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Dielectric properties of amorphous Bi–Ti–O thin films

R. Sun*, W. Xu† and R. B. van Dover*,‡

*Department of Materials Science and Engineering
Cornell University, Ithaca, NY 14853, USA

†Department of Applied and Engineering Physics
Cornell University, Ithaca, NY 14853, USA

‡vandover@cornell.edu

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We report the unexpectedly excellent dielectric properties of amorphous thin films with compositions in the Bi–Ti–O system. Films were deposited by RF magnetron reactive co-sputtering. In the composition range of $0.5 < x < 0.7$, amorphous $Bi_{1-x}Ti_xO_y$ exhibits excellent dielectric properties, with a high dielectric constant, $\varepsilon_r \sim 53$, and a dissipation factor as low as $\tan\delta = 0.007$. The corresponding maximum breakdown field reaches ~1.6 MV/cm, yielding a maximum stored charge per unit area of up to 8 μC/cm^2. This work demonstrates the potential of amorphous Bi–Ti–O as a high-performance thin-film dielectric material that is compatible with high-performance integrated circuits.

Keywords: Bismuth titanate; amorphous; thin films; composition spread; co-sputtering.

1. Introduction

The development of new thin-film dielectric materials has been of great importance for circuit applications in various electronic devices.[1,2] In silicon-based integrated circuit (IC) technology, the discovery of alternative dielectrics with desirable dielectric properties can lead to improved performance. In many applications, a good candidate for a thin-film capacitor dielectric must exhibit a high dielectric constant and a low dissipation factor, and for charge storage (as in dynamic random-access memory), it is also important that the material exhibit a high breakdown field.[2,3]

Titanium dioxide (TiO_2) has been extensively studied due to its high dielectric constant, but its dissipation factor has generally been found to be high as well.[4–6] Incorporating other metal oxides in TiO_2, such as Ta, Ba, Sr and Zr, can enhance the electric and dielectric properties. Amorphous bismuth titanium oxide (Bi–Ti–O) compositions are plausible candidates for dielectric applications. Crystalline $Bi_4Ti_3O_{12}$ has been reported to show a high dielectric constant with a low dissipation factor and $Bi_4Ti_3O_{12}$ ceramics have a low melting temperature and a high dielectric constant of 150.[7,8] Sillenite-type $Bi_{12}TiO_{20}$ single crystals exhibit a dielectric constant of ~47 at room temperature.[9] Furthermore, crystalline pyrochlore $Bi_2Ti_2O_7$ thin films have been reported with dielectric constants as high as 154.[10] Amorphous thin-film dielectrics are compatible with the low-temperature processing requirements associated with, for example, back-end-of-the-line IC processing. In other applications, amorphous thin films can be advantageous over polycrystalline materials because they avoid inhomogeneity in local charge density due to anisotropy.[7] Furthermore, grain boundaries can act as preferential paths for impurity diffusion and leakage current, so polycrystalline oxides tend to exhibit lower breakdown fields than those of amorphous dielectrics.[11]

Compared to crystalline materials, amorphous materials are also generally less expensive and easier to fabricate on modern circuitry containing nanoscale features. However, there is no systematic study of the properties of thin films in the amorphous Bi–Ti–O system in published literature. In this study, we report the properties of $Bi_{1-x}Ti_xO_y$ over the range of $0.1 < x < 0.85$. We employed the composition-spread technique for thin-film growth to characterize electrical properties with low composition-to-composition process variation and very fine composition resolution.[12,11,16] The films were synthesized by off-axis reactive RF magnetron sputtering. Amorphous $Bi_{1-x}Ti_xO_y$ thin films with a composition $0.5 < x < 0.7$ exhibit a high dielectric constant and a low dissipation factor, and therefore have great potential as a thin-film capacitor dielectric. The breakdown field is at least as high as 1.6 MV/cm, which implies a good maximum stored charge of about 8 μC/cm^2.

2. Experimental Methods

Thin-film composition spreads of Bi–Ti–O were synthesized on an Si wafer using 90° off-axis reactive RF co-sputtering

‡Corresponding author.

with two planar magnetron sputter guns arranged in the facing-targets configuration. The 90° off-axis configuration results in low bombardment of the substrate by reflected Ar atoms and oxygen ions. Two-inch-diameter metallic Bi and Ti targets were used, powered with 15 W and 125 W of RF excitation, respectively.[13] The ambient pressure in the chamber was 30 mTorr (4 Pa). The deposition rate varies rapidly as a function of the distance from the target, so a natural continuous composition gradient, approximately 1 at.% per mm, is obtained across the substrate.

