# *In situ* growth of *c*-axis-oriented $Ca_3Co_4O_9$ thin films on Si (100)

Y. F. Hu
*Materials Science Department, Brookhaven National Laboratory, Upton, New York 11973*

W. D. Si
*Physics Department, Brookhaven National Laboratory, Upton, New York 11973*

E. Sutter
*Center for Functional Nanomaterials, Brookhaven National Laboratory, Upton, New York 11973*

Qiang Li[a)]
*Materials Science Department, Brookhaven National Laboratory, Upton, New York 11973*

(Received 1 November 2004; accepted 4 January 2005; published online 16 February 2005)

High-quality *c*-axis-oriented $Ca_3Co_4O_9$ thin films have been grown directly on Si (100) wafers by pulsed-laser deposition without prechemical treatment of the substrate surface. Cross-sectional transmission electron microscopy shows good crystallinity of the $Ca_3Co_4O_9$ films. The Seebeck coefficient and resistivity of the $Ca_3Co_4O_9$ thin films on Si (100) substrate are 126 $\mu$V/K and 4.3 m$\Omega$ cm, respectively, at room temperature, comparable to the single-crystal samples. This advance demonstrates the possibility of integrating the cobaltate-based high thermoelectric materials with the current state-of-the-art silicon technology for thermoelectricity-on-a-chip applications.  [DOI: 10.1063/1.1868873]

Layered cobaltates have been the subject of extensive interest in the solid state physics and materials research community for several years, due to the wide variety of electrical, magnetic, and structural properties and phenomena associated with their tilted octahedral $CoO_2$ layer. The most important property pertinent to the practical applications at current stage is the unique combination of extraordinarily high thermopower with metallic transport properties, which was first discovered in $NaCo_2O_4$ with Seebeck coefficient (thermoelectric power) $S \sim 100$ $\mu$V/K at 300 K.[1] The quality of a thermoelectric material is quantified by the thermoelectric figure of merit $ZT = S^2T/(\rho\kappa)$, where $T$, $\rho$, and $\kappa$ are absolute temperature, electric resistivity, and thermal conductivity, respectively. $Ca_3Co_4O_9$ and $Ca_2Co_2O_5$ are among the cobaltates exhibiting best thermoelectric properties,[2–6] challenging the best conventional thermoelectric materials such as $Bi_2Te_3/Sb_2Te_3$ alloys.[7]

In electronics applications, such as thermochemistry-on-a-chip, biothermoelectric chips, and active cooling for microelectronic processors, thin-film devices are required that allow localized cooling/heating at points of interest. Miniature thermoelectric thin-film devices have already been produced for commercial applications, for example, the cardiac pacemaker. To retain an economically viable fabrication process, it is desirable to construct the thermoelectric elements from current silicon technology. Although $Ca_3Co_4O_9$ thin films have been grown on single-crystal substrates,[8–10] such as $SrTiO_3$, Y-stabilized $ZrO_2$ (YSZ), MgO, and $TiO_2$, there is no reported growth of high-quality cobaltate films on Si substrate. Here we demonstrate that this can be achieved by pulsed-laser deposition (PLD) without prechemical treatment of the substrate surface or buffer layers. The *c*-axis-oriented $Ca_3Co_4O_9$ thin films grown on Si (100) show high Seebeck coefficient and low resistivity, comparable to the best single-crystal samples.

[a)]Electronic mail: qiangli@bnl.gov

Our $Ca_3Co_4O_9$ thin films were grown *in situ* by the PLD process. The $Ca_3Co_4O_9$ target was prepared from the high-purity $CaCO_3$ and $Co_3O_4$ powders. The stoichiometrically mixed powders were calcined two times at 880–890 °C for 24 h in flowing air with intermediate grinding, and then pressed into a disk for final sintering at 900 °C for 24 h in flowing $O_2$ gas. Single-crystal Si (100) (commercial wafer) was used as the substrate. The substrates were cleaned in acetone and methanol prior to the deposition, but not chemically treated to remove the native oxide layer on the Si substrate surface. Films about 2300 Å thick were deposited at a substrate temperature of 700 °C with a laser energy density of $\sim$1.5 J/cm$^2$, under an oxygen pressure of 300 mTorr. After deposition, films were cooled to room temperature in $\sim$1 atmosphere of oxygen.

Figure 1 shows the x-ray diffraction (XRD) patterns for the $Ca_3Co_4O_9$ film grown on single crystalline Si (100) substrate. The XRD patterns exhibit nearly perfect *c*-axis alignment for the thin film (note: the log-scale used for counts). No diffraction peaks due to impurity phases were observed.

