Low-loss crystal-ion-sliced single-crystal potassium tantalate films

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The dielectric response has been studied in 10-μm-thick, single-crystal potassium tantalate films formed by crystal ion slicing. Scanning microwave microscopy shows that the implanted, pre-etched samples exhibit a bulk-like permittivity and low-loss tangent (0.0009) at 1.7 GHz. The separated free-standing films have somewhat higher loss tangents due to residual-ion-induced stress. Selective relaxation of this stress by etching or annealing reduces the dielectric loss. [DOI: 10.1063/1.1446214]

One important potential application for high-quality ferroelectric films is as tunable elements for microwave phased-array radars and wireless communications. Various thin-film fabrication methods have been investigated for the low-loss frequency-agile materials needed for these integrated microwave devices. It is important that these ferroelectric materials be single crystal in order to have low loss or high Q at microwave frequencies. For example, the high Q of single-crystal potassium tantalate ($KTaO_3$) allows its permittivity to be easily tuned with an external voltage at the transition temperature of high-T_C superconductors, <90 K.[1] This makes $KTaO_3$ a useful material for tunable elements in certain high-T_C resonant filters. In this connection, recent papers have reported on the use of ion implantation followed by selective etching to form free-standing thin films, 1–10 μm in thickness from ferroelectric and ferrite single crystals, including $KTaO_3$.[2,3] These films have been found to have fully single-crystal optical and magnetic properties.

In this letter, we report on the dielectric properties of ion-sliced $KTaO_3$ at microwave frequencies. The films are studied by microwave microscopy using a near-field-based technique[4] to determine and understand the effect of ion implantation and subsequent lift off on their electrical properties at a microscopic scale. $KTaO_3$ is chosen for this work, not only because of the application mentioned, but also because the physics of microwave loss in this crystal has been investigated carefully both theoretically and experimentally. This allows us to gain more generalizable insight into the effect of ion processing on film dielectric properties.

To prepare the samples for crystal ion slicing, singly charged 3.8 MeV helium ions are implanted at 5° from the surface normal on (001) $KTaO_3$ surfaces. The energy of the implantation can be adjusted to select the desired film thickness over a range from 4–10 μm; an implantation dose of 9×10^{15} cm^{-2} is used for optimum etching.[5] The samples are mounted on a 2 in. diameter water-cooled target holder, maintained at 56 °C. Etching is accomplished with dilute 5% hydrofluoric (HF) acid such that a deep undercut develops in the $KTaO_3$ after several hours, centered 10 μm below the top surface. As discussed before,[6] the localization of stress in the implantation region allows for selective lateral etching based upon stress-induced etch-rate enhancement, a similar process to that in stress-induced corrosion. Etch selectivity depends critically on the implantation dose, with very slow evolution below 8×10^{15} cm^{-2}. Higher doses can be used to promote faster etching, with a maximum rate near 300 μm/h per facet, limited by stress-induced fracturing of the film. More details and the fundamental basis for crystal ion slicing are discussed in Ref. 2.

The microwave properties of the free-standing film are measured using near-field microwave microscopy to determine both the room-temperature dielectric response and loss tangent of these films at 1.7 GHz. The technique couples the electromagnetic radiation to the sample from a resonant or weakly resonant structure via a scanning tunneling microscope (STM) tip. Changes in frequency, as the sample is scanned 10–20 nm beneath the tip, reflect microscopic variations in the measured dielectric properties. The estimated accuracy of the permittivity measurements is 5%, with a 0.2% relative precision. This technique is extremely sensitive to a small volume close to the end of the STM tip; see related experiments on bulk $PbTiO_3$.[7] In our experiments, the high-field region is limited to the first 10 μm beneath the sample surface, so the measured volume encompasses only the implantation region. Thus, we are able to make high-precision permittivity maps with a spatial resolution as fine as 1 μm and to observe features as small as 200 nm, even with a 19-cm-probe-radiation wavelength.

