Dielectric response of asymmetric $KNbO_3/KTaO_3$ superlattices

J. Sigman, H. J. Bae, and D. P. Norton[a)]
Department of Materials Science and Engineering, University of Florida, P.O. Box 116400, Rhines Hall, Gainesville, Florida 32606

J. Budai and L. A. Boatner
Oak Ridge National Laboratory, P.O. Box 2008, Oak Ridge, Tennessee 37831

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The synthesis and properties of asymmetric $KNbO_3/KTaO_3$ superlattices is examined. Interdigitated electrodes are fabricated for temperature-dependent capacitance measurements. The nonlinear dielectric response of $1/N$ superlattice exhibits the anomalous positive tunability behavior indicative of antiferroelectricity. In contrast, the $N/1$ $KNbO_3/KTaO_3$ structures ($N>1$) appear to be either ferroelectric or paraelectric, depending on the temperature. Discussion of possible mechanisms for this behavior is given. © *2004 American Vacuum Society.* [DOI: 10.1116/1.1778403]

I. INTRODUCTION

Ferroelectricity is a collective phenomenon in which the alignment of electric dipoles depends on their mutual interaction. It is the interaction of these dipoles that is key to determining the overall ferroelectric response of a material.[1] Yet, when considering ferroelectric thin films, extrinsic size effects, such as surface charges, nonuniform strains, and structural defects, can hinder these dipole interactions and modify the films' dielectric response.[2] Recent advances in oxide film growth, particularly for perovskites, have enabled the use of superlattices and heterostructures for investigating intrinsic and extrinsic size effects.[3–5] As a result of superlattice formation, radical changes in the ferroelectric response can be realized.[6] For epitaxial (001) oriented $BaTiO_3/SrTiO_3$ superlattices, an enhancement of the dielectric properties has been observed.[7] The remanent polarization is enhanced in asymmetric superlattice structures, attributed to the Ba/Sr ratio in the structure as well as a strain-induced increase in the *c*-axis lattice constant.[8] For (111) oriented symmetric $BaTiO_3/SrTiO_3$ superlattices, the dielectric constant has been measured to be twice that of the $Ba_{0.5}Sr_{0.5}TiO_3$ alloy films, again reflecting the effects of strain on ferroelectric properties.[9] Theoretically, first-principles density functional theory within the local density approximation has been used to investigate spontaneous polarization in ferroelectric superlattices, namely $BaTiO_3/SrTiO_3$ superlattices. These calculations suggest that the polarization of the superlattices can be larger than alloy structures with comparable $BaTiO_3$ content., and that the $SrTiO_3$ layers should be distorted to a tetragonal, polar structure.[10] The nonlinear dielectric behavior of superlattices has also been investigated experimentally. For $BaTiO_3/SrTiO_3$ structures, the voltage tunability increased with decreasing periodicity for superlattice periods less than 24 unit cells.[11] Clearly, superlattice structures can yield properties that differ from the bulk, and provide a unique tool for probing fundamental properties.

Another interesting ferroelectric superlattice to consider is $KTaO_3/KNbO_3$. $KTa_{(1-x)}Nb_xO_3$ (KTN) is in many ways similar to $(Ba,Sr)TiO_3$. $KTaO_3$, like $SrTiO_3$, is an incipient ferroelectric and remains cubic and paraelectric over all temperatures ranges.[12] $KNbO_3$ undergoes a first order ferroelectric phase transition at 701 K from the cubic to the tetragonal state with additional structural transitions to the orthorhombic state at 498 K and to the rhombahedral state at 263 K.[13] As a solid solution, KTN exhibits a continuous Curie temperature that varies according to the formula $T_c(\mathrm{K})=676x+32$ ($x>0.047$).[14] The lattice mismatch between the two materials is only 0.6%, considerably less than what is seen in $(Ba,Sr)TiO_3$.[3] Because of this low lattice mismatch, superlattice structures of alternating $KTaO_3$ and $KNbO_3$ layers have been grown by pulsed laser deposition (PLD) in which the strain in the structure is uniform and thickness independent up to a layer thickness of 17 nm.[4,5] A tetragonal-to-tetragonal structural phase transition is observed in the superlattices using temperature dependent x-ray diffraction for $KNbO_3$ layer thickness less than the critical thickness.[5] The structural phase transition temperature T_c, decreases with decreasing superlattice periodicity (Λ) in symmetric superlattices until $\Lambda=12$ unit cells.[4] Below this, the T_c of the superlattice is 200 °C, the same T_c as for a $KTa_{0.5}Nb_{0.5}O_3$ alloy film. Using molecular-dynamics simulation, the dynamical and phase transition behavior of $KTaO_3/KNbO_3$ superlattice structures has been examined.[15–17] It is predicted that the Curie temperature should decrease for small superlattice modulation lengths.[17] For modulation lengths less than 12 unit cells, the superlattice is predicted to respond as a single artificial structure.[16]

