Synthesis of Semiconducting $KTaO_3$ Thin films

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Abstract

In this study, the synthesis and semiconducting properties of cation and defect-doped $KTaO_3$ film is reported. $KTaO_3$ is an important material for optoelectronic and tunable microwave applications. It is an incipient ferroelectric with a cubic structure that becomes ferroelectric when doped with Nb. While numerous studies have investigated the thin-film growth of semiconducting perovskites, little is reported about semiconducting $KTaO_3$ thin films. In this work, the films were grown on (001) MgO single crystal substrates using pulsed-laser deposition. Semiconducting behavior is achieved by inducing oxygen vacancies in the $KTaO_3$ lattice via growth in a hydrogen atmosphere. The resistivity of semiconducting $KTaO_3$:Ca films was as low as 10cm, and n-type semiconducting behavior was indicated. Hall mobility and carrier concentration were 0.27 cm^2/Vs and 3.21018cm^{-3}, respectively. Crystallinity and microstructure of the $KTaO_3$:Ca films were examined using X-ray diffraction and field-emission scanning microscopy.

I. Introduction

Perovskites represent an important class of oxide materials, exhibiting many interesting properties, including piezoelectric, pyroelectric, ferroelectric, and electro-optic[1]. Many of these materials can be doped with charge carriers to yield semiconducting behavior as well. At elevated temperatures, semiconducting perovskites are useful in gas sensor and fuel cell applications [2-3]. Recently, both metallic and semiconducting perovskites have been explored as conducting oxide electrodes in ferroelectric memory devices as well as a channel material in novel electric field-effect device structures [4-5]. Among the perovskite materials, $KTaO_3$ has several properties that make it attractive for study as a semiconducting thin film material. The insulating $KTaO_3$ system has been investigated for use in optical waveguides and tunable microwave applications. $KTaO_3$ is an incipient ferroelectric material with a cubic perovskite structure (a=3.9885 A) and formal ionic charges of K^+, Ta_5^+, and O_2 [6]. The dielectric constant of $KTaO_3$ is 4500 at 4.2K (200kHz) and 243 at 25°C (200kHz). In comparison to other perovskite materials, such as the titanantes or zirconates, achieving semiconducting behavior in $KTaO_3$ is relatively difficult. This is due, in large part, to the strong tendency of Ta to assume the +5 oxidation state. Nevertheless, n-type semiconducting behavior has been reported in bulk material either by cation doping or through the introduction of O vacancies in reduced conditions. One candidate donor dopant is Ca_2^+, as substitution on the K^+ site should yield electron doping. While pure $KTaO_3$ bulk crystals exhibit a high resistivity due to the large bandgap,

reduction of the crystal to $KTaO_3$-x can result in a resistivity of 10-1 cm, a Hall mobility as high as 30 cm^2/Vs at room temperature and 2.3 x 104 cm^2/ Vs at 4.2K, and a carrier concentration of 1017 1019 cm^{-3} 101,10. The bandgap of $KTaO_3$ is 3.8 eV. From electron tunneling measurements, the density of states effective mass was estimated to be 0.5-0.7 me, which is remarkably low for a semiconducting perovskite oxide.

II. Experimental Methods

Given these attractive semiconducting properties in bulk materials, it would be interesting to investigate the synthesis of semiconducting $KTaO_3$ thin films for potential semiconducting oxide applications. Numerous semiconducting perovskite materials have been grown as thin films, including cation-doped $BaTiO_3$ and $SrTiO_3$. However, the synthesis of semiconducting $KTaO_3$ films has not been reported. In this paper, we examine the growth of semiconducting $KTaO_3$ thin films using pulsed-laser deposition. Single crystal MgO (100) was used as the substrate material. Prior to deposition, the MgO substrates were ultrasonically cleaned with trichloroethylene, acetone, and methanol, followed by compressed N_2 drying. For the growth of both undoped and 1 at. % Ca doped $KTaO_3$ films, segmented laser ablation targets were prepared. In the growth of $KTaO_3$ films, potassium deficiency is a significant issue due to the high vapor pressure of potassium at the deposition temperature range of 650 -750°C. In order to compensate for potassium loss, a segmented target, consisting of 50% $KTaO_3$ and 50% KNO_3, was used. Schematic diagram of the segmented $KTaO_3$/KNO_3 target was shown in Figure 1. Base pressure of the deposition chamber was 4.5 x 10^{-6} Torr. A KrF (248nm) laser was used at a frequency of 5Hz and energy density of 5J/cm2. Distance between target and substrate was ~6cm. Prior to growth, the laser target was cleaned in situ by preablating with approximately 2000 shots. Film thickness was 200 nm with a growth rate of 0.11 Å/pulse. The deposited films were characterized using X-ray diffraction, atomic force microscopy, field-emission scanning electron microscopy, and Hall measurement.

