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Stoichiometry control in molecular beam epitaxy of BaSnO₃

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La-doped BaSnO₃ films were grown on DyScO₃ substrates by molecular beam epitaxy using La, Ba, and SnO₂ sources with and without additional oxidant, respectively. Lattice parameter measurements as a function of growth conditions show a reduced lattice parameter that is likely due to substitution of Sn²⁺ on the Ba site. The propensity for the antisite defect is discussed as being due to the combination of oxygen-poor, Sn-rich conditions and the dual valence of Sn. Although electron mobilities are highest for films with reduced lattice parameters, antisite defects will pose an upper limit to thin film mobility. Less Sn-rich conditions lead to the formation of another defect that causes a lattice expansion. The combined effects of these defects on the lattice parameter can compensate each other and cause the appearance of a stoichiometric lattice parameter for nonstoichiometric films with poor electrical behavior.

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I. INTRODUCTION

The cubic perovskite BaSnO₃ has gained significant interest for applications as a transparent conducting oxide and as a candidate material for next-generation high-frequency and high-power electronics applications [1–6]. Its promise for these applications stems from the combination of a relatively wide bandgap (~3 eV) [1–3,7–9], low effective conduction band mass [10], high electron mobility at high carrier densities [1–3], and epitaxial integration with other perovskite oxides [5]. La-doped BaSnO₃ single crystals exhibit room temperature electron mobilities as high as 320 cm² V⁻¹ s⁻¹ at a doping density of 8 × 10¹⁸ cm⁻³, a record among perovskite oxides [1,2].

Epitaxial thin films are needed for devices, but have yet to reach single-crystal mobilities. Low carrier densities have also been difficult to achieve, a clear indication of the presence of compensating defects. To-date, the highest mobility films are grown via molecular beam epitaxy (MBE) using a SnO₂ effusion cell as Sn (and oxygen) source. These films show Hall mobility values around 150 cm² V⁻¹ s⁻¹ to 180 cm² V⁻¹ s⁻¹ [11,12]. The use of the SnO₂ source proved crucial for high-mobility films [11]. It addresses a key challenge in the MBE of stannates, namely that Sn reacts with co-supplied oxygen to form volatile SnO, leaving unoxidized Sn behind [13,14]. The difficulty in oxidizing Sn in MBE conditions is the likely culprit for the low mobilities of BaSnO₃ films grown using a metallic Sn source [15] or metal-organic Sn precursor [16,17].

Ultimately, one of the most significant hindrances to high mobilities will be the high density of threading dislocations that are typical for epitaxial films grown on highly mismatched substrates. The relatively large lattice constant of BaSnO₃ (~4.117 Å–4.115 Å [8,18,19]) results in a significant lattice mismatch with commercially available perovskite substrates such as SrTiO₃ (~5.1%) and DyScO₃ (~4.2%). Nevertheless, a large variation in mobility values is observed even for films grown on identical substrates under similar conditions. Furthermore, mobilities on different substrates do not scale with lattice mismatch, even though the threading dislocation densities roughly do [11,12]. These findings indicate that BaSnO₃ films contain high concentrations of point defects, most likely arising from nonstoichiometry, that negatively impact thin film mobilities. While adsorption-controlled growth [12,17] ensures the formation of the BaSnO₃ perovskite phase, there is as yet no evidence that these films are perfectly stoichiometric.

The dual valence state of Sn is one of the main challenges in MBE of stoichiometric BaSnO₃. While Sn⁴⁺ is favored in oxidizing conditions, reducing conditions promote Sn²⁺ [20]. As a result, II-IV perovskites such as BaSnO₃, where the cations take on formal charges A²⁺B⁴⁺O₃, may allow Sn to occupy both the A and B sites [21]. Consistent with this possibility, density functional theory (DFT) calculations show that the antisite defect, SnBa, is a low-energy defect in BaSnO₃ in oxygen-poor conditions [22].

The goal of this study was to develop an improved understanding of the challenges in growing stoichiometric BaSnO₃ films in MBE from a SnO₂ source. To this end, we grew films both with and without the presence of an additional oxidant. The fact that perovskite BaSnO₃ can be grown without any additional oxygen shows that the SnO₂ source supplies not only Sn but is also the main source of oxygen in BaSnO₃ MBE. Lattice constants of almost all films were lower than the stoichiometric value, and it is posited that a significant amount of SnBa antisite defects are the cause. Shifts in the growth parameters when oxidants co-supplied provide additional insights into the challenges in stoichiometry control.

