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Growth optimization of $CeCoIn_5$ thin films via pulsed laser deposition

Elmeri Rivasto[†,a,b], Jihyun Kim[†,c], Le Minh Tien[d], Ji-Hoon Kang[d], Sungmin Park[d], Woo Seok Choi[d], Won Nam Kang[d], and Tuson Park[*,d]

[a] *Wihuri Physical Laboratory, Department of Physics and Astronomy, University of Turku, 20014 Turku, Finland*
[b] *University of Turku Graduate School (UTUGS), University of Turku, 20014 Turku, Finland*
[c] *Institute of Basic Science, Sungkyunkwan University, Suwon 16419, South Korea*
[d] *Department of Physics, Sungkyunkwan University, Suwon 16419, Republic of Korea*

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Abstract

We developed an optimization process of the pulsed laser deposition method to grow epitaxial $CeCoIn_5$ thin films on MgF_2 substrates. The effects of different deposition parameters on film growth were extensively studied by analyzing the measured X-ray diffraction patterns. All the deposited films contained small amounts of $CeIn_3$ impurity phase and misoriented $CeCoIn_5$, for which the *c*-axis of the unit cell is perpendicular to the normal vector of the substrate surface. The deposition temperature, target composition, laser energy density, and repetition rate were found effective in the formation of (00*l*)-oriented $CeCoIn_5$ as well as the undesired phases such as $CeIn_3$, misoriented $CeCoIn_5$ along the (112) and (*h*00). Our results provide a set of deposition parameters that produce high-quality epitaxial $CeCoIn_5$ thin films with sufficiently low amounts of impurity phases and can serve as a reference for future studies to optimize the deposition process further.

Keywords: Pulsed laser deposition, thin-film, heavy fermion superconductor

1. INTRODUCTION

Heavy-fermion superconductors belong to the class of unconventional superconductors for which the simple Bardeen–Cooper–Schrieffer theory is not applicable. They remain to be of considerable interest to researchers as they provide a platform to study the unexplained origin of unconventional superconductivity and the interplay between superconductivity and magnetic quantum critical fluctuations related to the competition between Rudermann–Kittel–Kasuya–Yoshida (RKKY) interaction and the Kondo effect [1, 2]. Several recent studies on artificially grown Kondo superlattices of heavy fermion compounds, such as $CeCoIn_5/YbCoIn_5$ [3-6], $CeCoIn_5/CeRhIn_5$ [7, 8], and $CeCoIn_5/CeIn_3$ [9], wherein superconducting heavy electrons are confined within 2D block layers have provided a new method for exploring exotic superconducting states and the relationship between spin fluctuations and superconductivity. Nevertheless, the fabrication of epitaxial heavy-fermion thin films has not been widely investigated because of the difficulty in balancing layer-by-layer growth and crystallinity.

This study examined the effects of various deposition parameters on the growth of $CeCoIn_5$ thin films on MgF_2 substrates by using the pulsed laser deposition (PLD) technique [10]. The parameters include the deposition temperature (T_D), the stoichiometry ratio of the target materials, energy density (E_L) and repetition rate (f_P) of the laser. The deposited films were analyzed by X-ray diffraction (XRD) measurements, which provide detailed information about the growth of $CeCoIn_5$ and the presence of impurity phases. Conclusions pertaining to the effects of the aforementioned parameters on the formation of impurity phases were drawn, guiding further optimization.

* Corresponding author: tp8701@skku.edu
†These authors contributed equally to this work.

2. EXPERIMENTAL DETAILS

$CeCoIn_5$ thin films were grown via PLD on *c*-axis-oriented single-crystalline MgF_2 substrates using a KrF pulsed laser with a wavelength of 248 nm. The target materials were grown using an electrical arc melting furnace with a stoichiometric ratio of Ce:Co:In = 1:1:5+x (x = 0.5, 1.0, 1.5). The targets were encapsulated by quartz ampoule were annealed at 600 ℃ for a week to form the $CeCoIn_5$ structural phase with additional indium, and their surfaces were polished to be flat. The substrates were annealed at 800 ℃ for 2 h in a high-vacuum chamber before deposition. The films were grown under selective growth conditions of T_D (400–500 ℃), E_L (1.6–2.8 J/cm^2), and f_P (3–10 Hz) under a base pressure of 5×10^{-9} Torr. The structural information of $CeCoIn_5$ thin films on MgF_2 substrates was characterized by XRD.

