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Deposition of thermoelectric strontium hexaboride thin films by a low pressure CVD method

Tommi Tynell, Takashi Aizawa, Isao Ohkubo, Katsumitsu Nakamura, Takao Mori*

International Center for Materials Nanoarchitectonics (MANA), National Institute for Materials Science (NIMS), 1-1 Namiki, 305-0044 Tsukuba, Japan

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ABSTRACT

Thin films of SrB_6 were deposited on sapphire substrates using a chemical vapor deposition method, with elemental strontium and decaborane, $B_{10}H_{14}$, used as the strontium and boron sources, respectively. The formation of highly crystalline, phase-pure SrB_6 films was confirmed with X-ray diffraction and reflection high energy diffraction (RHEED) analysis, and the films' thermoelectric transport properties were measured. A relatively high deposition temperature of 850–950 °C was found to be optimal for obtaining well-crystallized films at an extremely high deposition rate. The thermoelectric transport properties of the SrB_6 thin films were observed to be comparable to those reported for bulk materials, but an unexpectedly high electrical resistivity led to a reduced power factor value for the thin films.

1. Introduction

Boron-rich metallic borides are known for often having very complex crystal structures, but hexaborides, MB_6, form an exception with their relatively simple cubic crystal structure. Despite this structural simplicity, metallic hexaborides have been found to exhibit a number of interesting properties, such as the ferromagnetism observed in EuB_6 [1] and, more controversially, La-doped CaB_6 [2,3], or the low work function and vacuum stability which makes hexaborides such as LaB_6 or CeB_6 suitable for use as hot cathode materials in electron field emission applications [4,5]. Alkaline earth hexaborides have also been identified as n-type thermoelectric materials, and a thermoelectric figure of merit as high as 0.35 has been reported for their bulk samples [6–10]. This performance along with the borides' general high capability to withstand high temperatures makes alkaline earth hexaborides among the promising materials [11] for possible usage in high temperature thermoelectric energy harvesting applications such as topping cycles of thermal power plants [12], where conventional state of the art materials are unusable. However, improving the thermoelectric performance of the materials remains a priority if they are to be used in applications on a large scale. Nanostructuring approaches such as the fabrication of layered superlattices offer a straightforward way to achieve improvements in thermoelectric performance even at room temperature [13–15], but a suitable thin film process is required to realize this goal.

Previous studies on hexaboride thin film depositions have largely concentrated on LaB_6 and CeB_6 [16,17], and CaB_6 thin film processes have also been studied on several occasions [18,19], but SrB_6 thin films have seen relatively little study. A previous study has looked at the thermoelectric performance of alkaline earth hexaboride thin films deposited via pulsed laser deposition [20], but otherwise the thermoelectric properties of hexaboride thin films have remained unexplored. Chemical vapor deposition (CVD) offers a robust process for depositing boron films through the use of various boron hydride precursors [21,22], and the method has been utilized before to deposit thin films of borides such as LaB_6 [23], NdB_6 [24] and MgB_2 [25]. While CVD generally utilizes volatile compounds that react to form the desired thin film, the MgB_2 study reported that an elemental Mg source can be used together with decaborane in a process to deposit boride films [25]. Here we demonstrate that a similar method, based on elemental strontium and decaborane sources, can be used to deposit films of SrB_6 and report the thermoelectric properties of the films.

2. Materials and methods

Thin films of SrB_6 were deposited on single-crystal sapphire (0001) substrates (Shinkosha) using a custom-built CVD reactor. The reactor consisted of a molybdenum sample stage/heater and two heated precursor sources: one valve-controlled source containing decaborane ($B_{10}H_{14}$) and one source consisting of an open Al_2O_3 crucible with a tungsten heating wire within the reaction chamber. Hence, the decaborane flow into the reaction chamber could be controlled with the valve, but the Sr flow onto the

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* Corresponding author.
E-mail address: MORI.Takao@nims.go.jp (T. Mori).

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substrate was determined entirely by its heating temperature. The walls of the reaction chamber where unheated, and the system was kept at a base pressure of around 10^{-3} Pa using a turbomolecular pump. The films were deposited using substrate temperatures of 700–950 °C, while the source temperatures for decaborane and Sr were kept at 110 °C and 750–770 °C, respectively. It should be noted that the reported temperature for the Sr source was measured from the bottom of the crucible, so the actual Sr temperature could be as much as 200 °C lower. Thus, the vapor pressure of the heated Sr metal was expected to be in the 1–10 Pa range, which would result in quite a strong Sr flow onto the substrate. While precise precursor flows could not be measured, the pressure in the reaction chamber (measured using an ion gauge) was monitored and kept constant at $2\text{–}3\times10^{-2}$ Pa by adjusting the decaborane precursor valves. The deposition time was 10 minutes for all the depositions, which already resulted in films around 2.5–3.5 μm thick, corresponding to a very fast deposition rate of 0.25–0.35 μm/min.

For structural characterization, X-ray diffraction (XRD) measurements were performed using a Rigaku Rind-Ultima III X-ray diffractometer in $2\theta/\theta$ mode. For one of the samples, the surface crystal structure was also studied using a reflection high energy electron diffraction (RHEED) apparatus, performed in ultra-high vacuum conditions of around 10^{-8} Pa. This sample was heated to 600 °C for two hours inside the vacuum chamber of the RHEED system in order to eliminate potential surface contamination during exposure to the atmosphere. The thicknesses of the SrB_6 films were determined by using a Dektak 6M surface profiler system and confirmed with a JEOL JSM-6700F scanning electron microscope (SEM). A Rutherford backscattering spectrometry (RBS) setup was also used to evaluate the distribution of the elements within the films. Finally, the thermoelectric transport properties (Seebeck coefficient and electrical resistivity) were simultaneously measured with an ULVAC ZEM-2 apparatus from room temperature to 700 °C under a helium atmosphere.

