# **RSC Applied Interfaces**



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# PAPER

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Cite this: RSC Appl. Interfaces, 2025, **2**, 822

Received 28th October 2024 Accepted 8th March 2025

DOI: 10.1039/d4lf00367e

rsc.li/RSCApplInter

### Introduction

Rare-earth hydrides have been widely studied for their interesting physical properties, such as electrochromic switchable mirrors and near-room-temperature superconductivity under high pressure.<sup>1-5</sup> High hydride ion conduction in rare-earth hydrides has attracted much attention for its electrochemical implications in battery applications.<sup>6-8</sup> Complex rare-earth hydrides are also anticipated to serve as a platform for exploring novel physical properties.<sup>9-11</sup> Owing to these interesting properties, recent studies have also focused on thin film growth to expand the range of applications for various rare-earth hydrides.<sup>12-16</sup>

Fluorite-type LaH<sub>2</sub>, which consists of a face-centered-cubic (fcc) La lattice with tetrahedral sites occupied by H atoms, is known to possess a metallic band structure due to the 5d<sup>1</sup> electron configuration of the divalent La ion.<sup>17</sup> The metallic ground state of LaH<sub>2</sub> has been confirmed through specific heat and magnetic susceptibility measurements at low

# Thickness-induced metal-semiconductor transition in LaH<sub>2</sub> epitaxial thin films grown by reactive rf magnetron sputtering<sup>+</sup>

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Rare-earth hydrides have been extensively studied for their metal-insulator transition, high-temperature superconductivity and high hydride ionic conduction. Hence, research on their thin films is of great interest for exploring future-/next-generation device applications. In this study, (111)-oriented LaH<sub>2</sub> epitaxial thin films with varying thicknesses were grown for the first time via reactive rf magnetron sputtering. In the thicker films, the out-of-plane and in-plane lattice spacings were almost similar to those of bulk LaH<sub>2</sub>. As the thickness decreased, the out-of-plane lattice spacing increased significantly, probably due to lattice strain, while the in-plane lattice spacing increased slightly. The thicker films exhibited metallic behavior similar to bulk LaH<sub>2</sub>, whereas the thinner films were narrow band-gap semiconductors with a direct transition, indicating a thickness-induced metal-semiconductor transition without altering the hydrogen composition. These results suggest that strain engineering of rare-earth hydrides could enable the control of their physical properties even under ambient conditions.

> temperatures using polycrystalline bulk specimens.18,19 Regarding the electrical conduction of LaH<sub>2</sub>, superconductivity has been reported in polycrystalline bulk specimens, although clear experimental evidence, such as zero resistance, has not been demonstrated. In addition, theoretical calculations have predicted recent superconductivity in LaH<sub>2</sub> due to the rearrangement of H atoms into the interstitial octahedral sites of the fcc La lattice in fluorite-type LaH<sub>2</sub>.<sup>20</sup> Additionally, a LaH<sub>2</sub> monolayer with a hexagonal lattice has been predicted to be a direct semiconductor.<sup>21</sup> Therefore, it is of interest to evaluate the intrinsic electrical conduction of LaH<sub>2</sub> at low temperatures using single crystalline specimens, such as epitaxial thin films. However, LaH<sub>2</sub> has so far been synthesized as polycrystalline bulks and thin films by heating La metal with a Pd capping layer in a hydrogen atmosphere<sup>1,2,15-17,19-25</sup> or, more recently, through a mechanochemical approach.<sup>26</sup> In addition, rare-earth hydrides, such as LaH<sub>2</sub>, are unstable in air, making it difficult to synthesize single-phase specimens free of impurities.9,18,21

> Recently, rare-earth hydride thin films have been directly grown using new approaches, such as pulsed laser deposition or reactive sputtering, without the need for a Pd capping layer.<sup>9</sup> For example, single-phase YH<sub>2</sub> epitaxial thin films have been successfully synthesized by reactive rf magnetron sputtering.<sup>11</sup> By using an *in situ* grown capping layer, the stability of the YH<sub>2</sub> films in air has been improved, resulting in higher electron mobility than polycrystalline bulk YH<sub>2</sub>.<sup>11</sup>