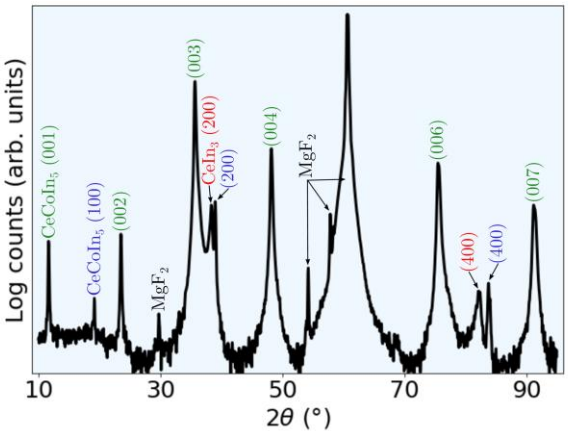

Fig. 1. An example of a measured XRD 2θ–ω scan with identified peaks belonging to the desired *c*-axis oriented $CeCoIn_5$ (green), misoriented $CeCoIn_5$ (blue) and impurity phase $CeIn_3$ (red).

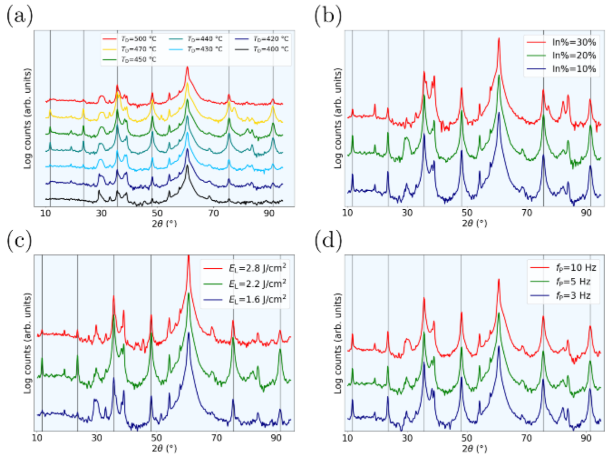

Fig. 2. 2θ–ω scans for varying (a) T_D, (b) excess indium concentrations of the target, (c) E_L, and (d) f_P. The vertical lines indicate the positions of the visible $CeCoIn_5$ (00*l*) peaks.

3. RESULTS AND DISCUSSION

The optimization process was started from a set of initial parameters based on the findings of our previous study [10]. Consequently, the optimal temperature was in the range of 400–500 ℃ with approximately 2.2 J/cm^2 laser energy density and the repetition rate of 5 Hz. The target was initially doped with a 20 % excess indium, which was necessary to avoid the formation of the $CeIn_3$ impurity phase. With such parameters, the growth of *c*-axis-oriented $CeCoIn_5$ was detected by the XRD 2θ–ω scan, although the films were far from optimal because of the presence of impurity phases. The 2θ–ω scan is representatively shown in Fig. 1 to identify peaks, while all measured 2θ–ω scans as functions of different growth parameters are presented in Fig. 2a–d. The diffraction pattern contains (00*l*) orientation of $CeCoIn_5$, except for the (005) peak that is submerged by the substrate peak, which indicates the presence of a *c*-axis-oriented $CeCoIn_5$. In contrast, (*h*00)-oriented $CeCoIn_5$ and small $CeIn_3$ peaks were observed in all the grown films. Optimally grown $CeCoIn_5$ thin films crystallize with lattice parameters of a= 4.619 Å and c= 7.545 Å, which are comparable with the values of a= 4.613 Å and c= 7.551Å in single crystal [11, 12]. The electrical transport measurement has been performed for a couple of films and showed similar superconducting properties with bulk $CeCoIn_5$.

The critical thickness of a thin film is defined as the thickness above which it becomes energetically favorable for the film to release lattice strain by forming dislocations. We have numerically estimated the critical thickness as a function of lattice mismatch using a self-contained expression derived by Matthews and Blakeslee for the critical thickness [13, 14]. Since the lattice constant of the MgF_2 substrate is a= 4.621 Å , the lattice mismatch between the $CeCoIn_5$ film and the MgF_2 substrate is f= 0.17%, indicating that the critical thickness is between 50-100 nm. The thickness of the samples determined by Scanning Electron Microscopy (SEM) technique through the cross-section of the samples is around 70-80 nm. Since the film thickness is comparable with the estimated critical thickness, it can be expected that most of the films are strained. It explains the reason why the lattice parameter along the *a*-axis of $CeCoIn_5$ is a bit larger than the bulk value while the lattice parameter along the *c*-axis behaves oppositely owing to the Poisson effect.

