Thermopower modulation clarification of the intrinsic effective mass in transparent oxide semiconductor BaSnO₃

Anup V. Sanchela,¹,*, Takaki Onozato,² Bin Feng,³ Yuichi Ikuhara,³ and Hiromichi Ohta¹,†

¹Graduate School of Information Science and Technology, Hokkaido University, N14W9, Kita, Sapporo 060-0014, Japan
²Institute of Engineering Innovation, The University of Tokyo, 2-11-16 Yayoi, Bunkyo, Tokyo 113-8656, Japan

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The exact intrinsic carrier effective mass $m^*$ of a well-studied transparent oxide semiconductor BaSnO₃ is unknown because the reported $m^*$ values are scattered from 0.06$m_0$ to 3.7$m_0$. This paper identifies the intrinsic $m^*$ of BaSnO₃, $m^* = 0.40 \pm 0.01m_0$, by the thermopower modulation clarification method and determines the threshold of the degenerate/nondegenerate semiconductor. At the threshold, the thermopower values of both the La-doped BaSnO₃ and BaSnO₃ thin-film transistor structures are 240 $\mu$VK⁻¹, the bulk carrier concentration is $1.4 \times 10^{19}$ cm⁻³, and the two-dimensional sheet carrier concentration is $1.8 \times 10^{12}$ cm⁻². When the Fermi energy $E_F$ is located above the parabolic shaped conduction band bottom, the mobility is rather high. In contrast, $E_F$ below the threshold exhibits a very low carrier mobility, most likely because the tail states suppress the carrier mobility. The present results are useful to further develop BaSnO₃-based oxide electronics.

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Transparent oxide semiconductors (TOSs) with a relatively high electrical conductivity and a large band gap ($E_g > 3.1$ eV) are commonly used as transparent electrodes and channel semiconductors for thin-film transistor (TFT) driven flat panel displays (FPDs) such as liquid crystal displays (LCDs) and organic light emitting diodes (OLEDs) [1]. TOS materials include Sn-doped In₂O₃ (ITO) and InGaZnO₄-based oxides. Novel TOSs exhibiting higher carrier mobilities have been intensively explored since the TFT performance strongly depends on the carrier mobility of the channel semiconductor. In 2012, Kim et al. reported that a La-doped BaSnO₃ (space group $Pm\bar{3}m$, cubic perovskite structure, $a = 4.115$ Å, $E_g \sim 3.1$ eV) single crystal grown by the flux method exhibits a very high mobility ($\mu_{Hall} \sim 320$ cm² V⁻¹ s⁻¹) at room temperature [2,3]. This report inspired the current interest in BaSnO₃ films and BaSnO₃-based TFTs [4–9]. Since the mobility is expressed as $\mu = e\tau m^{∗−1}$, where $e$, $\tau$, and $m^{∗}$ are the electron charge, carrier relaxation time, and carrier effective mass, respectively, the high mobility of the La-doped BaSnO₃ single crystal should be due to both a small $m^{∗}$ and a large $\tau$. Generally, the $\tau$ value of epitaxial films is smaller than that of the bulk single crystal due to the fact that the carrier electrons are scattered at dislocations, which originated from the lattice mismatch ($\delta$) and at other structural defects, in addition to optical phonon scattering. The estimated misfit dislocation spacing $d$ is 7.4 nm because $\delta$ between BaSnO₃ and SrTiO₃ ($a = 3.905$ Å) is +5.3%. BaSnO₃ films grown on (001) SrTiO₃ substrates exhibit rather small mobilities ($\mu_{Hall} \sim 26$–100 cm² V⁻¹ s⁻¹) [3,7,10] compared with those grown on (001) PrScO₃ ($a = 4.026$ Å, $\delta = +2.2\%$, $d \sim 17.7$ nm) ($\mu_{Hall} \sim 150$ cm² V⁻¹ s⁻¹) [7]. On the other hand, $m^{∗}$ only depends on the electronic structure of the material. Many theoretical and experimental values of $m^{∗}$, which were mostly determined from the optical properties, have been reported (e.g., theoretical values of $\sim 0.06m_0$ [11], $\sim 0.4m_0$ [3], and $\sim 0.2m_0$ [12], and experimental values of 3.7$m_0$ [13], 0.61$m_0$ [14], $\sim 0.35m_0$ [15], $\sim 0.396m_0$ [16], 0.27 $\pm$ 0.05$m_0$ [10], 0.19 $\pm$ 0.01$m_0$ [8]). Consequently, determining the intrinsic $m^*$ value is almost impossible.