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<sup>†</sup> Electronic supplementary information (ESI) available. See DOI: https://doi.org/ 10.1039/d4lf00367e

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In this study, (111)-oriented  $LaH_2$  epitaxial thin films were synthesized for the first time by reactive rf magnetron sputtering with an *in situ* grown  $SiN_x$  capping layer. The outof-plane lattice spacing increased significantly as the thickness decreased, suggesting the presence of thicknessdependent lattice strain. From electrical resistivity and optical absorption spectroscopy, the thicker films exhibited metallic behavior similar to bulk  $LaH_2$ , while the thinner films were semiconductors, a behavior not previously reported for bulk  $LaH_2$ . These results indicate a thicknessinduced metal-semiconductor transition, probably attributed to lattice strain.

### Experimental

LaH<sub>2</sub> (111) epitaxial thin films with varying thicknesses (38-121 nm) were grown on  $CaF_2$  (111) single crystal substrates by reactive rf magnetron sputtering using an La metal target at a substrate temperature of 300 °C in an Ar/H2 mixed gas atmosphere with a pressure of 0.02 Torr (H<sub>2</sub> concentration: 3.6%) and a typical deposition rate of 1.1 nm min<sup>-1</sup>. Subsequently,  $SiN_x$  (5 nm) thin films were grown in situ on the  $LaH_2$  (111) epitaxial thin films as a capping layer by rf magnetron sputtering using a SiN<sub>x</sub> target at room temperature ( $\sim 25$  °C) in the same gas pressure. The thickness of the films was measured by X-ray reflectivity measurement (D8 DISCOVER, Bruker AXS). The crystal structure was evaluated by X-ray diffraction (XRD) using Cu Kα radiation (D8 DISCOVER, Bruker AXS; SmartLab, Rigaku). The chemical composition was evaluated using hydrogen forward scattering spectrometry (HFS) and Rutherford backscattering spectrometry (RBS), which were nondestructive analysis methods that did not require removal of the  $SiN_x$  capping layer to prevent film degradation. The surface morphology was observed using an atomic force microscope (SPI4000, Hitachi High Technologies). Electrical resistivity was evaluated using the van der Pauw method with a physical property measurement system (PPMS, Quantum Design). The absorption spectra were evaluated from the transmittance and reflectance spectra at room temperature ( $\sim$ 20 °C) using a Fourier transform infrared spectrometer (FT/IR-6600, JASCO) and an ultraviolet-visible-near-infrared spectrometer (V-770, JASCO).

### Results and discussion

Fig. 1a shows the X-ray diffraction patterns of the thin films. In all the thin films, only the 111 and 222 diffraction peaks of LaH<sub>2</sub> were observed, in addition to the diffraction peaks of the CaF<sub>2</sub> substrate, representing the single-phase nature of  $LaH_2$  in the films. The full width at half maximum (FWHM) of the diffraction peaks for the LaH<sub>2</sub> epitaxial thin films decreased as the film thickness increased (Fig. S1<sup>†</sup>). This trend is reasonably explained using the Debye-Scherrer equation, which represents the relationship between the FWHM and the film thickness. No diffraction peak corresponding to the  $SiN_x$  phase was observed, indicating the amorphous nature of the capping layer. Fig. 1b and c show the depth profile of the chemical composition for the thin films, including the SiN<sub>x</sub> capping layers and CaF<sub>2</sub> substrates, as measured by RBS and HFS. For the 39 nm-thick film (Fig. 1b), Si and N were homogeneously distributed near the surface up to a depth of 5 nm, corresponding to the  $SiN_x$ capping layer. From a depth of 5-40 nm, only La and H were homogeneously distributed, with an atomic ratio of H/La of 2.15, corresponding to the LaH<sub>2</sub> thin film. Above 40 nm, only Ca and F signals were homogeneously distributed, corresponding to the CaF2 substrate. This depth profile



Fig. 1 (a)  $2\theta - \omega$  X-ray diffraction patterns of LaH<sub>2</sub> epitaxial thin films with different film thicknesses. Depth profiles of the chemical composition of the (b) 39- and (c) 122 nm-thick LaH<sub>2</sub> films with SiN<sub>x</sub> capping layers grown on CaF<sub>2</sub> substrates. The zero depth corresponds to the surface of the SiN<sub>x</sub> capping layer.