Maximizing (00*l*) oriented $CeCoIn_5$ peaks ($\Sigma I^{(00l)}_{CeCoIn_5}$) and minimizing (*h*00) oriented $CeCoIn_5$ ($\Sigma I^{(h00)}_{CeCoIn_5}$) and $CeIn_3$ peaks ($\Sigma I^{(hkl)}_{CeIn_3}$) are needed to optimize PLD parameters to fabricate epitaxial $CeCoIn_5$ thin films with high crystallinity. In order to quantitatively compare the crystallinity and amount of a particular substance in the sample, we propose a parameter (referred to as *R*-parameter herein) that can be tested experimentally as

$$R = \frac{\Sigma I^{(00l)}_{CeCoIn_5}}{\Sigma I^{(h00)}_{CeCoIn_5} + \Sigma I^{(hkl)}_{CeIn_3}} \quad (1).$$

The advantage of this approach is that *R* is independent of the film thickness and peak background, making it straightforward to calculate. However, the individual sums of the aforementioned peak intensities, which are affected by the film thickness and backgrounds of the nearby peaks, are also of interest.

Considering the thicknesses of the films constant, the peak sums of different films can be compared by considering the possible background of other nearby peaks. To calculate the peak heights reliably, one should either consider isolated peaks that are not affected by the background of other peaks in their vicinity or consider the effect of backgrounds of other peaks by fitting a double pseudo-Voigt function to the corresponding data [15]. In this study, we utilized both of these approaches by calculating $\Sigma I^{(00l)}_{CeCoIn_5}$ from the $CeCoIn_5$ (003) peak, calculating $\Sigma I^{(hkl)}_{CeCoIn_5}$ from the $CeCoIn_5$ (100) and (112) peaks, and calculating $\Sigma I^{(hkl)}_{CeIn_3}$ from the $CeIn_3$ (111) peak. The only cases in which the background of another peak had to be considered by fitting a double pseudo-Voigt function were the $CeCoIn_5$ (003) and $CeCoIn_5$ (112) peaks.

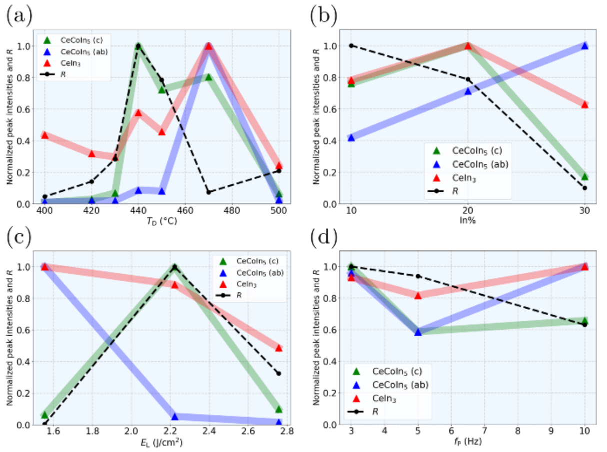

Fig. 3. The sums of the normalized peak intensities and the calculated *R*-parameter functions of (a) T_D, (b) excess indium concentration of the target, (c) E_L and (d) f_P.

The measured sums of the peak heights and the calculated *R*-parameters are presented in Fig. 3a–d as functions of the different control parameters.

The first control parameter to be optimized was the deposition temperature (T_D), achieved by growing films in the temperature range of 400–500 ℃ with 2.2 J/cm^2 laser energy density, the repetition rate of 5 Hz, and 18,000 pulses using a 20 % excess indium target. Based on the measured 2θ–ω scan in Fig. 2a, the peak intensities along with the *R*-parameter are presented in Fig. 3a. The intensities of the desired $CeCoIn_5$ (00*l*) peaks reach their maximum values in the range 440–470 ℃, inside which the peak intensities are approximately 80 % higher than those at other temperatures. This suggests that the optimal deposition temperature range for $CeCoIn_5$ is relatively wide, at least 30 ℃. The amount of misoriented $CeCoIn_5$ is increased by 90 % only at 470 ℃, manifested by the sudden emergence of an intense $CeCoIn_5$ (112) peak. The amount of $CeIn_3$, in contrast, stays approximately constant at lower temperatures before suddenly increasing around 470 ℃. All the peak intensities drop suddenly as the deposition temperature is increased up to 500 ℃. This indicates a critical temperature above which the emitted particles from the target cannot attach to the substrate surface. When considering the presence of impurity phases, the optimal deposition temperature is manifested as the value of the *R*-parameter reaches a sharp maximum at 440 ℃. The sharpness of the *R*-peak illustrates how the optimal temperature range can be as narrow as a few degrees. Even at the optimal temperature, at which the *R*-parameter is increased by approximately 90 % compared to other temperatures, the amounts of both impurity phases are significant. These results suggest that varying the deposition temperature is not effective in eliminating these impurity phases entirely.

