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Epitaxial Liftoff for Fully Single Crystal Ferroelectric Thin Films

Contract # N00173-98-1-G014

R. M. Osgood, Jr., M. Levy, H. Bakhru, E. Cross

FINAL REPORT

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Abstract

High-frequency signal transmission demands in RF and microwave systems, such as electronic phased-array radar and scanning antennas, call for innovative approaches in materials technology. Among the outstanding issues that need to be addressed in such systems are the fabrication of low-loss, highly tunable capacitive elements made of thin-film ferroelectrics. This program used a new epitaxial liftoff technique developed at Columbia University to produce high-quality, single-crystal films of ferroelectrics such as strontium titanate (ST), potassium tantalate ($KTaO_3$), and potassium tantalate niobate (KTN) for use in tunable microwave devices. Development of this single-crystal thin-film technology, produces thin films with "bulk-crystal" high-frequency-capacitive and piezoelectric properties, and thus is an important new approach to obtaining high-quality thin films of these materials.

1. Goal

This program investigated the use of a new epitaxial liftoff technique, recently developed at Columbia University, to produce high-quality, single-crystal films of ferroelectrics such as strontium titanate, potassium tantalite, and potassium tantalite niobate for use in tunable microwave devices. Development of this single-crystal thin-film technology has produced thin films with "bulk crystal" high-frequency capacitive and piezoelectric properties and, thus, has provided an important new approach to obtaining high-quality thin-films of these materials.

Specifically, the objective of this research effort has been to demonstrate epitaxial liftoff of thin, i.e. 1-10μm, single-crystal layers of ferroelectric materials, with subsequent bonding to a semiconductor or insulator substrate. The technique to be used in the process will be the recently developed crystal ion slicing (CIS) technique developed at Columbia in collaboration with SUNY Albany. Characterization of the thin-film electrical properties has been done in part at Penn State.

2. The Program's Motivation: Improved Thin-film Ferroelectric Material

High-quality ferroelectric thin films are an important technology for future, advanced RF systems. For example, most microwave phased-array electronic scanning antennas and radar systems are controlled by phase shifters. A typical system may have several thousand elements, with a phase shifter for every antenna element. Therefore low cost, high reliability and low complexity are very important considerations in the design of phased–array components. Until recently, ferrite phase shifters have been used for phased arrays, but their size, cost and complexity have limited their widespread use. Phase shifters employing ferroelectric materials promise to give much better performance as compared with ferrite shifters because of their high power handling capacity, low drive power, full military temperature range of operation and low cost. Moreover, the development of thin film ferroelectrics of superior quality can also potentially lead to the implementation of planar electro-optic phased-array systems. Such systems would use microstrip transmission lines, in conjunction with integrated or near-integrated thin film elements and sources and would, thus, yield a system, which is both extremely compact and highly reliable.

However, the growth of thin, stoichiometric, transition-metal-oxide films remains a difficult challenge for obtaining tunable microwave and RF components. For example, films of $SrTiO_3$ exhibit much higher loss tangents in thin-film form than as bulk single-crystals. Present day techniques for obtaining thin film ferroelectrics, such as the use of RF sputtering on wafer targets, or the growth of ceramic films, result in polycrystalline materials, with excess intergranular transmission losses. In fact, prior measurements on barium strontium titanate ceramic films find a thickness-dependent loss-tangent, which increases with decreasing thickness.

3. Approach

This program uses a promising technique, which has recently been invented and researched at Columbia by Profs. Levy and Osgood, for obtaining very high-quality films for RF device applications. This approach is "ion slicing" shown in Fig. 1. Initially a bulk crystal or LPR, MBE or MOCVD grown layer is exposed to a flux of high-energy light-weight ions, typically He+. The use of deep, high-energy implantation results in a change in the reactive chemistry of a deeply buried sacrificial layer. This change enables the top undamaged thin film to be "sliced off" by exposure to a selective etching solution. Note that in contrast to the usual liftoff techniques for semiconducting materials, ion-slicing does not require the growth of a sacrificial layer. The sliced film is then carefully placed onto the desired platform substrate and bonded to the desired substrate via one of the variety of methods including natural Van der Waals forces, chemical adhesive, or metal thin film, where the choice depends on the desired application.

