



**HAL**  
open science

## Growth of *c* -Axis-Oriented BiCuSeO Thin Films Directly on Si Wafers

Xiaolin Wu, Linjie Gao, Pascal Roussel, El Hadj Dogheche, Jianglong Wang,  
Guangsheng Fu, Shufang Wang

► **To cite this version:**

Xiaolin Wu, Linjie Gao, Pascal Roussel, El Hadj Dogheche, Jianglong Wang, et al.. Growth of *c*-Axis-Oriented BiCuSeO Thin Films Directly on Si Wafers. *Journal of the American Ceramic Society*, 2016, 99 (10), pp.3367-3370. 10.1111/jace.14359 . hal-02263699

**HAL Id: hal-02263699**

**<https://hal.science/hal-02263699v1>**

Submitted on 3 Oct 2024

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

# Growth of *c*-Axis-Oriented BiCuSeO Thin Films Directly on Si Wafers

Xiaolin Wu,<sup>‡</sup> Linjie Gao,<sup>‡,†</sup> Pascal Roussel,<sup>§</sup> Elhadj Dogheche,<sup>¶</sup> Jianglong Wang,<sup>‡</sup> Guangsheng Fu,<sup>‡</sup> and Shufang Wang<sup>‡,†</sup>

<sup>‡</sup>Hebei Key Lab of Optic-Electronic Information and Materials, The College of Physics Science and Technology, Hebei University, Baoding 071002, China

<sup>§</sup>Unite de Catalyse et Chimie du Solide (UCCS) – UMR CNRS 8181, Villeneuve d'Ascq 59655, France

<sup>¶</sup>Institute of Electronic Microelectronic Nanotechnology (IEMN), CNRS, University of Valenciennes & Hainaut Cambrésis, Le Mont Houy, Valenciennes 59309, France

**Single-phase, *c*-axis-oriented BiCuSeO thin films have been directly grown on the commercial silicon (001) wafers without any surface pretreatment by using pulsed laser deposition. X-ray diffraction pole figure confirms that the film does not have any *ab*-plane texture, whereas cross-sectional transmission electron microscopy shows good crystallinity of the film even if there exists an amorphous native oxide layer on the wafers surface. At room temperature, the resistivity of the film is about 14 mΩ cm, which is much lower than that reported for corresponding single crystals as well as polycrystalline bulks. This work demonstrates the possibility of using the available state-of-the-art silicon processing techniques to create BiCuSeO-based thin-film thermoelectric devices.**

**Keywords:** BiCuSeO thin films; *c*-axis oriented; Si wafers; pulsed laser deposition

## I. Introduction

**T**HERMOELECTRIC (TE) materials have attracted great attention because of their potential applications in waste

heat conversion and Peltier cooling. The performance of TE materials is qualified by the dimensionless figure of merit  $ZT = (S^2/\rho\kappa)T$ , where  $S$  is the Seebeck coefficient,  $\rho$  the electrical resistivity,  $\kappa$  the thermal conductivity, and  $T$  the absolute temperature. Until the present, most investigations on TE materials have been devoted to conventional semiconductors or alloys, primarily due to their high efficiency.<sup>1–4</sup> However, these materials often suffer from element scarcity, thermal instability at moderate or high temperatures, oxidation in air, and toxicity, preventing them from large-scale applications. Recently, the BiCuSeO-based compounds were reported as promising oxide-based TE materials due to their intrinsically very low thermal conductivity.<sup>5–15</sup> These compounds have a layered tetragonal crystal structure with  $P4/nmm$  space group, which consists of the insulating  $(\text{Bi}_2\text{O}_2)^{2+}$  layers and the conductive  $(\text{Cu}_2\text{Se}_2)^{2-}$  layers alternatively stacked along the *c*-axis. This layered structure leads to an anisotropy in their electrical transport properties, with a low electrical resistivity in the *ab* plane and a large electrical resistivity along the *c*-axis. Large value of  $ZT$ , as high as 1.4 at about 923 K, has been achieved in textured polycrystalline bulk samples with preferred *c*-axis orientation.<sup>15</sup> This value is

among the best ever reported for lead-free *P*-type polycrystalline bulks in this temperature range.