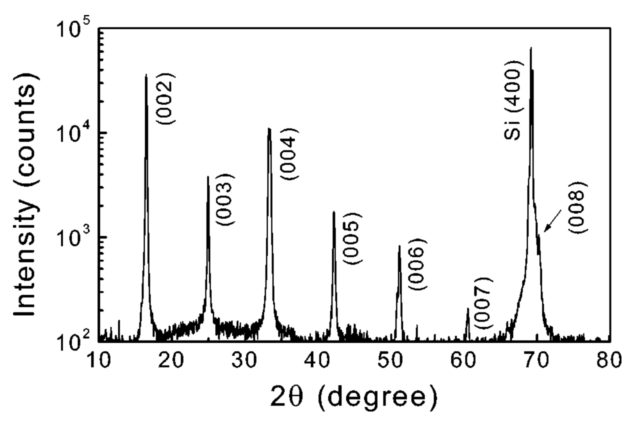
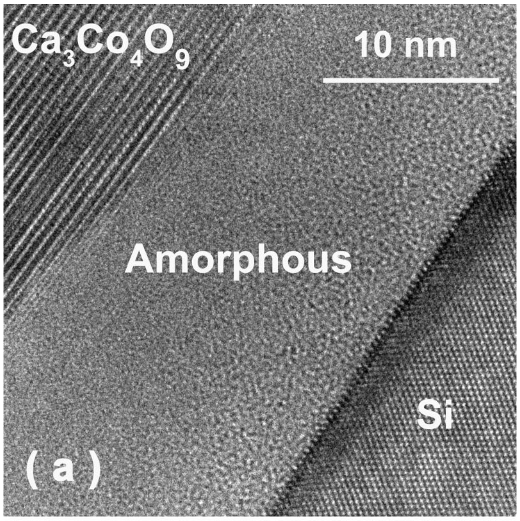



FIG. 1. XRD patterns for a 2300-Å-thick $Ca_3Co_4O_9$ film grown on single-crystalline Si (100) substrate.



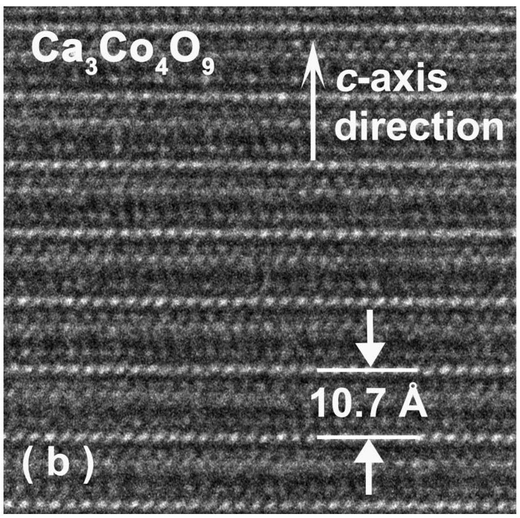




FIG. 2. (a) The HREM overview image of the $Ca_3Co_4O_9$/Si interface region for the film grown on Si (100) substrate, showing the atomic $Ca_3Co_4O_9$ layered structure and single-crystalline Si structure. Between the $Ca_3Co_4O_9$ film and Si (100) substrate, there is an amorphous layer ~20 nm thick. (b) The HREM image of the $Ca_3Co_4O_9$ film grown on Si (100) substrate, demonstrating a good crystallinity of the $Ca_3Co_4O_9$ film.

Cross-sectional transmission electron microscopy (TEM) images of a $Ca_3Co_4O_9$ film on Si (100) substrate are shown in Fig. 2. Figure 2(a) is the high-resolution electron microscopy (HREM) overview image of the $Ca_3Co_4O_9$/Si interface region, where the atomic $Ca_3Co_4O_9$ layered structure and single-crystal Si structure can be seen. Between the $Ca_3Co_4O_9$ film and Si substrate, there is an amorphous layer with a thickness of ~20 nm. The exact compositional nature of this amorphous layer is not clear yet, but extensive TEM investigation along the interface at various locations suggests that there are two distinct regions. The region adjacent to the Si substrate (~5 nm thick) is likely the $SiO_x$ amorphous layer, while the region adjacent to the $Ca_3Co_4O_9$ film is a predominantly amorphous material related to $Ca_3Co_4O_9$, within which some nanoscaled crystalline domains can be found. Figure 2(b) shows well ordered layer structures of $Ca_3Co_4O_9$ stacked along the *c* axis. These structures were invariably observed near the interface and deep inside the $Ca_3Co_4O_9$ films. No intergrowth defects were detected. The periodicity of the $CoO_2$ layers was estimated to be 10.7 Å, in consistence with the *c*-axis lattice parameter of $Ca_3Co_4O_9$