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confirmed negligible atomic diffusion between the  $SiN_x$  capping layer, the LaH<sub>2</sub> thin film, and the CaF<sub>2</sub> substrate. Similarly, the 122 nm-thick film showed negligible atomic diffusion at each interface, with La and H homogeneously distributed from 5–125 nm, maintaining an atomic ratio of H/La of 2.18 (Fig. 1c). These results indicated that the chemical composition of the thin films remained approximately the same regardless of their thickness. It was noted that the H/La ratio greater than 2 suggested the presence of excess H at the interstitial octahedral sites in the fluorite-type LaH<sub>2</sub>. For LaH<sub>2</sub> thin films, the root mean square roughness was approximately 1.0 nm (Fig. S2†), indicating good surface flatness independent of thickness. Additionally, the crystal domain size was found to be approximately 100 nm.

Fig. 2a–d show the reciprocal space mappings near the 311 diffraction of LaH<sub>2</sub> thin films with different thicknesses. For all the thin films, the LaH<sub>2</sub> 311 diffraction appeared as a spot shape, representing the epitaxial growth of LaH<sub>2</sub> thin films with the in-plane orientation of LaH<sub>2</sub>[11–2]//CaF<sub>2</sub>[11–2]. As the thickness increased, the  $Q_x$  and  $Q_z$  values of the LaH<sub>2</sub> 311 diffraction peak decreased, indicating thickness-dependent lattice strain.

Fig. 3 shows the relationship between the lattice spacings of  $d_{111}$  and  $d_{11-2}$  for LaH<sub>2</sub> epitaxial thin films with different thicknesses. Both  $d_{111}$  and  $d_{11-2}$  were calculated from the LaH<sub>2</sub> 311 diffraction peak in the reciprocal space mappings (Fig. 2a–d), corresponding to the lattice spacings along the out-of-plane and in-plane directions (see the inset of Fig. 3), respectively. Both  $d_{111}$  and  $d_{11-2}$  were the shortest for the 123 nm-thick film. For thicknesses down to 55 nm, the  $d_{111}$ remained almost constant at around 0.326 nm, while the  $d_{11-2}$  slightly increased. Both  $d_{111}$  and  $d_{11-2}$  for the 55-, 90-, and 123 nm-thick films were similar to those of bulk LaH<sub>2.15</sub> and LaH<sub>2.18</sub>. However, the  $d_{111}$  of the 42 nm-thick film significantly increased compared to the thicker films,



Fig. 2 (a)-(d) Reciprocal space mappings near the 311 diffraction for LaH<sub>2</sub> epitaxial thin films with thicknesses of (a) 42, (b) 55, (c) 90, and (d) 123 nm.



**Fig. 3** Lattice spacings of (111) and (11–2) planes, denoted by  $d_{111}$  and  $d_{11-2}$ , respectively, for LaH<sub>2</sub> epitaxial thin films with different thicknesses. Gray circles and triangles denote the  $d_{111}$  and  $d_{11-2}$  of bulk LaH<sub>2.15</sub> and LaH<sub>2.18</sub>, respectively, which are calculated from the lattice parameters of bulk LaH<sub>2</sub> and LaH<sub>3</sub> using Vegard's law.<sup>31,32</sup> Gray crosses denote the  $d_{111}$  and  $d_{11-2}$  of bulk LaH<sub>2</sub> and LaH<sub>3</sub> and LaH<sub>3</sub>.<sup>31,32</sup>

while the  $d_{11-2}$  remained similar to that of the thicker films. These results indicated that the  $d_{111}$  was largely modulated as a function of thickness compared to the  $d_{11-2}$ . The large elongation of  $d_{111}$ , reproducibly observed for different thin films (Fig. S3<sup>†</sup>), could be attributed to lattice strain, probably due to the smallest thickness, since all these films had almost the same chemical composition. From firstprinciples calculations of the bulk modulus (77.5 GPa) and Poisson's ratio (0.285) for LaH<sub>2</sub>,<sup>27</sup> the out-of-plane strain was estimated to be approximately 1 GPa (Fig. S4<sup>†</sup>). Such significant strain effects were achieved despite a relatively large lattice mismatch of 3.7%, which could be a unique characteristic of hydrides. The origin of the lattice strain was unlikely to be simple epitaxial strain, as the lattice mismatch between CaF2 and LaH2 was as large as 3.7%. Moreover, it was unlikely that these strain effects were caused by the heating or cooling processes during thin film growth, since the thermal expansion coefficients of LaH<sub>2</sub> and CaF<sub>2</sub> were comparable.<sup>28,29</sup> Thus, the origin of the lattice strain could be domain matching epitaxy due to the shared fluorite-type structure of LaH<sub>2</sub> and CaF<sub>2</sub>.<sup>30</sup>