Prior to film deposition, the vacuum chamber was evacuated to a pressure of 10^{-6} Torr. Gas flow rates during deposition were 15-sccm (std. cm^3/min) Ar and 10-sccm O_2. The high O_2 partial pressure was chosen to minimize the possibility of Bi or Ti ions being present in the film in a low oxidation state that could potentially cause hopping conductivity. An RF power level of approximately 10 W was applied to the substrate to achieve roughly −80 V DC bias, which ensures the formation of dense films.[15] During film deposition, the substrate temperature was maintained below 60 °C by mounting the substrate on a heatsink. The deposition rate was roughly 0.1 nm/s, and the deposition time was 20 min. The thickness of amorphous film at the center of the substrate was roughly 100 nm.

The composition of the films as a function of position along the composition spread axis was quantitatively determined using calibration samples on which a single element was reactively sputtered under the same conditions used for co-sputtering. The thicknesses of the reference Bi–O and Ti–O samples were measured as a function of position with a profilometer. The Bi and Ti cation fractions of the co-sputtered sample were inferred by calculating the ratio of arrival rates of the two cation species.

The thickness of the film also varies along the composition-spread axis since the sum of the deposition rates from each target is not constant. The thickness was determined as a function of position by preparing a co-deposited sample with a lift-off strip mask across the substrate. The mask was then removed, and the thickness of this sample was measured at 15 positions along the composition-spread axis using a profilometer. The position–thickness relationship was modeled by a cubic polynomial.

The dielectric properties of amorphous Bi–Ti–O thin films were characterized using a metal–insulator–metal (MIM) capacitor structure.[14] The silicon substrates were precoated with a uniform platinum layer before deposition of the amorphous dielectric film. After film deposition, an array of silver dot contacts with a diameter of 200 μm was deposited by thermal evaporation through a shadow mask. The capacitance and dissipation factor (tan δ) were measured using an automated probing station and HP4284 LCR meter. Current–voltage characteristics were also measured on the Ag–dielectric–Pt capacitor structures using a Keithley 617 electrometer to apply a voltage across the capacitor in 0.2 V steps while measuring the resulting leakage current. The breakdown voltage was then identified as the voltage for which the current jumped by at least two orders of magnitude between steps or exceeded 0.1 A/cm^2, whichever was lower.

The samples were not prepared in a clean room environment, and as a result we expect that many of the MIM capacitors may contain defects, including small pinholes caused by dust. When the film is coated with the counter-electrode layer, these pinholes can lead to random discrepancies in electrical measurements. For example, small pinholes completely dominate a quasi-DC *I–V* measurement. However, capacitance and dissipation factor measurements are much less affected, since the effect of parallel conduction channels created by small pinholes is often negligible compared to the capacitive admittance at 1 kHz or greater.

3. Results and Discussion

3.1. *Dielectric constant and dissipation factor*

To evaluate the dielectric performance and characterize the dispersion of amorphous Bi–Ti–O thin film compositions, the capacitance and dissipation factor were measured from 100 Hz to 1 MHz. Typically, 10–40 capacitors were measured at each composition in the Bi–Ti–O composition spread. The median capacitance value was chosen as representative. The dielectric constant was calculated from the measured capacitance and modeled film thickness. The dissipation factor (defined to be the ratio of the imaginary part of the dielectric constant to the real part) was reported directly by the LCR meter. High-quality thin-film dielectrics are associated with dissipation factors below 0.05.[7,13] Raw capacitance and dissipation factor data for all 560 capacitors are illustrated in Appendix A.