II. EXPERIMENTAL

La-doped BaSnO₃ films were grown by MBE on (110) DyScO₃ substrates. High-purity Ba, SnO₂, and La-dopant were co-evaporated from separate effusion cells, as described...
A intentionally doped (UID) BaSnO$_3$ buffer layer was grown first, Ba-limited for all films (Fig. 1). For each sample, an unin-

10

Son different SnO$_2$

sources. For each condition, a series of films were grown at

constant and varying the Ba flux. This avoids changing the

layer in this regime is negligible.

High mobility films and that the precise thickness of the buffer

half maxima (FWHM) values of 0$^\circ$14604-2

a Ba-rich phase, possibly Ruddlesden-Popper Ba$_2$SnO$_4$ [28].

This peak may belong to

wide-angle scans. This peak may belong to

The La flux was adjusted to keep the doping density

within the $\sim$1 $\times$ 10$^{10}$$^{-3} \times$ 10$^{20}$ cm$^{-3}$ range, in which mo-

bility is relatively independent of the carrier density. It is

important to note that the mobile carrier density is af-

fected by the growth parameters that were varied in these

experiments, not just the La flux. These include cation flux

ratios and oxygen supply, which determine dopant activation

and the concentration of compensating defects [22,26], and

the growth rate. In addition, effects from sample nonuniform-

ity as well as variability in the electrical properties between

samples grown under nominal identical growth conditions is

a general issue for state-of-the-art BaSnO$_3$ films, as is also

seen in the literature [12]. For this reason, differences in

mobility values of a few 10’s of cm$^2$ V$^{-1}$ s$^{-1}$ are not taken as

significant for the purpose of this growth study, which focuses

on systematic trends. We only use relative robust indicators

in the electrical properties, such as insulating behavior and

large deviations from high mobility—which we will define as

$\mu > 120$ cm$^2$ V$^{-1}$ s$^{-1}$—within this doping range as being

indicative of the introduction of defects.

Reflection high energy electron diffraction (RHEED) was

used to monitor the growth. Structural characterization was

performed via high resolution x-ray diffraction (XRD): out-

of-plane lattice parameters ($a_{\perp}$) were measured in a triple-

axis configuration and film perfection was assessed using

open detector scans. Straight-beam alignments were per-

formed prior to every measurement to eliminate any residual

instrument offset. All films were found to be relaxed (see

Supplemental Material [27]). Film thicknesses were calcu-

lated from x-ray reflectivity (XRR) data. For films with poor

XRR due to surface morphology (see Ref. [27] for atomic

force microscopy of the film surfaces), the thickness was

estimated from the Ba flux, as the growth rate is Ba-limited

(Fig. 1). For electrical measurements, Ti/Au ohmic contacts

were deposited in van der Pauw geometry via electron beam

evaporation. Sheet carrier densities and Hall mobilities were
determined at room temperature using a LakeShore Hall Mea-
surement System. To determine the reliability of the van der

Pauw measurements, smaller Hall bar structures were fabrica-
cated from selected samples, which provide a measure of the

variability in the mobility data due to film nonuniformity [27].

III. RESULTS

Figure 2 shows XRD data of films grown with different

SnO$_2$/Ba flux ratios, without any co-supplied oxidant, with

molecular oxygen, and with oxygen RF-plasma, respectively.

All films exhibit the 002 BaSnO$_3$ reflection, indicating suc-

cessful epitaxial growth of the BaSnO$_3$ perovskite phase

for all growth conditions. The no-oxygen sample grown at

SnO$_2$/Ba = 15 also exhibits a wide hump on the low-angle

side of the 002 BaSnO$_3$ peak, which can be seen more clearly

in the wide-angle scans (not shown). This peak may belong to

a Ba-rich phase, possibly Ruddlesden-Popper Ba$_2$SnO$_3$ [28].

Films grown with oxygen do not exhibit Ba-rich peaks in

XRD. Some films also exhibit weak SnO$_2$ peaks in wide-angle

scans.