When the temperature dependent capacitance is measured for a $\Lambda=0.8$ nm (1 unit cell $\times$ 1 unit) $KNbO_3/KTaO_3$ superlattice, three distinct regions are seen in the dielectric response.[18] An anomalous nonlinear dielectric behavior is observed with the dielectric constant increasing with applied bias voltage for temperatures between 120 and 220 °C.[18] In conventional paraelectrics, ferroelectrics, and tunable dielectrics, however, the maximum capacitance is seen at zero bias

[a)]Author to whom correspondence should be addressed; electronic mail: dnort@mse.ufl.edu

and then decreases as the bias voltage is increased, also referred to as negative tunability. Although the measured response in the superlattice is inconsistent with the bulk behavior of $KNbO_3$, $KTaO_3$, and their alloys, it is similar to the behavior seen in aniferoelectric perovskites, most notably $Pb(Zr,Ti)O_3$.[19,20] Since neither $KTaO_3$, $KNbO_3$, nor their alloys exhibit antiferroelecticity, the response appears to be a result of the artificial B-site ordering created in the superlattice structure. Recent reports of second harmonic generation in $BaTaO_3/SrTiO_3$ superlattices seem to support these conclusions.[21] For temperatures below 120 °C, the behavior is consistent with that of a material in the ferroelectric state. For $T>220$ °C, a conventional negative tunability as high as 50% is observed in a field of only 2 kV/cm. Similar positive tunability has also been observed in $SrTiO_3/BaZrO_3$ superlattice structures with superlattice periods less than 30 unit cells.[22] Superlattices with periods greater than 30 unit cells exhibit ferroelectric behavior. Interestingly, neither of these materials is either ferroelectric or antiferroelectric in bulk.

II. EXPERIMENTAL PROCEDURE

Previous work has focused on the properties and response of symmetric $KNbO_3/KTaO_3$ superlattices. In this article we focus on the nonlinear dielectric response of asymmetric $KNbO_3/KTaO_3$ superlattices. The superlattice films were grown by PLD on $KTaO_3$ (001) substrates. To prevent the loss of potassium during growth and to maintain stoichiometry in the films, the targets consisted of two semicircular pieces: one KNO_3 and one either $KNbO_3$ or $KTaO_3$.[23] A KrF laser ($\lambda=248$ nm) with an energy of 1–1.5 J/cm^2 and pulse rate of 1 Hz was used for deposition. At this pulse rate, a laser pulse strikes the segments twice per target rotation. The average deposition rate was 0.5 Å/pulse and substrate to target distance was 6 cm. All films were grown at a substrate temperature of 750 °C in an oxygen atmosphere of 100 mTorr. Films were cooled in an atmosphere of 200 Torr of oxygen. All films were 160 nm thick. RF sputter deposited Al/Cr interdigitated electrodes were patterned by wet photolithography and liftoff. Each electrode had 26 500 μm long fingers with a finger separation and width of 10 μm. Capacitance–voltage measurements were performed at 100 kHz and 1 MHz for temperatures of 20–300 °C in air.

III. RESULTS AND DISCUSSION

Several superlattice structures were grown in which the thickness of the $KNbO_3$ layer was held at 1 unit cell per period and the $KTaO_3$ layer thickness was varied. The temperature-dependent capacitance at 100 kHz for 1/3 and 1/6 $KNbO_3/KTaO_3$ superlattice structures is shown in Figs. 1 and 2, respectively. Although only the 5 V applied bias is represented in these figures, the same trends have been seen for dc bias voltages of 1–20 V. As with the 1/1 $KNbO_3/KTaO_3$ superlattice,[18] there are three distinct temperature regions in the response. At low temperatures, there is little temperature or bias voltage dependence of the capacitance for both structures. For the temperature range of 125–220 °C, the 1/3 $KNbO_3/KTaO_3$ superlattice exhibits a positive tunability as seen in the 1/1 structure. For the 1/6 $KNbO_3/KTaO_3$ superlattice, the positive tunability is less pronounced, but nevertheless present for 100 °C$<T<$160 °C. These changes in the slope of the capacitance at about 200 °C correspond to the previously mentioned structural phase transition seen in superlattices with periodicities less than 12 unit cells.[4] For temperatures above this, a conventional, yet large, voltage tunability is observed in both structures. Above 220 °C, the response shows a negative tunability as high as 30% in the 1/3 $KNbO_3/KTaO_3$ superlattice and 55% in the 1/6 $KNbO_3/KTaO_3$ structure.