We hypothesized that the experimental values include errors since the substrate contributes to the optical spectra of the BaSnO₃ films. To overcome this difficulty, we use the thermopower $S$ modulation clarification method to determine the intrinsic $m^*$ of BaSnO₃ as $S$ clearly reflects the energy derivative of the density of states (DOS) at the Fermi energy $E_F$. This study measures the $S$ of La-doped BaSnO₃ films and BaSnO₃ with a TFT structure as functions of carrier concentration. The carrier concentration can be modulated by applying an electric field. The intrinsic $m^* = 0.4 \pm 0.01m_0$ is clarified when $E_F$ is located above the degenerate/nondegenerate threshold of BaSnO₃.

La-doped BaSnO₃ films (thickness $\sim 200$ nm) were heteroepitaxially grown on (001) SrTiO₃ single crystal substrates by pulsed laser deposition (PLD, KrF excimer laser, $\lambda = 248$ nm, 10 Hz, fluence $\sim 2$ cm⁻² pulse⁻¹) technique using dense ceramic disks of Ba₁₋ₓLaₓSnO₃ (0.001 $\leq x \leq 0.07$) as the targets. The substrate temperature and oxygen pressure during film growth were 700 °C and 10 Pa, respectively. Since the surface of the as-deposited BaSnO₃ films was composed of tiny ($\sim 50$ nm) grains, the film was annealed at 1200 °C in air to obtain atomically smooth surfaces [17]. High-resolution x-ray diffraction (Cu $K\alpha_1$, ATX-G, Rigaku) measurements revealed that the resultant films were heteroepitaxially grown on (001) SrTiO₃ substrates with a cube-on-cube epitaxial relationship (see Fig. S2 in the Supplemental Material [18]). The film thickness of the resultant films was calculated from the Pendellösung fringes, which were observed around the 002 diffraction peak of La-doped BaSnO₃. The topographic atomic force microscopy (AFM) image of the resultant films showed a stepped and terraced surface.

We then measured the electrical conductivity $\sigma$, carrier concentration $n$, and Hall mobility $\mu_{Hall}$ of the La-doped BaSnO₃ films at room temperature by the conventional dc four-probe method using an In-Ga alloy electrode with van...
der Pauw geometry. \( S \) was measured at room temperature by creating a temperature gradient \( \Delta T \) of \( \sim 4 \) K across the film using two Peltier devices (and two small thermocouples were used to monitor the actual temperatures of each end of the Ba_{1−x}La_{x}SnO_{3} films). The thermoelectromotive forces \( \Delta V \) and \( \Delta T \) were measured simultaneously. The \( S \) values were obtained from the slope of the \( \Delta V - \Delta T \) plots.

Table I summarizes the electrical properties of the La-doped BaSnO_{3} films at room temperature. \( \sigma \) rapidly increased with \( x \) in Ba_{1−x}La_{x}SnO_{3} and reached a maximum value of 6910 S \text{ cm}^{-1} \text{ in the } x = 0.05 \text{ sample. At the same time, } n \text{ and } \mu_{\text{Hall}} \text{ achieved the highest values of } 6.41 \times 10^{20} \text{ cm}^{-3} \text{ and } 67.3 \text{ cm}^{2} \text{ V}^{-1} \text{ s}^{-1}, \text{ respectively. It should be noted that the } \mu_{\text{Hall}} \text{ value increased with increasing } n, \text{ which is consistent with the data reported by Kim et al. [2]. The sign of } S \text{ was negative in all samples, which agreed with the fact that La-doped BaSnO}_{3} \text{ is an } n\text{-type semiconductor. The absolute value } |S| \text{ gradually decreased with } n. \)

To clarify the intrinsic \( m^{*} \), we plotted the relationship between \( n \) and \( S \). As outlined in Eqs. (1)–(3), the DOS effective mass \( m^{*} \) was calculated. When \( n \) exceeded \( \sim 10^{19} \text{ cm}^{-3}, \text{ } |S| \text{ monotonically decreased with increasing } n \text{ (Fig. 1). We then calculated } m^{*} \text{ using the following relation between } n \text{ and } S \text{ [19],}

\[
S = -\frac{k_{B}}{e} \left( \frac{(r + 2)F_{r+1}(\xi)}{(r + 1)F_{r}(\xi)} - \xi \right),
\]

where \( k_{B}, \xi, r, \text{ and } F_{r} \) are the Boltzmann constant, chemical potential, scattering parameter of relaxation time, and Fermi integral, respectively. \( F_{r} \) is expressed as