Crystal Ion Slicing (CIS)

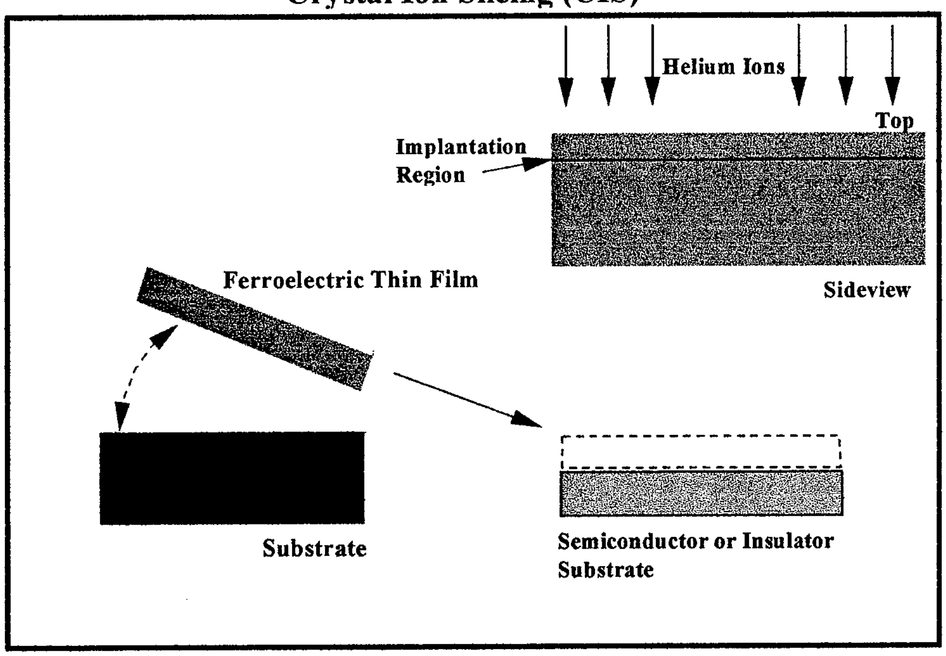

Fig. 1. Sketch of the CIS process for obtaining thin (1-10μm) single-crystal, stoichiometric films of ferroelectrics

4. Results

During this program we have demonstrated the fabrication of single-crystal $KTaO_3$ films, begun testing the dielectric and loss characteristics of these films, and begun examining anodic and palladium bonding to various substrates for the production of large-area films.

We have shown that ion slicing can be extended to ferroelectric crystals and specifically, we have demonstrated crystal ion slicing of single-crystal potassium tantalite and strontium titanate. *These are the first fully single crystal thin films made of these materials.* In brief, for these studies, transport-of ions-matter (TRIM) simulations and ion implantation at 3.8MeV and various dosages were first done and removal of the sacrificial layer tested in a number of etchants. Potassium tantalite films were then fabricated and characterized; sacrificial-layer etching studies in $SrTiO_3$ for (110) crystals were also carried out. In addition, a new approach to enhancing ion slicing has been developed using $LiNbO_3$ samples as a model crystal. Finally, careful testing of the thin film properties of all materials studied here has been accomplished. Thus, we have done extensive characterization of these films using optical probing and microscopy, electron microscopy, and x-ray microdiffraction at Columbia and in close collaboration with Penn State. A more detailed account of our recent progress is as follows:

a) Potassium Tantalate

- *Single-Crystal Film Fabrication - Etch Selectivity and Implantation Dosage*

One of the most difficult challenges of the CIS liftoff process is to achieve the correct level of stress without cracking the film. An excellent example of how this stress tuning can be successfully accomplished is shown in the case of KTO. Thus careful adjustment of the ion dosage was required to tune the He-implant stress level. 10μm thick films were fabricated at an implantation energy of 3.8MeV and a dosage of 1×10^{16} cm^{-2}. Below this point, the etch selectivity in diluted HCl increased dramatically between 5×10^{15} cm^{-2} and 1×10^{16} cm^{-2}. The undercut evolution rate ranged from less than a micron per hour at the low end, to 300 μm/h near the exfoliation threshold. At high dosages the films tended to cleave during etching, possibly as a result of implantation-induced stress. Films up to 0.5 x 1.0 mm^2 in size have been fabricated so far. The effect of heat treatment on etch selectivity has yet to be investigated.