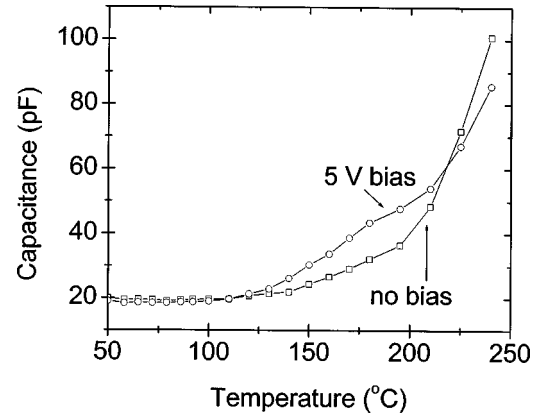

FIG. 1. Temperature dependent capacitance of a 1/3 $KNbO_3/KTaO_3$ measured at 100 kHz.

For a second set of superlattices, the thickness of the $KTaO_3$ ayer was held at 1 unit cell while the thickness of the $KNbO_3$ ayer was varied. Figure 3 shows the temperature-dependent capacitance at 100 kHz for a 2/1 $KNbO_3/KTaO_3$ superlattice. Figure 4 shows the response for a 3/1 $KNbO_3/KTaO_3$ superlattice. The nonlinear dielectric response for these $N/1$ structures differs significantly from that for the $1N$ structures. For the 2/1 $KNbO_3/KTaO_3$ structure, there is no significant dependence of the capacitance on bias voltage for $T<125$ °C. At $T=125$ °C, the capacitance increases with increasing with temperature, peaking at

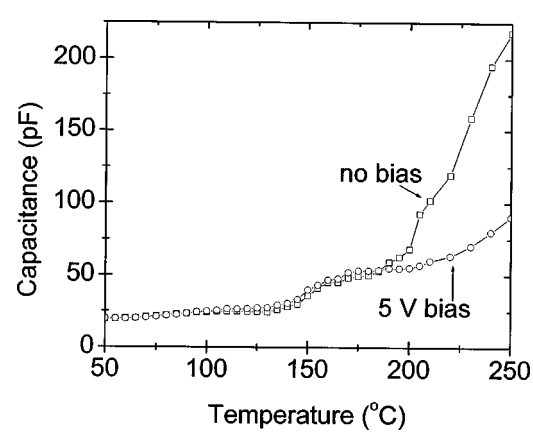

FIG. 2. Temperature dependent capacitance of a 1/6 $KNbO_3/KTaO_3$ measured at 100 kHz.

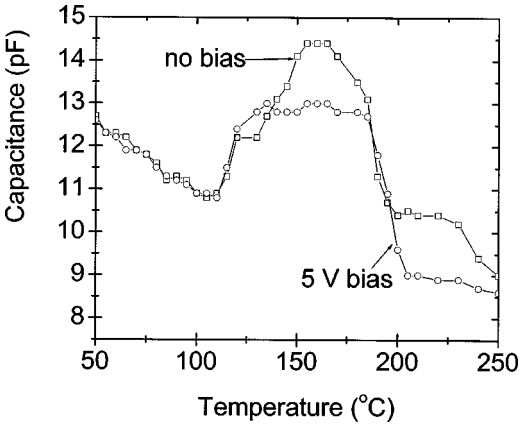

FIG. 3. Temperature dependent capacitance of a 2/1 $KNbO_3/KTaO_3$ measured at 100 kHz.

~160 °C. However, the positive tunability is barely observable over a narrow temperature range. Only through a 10 °C range around the previous transition temperatures of 125 and 200 °C does the 2/1 $KNbO_3/KTaO_3$ structure show a positive tunability. Because the trends at these two temperatures appear to be equal, this behavior provides evidence for an additional structural transition at 125 °C that has not previously been measured. Once the superlattice passes through these transition temperatures, it reverts back to negative tunability behavior. Above 210 °C, the response shows a negative tunability that is smaller than that seen in the 1/3 or 1/6 $KNbO_3/KTaO_3$ superlattices. The capacitance also exhibits negative tunability between 140 and 190 °C.

For the 3/1 $KNbO_3/KTaO_3$ superlattice structures, the temperature-dependent dielectric response of Fig. 4 shows very little dependence on applied bias voltage. There is some evidence for a maximum in the capacitance at 210 °C, but no distinctive voltage tunability is observed.

