Epitaxial growth of hexagonal tungsten bronze Cs$_2$WO$_3$ films in superconducting phase region exceeding bulk limit

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We report epitaxial synthesis of superconducting Cs$_2$WO$_3$ ($x = 0.11, 0.20$, and $0.31$) films on Y-stabilized ZrO$_2$ (111) substrates. The hexagonal crystal structure was verified not only for the composition within the stable region of the bulk ($x = 0.20$ and $0.31$), but also for the out-of-range composition ($x = 0.11$). The onset of the superconducting transition was recorded at 5.8 K for $x = 0.11$. We found a strong correlation between the superconducting transition temperature ($T_c$) and the $c$-axis length, irrespective of the Cs content. These results indicated that the hidden superconducting phase region of hexagonal tungsten bronze is accessible using epitaxial synthesis of lightly doped films.

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Tungsten bronzes A$_x$WO$_3$ have been synthesized with a wide variety of A-site ions (H$^+$, Li$^+$, Na$^+$, K$^+$, Rb$^+$, Cs$^+$, Ca$^{2+}$, In$^+$, and complex ions such as NH$_4^+$). In bulk Cs$_2$WO$_3$, superconductivity completely vanishes when $x$ exceeds either the lower or upper bounds in the HTB-phase region; $T_c$ increases from 1.0 K ($x = 0.33$) to 6.7 K ($x = 0.19$), which is the highest among the HTBs. The upper bound at $x = 0.33$ corresponds to the crystallographic limit, where all the A sites are filled, while the lower bound corresponds to the structural stability limit of the HTB phase ($x = 0.17$ for K and 0.16 for Rb). Therefore, the optimal ranges of A-site doping in HTBs have been thought to be hidden beyond the structural stability limit.

Epitaxial synthesis of metastable compounds is a powerful approach to paving the way for exploring exotic properties. It is worth testing this approach so as to reach the hidden superconducting states in HTBs. Wu et al. first fabricated superconducting hexagonal K$_{0.33}$WO$_3$ films on LaAlO$_3$ and Y-stabilized ZrO$_2$ (YSZ) substrates using pulsed-laser deposition (PLD). Recently, undoped hexagonal WO$_3$ films have been epitaxially synthesized using sputtering and molecular beam epitaxy; however, superconductivity did not appear in the as-grown and liquid-iodinated-gated samples.

In this study, we fabricated the $c$-axis oriented hexagonal Cs$_2$WO$_3$ ($x = 0.11, 0.20$, and $0.31$) epitaxial films on YSZ (111) substrates. All of the films, even the one with a thermodynamically unstable composition ($x = 0.11$), exhibited superconductivity with a $T_C$ comparable to that of the bulk.

We found that post-annealing is essential for an improvement of the superconducting properties. Moreover, we showed that the $c$-axis length instead of the Cs content is a crucial factor affecting the superconducting properties.

Several Cs$_2$WO$_3$ films of hundreds of nanometers in thickness were grown on YSZ (111) substrates using PLD with a KrF excimer laser (0.6 J/cm²). Ceramic tablets were prepared with a conventional solid-state reaction method, starting by mixing Cs$_2$CO$_3$ and WO$_3$ powders with different compositions (Cs/W = 0.10, 0.20, and 0.33). The substrate temperature was set to 750 °C and the oxygen pressure ($P_{O_2}$) was controlled in the range of 5–50 mTorr with a continuous flow of pure oxygen (6N purity). After the growth, the films were cooled to room temperature with a constant $P_{O_2}$. Some of the films were annealed at the $P_{O_2}$ ranging from 10$^{-5}$ Torr to 0.1 mTorr. The annealing temperature and duration were varied in the range of 700–750 °C and 2–34 h, respectively.

The film composition was analyzed using scanning electron microscopy with an electron probe microanalyzer (EPMA). The Cs contents in the as-grown and annealed films were $x = 0.11, 0.20$, and 0.31 for each target used. The homogeneous distribution of the Cs atoms in the films was also confirmed using EPMA compositional mapping. The crystal structures and epitaxial relationship were investigated using laboratory X-ray diffraction (XRD) apparatus with Cu Kα radiations.
radiation. The temperature dependence of the resistivity was measured using the standard four-probe method with a physical property measurement system (Quantum Design PPMS).