High-quality TE thin film is of critical interest for realization of the thin-film TE devices for localized rapid heating or cooling.<sup>16,17</sup> But to our knowledge, most of the as-prepared BiCuSeO-based samples are polycrystalline bulks, and there are very few reports on thin films, especially thin films directly grown on the commercial silicon wafers. High-quality TE thin films on silicon wafers can provide the possibility of fabricating TE microscale devices by using the available state-of-the-art silicon processing techniques. In this work, for the first time, we report on the *in situ* growth of high-quality *c*-axis-oriented BiCuSeO thin films on commercial silicon wafers by pulsed laser deposition (PLD), without chemical removal of native surface oxide. The as-grown thin films showed good crystallinity, with a much lower resistivity than that reported for single crystals as well as polycrystalline bulks.

## II. Experimental Section

BiCuSeO thin films were deposited on a commercial Si (001) single-crystal wafers with dimensions of 5 mm (width) × 10 mm (length) × 0.5 mm (thickness) in an *in situ* manner using the PLD technique. The room temperature resistivity of these wafers is about  $10^5 \Omega \text{ cm}$ . Before being loaded into the PLD chamber, they were only simply cleaned with acetone and methanol, and no other pretreatment was made to remove the native oxide layer on the wafers surface. A 308-nm excimer laser was used for ablating the BiCuSeO ceramic target under the argon atmosphere. Here, the target was synthesized by the solid-state reaction method as described: stoichiometric mixtures of Bi<sub>2</sub>O<sub>3</sub> (99.99%, Alfa Aesar), Cu (99.9%, Alfa Aesar, Shanghai, China), Bi (99.99%, Aladdin, Shanghai, China), and Se (99.99%, Aladdin) powders were grinded for about 6 h by a ball-milling machine and pressed into a pellet with diameter of about 30 mm. Then the pellet was sealed in quartz tube under the pressure of  $10^{-5} \text{ Pa}$  and sintered at 573 K for 6 h and 973 K for 12 h. The current optimal experimental conditions for the film growth were listed as follows: the laser energy density on the target was about 1.5 J/cm<sup>2</sup>, the repetition rate of the laser was 5 Hz, the distance between the film and substrate was about 50 mm, the argon pressure was about 0.1 Pa, and the substrate temperature was about 330°C.

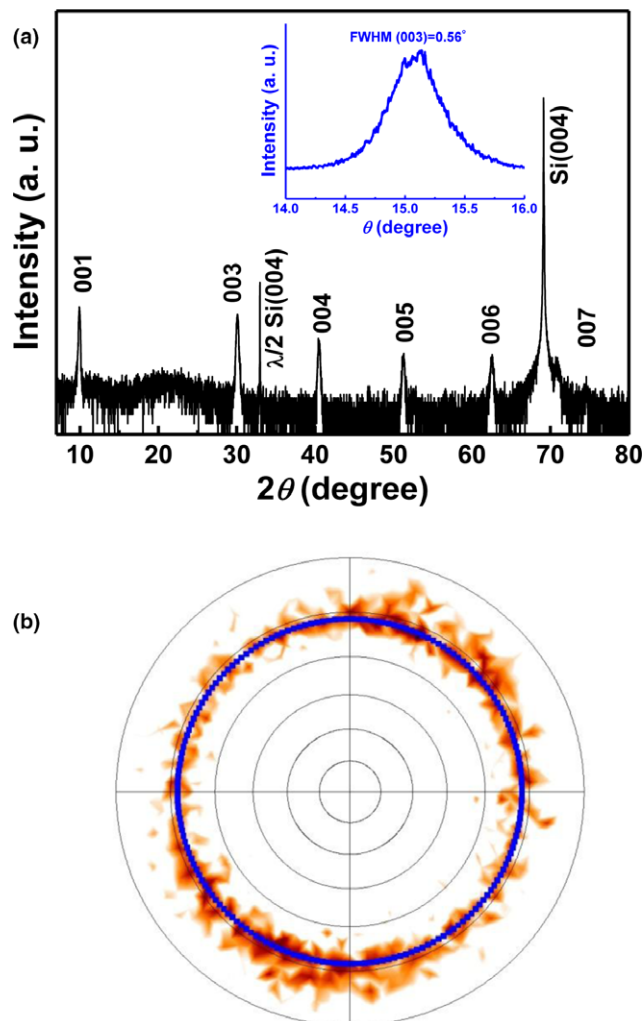
The crystal structure of the films was measured using a Bruker AXS D8 (Karlsruhe, Germany) advance X-ray diffractometer with  $\text{CuK}_\alpha$  radiation. The surface morphology and the elemental composition of the films were analyzed by a scanning electron microscope (SEM, Zeiss Ultra55; Carl zeiss AG, Oberkochen, Germany) equipped with an energy-dispersive X-ray spectroscopy (EDX) detector. The