3. Results and discussion

Black films with a uniform, opaque appearance were obtained across the investigated substrate temperature range of 700–950 °C. The formation of the SrB_6 structure was confirmed for all of the samples using XRD, with the XRD pattern of the 950 °C sample displayed in Fig. 1. The indexed peaks in the figure correspond to those resulting from the cubic structure of SrB_6, while the unindexed peaks are all from the sapphire substrate (including some impurities already present in the substrate). Thus, the films consisted of pure SrB_6, with no impurity phases detected, indicating a successful fabrication of SrB_6 thin films. There was also no shifting of diffraction peaks observed, which was expected because the films are so thick that any lattice strain inflicted upon the film by the substrate would be expected to be accommodated through defect formation mechanisms at a critical thickness far lower than the 2.5–3.5 μm deposited in this work. The lattice constant value of 4.194 Å calculated from the XRD pattern also closely matches the reported value for bulk SrB_6 of 4.198 Å [26], a difference of approximately 0.1%. The two main sapphire diffraction peaks are cut off from the pattern in Fig. 1 to make the film diffraction pattern visible in the figure; the intensity of the (100) SrB_6 peak was approximately 1–10% of the intensity of the sapphire (0006) peak, varying with the deposition temperature.

The most striking feature of the XRD pattern in Fig. 1 is how dominant the (100) direction diffractions are compared with the other peaks. Although all the expected SrB_6 diffractions are discernible, their peak intensities are far below those of the (100) peaks, indicating a strong preferred orientation towards the $<100>$ direction. The (110) peak especially is strongly suppressed; in a bulk powder diffraction pattern it would be expected to be the strongest peak, yet here it is barely 1/10 of the (100) peak intensity. The XRD patterns of all the analyzed samples were very similar to the one shown in Fig. 1, although the intensities of the diffraction peaks, particularly the (100) peak, varied with the deposition temperature.

The obtained XRD patterns were also used to observe changes in the crystallinity of the SrB_6 films based on the intensity and width of the (100) diffraction peak. Since a change in diffraction intensity under identical measurement conditions can be thought to arise either from a change in the crystallinity or thickness of the analyzed thin film, the evolution of the SrB_6 film crystallinity can be estimated by comparing the intensity of the (100) diffraction peak normalized in relation to the film thickness and sapphire (0006) peak intensity according to the formula $I_{\text{Norm}(100)}=I_{\text{SB}(100)}/I_{\text{Sapph}(0006)}d$, where d is the film thickness. Likewise, the width of the diffraction peak can be used to estimate the crystallinity of the film, with narrower peaks indicating larger grains and thus a higher crystalline quality. The normalized (100) peak intensities and measured peak widths at half maximum for films deposited between 700 and 950 °C are plotted in Fig. 2.

The normalized (100) peak intensity can be seen to rise with increasing deposition temperature until 850 °C, signifying an improving degree of crystallinity. After 850 °C the intensity starts to go down slightly, which could result from decreasing crystallinity.

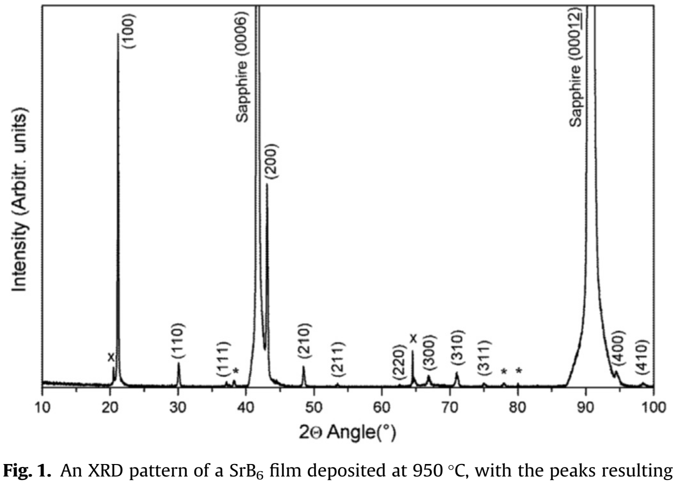

Fig. 1. An XRD pattern of a SrB_6 film deposited at 950 °C, with the peaks resulting from SrB_6 indexed. Peaks marked with × and * correspond to forbidden peaks of the sapphire substrate and unknown peaks from substrate impurities, respectively.

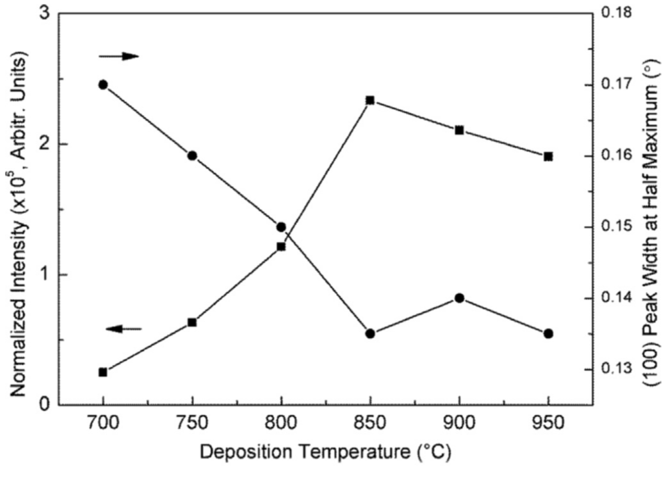

Fig. 2. The normalized (100) diffraction peak intensities (squares) and peak widths (circles) of the SrB_6 films deposited at different temperatures.