First Growth and Characterization of $KTaO_3$ Thin Films Using Molecular-Beam Epitaxy

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In this project, for the first time, oxide molecular-beam epitaxy (MBE) is employed to grow $KTaO_3$ (KTO) thin films. Early growths were conducted using (100) $SrTiO_3$ (STO) substrates in an attempt to fine-tune growth parameters. Furthermore, both a sub-oxide source of TaO_2 heated via furnaces and a Ta source heated via electron beam were used and their respective films were analyzed and compared. In-situ monitoring via reflection high-energy electron diffraction (RHEED), as well as post-growth characterization through atomic force microscopy (AFM) and x-ray diffraction (XRD), allowed for surface and crystal analysis throughout the project. Films from both sub-oxide and e-beam heated Ta sources displayed similar crystalline quality, however, a higher concentration of oxide impurities was found on sub-oxide grown KTO surfaces. After successful growth of KTO was achieved, rare-earth scandate (110) substrates $GdScO_3$ (GSO) and $DyScO_3$ (DSO) were used as their "cube-on-pseudocube" interface with KTO would induce a theoretical 0.55% and 0.93% compressive strain, respectively. Through reciprocal space mapping (RSM), GSO substrates displayed commensurate strain on KTO films, whereas DSO substrates only displayed partial strain. Overall, the growth of KTO using MBE allowed for high crystalline quality, pointing towards a bright future for KTO thin-film synthesis and ferroelectric KTO analysis.

Introduction

ABO_3-type perovskites have garnered attention in recent years as their integration into electronic devices has lent novel functionalities and performance enhancement [1]. $KTaO_3$ (KTO) in particular has been theorized to create interfaces that can offer several spin-optoelectronic properties. A study on $SrTiO_3$ (STO), a similar cubic perovskite, has shown success in using epitaxial strain to achieve a room temperature ferroelectric to paraelectric transition [2]. Furthermore, recent density functional calculations have predicted ferroelectric tuning of KTO by similar methods. Despite this promising news, success in KTO thin film synthesis has been particularly dire due to the non-stoichiometry of highly volatile K-atoms and non-volatile Ta-atoms [1].

In this study, oxide molecular-beam epitaxy is used to grow KTO for the first time as adsorption-controlled growth can be used to promote film growth – K-atoms flood the chamber, allowing for a Ta flux to set a KTO growth rate. Oxide MBE offers high oxidation, enhanced thin-film crystal quality, independent growth parameters, and interfacial control. Using oxide MBE to fine-tune KTO film growth methods and looking into strain in KTO lie at the forefront of this study.

Methods

Due to the novelty of MBE-grown KTO, previous literature regarding the MBE synthesis of $LiTaO_3$ (LTO) and other perovskite structures was referenced to lay the groundwork for growth parameters — notably, a ballpark flux ratio between the alkali source and Ta source [3]. For beginning growths, using STO (100) substrates, changes in source temperatures and substrate temperatures (T_{sub}) were made and monitored through x-ray diffraction (XRD) and x-ray reflectivity (XRR) to streamline consistent KTO synthesis and film thickness. The tuning of T_{sub} was particularly important as a balance between volatile K-atoms sticking to the film and crystallization occurring was needed to promote growth.

After initial calibration procedures, films made through the e-beam heating of a purely Ta source and a source furnace heating of a sub-oxide TaO_2 were compared. This was done through XRD techniques such as 2θ scans, rocking curves, and reciprocal space mapping (RSM) for analysis of interfacial and crystalline quality as well as atomic-force microscopy for surface morphology insight.

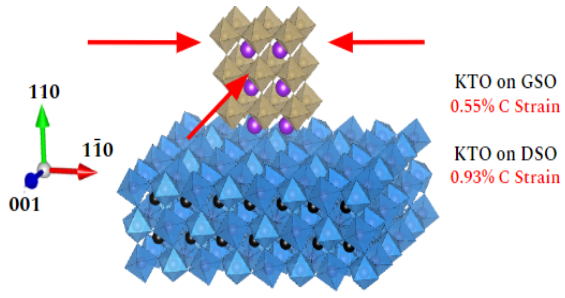

Figure 1: Interface of KTO (cubic lattice constant of 3.99Å) on GSO and DSO (110) substrates and theoretical compressive strain with pseudocubic lattice constants of 3.96Å and 3.94Å, respectively.

A final pillar for this study involves compressive epitaxial strain using rare-earth scandate (110) crystal substrates that create "cube-on-pseudocube" interfaces (Fig. 1) with KTO: $GdScO_3$ (GSO) and $DyScO_3$ (DSO). The KTO thin films grown onto these rare-earth scandates were measured through 2θ scans and RSM such that their crystalline quality and the extent to which compressive strain occurred could be assessed.

Results/Discussion

During the growth calibration process on (100) STO, source temperatures corresponding to a K:Ta flux ratio of around 10:1 and a T_{sub} range of 600℃-625℃ were found most successful, generally agreeing with previous literature on LTO [3].

Based on the intensity of (100) KTO peaks and fringe character, 10.5nm KTO films derived from both a sub-oxide TaO_2 source and an e-beam Ta source yielded comparable crystallinity — with the sub-oxide films edging by just a small margin (Fig. 2a). This was confirmed by extremely similar rocking curves with full width at half maximum (FWHM) values of 0.00940° and 0.00762°, respectively (Fig. 2b).