X-ray rocking curves are shown in Figs. 2(d)–2(f). Their

widths represent the crystal surface quality and crystal perfec-
tion of the films’ interiors. For example, for the films grown

without additional oxygen [Fig. 2(d)], the narrow curves are

also those that exhibit thickness oscillations in Fig. 2(a),

indicating smooth surfaces. These films are grown with the

highest SnO$_2$/Ba flux ratios and all have similar full width at

half maxima (FWHM) values of 0.097°, 0.068°, and 0.099°.
FIG. 2. [(a)–(c)] On-axis 2θ-ω scans around the BaSnO$_3$ 002 reflection for films grown with (a) no additional oxygen, (b) molecular oxygen, and (c) oxygen plasma. [(d)–(f)] Rocking curves around the BaSnO$_3$ 002 reflection for films grown with (a) no additional oxygen, (b) molecular oxygen, and (c) oxygen plasma. The triangles mark the 002 BaSnO$_3$ film reflections and the asterisks mark the 220 DyScO$_3$ reflections.

They differ, however, in the width of the lower portion of the rocking curve, which typically contains the diffuse scattering from point defects. The width the rocking curve wing correlates with the measured mobility, indicating that the point defects giving rise the intensity in this portion of the rocking curve are also the ones that affect the mobility.

Samples grown with additional oxidant show a less systematic relationship between carrier mobility and rocking curve widths. Oxygen tends to reduce the mobility of arriving adatoms species on the growing films surface [29]. This negatively affects crystalline perfection and surface quality and both cause broadening of the rocking curves. In addition, for some samples, the 220 peak from the DyScO$_3$ substrate displays a shoulder that is reflected in an asymmetry in the film rocking curve, such as for the 35.4 ratio film [Figs. 2(c) and 2(f)].

Figure 3 compares the measured out-of-plane lattice parameters ($a_{op}$) and Hall mobilities ($\mu$). Note that samples that were too resistive to reliably measure the Hall mobility are displayed as having $\mu = 0$ cm$^2$ V$^{-1}$ s$^{-1}$. Three important observations can be made: (i) most measured $a_{op}$ are smaller than the reported stoichiometric value for BaSnO$_3$ (indicated by the dotted line), (ii) the mobilities are highest near the minimum in $a_{op}$, rather than near the apparent stoichiometric value, and (iii) addition of oxygen shifts the growth conditions to achieve films that exhibit the highest mobility to lower SnO$_2$/Ba ratios, compared with films grown with no additional oxygen. In addition, slightly higher mobilities are achieved in the films grown with extra oxygen. We note that the small $a_{op}$ is not caused by residual epitaxial coherency strains, as compressively strained films would lead to an expanded $a_{op}$.

IV. DISCUSSION

A main result is the successful growth of BaSnO$_3$ without any co-supplied oxidant. This shows that oxygen-containing species needed to form the BaSnO$_3$ perovskite phase are mainly supplied by the flux from the SnO$_2$ cell. The main evaporating species from an SnO$_2$ source in a vacuum environment is SnO [23–25,30]. Mass spectrometric studies indicate that the flux from SnO$_2$ at 1420 K contains approximately 77% SnO, 21% O$_2$, 1.5% Sn$_2$O$_2$, with the rest belonging to SnO$_2$ and other molecules [30]. The small amount of O$_2$ in
FIG. 3. Out-of-plane lattice constants $a_{op}$ (orange circles, left axis) and measured Hall mobilities (blue triangles, right axis) as a function of SnO$_2$/Ba BEP ratio for films grown with (a) no additional oxygen, (b) molecular oxygen, and (c) oxygen plasma.

the flux from a SnO$_2$ cell suggests that films grown without an additional oxidant are grown in oxygen-poor conditions. If SnO is the main source of oxygen, then growth conditions are likely also Sn-rich. Sn-rich conditions are supported by the fact that growth rate remains Ba-limited for most films (Fig. 1). In the absence of a true MBE growth window or for compounds that are not true line compounds, nonstoichiometric growth conditions will induce native point defects, such as vacancies or antisite defects [31–33].

We next discuss possible defects, beginning with the films grown with no additional oxygen. The deviation of the lattice parameter from its stoichiometric value provides information about the prominent defect(s). Cation vacancies cause a lattice expansion in most perovskites and may in BaSnO$_3$ as well [16,34]. Oxygen vacancies cause virtually no variation in the lattice parameter of SrTiO$_3$ thin films [35], although there are indications that they may cause a moderate lattice expansion in BaSnO$_3$ [36]. In contrast, Sn$^{2+}$ incorporation on the Ba site may lead to a lattice contraction [17], because the Ba site is large compared to the ionic radius of Sn$^{2+}$. In general, perovskites that incorporate Sn on the A site are found to exhibit reduced lattice parameters [21,37,38]. Therefore we posit that the small $a_{op}$ are a fingerprint of SnBa formation in these films. Given oxygen-poor, Sn-rich conditions, SnBa is a likely mechanism to accommodate Sn excess in the high-mobility films. This is also consistent with DFT calculations for these conditions [22,26,39].