Figures 1(a) and 1(b) show a schematic of the crystal structures of Cs\(_2\)WO\(_3\) and YSZ projected along the [001] and [111] directions, respectively. The \(a\)-axis lattice constant (7.42 Å) of hexagonal Cs\(_{0.2}\)WO\(_3\) was close to double the \(d_{100}\) spacing (7.27 Å) of YSZ, and their mismatch was only 2.1%. Consequently, the \(c\)-axis oriented HTB films were obtained when a mixed valence state of W\(^{5+}\) was accommodated at an appropriate \(P_{O_2}\). Figure 2(a) shows the out-of-plane XRD patterns of the Cs\(_{0.2}\)WO\(_3\) films grown at various \(P_{O_2}\). For all of the films, the HTB 002 and 004 reflections were detected at \(2\theta \approx 23\) and 48°, respectively. The \(c\)-axis length for the film grown at \(P_{O_2} = 10\) mTorr was estimated to be 7.56 Å, which was close to that of the bulk (\(c = 7.57\) Å). However, small reflections of the secondary phases (marked with filled triangles) were also detected except for \(P_{O_2} = 10\) mTorr. The reflections at \(2\theta \approx 31\) and 46° observed for the film grown at \(P_{O_2} = 50\) mTorr could be attributed to fully oxidized compounds such as Cs\(_{3}\)W\(^{6+}\)O\(_4\) and W\(^{6+}\)O\(_3\). Correspondingly, the film was insulating. In contrast, the sharp peak at \(2\theta \approx 37°\) observed for the film grown at \(P_{O_2} = 5\) mTorr was assigned to the 020 reflection of rutile-type structured W\(^{4+}\)O\(_2\). These results reflected subtle oxygen nonstoichiometry arising from similar redox potentials of the tungsten-ion species.

Despite the thermodynamically unstable phase, HTB films with \(x = 0.11\) could be grown at \(P_{O_2} = 10\) mTorr [Fig. 2(b)]. The \(c\)-axis length was estimated to be 7.55 Å, slightly smaller than that of the Cs\(_{0.2}\)WO\(_3\) film. We also measured the asymmetric Cs\(_{0.1}\)WO\(_3\) 202 reflection to obtain the \(a\)-axis length as 7.44 and 7.43 Å for \(x = 0.11\) and \(x = 0.20\), respectively. The latter was close to that of the bulk (\(a = 7.42\) Å), indicating strain-free relaxing HTB films.

We carried out an XRD \(\theta\)-scan for the asymmetric reflections to confirm the epitaxial relationship shown in Fig. 1. The Cs\(_{0.3}\)WO\(_3\) 202 and YSZ 100 reflections showed six-fold and three-fold symmetry, respectively [Fig. 2(c)]. Thus, the epitaxial relationship of Cs\(_{0.3}\)WO\(_3\) [100] \(\parallel\) YSZ [110] was verified.

Figure 3(a) shows the temperature dependence of the resistivity for Cs\(_{0.1}\)WO\(_3\) films (\(x = 0\), 0.11, 0.20, and 0.31). The WO\(_3\) \((x = 0)\) film had a distorted ReO\(_3\)-type structure, details of which will be described elsewhere.\(^{15}\) Starting from a fairly high resistivity of \(x = 0\), the temperature-dependent resistivity systematically decreased with increasing \(x\), exhibiting an insulator-to-metal transition (IMT) for \(0.11 < x < 0.20\). We would like to emphasize that an IMT has not been reported for hexagonal Cs\(_{0.1}\)WO\(_3\) until now (although an IMT occurs in tetragonal and/or cubic Li\(_2\)WO\(_3\) for \(0.2 < x < 0.24\) and in cubic Na\(_2\)WO\(_3\) for 0.23 < \(x < 0.29\)).\(^{16}\) Furthermore, superconductivity was observed at low temperatures for the films with \(x = 0.11\) and 0.20. We also would like to emphasize that superconductivity in Cs\(_{0.1\_2}\)WO\(_3\) was observed for the first time. In contrast, superconducting transition was not observed in the Cs\(_{0.3}\)WO\(_3\) film above 1.9 K, which was consistent with previous reports.\(^{4}\)

We note that a number of factors, such as oxygen nonstoichiometry, disorder, and thickness, affect the sign of \(dp/dT\) and the smear intrinsic behaviors of the IMT. Indeed, an uncontrollable sign of \(dp/dT\) was reported for pulsed-laser deposited K\(_{0.33}\)WO\(_3\) films.\(^{10}\) In contrast, our Cs\(_{0.3}\)WO\(_3\) films showed reproducible transport properties: all of the Cs\(_{0.3}\)WO\(_3\) (Cs\(_{0.2}\)WO\(_3\)) films were insulating (metallic) even after the annealing. However, the metallic behavior disappeared when the thickness was reduced down to several tens of nanometers.