<sup>†</sup>Authors to whom correspondence should be addressed.  
e-mails: LinjieGao@hotmail.com and sfwang@hbu.edu.cn

microstructure was analyzed with a field-emission transmission electron microscopy (TEM, Tecnai G2 F20; FEI, Hillsboro, OR). The thickness of the films was about 90 nm, which was determined by the Step Profiler (Dektak 150; Veeco, Plainview, NY) and further confirmed by the cross-sectional TEM measurements. The room temperature carrier concentration  $n$  and carrier mobility  $\mu$  were measured by using a physical properties measurement system (PPMS-9, Quantum Design Inc., San Diego, CA) with the Van Der Pauw method. The electrical resistivity  $\rho$  and Seebeck coefficient  $S$  were measured simultaneously in the PPMS-9 system with a thermal transport option (TTO). The measurement was carried out under vacuum with a four-probe steady-state mode.

### III. Results and Discussion

Figure 1(a) shows the typical X-ray diffraction (XRD)  $\theta$ - $2\theta$  scan for a BiCuSeO thin film directly grown on Si (001) wafer. Only peaks from diffractions of (00 $l$ ) BiCuSeO planes were observed besides the Si peaks, indicating that the film is single phase and well aligned along the  $c$ -axis. The  $c$ -axis lattice parameter calculated from the XRD measurement is about 0.892 nm, similar to the values that were previously reported in the literature.<sup>18</sup> The  $\omega$ -scan of the BiCuSeO (003) peak, as seen in the inset of Fig. 1(a), shows a full width at half maximum of  $0.56^\circ$ , further confirming the good  $c$ -axis alignment of the film. The  $ab$ -plane texture information of the film was investigated by XRD pole figures. Figure 1(b)

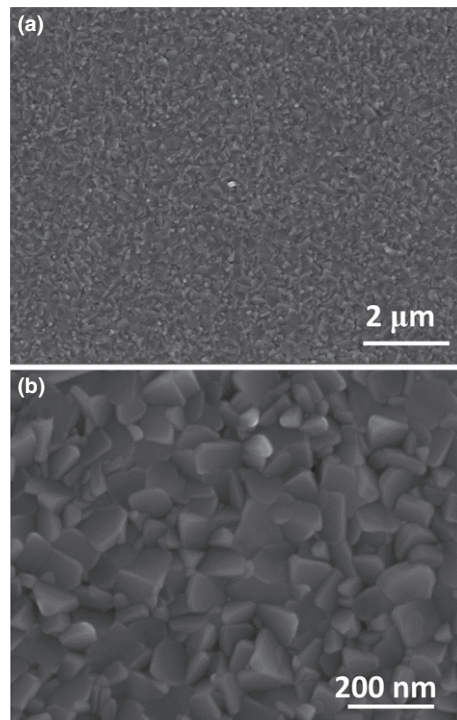


**Fig. 1.** (a) XRD  $\theta$ - $2\theta$  scan of the BiCuSeO thin film on Si (001) wafer. The inset is the rocking curve of BiCuSeO (003) peak. (b) (111) pole figure of the BiCuSeO thin film on Si (001) wafer.