\[
F_{r}(\xi) = \int_{0}^{\infty} \frac{x^{r}}{1 + e^{x-\xi}} \text{dx},
\]

and \( n \) is given by

\[
n_{-} = 4\pi \left( \frac{2m^{*}k_{B}T}{h^{2}} \right)^{3/2} F_{1/2}(\xi),
\]

where \( h \) and \( T \) are Planck’s constant and the absolute temperature, respectively. We used an \( r \) value of 0.5, which indicates the carrier electrons are dominantly scattered by the optical phonon. Using Eqs. (1)–(3), we obtained the degenerate/nondegenerate threshold of \( 1.4 \times 10^{19} \text{ cm}^{-3}. \) The intrinsic effective mass was obtained as \( m^{*} = 0.40 \pm 0.01m_{0} \) when \( n \geq 1.4 \times 10^{19} \text{ cm}^{-3}, \text{ though the } S-n \text{ plots at } n < 1.4 \times 10^{19} \text{ cm}^{-3} \text{ did not obey the } m^{*} = 0.4m_{0} \text{ line. The threshold of the degenerate/nondegenerate semiconductor appeared around } n = 1.4 \times 10^{19} \text{ cm}^{-3}. \) As shown in the inset, when \( n \) exceeded the threshold (≡ degenerate semiconductor, Fig. S1 [18]), \( E_{F} \) was located inside of the parabolic shaped conduction band. On the other hand, when \( n \) was less than the threshold (≡ nondegenerate semiconductor), \( E_{F} \) was located at the nonparabolic shaped extra DOS. At the threshold, the \( S \) value should be \( 240 \mu \text{V K}^{-1}. \)

To further clarify the intrinsic \( m^{*} \) of BaSnO_{3}, we measured the electric field modulated \( S \) of BaSnO_{3}-based TFT (Fig. 2). First, a 22-nm-thick undoped BaSnO_{3} film was prepared by PLD, as described above. The surface exhibited steps (~0.4 nm) and terraces [Fig. 2(d)]. Then, 30-nm-thick Ti films were deposited with a stencil mask by electron beam (EB; base pressure \( \sim 10^{-4} \text{, no substrate heating} \) evaporation, which was used as the source and drain electrodes. The channel length \( L \) and the channel width \( W \) of the TFT were 800 and 400 \text{um}, respectively. Next, an \( \sim 300\text{-nm-thick amorphous 12CaO \cdot 7Al}_{2}O_{3} \text{ (a-C12A7, } \varepsilon_{r} = 12) \text{ [20] film, which was used as a gate insulator, was deposited through a stencil mask by PLD. Finally, an } \sim 30\text{-nm-thick Ti film was deposited by}

![FIG. 1. Change in the thermopower \( S \) of La-doped BaSnO_{3} films grown on (001) SrTiO_{3} substrates as a function of the carrier concentration \( n \) at room temperature. The red line is to guide the eye. Effective mass \( m^{*} \) values, which are calculated using Eqs. (1)–(3), are shown. The gray line is the \( S-n \) curve calculated using \( m^{*} = 0.4 \pm 0.1m_{0}. \) The dotted line is the threshold of the degenerate/nondegenerate semiconductor around \( n = 1.4 \times 10^{19} \text{ cm}^{-3}. \) The inset shows a schematic explanation of the energy dependence of the DOS.](image_url)
BaSnO₃ is heteroepitaxially grown on the (001) SrTiO₃ substrate. The abrupt heterointerface between a-C12A7 and BaSnO₃ was clearly observed. The thicknesses of Ti, a-C12A7, and BaSnO₃ were 28, 280, and 22 nm, respectively.

A semiconductor device analyzer (Agilent B1500A) was used to measure the transistor characteristics of the undoped BaSnO₃ TFT at room temperature. Figure 3 summarizes the typical transistor characteristics such as the transfer and output characteristics, threshold voltage, and field effect mobility of the resultant BaSnO₃ TFT. The drain current $I_d$ increased markedly as the gate voltage $V_g$ increased [Fig. 3(a)], indicating that the channel was n-type and the electron carriers accumulated by a positive $V_g$. An on-off current ratio of $\sim 10^3$ was obtained for $V_d = 1$ V. A rather large threshold voltage ($V_{th}$) of +5.5 V was observed from the linear fit of the $I_d$-$V_g$ plot [Fig. 3(b)]. A clear pinch-off behavior and current saturation in $I_d$ revealed that the resultant TFT obeyed the standard field effect transistor theory [Fig. 3(c)].