This approach is used to examine the effects of ion implantation on the dielectric properties of the $KTaO_3$. First, an implanted sample was probed *before the films are separated from the mother crystal* over a wide, 360 000 μm^2 region of

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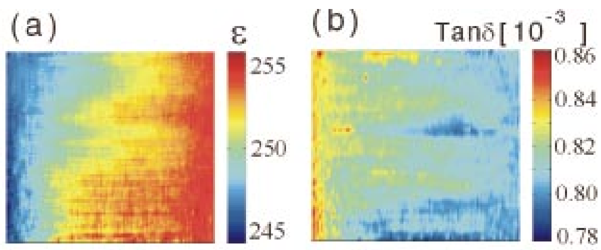

Sample	ε	Tanδ
Implanted bulk	245	0.0009
Film / No annealing	170	0.0060
Film / (1) 300°C for 3hrs/Ar+O_2	200	0.0040
Film / (2) 450°C for 4hrs	197	0.0055

FIG. 1. (Color) (a) Permittivity and (b) loss tangent in $KTaO_3$ over $600 \times 600\ \mu m^2$. From the left- to right-hand side, the scans move from the implanted to the unimplanted region. The average values for ϵ are 255 and 245 and for loss tangent are 0.0008 and 0.0009 for the virgin and implanted regions, respectively.

the surface and then averaged. Accurate values of permittivity are determined by comparing these data to data taken on a $SrTiO_3$ standard, and measuring in a differential-height mode.[8] Specifically, the average measured values of permittivity were 255 and 245 and of loss tangent, 0.0008 and 0.0009, taken at the center of the virgin and implanted regions, respectively. These are comparable to single-crystal bulk values reported in the literature as 240 for permittivity and between 0.0004 and 0.0010 for the room-temperature loss tangent in the GHz range.[9–11] Thus, the electronic properties of the implanted material remain very close to the virgin sample, i.e., they exhibit a remarkably low microwave loss. This shows that energetic helium ion implantation has only a minor deleterious effect on the permittivity and loss tangent. Figure 1 shows a $600 \times 600\ \mu m^2$ map of permittivity and loss tangent, which includes the boundary separating the implanted from an unimplanted region indicating the small variation in dielectric properties by the implantation.

In order to study the detached films, the implanted samples are etched and the films are removed from the substrate, and then rinsed in deionized water. Those stand-alone films are mounted on a MgO substrate, without bonding agents to avoid unnecessary contamination of the surface, for electrical testing using the same microwave probing technique described. Room-temperature data are taken on several films prepared under different conditions with and without annealing, since annealing is known to diffuse He within the ion-implanted samples. The table in Fig. 1 compares the averaged permittivity and loss tangent at 1.7 GHz for $KTaO_3$ films prepared under different postdetachment annealing conditions.

It is clear that the unannealed film has dielectric properties close to, but significantly degraded from, the bulk or as-implanted sample. However, annealing brings the values of permittivity and loss tangent closer to the virgin sample. Since the as-implanted samples retain the bulk properties, it is clear that the presence of interstitial He or residual radiation damage alone does not degrade the microwave properties of the detached samples. Instead the explanation could be either in some form of surface degradation or sample stress.

First, we study the effect of surface morphology on the dielectric measurements by using the STM in a scanning mode to simultaneously map the dielectric properties and the surface topography. By probing the sample topography simultaneously with frequency-shift measurements, we find that a small part of the change in frequency and, thus in the sample permittivity, correlates well with surface topography. In particular, the ion process is known to sometimes yield a locally corrugated surface on the etched side of stand-alone films.[6] Because of this morphology, a corrugated surface of a film from annealing condition 2 results in a correlated, 0.03% variation in the dielectric response. Measurements on the top side of the films reveal a smooth surface (<50 nm surface roughness) on which the observed variation in the dielectric response could be attributed to edge effects in the small ($2.2 \times 2.2\ mm^2$) samples measured. The values reported in the table (Fig. 1) have already been checked for surface morphology effects and corrected for the sample geometry. In all cases, however, the variation in permittivity is much less than the changes reported in the table in Fig. 1; thus much of the process-induced change is not attributable to surface morphology effects.

Instead, a second series of experiments show that the reduction in permittivity and increase in loss stem dominantly from bowing-induced stress in the free-standing films. In particular, these films are observed to have a small curvature; e.g., the top is concave, indicating that the implanted region is under tensile stress. The measured variation in this curvature with processing conditions is used to investigate the mechanism of curvature and its effect on dielectric properties. The film shape is recorded using an optical microscope and fitted to a quadratic curve, a profile expected for our conditions. Slicing under different acid concentrations at constant etch times shows that films have less curvature as the HF concentration increases. Moreover, thickness measurements on these films show that the more concentrated the acid, the deeper the sacrificial layer-etch and the smoother the etched surfaces. By comparing film thickness with transport-of-ions-in-matter (TRIM) simulations of the implantation, we confirm the removal of a large part of the implanted He by more highly concentrated HF solutions; see Fig. 2(a). Thus, we attribute the smaller curvature in more strongly etched films to the removal of residual He from the film surface and hence a relaxation of stress. Annealing the sliced films would be expected to yield the same result, since annealing would cause the residual helium ions to diffuse out and, thus, release the stress and curvature. In this connection, $KTaO_3$ films annealed under condition 1 in the table in Fig. 1 did exhibit a $25\% \pm 15\%$ reduction in curvature relative to unannealed films. Thus, annealed samples have less near-surface stress; these results correlate with a reduction in dielectric loss and an increase in permittivity for annealed films.

