Combinatorial pulsed laser deposition and thermoelectricity of \( \text{La}_{1-x}\text{Ca}_x\text{VO}_3 \) composition-spread films

Quinjiao Wang\(^a\), Kenji Itaka\(^{a,b,*}\), Hideki Minami\(^a\), Hitoshi Kawaji\(^a\), Hideomi Koinuma\(^{a,b,c}\)

\(^a\)Materials and Structures Laboratory, Tokyo Institute of Technology, 4259, Nagatsuta, Midori-ku, Yokohama 226-8503, Japan
\(^b\)CREST-Japan Science and Technology Agency, Tsukuba, 305-0044, Japan
\(^c\)Combinatorial Materials Exploration and Technology (COMET), Tsukuba, 305-0044, Japan

Received 5 January 2004; revised 20 February 2004; accepted 15 March 2004
Available online 21 July 2004

Abstract

\( \text{La}_{1-x}\text{Ca}_x\text{VO}_3 \) composition-spread film library was fabricated by combinatorial pulsed laser deposition and their thermoelectric properties were evaluated parallelly by the multi-channel probes of Seebeck coefficient and electric conductivity. Concurrent X-ray analysis verified the formation of solid soluted films in the full composition range \( 0 \leq x \leq 1 \) as judged from the linear variation of the lattice constants. The Seebeck coefficients of \( \text{La}_{1-x}\text{Ca}_x\text{VO}_3 \) changed from a large negative value to almost zero with the increase of \( x \); due presumably to the variation of valence in vanadium ions. The power factor in this library was as high as 0.6 \( \mu\text{W/cm K}^2 \), which was obtained at \( x = 0 \), i.e. pure \( \text{LaVO}_3 \) grown at 800°C.

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Keywords: Thermoelectric; Seebeck coefficient; Vanadium oxide; Combinatorial technology; Perovskite; Pulsed laser deposition; Composition-spread film

1. Introduction

Thermoelectric (TE) materials attract much interest for such applications as to heat pumps and power generators. At present, the materials with highest TE performance are intermetallic compounds such as \( \text{Bi}_2\text{Te}_3 \) [1–3]. However, their practical application to power generation from the waste heat has been drawn back by many material problems like a low melting point, poor oxidation resistance, and an insufficient conversion efficiency in the typical operating temperature range of the waste heat (300–800°C). The known material of \( \text{NaCo}_2\text{O}_4 \) was recently discovered to be a good TE material [4,5] to encourage researchers for exploring new TE materials in metal oxides. They are already in oxidized state and thermally stable, and therefore have the potential to overcome the problems mentioned above. The large Seebeck coefficient in \( \text{NaCo}_2\text{O}_4 \) is explained by the characteristic degeneracy due to spin and orbital degrees of freedom [6]. Thus, some 3d transition-metal oxides are candidates for new thermoelectric materials. Vanadium oxides possess various interesting properties due to the multivalent nature of vanadium. In general, heavy electron systems generate large thermopower due to the large density of state at the Fermi level. Thus, vanadium oxides are good candidates of highly efficient TE materials. A perovskite vanadate \( \text{LaVO}_3 \) is well-known as a typical Mott-insulator [7–10]. The substitution of divalent cations for \( \text{La}^{3+} \) sites can cause the vanadium cation to change the valence state from \( 3^+ \) to \( 4^+ \), leading to the enhancement of the vanadium valence state and the carrier density.

Combinatorial chemical technology started in drug industries for high throughput discovery of new drugs by the integrated organic synthesis [11] and now it is finding a wide possibility in solid state materials as a powerful tool for optimizing the compositions and fabrication conditions by systematically varying several process parameters [12–14]. A large number of samples (combinatorial library) can be fabricated and evaluated in a single run of experiments. We recently demonstrated the validity of this method for the investigation of \( \text{ZnO} \) based TE materials [15] among a lot of examples [16].
In this paper, we report on the combinatorial pulsed laser deposition (CPLD) and TE properties of $\text{La}_{1-x}\text{Ca}_x\text{VO}_3$ composition-spread films.

2. Experimental

$\text{La}_{1-x}\text{Ca}_x\text{VO}_3$ ($0 \leq x \leq 1$) composition-spread film library was fabricated on a $\text{SrTiO}_3$ (STO), substrate with a dimension of $15.0 \times 7.5 \times 1.0$ mm$^3$ using a CPLD system illustrated in Fig. 1(a). $\text{LaVO}_3$ and $\text{CaVO}_3$ targets of 15 mm in diameter and 5 mm in thickness were made from stoichiometric $\text{La}_2\text{O}_3-\text{V}_2\text{O}_5$, and $\text{CaCO}_3-\text{V}_2\text{O}_5$ mixed powders, respectively. These mixed powders were ground, pressed into pellets, pre-sintered at $600 \text{^\circ C}$ for 30 h in air, and sintered at $1000 \text{^\circ C}$ for 30 h in air. Although the sintering of bulk perovskite vanadates was conventionally carried out under such a reducing atmosphere as $\text{Ar}$ or $\text{Ar}/\text{H}_2$ mixture, we made the targets by sintering the pellets in air. The $\text{SrTiO}_3$ (100) single crystal (cubic, $a = 3.905$ Å) was used as a substrate, which has a small mismatch ($\sim 0.4\%$) to the lattice of bulk $\text{LaVO}_3$ (tetragonal, $a = b = 3.922$ Å, $c = 3.914$ Å) [17].