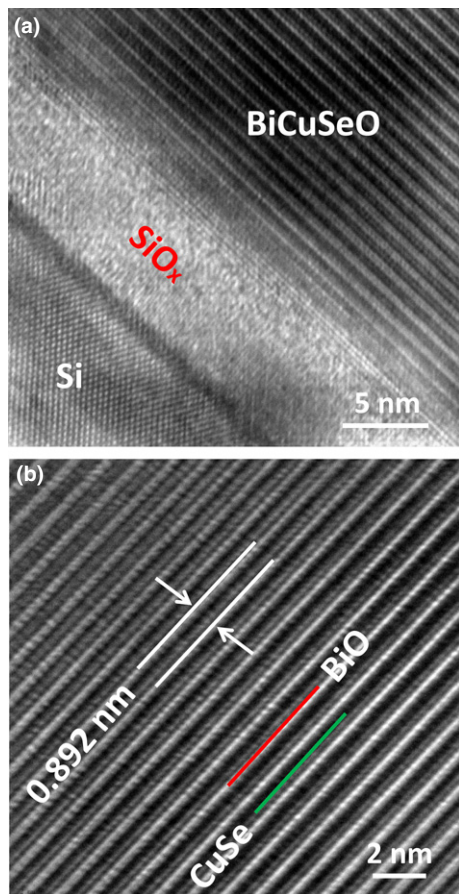
the (111) pole figure of the BiCuSeO film on Si (001) wafer recorded at  $33.75^\circ$ . In this pole figure, strong peaks that represent single-crystal-like texture are absent, whereas a continuous ring is observed, indicating random  $ab$ -plane orientation of the grains in the film. The Debye ring in Fig. 1(b) is around  $73^\circ$ , and can be modeled with the software Stereopole with a (001) fiber texture (blue ring).<sup>19</sup> It is therefore concluded that the film on Si (001) wafer does not have  $ab$ -plane texture, but has a strong (001) fiber texture.

Figures 2(a) and (b) display the SEM surface images of the BiCuSeO thin film on Si (001) wafer. Dense film composed of square-shaped grains can be seen in these images. The EDX measurements on a large-scale film surface reveal that the cation ion ratio of Bi:Cu:Se in the film is about 1:0.0:0.96:0.91, which is very close to the nominal composition of the film. We also performed EDX mapping measurements for Bi, Cu, Se, and O, and the results demonstrate the homogeneous distribution of these elements in the film (see the supplementary figure).

Figure 3(a) is a cross-sectional high-resolution TEM (HRTEM) image for the BiCuSeO film on Si (001) wafer. Good layered structure of the film and single crystalline cubic Si wafer can be observed. Between the film and the wafer, there is an amorphous layer with the thickness of no more than 10 nm, which is suggested to originate from the native  $\text{SiO}_x$  layer on the Si wafer surface. Figure 3(b) is the enlarged HRTEM picture taken from the film part. Different layers of BiO (marked with red line) and CuSe (marked with green line) are clearly visible with a well-ordered growth along the  $c$ -axis. The distance of the lattice is about 0.892 nm, in good agreement with the  $c$ -axis lattice parameter obtained from XRD measurement. It is surprising that nearly perfect crystalline structures with  $c$ -axis alignment of the BiCuSeO film can be formed on top of an amorphous  $\text{SiO}_x$  layer. As the film material always prefers to grow along the film planes with the lowest surface energy, the self-assembled  $c$ -axis-oriented growth of the present film might be because the (00 $l$ ) planes have the lowest surface energy in BiCuSeO. Similar self-assembly nature has also been observed in other layered materials such as  $\text{Ca}_3\text{Co}_4\text{O}_9$ ,  $\text{Bi}_2\text{Sr}_2\text{Co}_2\text{O}_y$ , and  $\text{Bi}_2\text{Sr}_3\text{Co}_2\text{O}_y$ .<sup>20-22</sup>