Figure 1 shows the dielectric constant and the dissipation factor of $Bi_{1-x}Ti_xO_y$ as a function of composition, specifically

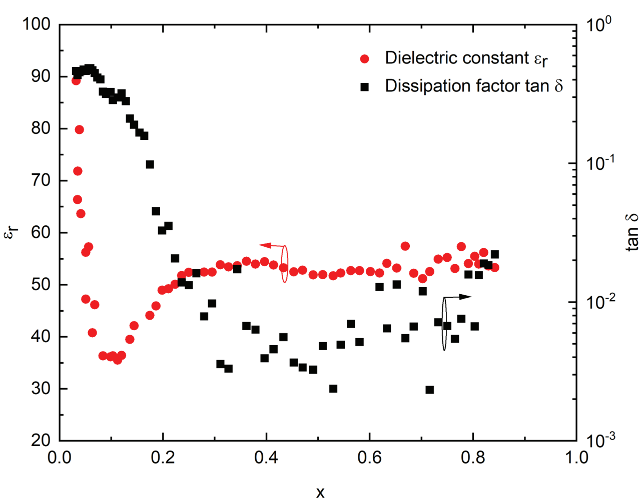

Fig. 1. Composition dependence of the dielectric constant and dissipation factor of amorphous thin-film $Bi_{1-x}Ti_xO_y$ measured at 10 kHz.

at 10 kHz. The dielectric constant in the Bi-rich region ($x < 0.3$) is high, but varies greatly with composition as well as frequency in the range of 100 Hz < f < 500 kHz. Films in this composition range also exhibit a high dissipation factor. These behaviors reflect the nature of Bi_2O_3, which exhibits ionic conductivity and possibly a hopping electronic conductivity as well.

Films with compositions in the range of $0.3 < x < 0.6$ exhibit a dielectric constant $\varepsilon_r \approx 53$, a value that is essentially frequency-independent up to 500 kHz. In this range, the dissipation factor is generally quite low — values as low as tan $\delta = 0.002$ were observed.

Films in the Ti-rich composition region also exhibit a dielectric constant in the vicinity of $\varepsilon_r \approx 53$, though with less reproducibility. The dielectric constant is still independent of frequency, as it is for the compositions in the middle of the spread, but the Ti-rich films exhibit markedly higher values for the dissipation factor, i.e., in the range of $0.006 < \tan \delta < 0.02$. This is consistent with the observation that nominal pure TiO_2 films typically incorporate O vacancies, leading to a small concentration of Ti^{3+} that supports dissipation due to hopping conductivity in the film.

3.2. *Breakdown field and maximum stored charge*

Current–voltage characteristics were measured to determine the composition-dependent trends in electrical leakage and breakdown in amorphous Bi–Ti–O. As in the capacitance measurements, data were collected from 10–40 devices with nominally identical compositions. For each composition, the maximum breakdown voltage was chosen as the best representative of behavior, since random defects that are unavoidable in films fabricated and processed in a noncleanroom facility can lead to premature (uncharacteristic) breakdown. The leakage current and breakdown field of dielectric materials are important parameters that determine suitability for applications in which charge storage is important.[7] The maximum stored charge for a parallel plate capacitor can be calculated as the product of the breakdown field E_{br} and the dielectric constant $\varepsilon_r\varepsilon_0$, or equivalently, the product of breakdown voltage V_{br} and capacitance C, normalized to the area of the capacitor A, i.e., $Q_{max} = \varepsilon_r\varepsilon_0 E_{br} = CV_{br}/A$.

Figure 2 illustrates the composition dependence of the breakdown field in amorphous thin film $Bi_{1-x}Ti_xO_y$. For compositions with the lowest Ti content ($x < 0.2$) the breakdown field is very low, consistent with the excessive conductivity and corresponding leakage inferred from the dissipation factor associated with the capacitance measurement. Similarly, for compositions with the highest Ti content ($x > 0.7$), the breakdown field rapidly decreases due to excessive conductivity associated with multivalent Ti.