Into the CPLD chamber with a base pressure of $1 \times 10^{-7}$ Torr, Ar-balanced 10 ppm oxygen gas was introduced to regulate a total pressure at $1 \times 10^{-4}$ Torr, i.e. $P_{\text{O}_2} = 1 \times 10^{-9}$ Torr during the film deposition. The substrate temperature during the deposition was varied from 600 to 800 °C. Films were fabricated by the pulsed KrF excimer laser (Lambda Physik Inc.; COMPeX 102, $\lambda = 248$ nm) with an energy density range of 2.5–5.7 J/cm$^2$ and a laser repetition of 5 Hz. The sintered $\text{LaVO}_3$ and $\text{CaVO}_3$ targets were alternately positioned at a laser focus to be ablated by the laser pulses as illustrated in Fig. 1(a). The moving masks were slid during the film deposition in synchronization with the target exchange and laser conditioning. These operations were controlled by a personal computer installed with our original LabVIEW™ program. The target switching and the mask motion were programmed to deposit films with the thickness gradient from zero to one unit cell ($0.4$ nm) and from one unit cell to zero in each cycle of $\text{LaVO}_3$ and $\text{CaVO}_3$ film deposition. In this way, the value of $x$ in $\text{La}_{1-x}\text{Ca}_x\text{VO}_3$ was changed linearly from 0 to 1 along one direction of the substrate and this cycle was repeated until the film thickness reached the programmed thickness (Fig. 1(c)). In order to make 10 different stripe patterned films, each of which are

![Fig. 1. Schematic diagram of the parallel synthetics and characterization system. (a) Combinatorial pulsed laser deposition process. The substrate is covered by a shadow mask during the film deposition. (b) The multi-channel thermoelectric measurement system. (c) Procedure for the fabrication of composition-spread films (see text).](image-url)
electrically isolated, the substrate was covered with a patterned shadow mask of Inconel alloy during the deposition (Fig. 1(b)).

The structure analysis was carried out by conventional X-ray diffractometry (XRD) and ‘concurrent X-ray diffractometry’ (CXRD) [14,18], which measures XRD spectra of the entire composition range simultaneously. Two axes in the detector are the Bragg angle \(2\theta\) and the film position, which directly corresponds to the composition, along the 10 mm substrate. For the high-throughput evaluation of TE properties of the 10 pieces of film samples simultaneously, we developed such a multi-channel measurement system as shown in Fig. 1(b)[15]. This system enabled us to measure the resistance and Seebeck coefficient of the combinatorial film library compared to the range close to CaVO₃ as compared to the range close to LaVO₃. This is consistent with the larger FWHM value for LaVO₃ films than the data reported for the bulk sample [17]. A compressive strain from the substrate is presumed to elongate the \(c\) lattice normal to the substrate. The XRD peak was broadened to a larger extent in the composition range close to CaVO₃ as compared to the range close to LaVO₃. This is consistent with the larger FWHM value in the rocking curve (\(\theta\) scan) for CaVO₃ film than the value for LaVO₃.

The crystal lattice of LaVO₃ films was elongated along the \(c\)-axis, as the \(c\)-axis length of LaVO₃ films was larger than the data reported for the bulk sample [17]. A compressive strain from the substrate is presumed to elongate the \(c\) lattice normal to the substrate. The XRD peak was broadened to a larger extent in the composition range close to CaVO₃ as compared to the range close to LaVO₃. This is consistent with the larger FWHM value in the rocking curve (\(\theta\) scan) for CaVO₃ film than the value for LaVO₃.

3. Results and discussions

Despite the detection of such impurity phases as VO₂, V₂O₅ in X-ray diffraction patterns of sintered targets, the epitaxial uniform films of LaVO₃ and CaVO₃ grown by CPLD did not contain an impurity phase. The full widths at half maximum (FWHM) in the rocking curve (\(\theta\) scan) of the both films obtained at 800 °C were 0.032 and 0.44°, respectively. The thickness of the \(La_{1-x}Ca_xVO_3\) composition-spread films was approximately 2000 Å, and the deposition rates of LaVO₃ and CaVO₃ were 0.11 and 0.14 Å/pulse, respectively.