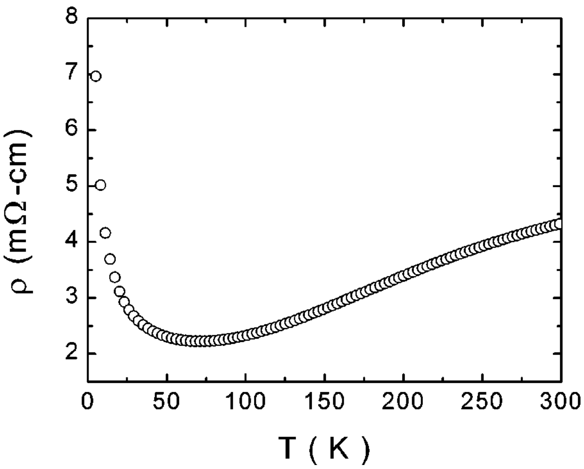



FIG. 3. The temperature dependence of the resistivity $\rho$ for the $Ca_3Co_4O_9$ film grown on Si (100) substrate.

determined from XRD pattern, as well as the reported value of 10.833 Å for the single-crystal sample.[6]

The growth mechanism of these *c*-axis-oriented $Ca_3Co_4O_9$ films on Si is of interest. Note that Si (100) substrate has a cubic structure with the lattice parameter $a=5.429$ Å, which is hardly a match for the $Ca_3Co_4O_9$ lattice. $Ca_3Co_4O_9$ consists of alternating layers of the triple rocksalt-type $[Ca_2CoO_3]$ subsystem (in-plane lattice parameters: $a\approx 4.8$ Å, $b\approx 4.5$ Å) and the single $CdI_2$-type $[CoO_2]$ subsystem (in-plane lattice parameters: $a\approx 4.8$ Å, $b\approx 2.8$ Å) stacked along the *c* axis. In addition, there is also a thin layer (a few nanometers) of native $SiO_x$ amorphous layer on the surface of the Si substrate prior to the thin-film deposition. Clearly, we should not expect epitaxial growth of $Ca_3Co_4O_9$ on Si. The fact that such well ordered $Ca_3Co_4O_9$ films do form on the top of the $SiO_x$ amorphous layer is perhaps the consequence of the nature of self-assembly intrinsic to the cobaltate system. $Ca_3Co_4O_9$ itself can be looked as self-assembled nanocomposites of misfit layers stacked alternately with bonding crystallographically incoherent. A behavior bearing some similarity to this case was observed in the growth of YSZ thin film on a $SiO_x$/Si(001) substrate at the very early stages of crystallization and growth.[11] However, the disordered regions ($SiO_x$ and YSZ amorphous layer) disappeared when the YSZ film was thicker than 6.5 nm.

Figure 3 shows the temperature dependence of the resistivity $\rho$ for $Ca_3Co_4O_9$ films grown on Si (100) substrate. The film shows a metallic behavior as $T$ decreases from 300 to 70 K. The value of $\rho$ at 300 K is 4.3 mΩ cm for the film with thickness of 2300 Å. This temperature dependence is very similar to that for the $Ca_3Co_4O_9$ single-crystal in-plane resistivity $\rho_{ab}(T)$.[6] The fact that the resistivity of the $Ca_3Co_4O_9$ films on Si substrates is actually smaller than that of the single crystal (~10–40 mΩ cm)[6] and other $Ca_3Co_4O_9$ films (>10 mΩ cm)[8,9] suggests that these films are of excellent quality.