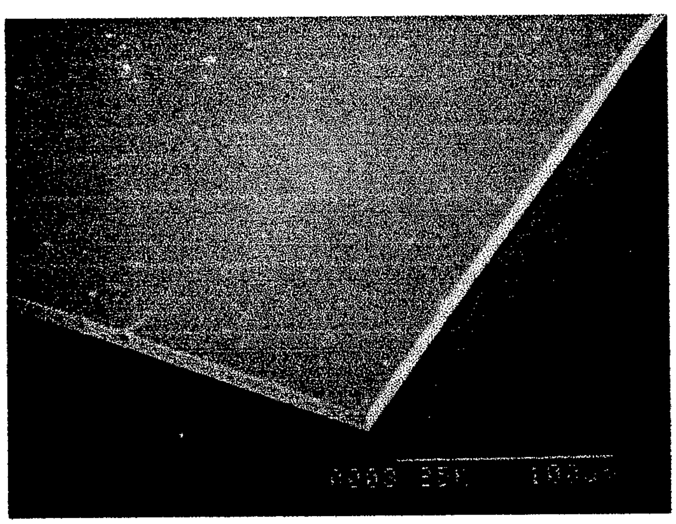

Fig. 2. Single-crystal KTO film obtained by crystal ion slicing

Figure 2 shows a fully detached KTaO3 film. While the film's surface is smooth, its undersurface exhibits regular narrow grooves, less than 0.2 μm in depth. These lines are thought to result from charged line dislocations in the sacrificial layer as a result of the ion implantation.

- *Crystallographic Studies*

We have initiated a series of crystallographic tests to probe the effect of implantation dosage on crystal structure in $KTaO_3$. Our aim is to better understand the evolution of strain leading to exfoliation at a threshold dosage of 1×10^{16} cm^2. X-ray rocking curve measurements have been obtained at three different dosages below threshold. These experiments were done in collaboration with A. Kumar and H. Bakhru at SUNY, Albany. The plots show a pronounced shift in peak position in the implanted region, from $2\theta = 22.4°$ at 5×10^{15} cm^{-2} dosage. This corresponds to a strain of $\Delta a =$ 0.018A in the lattice parameter a at the implantation layer. Rutherford back scattering (RBS) measurements are also planned in these samples.

- *Measurement of the Free-Standing $KTaO_3$ Films*

It is important to study the dielectric properties of single-crystal thin ferroelectric films, in order to determine whether they perform as bulk material, or whether deviations are brought about by purely geometrical factors. This is an issue central to the goals of the FAME program. In particular, are these films highly tunable, and are the values of dielectric constant and loss tangent comparable to that of bulk material? To answer these questions, we have started a study of the electrical properties in crystal ion sliced $KTaO_3$ films in collaboration with R. Guo, A. Bhalla and L.E. Cross of Penn State University. Capacitance measurements have been done initially on films with electrodes placed on top and bottom surfaces using conductive epoxy. Low-temperature data was obtained showing the expected Curie-Weiss behavior, with a Curie point near 20K as in single-crystal bulk material. A secondary peak, observable near 60K in some films shown in Fig. 3(a) has been tentatively identified with the presence of strain leading to weak ferroelectic behavior. Figure 3(b) shows the temperature dependence of the capacitance and loss tangent in these films. Notice that a low value of 0.006 is found for the loss tangent at low temperature. Further tests are underway, including prior annealing to eliminate residual implantation strain, which should reduce the loss even further. Presently we are preparing the deposition of Cr/Au electrodes to improve electrical contact. This is important to get an accurate reading of the absolute value in the dielectric constant and to eliminate spurious excess losses due to contact resistance.