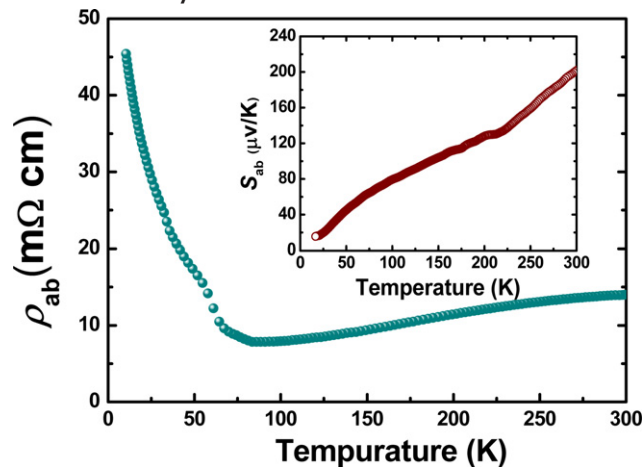
**Fig. 2.** (a) Low- and (b) high-resolution SEM surface images of the BiCuSeO thin film on Si (001) wafer.



**Fig. 3.** (a) Cross-sectional high-resolution transmission electron microscopy (HRTEM) image of the BiCuSeO/Si interface region for the BiCuSeO thin film on Si (100) wafer. (b) Enlarged HRTEM image taken from the film part.

The temperature dependence of  $ab$ -plane resistivity  $\rho_{ab}$  and Seebeck coefficient  $S_{ab}$  of the  $c$ -axis-oriented BiCuSeO film on Si wafer is shown in Fig. 4. There is a broad minimum near 80 K in the resistivity–temperature ( $\rho$ - $T$ ) plot of BiCuSeO thin film, exhibiting a transition from the high-temperature metallic-like conducting to the low-temperature insulating-like one. Similar metal–insulator transition was also observed in  $\rho$ - $T$  plots of some BiCuSeO bulk samples with Cu vacancies [see Supporting Information of Ref. (14)].<sup>14,23</sup> It might be caused by the disorder-induced carrier localization effects due to the existence of Cu vacancies or other defects in the films.<sup>24,25</sup> In addition, we suggest that the low-temperature carrier transport of the present BiCuSeO thin film is mainly dominated by the variable range hopping mechanism, which leads to the tendency between the resistivity and the Seebeck coefficient of the film is deviated from the Drude model (from the Drude model, it is expected that the Seebeck coefficient will be enhanced with resistivity).<sup>26,27</sup>

Figure 4 shows that the room temperature  $\rho_{ab}$  and  $S_{ab}$  of the film are about 14 m $\Omega$  cm and 210  $\mu$ V/K, respectively, which are comparable to those of high-quality epitaxial thin-film samples grown on SrTiO<sub>3</sub> single-crystal substrate.<sup>28</sup> Moreover, the room temperature  $\rho_{ab}$  of the present film is found to be much lower than those obtained from polycrystalline bulks (~0.1–40  $\Omega$ ·cm)<sup>10–14,23</sup> as well as the recently reported value for single-crystal samples (~90–770 m $\Omega$ ·cm).<sup>29</sup> The very low resistivity of the thin-film sample in comparison with the single crystals remains unclear now as most data, including the carrier concentration  $n$  and the carrier mobility  $\mu$ , are still not available for single-crystal samples.<sup>18,29</sup> When compared with the BiCuSeO polycrystalline bulk samples, the reduced resistivity of the thin film can be partially ascribed to the  $c$ -axis-orientated nature of the film. In addition, the high carrier concentration of