The field effect mobility $\mu_{FE}$ was calculated from $\mu_{FE} = \frac{\partial I_d}{\partial V_g} \cdot \frac{C}{g_m} \cdot \frac{1}{W/L}$, where $g_m$ is the transconductance $\partial I_d/\partial V_g$ and $C$ is the capacitance per unit area (39 nF cm⁻²) [Fig. 3(d)]. $\mu_{FE}$ drastically increased with $V_g$ and became saturated at $\sim 40$ cm² V⁻¹ s⁻¹, which was $\sim 60\%$ of the room temperature $\mu_{Hall}$ of La-doped BaSnO₃ ($\mu_{Hall} \sim 67$ cm² V⁻¹ s⁻¹).

Then, we measured the electric field modulated $S$ of the resultant BaSnO₃ TFT (Fig. 2). For the $S$ measurements, we used two Peltier devices, which were placed under the TFT, to generate a temperature difference between the source and drain electrodes [Fig. 2(b)]. Two thermocouples (K type, 150 μm in diameter, SHINNETSU), which were mechanically attached at both edges of the channel, monitored the temperature difference. (d) Stepped and terraced SHINNETSU, which are mechanically attached at both edges of the channel, monitored the temperature difference. (d) Stepped and terraced SHINNETSU, which are mechanically attached at both edges of the channel, monitored the temperature difference.
The inflection point occurs around (gray line) when \( n \) (films; the degenerate/nondegenerate threshold was around \( S \)). This observation is similar to that of the La-doped BaSnO\(_3\) films (Fig. 1). It is consistent with the La-doped BaSnO\(_3\) films (Fig. 1). It should be noted that a deflection point occurred around (240 \( \mu \)V K\(^{-1}\), 1.8 \( \times \) 10\(^{12}\) cm\(^{-2}\)). An almost linear relationship with a slope of \( -200 \mu \)V K\(^{-1}\)/decade was observed in the \( S \)-log \( n \) plot when \( n \) exceeded 1.8 \( \times \) 10\(^{12}\) cm\(^{-2}\). Below 1.8 \( \times \) 10\(^{12}\) cm\(^{-2}\), the slope was not linear. This observation is similar to that of the La-doped BaSnO\(_3\) films; the degenerate/nondegenerate threshold was around (240 \( \mu \)V K\(^{-1}\), 1.8 \( \times \) 10\(^{12}\) cm\(^{-2}\)). In the degenerate region, the \( E_F \) was located above the threshold and \( S \) obeyed Eqs. (1)–(3). The conduction band bottom was parabolic shaped and the intrinsic \( m^* \) was 0.40 \( \pm \) 0.01\( m_0 \).

In the nondegenerate region, \( E_F \) was below the threshold. The \( S \) value did not show a clear \( n \) dependence. Similar phenomena were also observed in amorphous TOSs, \( a \)-InGaZnO\(_4\), and \( a \)-In\(_2\)MgO\(_4\) [22]. In the case of these amorphous TOSs, structural imperfections led to the formation of an antiparabolic shaped extra state just below the original conduction band bottom, which played an essential role in the transistor switching of TOS-based TFTs [27,28]. In the present case, the almost linear shaped extra DOS (i.e., tail states) formed just below the conduction band bottom, possibly due to an oxygen deficiency. Because these tail states suppressed the carrier mobility, BaSnO\(_3\) films exhibited a very low mobility when \( E_F \) was below the threshold.

In summary, we have clarified the intrinsic effective mass of a transparent oxide semiconductor BaSnO\(_3\), \( m^* = 0.40 \pm 0.01m_0 \), using the thermopower modulation clarification method. We also determined the threshold of the degenerate/nondegenerate semiconductor of BaSnO\(_3\). At the threshold, both La-doped BaSnO\(_3\) and the BaSnO\(_3\) TFT structures have a thermopower value of 240 \( \mu \)V K\(^{-1}\), a bulk carrier concentration of 1.4 \( \times \) 10\(^{19}\) cm\(^{-3}\), and a two-dimensional sheet carrier concentration of 1.8 \( \times \) 10\(^{12}\) cm\(^{-2}\). A rather high mobility occurs when \( E_F \) is located above the parabolic shaped conduction band bottom. On the contrary, a very low carrier mobility is observed when the \( E_F \) is below the threshold, most likely because the tail states suppress the carrier mobility.

We hope the present results will lead to further developments of BaSnO\(_3\)-based oxide electronics.

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