However, for intermediate compositions ($0.3 < x < 0.7$), the breakdown field can be very high, rising to values as high as 1.6 MV/cm at $x = 0.7$. One capacitor exhibited a breakdown field of 2.2 MV/cm, suggesting the possibility that an

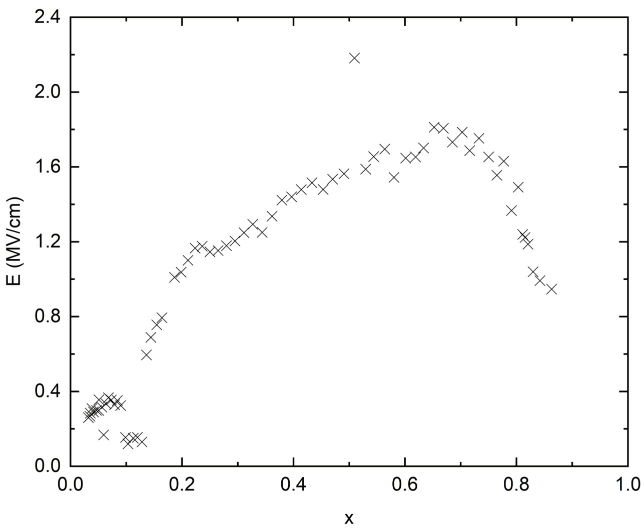

Fig. 2. Composition dependence of the breakdown field and maximum stored charge in amorphous $Bi_{1-x}Ti_xO_y$.

even higher breakdown field might be attained with process conditions that minimize pinholes. Amorphous $Bi_{0.3}Ti_{0.7}O_{1.85}$ is a promising dielectric material and worthy of further investigation and optimization.

For compositions in the range of $0.3 < x < 0.8$, the dielectric constant is approximately constant at $\varepsilon_r \approx 53$, so the maximum stored charge is simply proportional to the breakdown field. Thus, in the range where the breakdown field is highest, $0.6 < x < 0.7$, amorphous Bi–Ti–O films can support a maximum stored charge of approximately 8 $\mu C/cm^2$. For the single capacitor with the highest breakdown field, the maximum stored charge is 10 $\mu C/cm^2$. These values compare favorably with the maximum stored charge achieved in carefully optimized amorphous Ta_2O_5 films, for which $Q_{max} \sim 8$ $\mu C/cm^2$.

4. Conclusion

This work documents the composition dependence of the dielectric properties of amorphous Bi–Ti–O thin films over a wide range of compositions. Bi-rich and Ti-rich compositions yield capacitors with inferior properties mainly associated with excess parasitic conductivity. Although the endmembers are not promising, oxide films with intermediate Bi/Ti ratios have surprisingly excellent properties. For compositions in the range of $0.4 < x < 0.6$, amorphous $Bi_{1-x}Ti_xO_y$ exhibits the highest dielectric constant with the lowest dissipation factor, while in the range of $0.6 < x < 0.7$, it exhibits the highest breakdown field. Compositions with Ti cation fraction of $0.5 < x < 0.7$ have excellent properties, with a dielectric constant $\varepsilon_r \sim 53$ and a dissipation factor tan $\delta < 0.01$. The breakdown field is in the vicinity of 2 MV/cm, resulting in a maximum stored charge of ~8 $\mu C/cm^2$. Some capacitors exhibited even higher breakdown fields, which suggests that optimized deposition conditions might lead to even better performance.

We conclude that amorphous $Bi_{1-x}Ti_xO_y$ with $0.5 < x < 0.7$ is a material that shows unexpected promise for application in IC technology.

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Appendix A

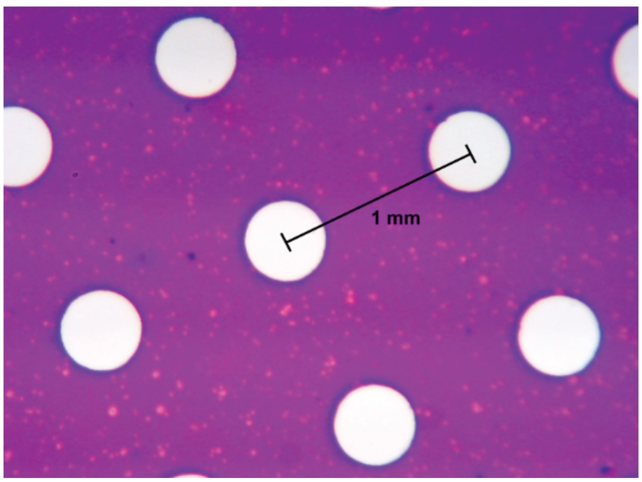

Fig. A.1. Micrograph showing Ag dot electrodes 200 μm in diameter with 1-mm spacing between the dot centers, as deposited on the Bi–Ti–O composition-spread thin film. The film color is due to optical interference.