The thermoelectric power of the $Ca_3Co_4O_9$ films was measured using a four-terminal steady state method in a Quantum Design physical property measurement system. Figure 4 shows the thermoelectric power as a function of temperature for a $Ca_3Co_4O_9$ film on Si (100) substrate between 100 and 400 K. As a reference, thermoelectric power of a single-phase $Ca_3Co_4O_9$ polycrystalline sample was also measured and shown in Fig. 4. The contribution of Si sub-

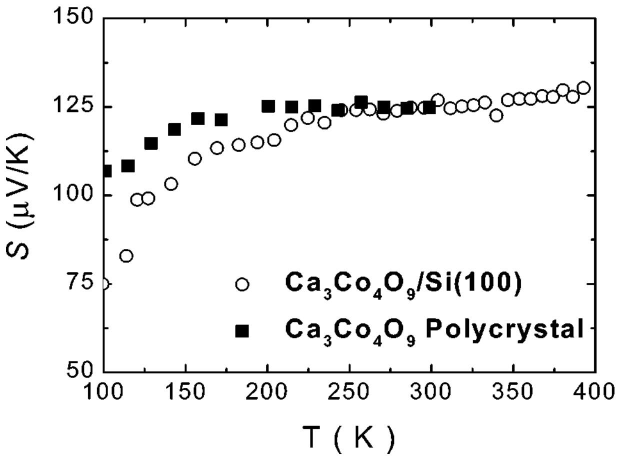



FIG. 4. The thermoelectric power as a function of temperature for a $Ca_3Co_4O_9$ film on Si (100) substrate and a $Ca_3Co_4O_9$ polycrystalline sample.

strate to the total thermoelectric power of the film is negligible in this temperature region, which was confirmed by a direct measurement of the thermoelectric power of a bare Si substrate. The thermoelectric power monotonically increases with temperature. At 300 K, the thermoelectric power for the $Ca_3Co_4O_9$ film on Si (100) and that for the polycrystalline samples are $\sim 126\ \mu V/K$, very close to that of the single-crystal sample ($\sim 125\ \mu V/K$).[6] The temperature dependence of thermoelectric power for the $Ca_3Co_4O_9$ film follows that of the bulk samples, with a slightly lower value at the low-temperature regime. Further improvement on the thermoelectric performance of these films may be possible by optimizing deposition conditions.

In summary, we demonstrated that high-quality *c*-axis-oriented thin films of $Ca_3Co_4O_9$ can be grown on Si substrates by pulsed-laser deposition without any chemical pretreatment of the substrate surface. The resistivity and thermoelectric power measurements show that these films have superior thermoelectric properties, similar to that found in the bulk samples. This advance suggests that the cobaltates can potentially be incorporated into the existing thin-film thermoelectric technology with a good scalability. In addition, TEM characterization revealed nearly perfect crystalline structures of the $Ca_3Co_4O_9$ film formed on top of $SiO_x$ amorphous layer, suggesting self-assembly is a viable technique for cobalt oxide-based thermoelectrics.

The authors would like to thank Drs. A. R. Moodenbaugh and V. Solovyov for technical assistance. This work was supported by the U. S. Dept. of Energy, Office of Basic Energy Science, under Contract No. DE-AC-02-98CH10886.

[1] I. Tersaki, Y. Sasago, and K. Uchokura, Phys. Rev. B **56**, 12685 (1997).
[2] S. Li, R. Funahashi, I. Matsubara, K. Ueno, and H. Yamada, J. Mater. Chem. **9**, 1659 (1999).
[3] S. Li, R. Funahashi, I. Matsubara, K. Ueno, and H. Yamada, J. Mater. Chem. **12**, 2424 (2000).
[4] R. Funahashi, I. Matsubara, S. Sodeoka, H. Ikuta, T. Takeuchi, and U. Mizutani, Jpn. J. Appl. Phys., Part 2 **39**, L1127 (2000).
[5] Y. Miyazaki, K. Kudo, M. Akoshima, Y. Ono, Y. Koike, and T. Kajitani, Jpn. J. Appl. Phys., Part 2 **39**, L531 (2000).
[6] A. Masset, C. Michel, A. Maignan, M. Hervieu, O. Toulemonde, F. Studer, B. Raveau, and J. Hejtmanek, Phys. Rev. B **62**, 166 (2000).
[7] G. Mahan, B. Sales, and J. Sharp, Phys. Today **50**, 42 (1997).
[8] Y. Yoshida, T. Kawai, Y. Takai, and M. Yamaguchi, J. Ceram. Soc. Jpn. **110**, 1080 (2002).
[9] I. Matsubara, R. Funahashi, and M. Shikano, Appl. Phys. Lett. **80**, 4729 (2002).
[10] H. Minami, K. Itaka, H. Kawaji, Q. J. Wang, H. Koinuma, and M. Lippmaa, Appl. Surf. Sci. **197–198**, 442 (2002).
[11] A. Bardal, Th. Matthée, J. Wecker, and K. Samwer, J. Appl. Phys. **75**, 2902 (1994).