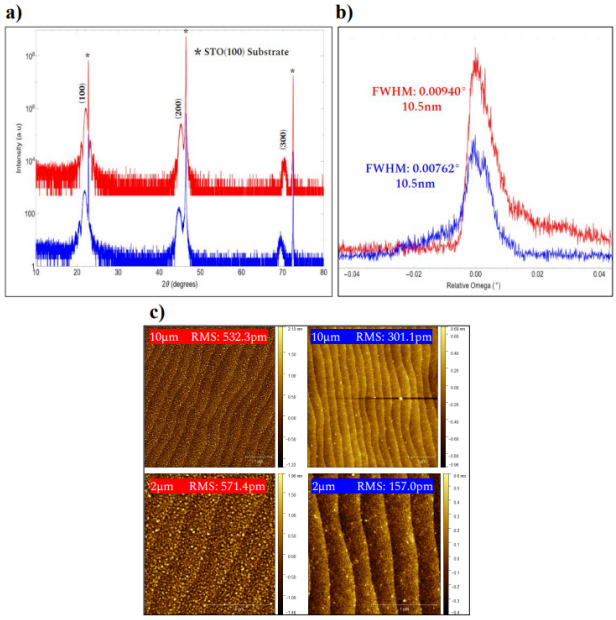

Figure 2: Crystalline and surface comparisons of furnace-heated TaO_2 source (red) and e-beam-heated Ta source KTO films (blue). (a) 2θ scans (logarithmic scale) (b) ω scan rocking curves (linear scale). (c) 10μm and 2μm AFM images and RMS values.

Although crystalline character posed no strong discrepancy in film quality, an image of each growing method's respective KTO surface aided in the comparison. 10μm AFM scans revealed high concentration of impurities on the sub-oxide films compared to e-beam films – a phenomenon that was further illustrated with 2μm scans (Fig. 2c). Previous literature suggests that these impurities are KO agglomerates that formed due to the increased introduction of O_2 into the system with sub-oxide species [1].

Transitioning from the (100) STO substrates to (110) rare-earth scandates, the crystalline quality of the KTO films excelled, demonstrating high intensity (100) peaks and numerous thickness fringes (Fig. 3).

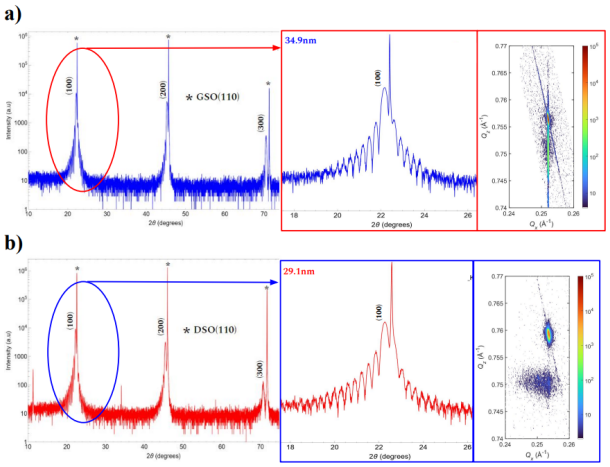

Figure 3: Broad 2θ scans, fine 2θ scans, and RSM scans (logarithmic scale). (a) KTO on GSO substrate. (b) KTO on DSO substrate.

In terms of epitaxial strain, (100) 34.9nm thick KTO films demonstrated full 0.55% compressive strain on GSO substrates as confirmed by perfect RSM Q_x alignment (Fig. 3a). In contrast, RSM scans suggest KTO films on DSO had only partial strain (Fig. 3b). This may be explained by the 29.1nm film thickness lying outside of a strainable range for a 0.93% lattice mismatch.

Conclusions/Future Work

This study has shown a successful growth of KTO using MBE, comparable crystallinity and differing surface character with e-beam and sub-oxide Ta heating methods, as well as full strain with (110) GSO substrates and partial strain with (110) DSO substrates. Overall, successful growths of KTO using MBE yielded high crystalline quality, pointing towards a bright future for KTO thin-film synthesis.

For future work, additional RSM analyses must be made with thinner films to gain further knowledge regarding compressive strain behavior and limitations. Additionally, the ferroelectric behavior of KTO thin films made through MBE should be tested to point toward the usability/application of the material.

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References

[1] Gupta, Anshu, et al. "$KTaO_3$—the New Kid on the Spintronics Block." Advanced Materials, vol. 34, no. 9, 2022, p. 2106481., doi.org/10.1002/adma.202106481.
[2] Haeni, J. H., et al.. "Room-Temperature Ferroelectricity in Strained $SrTiO_3$." ChemInform, vol. 35, no. 42, 2004, doi.org/10.1002/chin.200442012.
[3] Sitar, Z., Gitmans, F., Liu, W. et al. Homo and Heteroepitaxial Growth of $LiTaO_3$ and $LiNbO_3$ by MBE. MRS Online Proceedings Library 401, 255–260, 1995. doi.org/10.1557/PROC-401-255