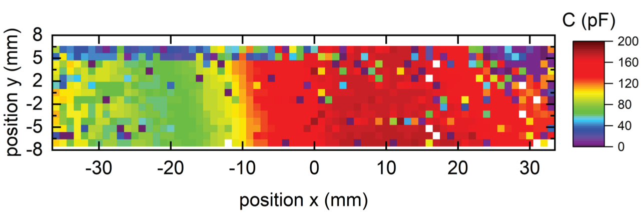

Fig. A.2. Color map of the capacitance of devices measured at 10 kHz. The x-axis represents position on the wafer (Bi-rich region on the left-hand side, Ti-rich region on the right-hand side). Measurements along the vertical axis represent capacitors with the same nominal composition and thickness. Since the thickness of the film varies along the horizontal axis, the dielectric constant is not directly proportional to the capacitance. Individual capacitors that were short circuits or were otherwise unmeasurable are represented using white.

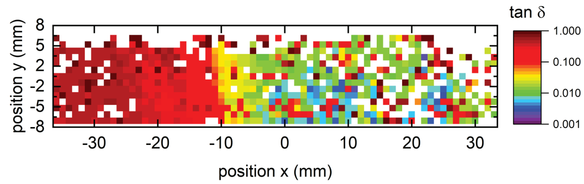

Fig. A.3. Color map of the dissipation factor measured at 10 kHz with respect to position on the wafer; x- and y-axes are as in Fig. A.2. Notice the variability of values measured for a given composition, especially in the range between −2 mm and +13 mm. Subtle variations in the deposition process can apparently have a significant effect on the properties of the dielectric. Note the logarithmic scale for the color bar; devices for which the measurement was off scale are represented using white.

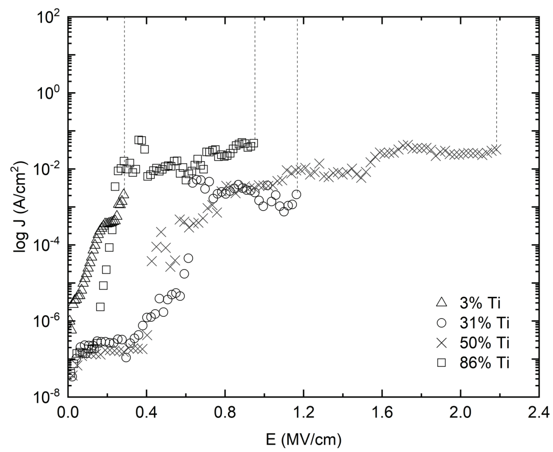

Fig. A.4. J–E characteristics in $Bi_{1-x}Ti_xO_y$ capacitors, with four representative compositions: Bi-rich (Ti cation fraction of $x \approx 0.03$), center of the composition spread ($x \approx 0.31$), an exceptional capacitor with roughly equimolar composition, and a capacitor in the Ti-rich ($x \approx 0.86$) region. The dashed line represents the point beyond which the current density rises above 10^{-1} A/cm² (i.e., breakdown).

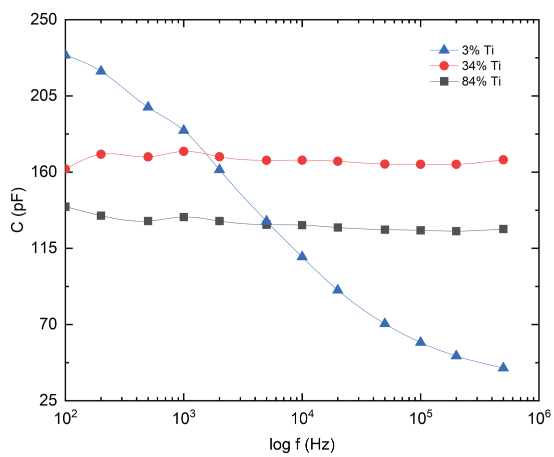

Fig. A.5. Frequency dependence of the capacitance, with three representative cases. Only the Bi-rich (e.g., Ti cation fraction of $x \approx 0.03$) capacitors show large dispersion in the dielectric constant. The capacitors at the center of the composition spread ($x \approx 0.34$) and the Ti-rich ($x \approx 0.84$) compositions have a dielectric constant that is essentially independent of frequency.

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