Two trends are immediately apparent from the capacitance data. Decreasing the $KNbO_3$ layer thickness to 1 unit cell has a dramatic effect on the dielectric characteristics of the superlattice structure for a variety of $KTaO_3$ layer thicknesses. Increasing the $KNbO_3$ layer thickness to 2 unit cells

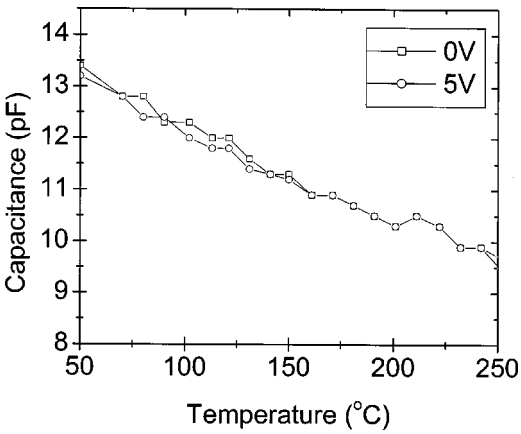

FIG. 4. Temperature dependent capacitance of a 3/1 $KNbO_3/KTaO_3$ measured at 100 kHz.

or greater essentially eliminates the positive tunability seen in the structures. The observation that superlattices with single unit cell $KNbO_3$ layers and variable $KTaO_3$ layer thicknesses behave similarly is difficult to resolve within the context of long-range ferroelectric interactions. Interfacial effects might play a role in the tunability response of these superlattices. Since a 1/1 superlattice structure possesses the highest number of periods and thereby interfaces, it would be reasonable to consider this as a possible source of the antiferroelectric behavior. However, it is unclear how antiferroelectric coupling could be interface related. Contradiction occurs when the 3/1 $KNbO_3/KTaO_3$ and the 1/3 $KNbO_3/KTaO_3$ superlattices are compared. Here the number of interfaces is equal, yet the responses are dramatically different. The structural difference lies in what nearest neighbors the $KNbO_3$ dipole will see in each superlattice. In the 1/3 $KNbO_3/KTaO_3$ structure, the nearest neighbor for every $KNbO_3$ dipole is an induced dipole of the $KTaO_3$ layer. For a 3/1 $KNbO_3/KTaO_3$ superlattice, one third of the $KNbO_3$ dipoles have $KNbO_3$ nearest neighbors.[17]

Besides a dipole moment each Nb atom in the $KNbO_3$ layer possesses an elastic quadropole moment.[24] Because of the piezoelectric nature of ferroelectric materials, a reorientation of one always results in a reorientation of the other. Previous x-ray diffraction measurements of $KNbO_3/KTaO_3$ superlattices indicate that the nature of the structural phase transition is dependent upon the thickness of the $KNbO_3$.[4,5] Changes in structure create changes in lattice parameters and thereby changes in strain in the layers. However, changes in strain create change in polarization and thereby changes in the dipole interactions. Such structure, strain and polarization relationships have been observed in $BaTiO_3/SrTiO_3$ superlattices.[8] Therefore, the structural change that occurs as the $KNbO_3$ layer thickness is decreased from 3 to 1 unit cell creates enough changes in the polarization and dipole interaction to favor antiferroelectric coupling. Further understanding of this antiferroelectric coupling will require additional x-ray diffraction measurements as well theoretical simulations of the dipole moment configurations.

It is interesting to note that the 180° stripe domains have recently been observed from x-ray diffraction of ultrathin $PbTiO_3$ films.[25] Upon cooling below the Curie temperature, satellites around the Bragg peaks are reported, indicating stripe domains whose period decreases with decreasing film thickness. For the smallest film thickness considered (1.6 nm), the 180° stripe domains period is only 3.7 nm. Extrapolating the measurements to a single unit cell thick film, the stripe domain period should be less than 2 nm. As the period of the 180° stripe domain structure approaches 2 units cells, it becomes equivalent to antiferroelectric ordering of the dipole moments. Here it is suggested that the stripe domain occurs because of depolarization fields that have not been otherwise neutralized by other means such as surface charges. As the temperature is raised in these samples, distinct structural changes do occur in these films where the stripe domain become more diffuse. With further increases in temperature, a monodomain ferroelectric phase is formed,

indicating that increases in thermal energy can relax or neutralize the depolarization field. It is interesting that transition temperatures, which change both the structure and ferroelectric ordering of the system, appear to exist in both the KT/KN superlattices and these very thin lead–zirconate–titanate films This may, in fact, provide a possible explanation for the dielectric tunability of the single unit cell thick $KNbO_3$ layers, assuming that a stripe domain structure similar to that for $PbTiO_3$ appears in this material as well.

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