**Fig. 4.** The temperature dependence of  $ab$ -plane resistivity  $\rho_{ab}$  and Seebeck coefficient  $S_{ab}$  of the BiCuSeO thin film on Si (100) wafer.

the film ( $n \sim 6.6 \times 10^{19} \text{ cm}^{-3}$  at 300 K), which is nearly an order of magnitude larger than those reported in most polycrystalline bulks,<sup>5–7,10–12</sup> should be also responsible for its decreased resistivity. The large concentration of holes obtained in the present unintentionally doped BiCuSeO thin film is very likely due to the small number of Cu vacancies in the film.<sup>23</sup> It is noteworthy that the resistivity of the present film can be further strongly decreased by a partial substitution of Bi<sup>3+</sup> by a divalent element (alkaline-earth metal or Pb).<sup>28</sup> For example, the room-temperature resistivity of the film can be decreased to about 2.2 m $\Omega$  cm when doping 1% Pb into the film. The effect of the element doping on the electrical transport properties as well as the thermoelectric performance of the films will be investigated in detail and described in a future study.

#### IV. Conclusion

In conclusion, we reported the *in situ* growth of BiCuSeO thin films on commercial silicon (001) wafers by PLD technique without any surface pretreatment. XRD measurements revealed the as-grown films were single phase with a strong (001) fiber texture. HRTEM showed that the films exhibited nearly perfect crystalline structure even there was a native amorphous SiO<sub>x</sub> layer on the top of Si wafers. As compared to the single-crystal samples or polycrystalline bulks, the as-grown  $c$ -axis-oriented films showed very low resistivity and moderate Seebeck coefficient. This work demonstrated the possibility integrating thin film of BiCuSeO, a newly discovered promising oxide TE material, into the current conventional silicon technology for novel TE thin-film devices.

#### Acknowledgments

This project was supported by the National Natural Science Foundation of China (no. 51372064), the Nature Science Foundation of Hebei Province, China (no. 2013201249 and no. A2014201176), the One Hundred Talent Project of Hebei Province (no. E2013100013), and the Fostering Foundation for the Distinguished Ph.D. Dissertation of Hebei University (YB201502).

#### Supporting Information

Additional Supporting Information may be found in the online version of this article:

**Fig. S1.** The EDX mappings of Bi, Cu, Se and O elements of the BiCuSeO thin film on Si (001) wafer.

#### References

1. Y. Z. Pei, X. Y. Shi, A. LaLonde, H. Wang, L. D. Chen, and G. J. Snyder, "Convergence of Electronic Bands for High Performance Bulk Thermoelectric," *Nature*, **473**, 66–9 (2010).