To reduce the amount of impurity phases in the films, the effect of the target morphology was studied by depositing films from targets containing 10–30 % excess indium. The films were deposited with 2.2 J/cm^2 pulses and the repetition rate of 5 Hz at a previously optimized temperature of 440 ℃. The results are presented in Fig. 2b and 3b, where the amount of *c*-axis-oriented $CeCoIn_5$ and the $CeIn_3$ impurity phase is observed at their maximum at 20 % excess indium. In contrast, the amount of the misoriented $CeCoIn_5$ increases linearly with the excess indium concentration, suggesting that it is possible to reduce the amount of the misoriented phase by reducing the amount of excess indium in the target. However, previous studies suggested that the excess indium in the target is needed for phase formation and considering a poor sticking coefficient of indium [16, 17]. Excess indium above 10 % apparently has no advantage as the *R*-parameter decreases approximately linearly as the doping increases owing to the increased amount of the misoriented $CeCoIn_5$ phase. Doping concentrations in the range of 0–10 % may be of interest for future studies.

Next, the effect of laser energy density (E_L) was examined by growing films with energies in the range of 1.6-2.8 J/cm^2 at 440 ℃ with a repetition rate of 5 Hz using a 10 % excess indium target that was previously found to be optimal. As observed in Fig. 2c and 3c, the amount of $CeCoIn_5$ reaches an apparent maximum of around 2.2 J/cm^2, at which it attains approximately 90 % higher values than other laser energies. The amount of both of the impurity phases decreases as the energy of the laser is increased. The optimal laser energy density determined by the highly increased amount of *c*-axis-oriented $CeCoIn_5$ is 2.2 J/cm^2, as the *R*-parameter also reaches a maximum value at this energy level.

Furthermore, the effect of the repetition rate (f_P) was investigated by depositing films with the repetition rates in the range of 3–10 Hz with previously optimized parameters of 440 ℃ deposition temperature and 2.2 J/cm^2 laser energy density, using the same 10 % excess indium target as before. As shown in Figs. 2d and 3d, the amount of the desired *c*-axis-oriented $CeCoIn_5$ clearly increases at the low repetition rates but drops by 40 % at the frequencies above 5 Hz. The amount of the misoriented $CeCoIn_5$ phase is minimized by 40 % at a frequency of 5 Hz, while the amount of $CeIn_3$ impurity phase is not significantly affected by the repetition rate. The *R*-parameter slowly decays as the frequency increases, indicating that the repetition rate is not a critical parameter that significantly affects the film properties in the growth process. However, the lower frequencies should be utilized as they are observed to produce slightly better results.

4. CONCLUSIONS

Heavy fermion superconductor $CeCoIn_5$ films were successfully deposited on the MgF_2 substrate via pulsed laser deposition. The deposition parameters were optimized to maximize the ratio of the well-oriented $CeCoIn_5$ peak intensities over the misoriented $CeCoIn_5$ and the $CeIn_3$ impurity peak intensities in the XRD spectra. The optimal deposition temperature was observed to be within a narrow range of around 440 ℃. The laser energy density was observed to have a critical effect on the film growth, with an optimal value of approximately 2.2 J/cm^2. The repetition rate (f_P), in contrast, was not observed to have a significant effect on the composition of the film, although lower frequencies produced slightly better results.

Increasing the amount of excess indium in the target seemed to have a negative effect on the film quality because of the greater amount of misoriented $CeCoIn_5$ in the deposited films. However, the excess indium may help the impurity phase suppressed, reducing the $CeIn_3$ impurity phase. Thus, further optimization below 10 % excess indium should be considered. Other future experiments include studying the effect of target doping with other elements, such as excess cobalt, along with optimizing the laser energy density in a narrower range.

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