Fig. 4a shows the temperature dependence of the electrical resistivity for the LaH<sub>2</sub> epitaxial thin films. The 121 nm-thick film showed the lowest electrical resistivity with a metallic temperature dependence, *i.e.*, positive  $d\rho/dT$ , consistent with the metallic ground state of LaH<sub>2</sub>. The electrical resistivity at room temperature of the 121 nm-thick film (600  $\mu\Omega$  cm) was higher than that of bulk LaH<sub>2</sub> (30  $\mu\Omega$  cm).<sup>1</sup> As the thickness decreased, the electrical resistivity increased monotonically, and the 38 nm-thick film exhibited a semiconducting temperature dependence,



Fig. 4 (a) Temperature dependence of electrical resistivity and (b) optical absorption spectra for  $LaH_2$  epitaxial thin films with different thickness. The inset of (b) shows the Tauc plot of the absorption edge, where the dotted line denotes the fitting line to evaluate the band gap.

*i.e.*, negative  $d\rho/dT$ , while the 55 nm-thick film showed a small hump around 230 K (Fig. S5<sup>†</sup>). Fig. 4b shows the optical absorption spectra for the LaH<sub>2</sub> epitaxial thin films. The 123 nm-thick film showed no absorption edge, indicating the metallic ground state. The absorption peak at 2.2 eV was also observed in a previous study, attributed to interband absorption for La.33 However, the 42 nm-thick film showed an absorption edge around 0.1 eV, consistent with the semiconducting behavior observed in the electrical resistivity of the 38- and 55 nm-thick films (Fig. 4(a)). The Tauc plot of the absorption edge indicated a direct band gap of 0.17 eV for the 42 nm-thick film (inset of Fig. 4b). The absorption peaks at 0.20 eV and 0.29 eV could be attributed to exciton absorptions, taking into account the structurally similar tetrahedral coordination between the fluorite-type LaH<sub>2</sub> and zinc-blende-type semiconductors, such as GaAs, which exhibit exciton absorption.<sup>34</sup> These results indicated a thickness-induced metal-semiconductor transition. The metallic behavior in the thicker films was consistent with bulk LaH2, while the semiconducting behavior in the thinner films was observed in bulk LaH<sub>2</sub>. Since the FWHM of the diffraction peaks did not largely depend on film thickness, the effects of micro-strain, stress, and dislocation density, which are often discussed in polycrystalline thin films, appeared to be insignificant. In addition, neither surface morphology nor composition showed dependence on thickness, suggesting that the outof-plane lattice spacing influenced this metal-semiconductor transition.

# Conclusions

In summary, we successfully grew (111)-oriented LaH<sub>2</sub> epitaxial thin films with varying thicknesses for the first time using reactive rf magnetron sputtering. The LaH<sub>2</sub> epitaxial thin films showed an increase in the out-of-plane lattice spacing with decreasing thickness, suggesting the presence of thickness-dependent lattice strain. From the electrical resistivity and optical absorption spectra, the thicker films exhibited metallic behavior similar to bulk LaH<sub>2</sub>, while the thinner films behaved as direct band gap semiconductors. These results indicated that the modulation of out-of-plane lattice spacing via lattice strain induced the metal-semiconductor transition in the LaH<sub>2</sub> epitaxial thin films, suggesting the potential for developing of novel physical properties in rare-earth hydrides through strain engineering.

## Data availability

The data supporting this article have been included as part of the ESI.†

## Author contributions

S. Uramoto: investigation, validation. H. Kawasoko: conceptualization, funding acquisition, investigation, validation, supervision, writing – original draft/review and editing. S. Miyazaki: investigation, validation. T. Fukumura: funding acquisition, resources, validation, supervision, writing – review and editing.