- <sup>2</sup>J. P. Heremans, V. Jovovic, E. S. Toberer, A. Saramat, K. Kurosaki, et al., "Enhancement of Thermoelectric Efficiency in PbTe by Distortion of The Electronic Density of States," *Science*, **321**, 554–7 (2008).
- <sup>3</sup>J. K. Chen, X. Y. Zhou, C. Uher, X. Shi, J. Jun, et al., "Structural Modifications and Non-Monotonic Carrier Concentration in  $\text{Bi}_2\text{Se}_{0.3}\text{Te}_{2.7}$  by Reversible Electrochemical Lithium Reactions," *Acta Mater.*, **61**, 1508–17 (2013).
- <sup>4</sup>C. G. Fu, T. J. Zhu, Y. T. Liu, H. H. Xie, and X. B. Zhao, "Band Engineering of High Performance p-Type FeNbSb Based Half-Heusler Thermoelectric Materials for Figure of Merit  $ZT > 1$ ," *Energy Environ. Sci.*, **8**, 216–20 (2015).
- <sup>5</sup>Y.-L. Pei, H. J. Wu, D. Wu, F. S. Zheng, and J. Q. He, "High Thermoelectric Performance Realized in a BiCuSeO System by Improving Carrier Mobility Through 3D Modulation Doping," *J. Am. Chem. Soc.*, **136**, 13902–8 (2014).
- <sup>6</sup>L.-D. Zhao, J. Q. He, D. Berardan, Y. H. Lin, J.-F. Li, et al., "BiCuSeO Oxyselelenides: New Promising Thermoelectric Materials," *Energy Environ. Sci.*, **7**, 2900–24 (2014).
- <sup>7</sup>J. L. Lan, B. Zhan, Y.-C. Liu, B. Zheng, Y. Liu, et al., "Doping for Higher Thermoelectric Properties in p-Type BiCuSeO Oxyselelenide," *Appl. Phys. Lett.*, **102**, 123905, 4pp (2013).
- <sup>8</sup>J. L. Lan, Y.-C. Liu, B. Zhan, Y.-H. Lin, B. P. Zhang, et al., "Enhanced Thermoelectric Properties of Pb-Doped BiCuSeO Ceramics," *Adv. Mater.*, **25**, 5086–90 (2013).
- <sup>9</sup>Y. C. Liu, J. X. Ding, B. Xu, J. L. Lan, Y. H. Zheng, et al., "Enhanced Thermoelectric Performance of La-Doped BiCuSeO by Tuning Band Structure," *Appl. Phys. Lett.*, **106**, 233903, 5pp (2015).
- <sup>10</sup>C. Barreateau, D. Bérardan, E. Amzallag, L. D. Zhao, and N. Dragoe, "Structural and Electronic Transport Properties in Sr-Doped BiCuSeO," *Chem. Mater.*, **24**, 3168–78 (2012).
- <sup>11</sup>Y. Liu, L.-D. Zhao, Y. C. Liu, J. L. Lan, W. Xu, et al., "Remarkable Enhancement in Thermoelectric Performance of BiCuSeO by Cu Deficiencies," *J. Am. Chem. Soc.*, **133**, 20112–5 (2011).
- <sup>12</sup>C. Barreateau, D. Berardan, L. D. Zhao, and N. Dragoe, "Influence of Te Substitution on the Structural and Electronic Properties of Thermoelectric BiCuSeO," *J. Mater. Chem. A*, **1**, 2921–6 (2013).
- <sup>13</sup>S. G. Tan, H. C. Lei, D. F. Shao, H. Y. Lv, W. J. Lu, et al., "Enhanced Low Temperature Thermoelectric Performance of Ag-Doped BiCuSeO," *Appl. Phys. Lett.*, **105**, 082109, 5pp (2014).
- <sup>14</sup>D. Berardan, L.-D. Zhao, C. Barreateau, and N. Dragoe, "Low Temperature Transport Properties of the BiCuSeO System," *Phys. Status Solidi A*, **209**, 2273–6 (2012).
- <sup>15</sup>J. H. Sui, J. Li, J. Q. He, Y.-L. Pei, D. Berardan, et al., "Texturation Boosts the Thermoelectric Performance of BiCuSeO Oxyselelenides," *Energy Environ. Sci.*, **6**, 2916–20 (2013).
- <sup>16</sup>R. Venkatasubramanian, E. Siivola, T. Colpitts, and B. O'Quinn, "Thin-Film Thermoelectric Devices With High Room-Temperature Figures of Merit," *Nature*, **413**, 597–602 (2001).