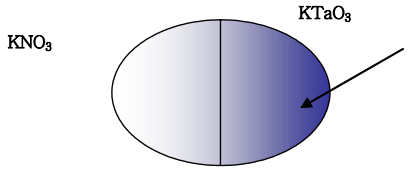

Figure 1. Schematic diagram of the segmented $KTaO_3$ /KNO_3 target

III. Results and Discussion

Initial efforts focused on the growth of epitaxial Ca doped $KTaO_3$ in an oxygen background ambient. Both crystallinity and transport were studied as a function of deposition temperature and oxygen pressure.

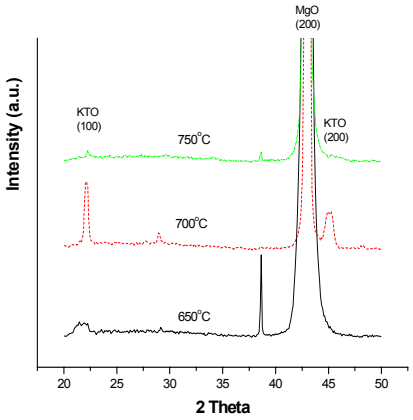

Figure 2. X-ray diffraction results of $KTaO_3$:Ca film grown on MgO (100) substrate as a function of deposition temperature

Figure 2 shows the X-ray diffraction results for $KTaO_3$:Ca films grown in 10^{-4} Torr of oxygen at various deposition temperatures. For the 50/50 Ca doped-$KTaO_3$/KNO_3 segmented target configuration, a deposition temperature of 700°C resulted in a high degree of crystallinity as determined by X-ray diffraction. The lack of good crystallinity for $KTaO_3$:Ca films deposited at 750°C may reflect potassium deficiency due to the high vapor pressure of potassium at this deposition temperature. Despite the inclusion of Ca as a donor impurity, the films deposited at 10^{-4} Torr were insulating and transparent with no measurable conductance.

In order to explore the doping behavior further, Ca doped films were grown at 700°C in an oxygen ambient ranging from vacuum (5 x 10^{-6} Torr) to 10^{-1} Torr of oxygen. Figure 3 shows the X-ray diffraction results for $KTaO_3$:Ca films grown on MgO substrate as a function of oxygen pressure at a deposition temperature of 700°C. Over this entire pressure range, the epitaxial growth of Ca-doped $KTaO_3$ was achieved. Note that the strongest intensity (0 0 l) $KTaO_3$ peaks were observed for an oxygen pressure of 10^{-3} Torr. However, for the entire pressure range, the Ca-doped $KTaO_3$ films were insulating. This result differs from that observed for other perovskites, such as the titanates, in which semiconducting behavior is observed for growth in vacuum.

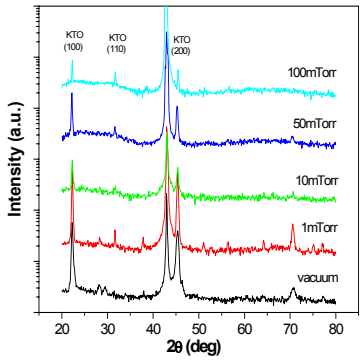

Figure 3. X-ray diffraction results of $KTaO_3$:Ca film grown on MgO (100) substrate as a function of different oxygen pressure at deposition temperature of 700°C.

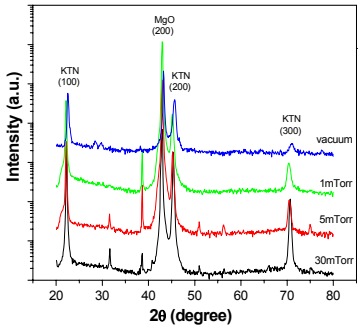

Figure 4. X-ray diffraction results of Ca doped $KTaO_3$ semiconducting film grown on MgO (100) substrate at deposition temperature of 700°C in reduced pressure of 96% Ar/4% H_2

In order to successfully reduce the Ca-doped $KTaO_3$ films and achieve semiconducting behavior, the use of hydrogen as a reactive background gas was implemented. It is well known that many oxides can be made oxygen deficient via hydrogen reduction. It is also true that hydrogen can serve as a shallow dopant in some oxides. Figure 4 shows the X-ray diffraction results of Ca doped $KTaO_3$ films on MgO (100) grown at a substrate temperature of 700°C at various pressures of 96% Ar/4% H_2. For Ar/H_2 pressure up to 30mTorr, epitaxial Ca-doped $KTaO_3$ films were obtained.