We studied other factors that influence the superconducting properties. As shown in Figs. 3(b) and 3(c), the as-grown films with \(x = 0.11\) and 0.20 exhibited the onset of \(T_C\) (\(T_{C,\text{onset}}\)) at 5.5 and 4.9 K, respectively. We note that \(T_{C,\text{onset}}\) for \(x = 0.20\) was considerably lower than \(T_C\) for bulk Cs\(_{0.3}\)WO\(_3\) (6.4 K). We attributed this discrepancy to a slight deviation from oxygen stoichiometry. For Rb\(_2\)WO\(_3\), a strong oxygen-content dependence of \(T_C\) was reported.\(^{17}\) We conducted annealing at \(P_{O_2} = 0.1\) mTorr so as to tune the oxygen stoichiometry carefully. The post-annealed films exhibited sharp transitions with a higher \(T_{C,\text{onset}}\) (5.8 and 5.4 K for three-fold symmetry, respectively [Fig. 2(c)]. Thus, the epitaxial relationship of Cs\(_{0.3}\)WO\(_3\) [100] \(\parallel\) YSZ [110] was verified.

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This unusual phase stability likely resulted from the nonequilibrium nature of PLD and the epitaxial stabilization effect. Therefore, further optimization of the PLD growth and annealing conditions may enhance $T_C$. Moreover, together with other approaches, the present study provides a further insight into the research of tungsten bronzes. For example, the indium content in HTB In$_x$WO$_3$ can be reduced to $x = 0.11$ by annealing with iodine without a structural phase transition. Other techniques such as electrostatic doping and electrochemical deintercalation in liquid electrolytes will also be useful.

In summary, we grew hexagonal Cs$_{0.31}$WO$_3$ ($x = 0.11, 0.20,$ and 0.31) epitaxial films on YSZ (111) substrates using PLD. The transport and XRD measurements revealed that superconductivity emerged even outside the structural stability region of the HTB Cs$_x$WO$_3$ bulk. By annealing under various conditions, a number of samples were prepared to elucidate a strong correlation between the superconducting transition temperature and the $c$-axis length. We concluded that the superconducting properties of HTBs Cs$_x$WO$_3$ were governed by lattice parameters instead of the Cs content. These results strongly suggested that epitaxial stabilization is a powerful approach to studying HTB systems.

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Fig. 4. Superconducting transition temperature as a function of the $c$-axis length for the as-grown and annealed Cs$_x$WO$_3$ films. The data for the bulks are also plotted for comparison. The bulk references are rearranged from the $x$ dependencies of $T_C$ and $c$, reported independently in Refs. 4 and 13, assuming Vegard’s law for $c$ versus $x$. The broken lines indicate a guide for eyes.

$x = 0.11$ and 0.20, respectively). Crystallinity of the films (namely, the full width at half maximum of the XRD $a$-scans) hardly changed after the annealing. In contrast, the $c$-axis length somewhat varied in a systematic fashion, as will be discussed later. These variations were caused neither by a lack of the Cs content nor by the stain relaxation, as described already. Therefore, we presumed that the lattice parameter is a crucial factor for the superconducting properties.

We tested this hypothesis for the nonsuperconducting Cs$_{0.31}$WO$_3$ film. The sample was first annealed at 750°C and $P_{O_2} \approx 0.1$ mTorr for extended durations. Surprisingly, superconductivity was observed: $T_{C,\text{onset}}$ increased from 3.5 K (after 4 h) to 4.6 K (after 16 h) and then was saturated at around 4.8 K (after 34 h). Meanwhile, the $c$-axis length significantly decreased and became comparable to that of bulk Cs$_{0.2}$WO$_3$ ($\approx 7.57 \text{ Å}$). However, the film showed no transition and the $c$-axis length was close to that of bulk Cs$_{0.33}$WO$_3$ after reducing in Ar/H$_2$ mixed gas (1 vol % H$_2$) at 750°C. Moreover, superconductivity ($T_{C,\text{onset}} = 3.0$ K) was observed again after annealing at 750°C and $P_{O_2} \approx 0.1$ mTorr. These results indicated that Cs doping is not a primary factor for modulation of the superconducting properties.

Now, we propose a new superconducting phase diagram as shown in Fig. 4, where $T_{C,\text{onset}}$ is plotted as a function of the $c$-axis length of the Cs$_x$WO$_3$ film. A conventional phase diagram of bulk Cs$_x$WO$_3$ is also shown.$^{43}$ As for the bulk, $T_C$ is scalable to both the Cs content $x$ and the $c$-axis length $c$ because $c$ versus $x$ obeys Vegard’s law.$^{13}$ Here, the structural stability limit of the bulk HTB phase is located at $c \approx 7.567 \text{ Å}$ (indicated by vertical broken line). Our Cs$_x$WO$_3$ films follow a similar trend irrespective of $x$, but those with a smaller $c$-axis length ($x = 0.11$ and 0.20) exceed the bulk limit.