- <sup>17</sup>I. Chowdhury, R. Prasher, K. Lofgreen, G. Chrysler, S. Narasimhan, et al., "On-Chip Cooling by Superlattice-Based Thin-Film Thermoelectrics," *Nat. Nanotechnol.*, **4**, 235–8 (2009).
- <sup>18</sup>A. P. Richard, J. A. Russell, A. Zakutayev, L. N. Zakharov, D. A. Kesler, and J. Tate, "Synthesis, Structure and Optical Properties of BiCuOCh (Ch=S, Se, AndTe)," *J. Solid State Chem.*, **187**, 15–9 (2012).
- <sup>19</sup>I. Salzmänn and R. Resel, "STEREOPOLE: Software for the Analysis of X-ray Diffraction Pole Figures With IDL," *J. Appl. Crystallogr.*, **37**, 1029–33 (2004).
- <sup>20</sup>Y. F. Hu, W. D. Si, E. Sutter, and Q. Li, "In Situ Growth of c-Axis-Oriented  $\text{Ca}_3\text{Co}_4\text{O}_9$  Thin Films on Si (100)," *Appl. Phys. Lett.*, **86**, 082103, 3pp (2005).
- <sup>21</sup>X.-B. Zhu, D. Q. Shi, S. X. Dou, Y. P. Sun, Q. Li, et al., "(00 l)-Oriented  $\text{Bi}_2\text{Sr}_2\text{Co}_2\text{O}_y$  and  $\text{Ca}_3\text{Co}_4\text{O}_9$  Films: Self-Assembly Orientation and Growth Mechanism by Chemical Solution Deposition," *Acta Mater.*, **58**, 4281–91 (2010).
- <sup>22</sup>X.-B. Zhu, X. W. Tang, D. Q. Shi, H. B. Jian, H. C. Lei, et al., "Synthesis and Characterization of Self-Assembled c-Axis Oriented  $\text{Bi}_2\text{Sr}_2\text{Co}_2\text{O}_y$  Thin Films by the sol-gel Method," *Dalton Trans.*, **40**, 9544–50 (2011).
- <sup>23</sup>T. Ohtani, Y. Tachibana, and Y. Fujii, "Electrical Properties of Layered Copper Oxyselelenides ( $\text{BiO}$ ) $\text{Cu}_{1-x}\text{Se}$  and ( $\text{Bi}_{1-x}\text{Sr}_x$ ) $\text{OCuSe}$ ," *J. Alloy. Comp.*, **262–263**, 175–9 (1997).
- <sup>24</sup>Y. Q. Feng, K.-J. Jin, L. Gu, X. He, C. Ge, et al., "Insulating Phase at low Temperature in Ultrathin  $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$  Films," *Sci. Rep.*, **6**, 22382, 9pp (2016).
- <sup>25</sup>Z. L. Liao, F. M. Li, P. Gao, L. Li, J. D. Guo, et al., "Origin of the Metal-Insulator Transition in Ultrathin Films of  $\text{La}_{2/3}\text{Sr}_{1/3}\text{MnO}_3$ ," *Phys. Rev. B*, **92**, 125123, 8pp (2015).
- <sup>26</sup>C. O. Yoon, M. Reghu, D. Moses, and A. J. Heeger, "Counterion-Induced Processibility of Polyaniline: Thermoelectric Power," *Phys. Rev. B*, **48**, 14080–4 (1993).
- <sup>27</sup>C.-J. Liu, L.-C. Huang, and J.-S. Wang, "Improvement of the Thermoelectric Characteristics of Fe-Doped Misfit-Layered  $\text{Ca}_3\text{Co}_{4-x}\text{Fe}_x\text{O}_{9+\delta}$  ( $x = 0, 0.05, 0.1, \text{ and } 0.2$ )," *Appl. Phys. Lett.*, **89**, 204106, 3pp (2006).
- <sup>28</sup>X. L. Wu, J.-L. Wang, H. R. Zhang, S. F. Wang, S. J. Zhai, et al., "Epitaxial Growth and Thermoelectric Properties of c-Axis Oriented  $\text{Bi}_{1-x}\text{Pb}_x\text{CuSeO}$  Single Crystalline Thin Films," *CrystEngComm*, **17**, 8697–702 (2015).
- <sup>29</sup>S.-T. Dong, Y.-Y. Lv, B.-B. Zhang, F. Zhang, S. H. Yao, et al., "Strong Correlation of the Growth Mode and Electrical Properties of BiCuSeO Single Crystals With Growth Temperature," *CrystEngComm*, **17**, 6136–41 (2015). □