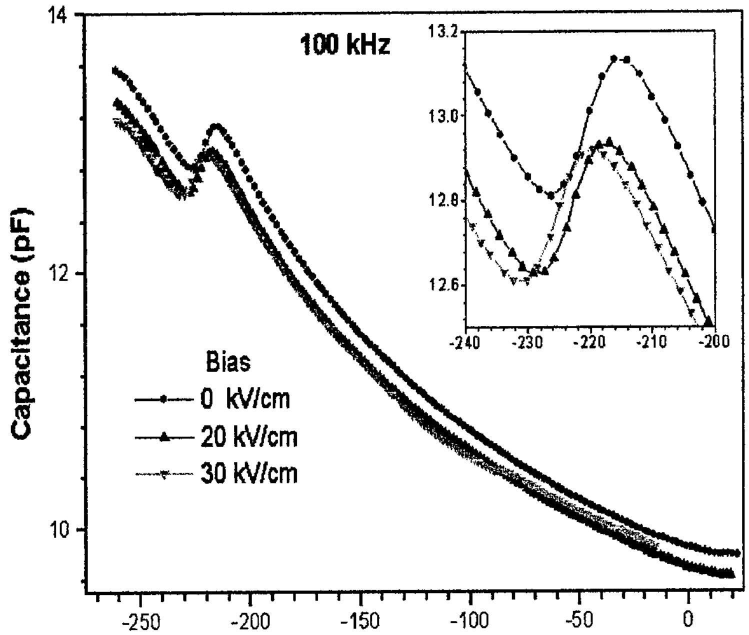

Fig. 3 (a) Capacitance versus temperature in a KTO CIS film showing ferroelectric signature

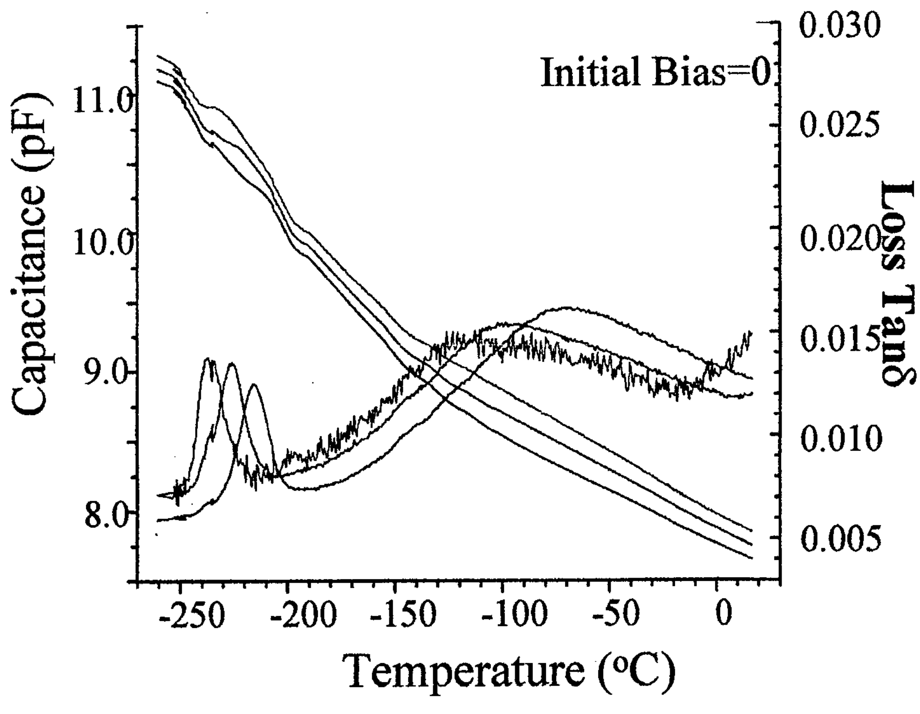

Fig.3 (b) Capacitance and Loss Tangent of KTO

b) Strontium Titanate

- *Etch Selectivity and Crystal Orientation*

(110) crystals were implanted with He^+ at 3.8 MeV, 5 x 10^{16} cm^{-2} and 1 x 10^{17} cm^{-2}. An undercut etch rate of 33μm/h was observed at the lower dosage and 65μm/h for 1 x 10^{17} cm^{-2} along the (110) direction. A lower etch rate was measured for (001) indicating crystallographic dependence to the etch selectivity. Some implantation induced cleavage occurred during the etching. Annealing studies are planned.

- *Technology of Processing Large-Area Films*

The formation of large-area films of potassium tantalate, strontium titanate and barium titanate is currently being explored using anodic bonding and palladium bonding to form handle wafers. Bonding is extremely important since it provides a rigid support to the films during detachment, thus allowing the fabrication of large area films. Anodic (KTO to glass) and palladium (KTO to Si and GaAs) bonding have already been successfully tested in KTO. Anodic bonding has also been tested for STO on glass. The bonding techniques may enable fabrication of films of materials otherwise too fragile to obtain large-area sliced samples.

c) Tunable Free-standing YIG Films

We have also fabricated and characterized narrow-FMR-linewidth single YIG films in collaboration with F. Rachford of NRL. The purpose of these experiments is to produce single-crystal ferrite films for use as integrated magnetically tunable low loss filters. Post-liftoff annealing was used successfully to obtain narrow linewidths (0.7G) comparable to that of the original LPR grown material (0,6G).

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