On the low SnO$_2$/Ba flux ratio side, some films appear to possess $a_{op}$ values that are closer to the stoichiometric values, though their poor electrical properties indicate that these films are not stoichiometric. A more likely scenario for the apparent stoichiometric $a_{op}$ is another defect, which causes a lattice expansion, compensates for the lattice contraction caused by SnBa. According to DFT [22,26], under Sn-rich conditions, Ba vacancies ($V'_{Ba}$) and SnBa are favorable. Donor dopants may under certain conditions also favor cation vacancies [40]. In contrast to SnBa, $V'_{Ba}$ are likely to cause a lattice expansion and furthermore to act as acceptors [39]. From the change in lattice parameter seen in Fig. 3(a), it is apparent that $V'_{Ba}$ are more favorable under conditions that are less Sn-rich and possibly also more oxygen poor (larger lattice parameter). As the SnO$_2$/Ba flux ratio is increased their concentration decreases, most likely by incorporation of Sn$^{2+}$ on the empty Ba sites, which causes the lattice parameter to decrease. The increase in mobility with increasing SnO$_2$/Ba flux can then be explained with SnBa filling the negatively charged $V'_{Ba}$, which should scatter more strongly by ionized impurity scattering and/or trap mobile carriers than the charge-neutral SnBa. Ultimately, however, even charge-neutral defects contribute to carrier scattering and reduce their mobilities. We note that another defect candidate causing a lattice expansion could be oxygen vacancies, $V^\circ\circ_{O}$. The high degree of La-doping should, however, suppress the formation of $V^\circ\circ_{O}$, while promoting compensating $V'_{Ba}$ [26].

This general picture is further confirmed by considering the trends in the films grown with additional oxygen. Lower-than-stoichiometric $a_{op}$ are exhibited by these films as well, pointing to the presence of SnBa defects. Therefore it appears that even in the presence of additional oxygen during growth, even in the form of an activated plasma, the conditions are still Sn-rich. The main effect of additional oxygen supplied by the molecular or plasma source is to shift the growth conditions. The extra oxygen shifts the growth conditions for high mobility films toward lower SnO$_2$/Ba ratios. This is consistent with the interpretation discussed above: the extra oxygen alleviates the need to supply a large amount of oxygen via SnO, making the conditions less Sn-rich. Thus, the only way to improve the cation stoichiometry of BaSnO$_3$ films would be achieve vastly more oxidizing conditions, which appears to be difficult to achieve within the constraints of MBE. Already, one difficulty for the films grown with additional oxygen supply is the oxidation of the Ba source material and associated Ba flux instabilities [41].
Finally, we note that based on the observed variations in carrier density ($n_{h,p}$), about $-1 - 4 \times 10^{19} \text{ cm}^{-3}$ for films grown at different cation flux ratios, the concentration of electrically active defects from non-stoichiometry is estimated to be less than 1%. This degree of nonstoichiometry is difficult to detect with most thin film physical characterization methods, while nevertheless significant in terms of the electrical properties.

V. CONCLUSIONS

To summarize, we have demonstrated that La-doped BaSnO$_3$ films can be grown by MBE using only Ba, La, and SnO$_2$ effusion sources. Even when additional oxygen is supplied, however, lattice parameter measurements indicate that film are nonstoichiometric. We have argued that the films are Sn-rich and that the origin of this twofold: SnO is a major source of the oxygen incorporated in the films and the dual valency of Sn facilitates the formation of Sn$_{\text{Ba}}$ antisite defects, which can accommodate Sn excess. Moreover, the study showed that films with an apparent stoichiometric lattice parameter are, in fact, also nonstoichiometric, most likely because the effects of two defects on the lattice parameter compensate each other. Thus, unlike materials that are much closer to line compounds and can be fully oxidized, such as SrTiO$_3$, care should be taken to make claims of an MBE growth window based on lattice parameter measurements. In addition to developing substrates that have a reduced lattice mismatch, the key to achieve BaSnO$_3$ films with higher mobilities will be more oxidizing conditions, which is challenging in MBE.

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