Fig. 2 shows a part of CXRD image (21.6° ≤ 2θ ≤ 24.1°) (a) for full composition area \((0 \leq x \leq 1)\) and the line profiles (b) at four \(x\)-positions of \((La_{1-x}Ca_x)_3VO_3\) composition-spread films on a STO substrate. The diffraction angle \(2\theta\) in this image is calibrated by the STO (200) peak positions in order to remove the error due to the substrate setup in the CXRD. It is noted that the CXRD (200) peak in this range is separated into 10 pieces because the films are patterned by a shadow mask as shown in Fig. 1(a). The CXRD peak of the composition-spread films changed linearly, thus indicating that the composition-spread films formed solid solution in the whole composition range \((0 \leq x \leq 1)\). Thus, the \(c\)-axis length obeyed Vegard’s law. The crystal lattice of LaVO₃ films was elongated along the \(c\) axis, as the \(c\)-axis length of LaVO₃ films was larger than the data reported for the bulk sample [17]. A compressive strain from the substrate is presumed to elongate the \(c\) lattice normal to the substrate. The XRD peak was broadened to a larger extent in the composition range close to CaVO₃ as compared to the range close to LaVO₃. This is consistent with the larger FWHM value in the rocking curve (\(\theta\) scan) for CaVO₃ film than the value for LaVO₃.

Fig. 3 shows the resistivity of \((La_{1-x}Ca_x)_3VO_3\) (0 ≤ \(x\) ≤ 0.05) composition-spread films grown in the temperature range from 600 to 800°C. With the decrease of the growth temperature, the resistivities of films (a) Concurrent X-ray diffraction patterns obtained with a line-focused Cu Kα X-ray source for \(La_{1-x}Ca_xVO_3\) (0 ≤ \(x\) ≤ 1.0) composition-spread films deposited at 800 °C. The gray scalebar indicates the X-ray diffraction intensity. The peak line of the films was divided into ten because these films were patterned by a metal shadow mask. The cross (+) markers show the peak positions of the films and the additional left axis shows the \(c\)-axis length calculated from the wavelength of Cu Kα (\(\lambda = 1.5418\) Å). The left arrow indicates the \(c\)-axis length of bulk LaVO₃ [17]. (b) Line profiles of (a) along dashed lines at \(x = 0.0, 0.125, 0.875, 1.0\), respectively.
increased, indicating that the crystallinity of the films was depressed at lower temperatures.

Fig. 4 shows the TE properties of La$_{1-x}$Ca$_x$VO$_3$ composition-spread films grown at 800 °C. The Seebeck coefficients of CaVO$_3$ side films were close to zero (0 ~ 5 μV/K), while those of LaVO$_3$ side films were large negative values (~ 310 μV/K). The heavy electron in the Mott-insulator of LaVO$_3$ is considered to cause the large Seebeck coefficient of LaVO$_3$ films [19], while CaVO$_3$ film appears to behave like a normal metal. The transition point from large negative value to almost zero is around $x = 0.2$, where the metal-insulator transitions was reported to occur [9].

The resistivity of La$_{1-x}$Ca$_x$VO$_3$ composition-spread films decreased monotonically from $x = 0.0$ to $x = 1.0$. The Seebeck coefficient of La$_{1-x}$Ca$_x$VO$_3$ close to CaVO$_3$ ($0.6 \leq x \leq 1.0$) was reported to be sensitive to the temperature and Ca content $x$; it could be positive and negative depending on these parameters. [20]. This means that La$_{1-x}$Ca$_x$VO$_3$ have both electron- and hole-type carriers and the dominant carrier represents the polarity of the Seebeck coefficient. In particular, the strong strain of LaVO$_3$ film on a STO may cause its large negative Seebeck coefficient opposite to the reported data of bulk samples [20, 21].

Fig. 5 shows the TE properties of LaVO$_3$ films grown at various temperatures $T_g$. There is little change in the Seebeck coefficients of LaVO$_3$ films grown at the different growth temperatures, while the resistivity of them increased with the decrease of the growth temperatures. It is considered that the low growth temperature caused to increase the grain boundaries of the films and increase the resistivity of them. The power factor in this library was as high as 0.6 μW/cm K$^2$, which was obtained at $x = 0$ composition (i.e. LaVO$_3$) grown at 800 °C.
4. Conclusion

La$_{1-x}$Ca$_x$VO$_3$ composition-spread films were fabricated by combinatorial pulsed laser deposition. Concurrent X-ray analysis showed that this material formed a solid solution. The Seebeck coefficient of La$_{1-x}$Ca$_x$VO$_3$ changed from a large negative value to almost zero, presumably depending on the variation of vanadium valence with the increase of x. The high power factor of 0.6 $\mu$W/cm$^2$K$^2$ suggests further increase in thermoelectric property in vanadium oxide systems.

Acknowledgements

Authors thank Dr Yasutaka Ban for fruitful discussions and critical readings.

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[21] These results were reproducible in the same fabrication condition. Preliminary, we found the substrate effect of the Seebeck polarity in LaVO$_3$ films. We will report on the detail of them elsewhere.