Four-circle X-ray diffraction was used to investigate in-plane alignment of the film. Figure 5(a) shows the -scan results for the $KTaO_3$:Ca film on MgO. The in-plane orientation of the film is evident via a -scan through the $KTaO_3$:Ca (110). The film is in-plane aligned with a cube on cube epitaxial relationship to the MgO substrate. The in-plane mosaic spread was 3.7o. Figure 5(b) shows the out-of-plane rocking curve of $KTaO_3$:Ca (200) peak. The full width at half maximum (FWHM) of $KTaO_3$:Ca was 2.3o. the lattice constant of the Ca-doped $KTaO_3$ was 3.9885 Å. Figure 6 shows a FE-SEM image of the surface morphology of semiconducting $KTaO_3$:Ca film on (100) MgO substrate deposited at 700°C for 1hr in 30 mTorr of 96% Ar/4% H2. The grain size is approximately 100-150nm.

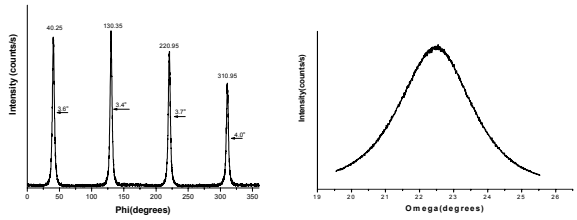

Figure 5. X-ray diffraction Phi scan and rocking curve data.

Semiconducting properties of $KTaO_3$:Ca film were measured for films grown at 30mTorr of 96% Ar/ 4% H2 atmosphere. $KTaO_3$ films grown under this condition were dark blue. This dark blue color is considered to be due to formation of impurity energy level inside the band gap of $KTaO_3$. The room temperature properties of the $KTaO_3$:Ca film

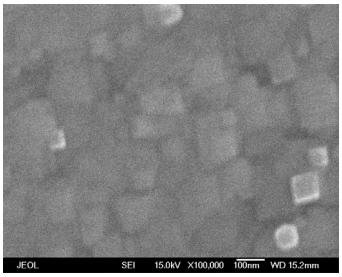

Figure 6. FE-SEM images of surface morphology of semiconducting KTO_3:Ca film on (100) MgO substrate, which was deposited at 700C for 1hr with 30mTorr of 96%Ar/4% H2 mixture gas using pulsed laser deposition

were investigated via Hall measurement in a Van der Pauw configuration. These measurements were performed using a 8 kG field and a measurement current of 1 mA. Also, temperature dependence of resistivity of Ca-doped $KTaO_3$ thin film on (001) MgO was seen in Figure 7. The resistivity of Ca-doped $KTaO_3$ film decreased as temperature increased from 180K to 300K. This behavior was consistent with semiconducting behavior. The film resistivity of the Ca-doped $KTaO_3$ film was 10.4 cm. conductivity was n-type with a Hall mobility of 0.27 cm2/Vs and a carrier density of 3 x 1018 cm^{-3}. Note that semiconducting behavior was also observed for $KTaO_3$ (no Ca) films grown in 30 mTorr Ar/H_2 at 700°C. This suggests that oxygen deficiency is responsible for n-type behavior in both materials.

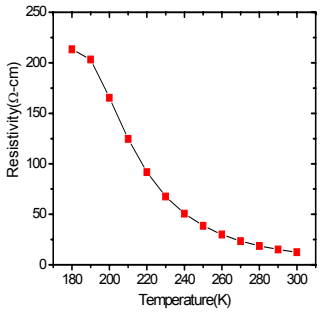

Figure 7. Resistivity of Ca doped $KTaO_3$ thin film as a function of temperature.

Ⅳ. Conclusion

In this study, conditions for growth of insulating and semiconducting $KTaO_3$:Ca film were investigated. Unlike other perovskites, such as the titanates, semiconducting behavior is not observed for growth in vacuum. This resistance to forming free carriers reflects the tendency for K and Ta to assume a specific valence state. The difficulty in varying the valence state of the cation greatly retards the ability to make the films semiconducting. Nevertheless, epitaxially grown $KTaO_3$:Ca films grown in 30 mTorr partial pressure of 96% Ar/ 4% H2 atmosphere at 700°C were semiconducting. The resistivity of $KTaO_3$:Ca film was 10.4 cm at room temperature and showed n-type semiconducting behavior.

References

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