These observations are in agreement with the fundamental understanding of microwave loss in bulk, single-crystal $KTaO_3$ reported by Tagantsev.[12,13] This work, along with other experimental studies, have shown that the microwave loss increase in $KTaO_3$ originates from the interaction of the

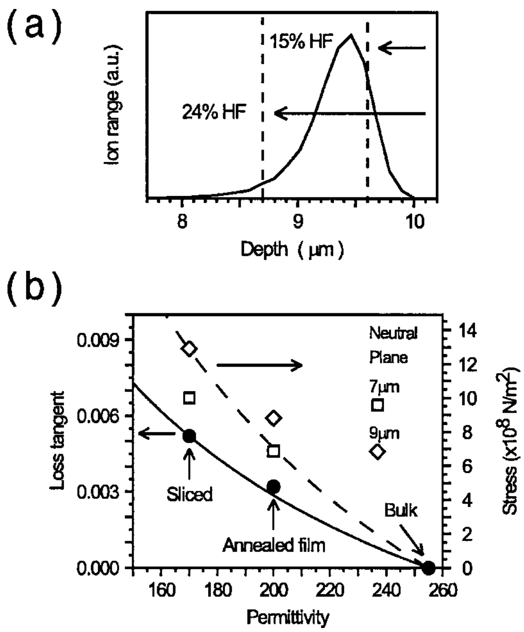

FIG. 2. (a) Comparison between ion distribution simulated by TRIM (solid curve) and ion-sliced film thickness shown by vertical lines with two HF concentrations. (b) Increase of loss tangent due to the quasi-Debye mechanism versus permittivity. The curve is fitted to the measured loss (disks) of the sliced film. A broken line shows stress versus ϵ with measured stress from curvatures.

electromagnetic wave with lattice vibrations. Of particular interest in the present study is the contribution introduced by the presence of internal electric fields originating from mechanical stress through converse electrostriction (a quasi-Debye contribution). This effect has been observed in bulk $KTaO_3$.[14]

In this connection, the improvement in dielectric properties following annealing can be calculated and then compared to the measured data. The changed permittivity, ϵ, in $KTaO_3$ under a stress, σ, is dominantly due to converse electrostriction. In this case, ϵ can be obtained from[15]

$$\epsilon = 1 + \frac{1/\epsilon_0}{\gamma_0 + 2Q\sigma}. \tag{1}$$

Here the permittivity is expressed in terms of the inverse susceptibility without stress, γ_0, the permittivity of vacuum, ϵ_0, and an electrostrictive constant, Q. The stress versus permittivity is plotted using Eq. (1), measured ϵ (stress free) for the bulk, and known $Q_{11} = 8.71 \times 10^{-2}$ m^4/C^2,[15] Fig. 2(b). The stress on the film surface can be calculated, Fig. 2(b), from the surface curvature and assuming a position of the neutral plane of stress at 7 and 9 μm. Note, diffusion of He by sample annealing causes the neutral plane to shift toward the center; diffusion would also improve uniformity. Finally, the increase in microwave loss due to the stress via the quasi-Debye mechanism is estimated. The quasi-Debye microwave loss in $KTaO_3$ is known to be a simple linear function of $\eta \equiv [\epsilon^{-1}(\text{stressed}) - \epsilon^{-1}]\epsilon$ for small η.[13] This linear relation can be obtained by subtracting the measured loss for stress-free bulk from that of the sliced films so as to obtain only the stress-induced contribution and then plotting the loss versus the permittivity, see Fig. 2(b). The fitted loss versus permittivity curve agrees with the measured improvement in loss for annealed films. Thus, we conclude that the relatively larger loss measured in ion-sliced films is stress induced, and can be minimized by removing the residual stress by annealing or etching.

In summary, the results in this letter using $KTaO_3$ as a ''model'' material have shown that crystal ion slicing fabricated dielectric films can have a bulk-like microwave response and thus high-Q thin films can be generated using this technique. The primary limitation on microwave loss appears to originate from stress formed in the free-standing film as a result of residual interstitial He. This can be reduced by additional etching of the ion-implant region or by additional annealing.

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