 kHz–2 MHz) and a 10% variation in capacitance over a range of temperatures (25–400°C). The capacitor device exhibited a low electrical loss and a very good stability when subjected to high temperature for a prolonged period of time.

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