## Conflicts of interest

There are no conflicts to declare.

## Acknowledgements

This study was supported by JSPS KAKENHI (21K14532).

### Notes and references

- J. N. Huiberts, R. Griessen, J. H. Rector, R. J. Wijngaarden, J. P. Dekker, D. G. de Groot and N. J. Koeman, *Nature*, 1996, 380, 231.
- 2 J. W. J. Kerssemakers, S. J. van der Molen, N. J. Koeman, R. Günther and R. Griessen, *Nature*, 2000, **406**, 489.
- 3 V. A. Maiorov, Opt. Spectrosc., 2020, 128, 148.
- 4 M. Somayazulu, M. Ahart, A. K. Mishra, Z. M. Geballe, M. Baldini, Y. Meng, V. V. Struzhkin and R. J. Hemley, *Phys. Rev. Lett.*, 2019, **122**, 027001.
- 5 P. Drozdov, P. P. Kong, V. S. Minkov, S. P. Besedin, M. A. Kuzovnikov, S. Mozaffari, L. Balicas, F. F. Balakirev, D. E. Graf, V. B. Prakapenka, E. Greenberg, D. A. Knyazev, M. Tkacz and M. I. Eremets, *Nature*, 2019, **569**, 528.

- 6 K. Fukui, S. Iimura, T. Tada, S. Fujitsu, M. Sasase, H. Tamatsukuri, T. Honda, K. Ikeda, T. Otomo and H. Hosono, *Nat. Commun.*, 2019, **10**, 2578.
- 7 K. Fukui, S. Iimura, A. Iskandarov, T. Tada and H. Hosono, *J. Am. Chem. Soc.*, 2022, **144**, 1523.
- 8 W. Zhang, J. Cui, S. Wang, H. Cao, A. Wu, Y. Xia, Q. Jiang, J. Guo, T. He and P. Chen, *Nature*, 2023, **616**, 73.
- 9 J. Ångström, R. Johansson, T. Sarkar, M. H. Sørby, C. Zlotea, M. S. Andersson, P. Nordblad, R. H. Scheicher, U. Häussermann and M. Sahlberg, *Inorg. Chem.*, 2016, 55, 345.
- 10 A. Werwein, H. Auer, L. Kuske and H. Kohlmann, Z. Anorg. Allg. Chem., 2018, 644, 1532.
- 11 A. Werwein, C. Benndorf, M. Bertmer, A. Franz, O. Oeckler and H. Kohlmann, *Crystals*, 2019, **9**, 193.
- 12 R. Shimizu, H. Oguchi and T. Hitosugi, J. Phys. Soc. Jpn., 2020, 89, 051012.
- 13 Y. Komatsu, R. Shimizu, M. Wilde, S. Kobayashi, Y. Sasahara, K. Nishio, K. Shigematsu, A. Ohtomo, K. Fukutani and T. Hitosugi, *Cryst. Growth Des.*, 2020, **20**, 5903.
- 14 N. Hasegawa, H. Kawasoko and T. Fukumura, *Chem. Lett.*, 2020, **49**, 1181.
- 15 Y. Komatsu, R. Shimizu, R. Sato, M. Wilde, K. Nishio, T. Katase, D. Matsumura, H. Saitoh, M. Miyauchi, J. Adelman, R. McFadden, D. Fujimoto, J. Ticknor, M. Stachura, I. McKenzie, G. Morris, W. Macfarlane, J. Sugiyama, K. Fukutani, S. Tsuneyuki and T. Hitosugi, *Chem. Mater.*, 2022, 34, 3616.
- 16 T. Yamasaki, R. Takaoka, S. Iimura, J. Kim, H. Hiramatsu and H. Hosono, *ACS Appl. Mater. Interfaces*, 2022, 14, 19766.
- 17 D. K. Misemer and B. N. Harmon, Phys. Rev. B: Condens. Matter Mater. Phys., 1982, 26, 5634.
- 18 K. Kai, K. A. Gschneidner Jr., B. J. Beaudry and D. T. Peterson, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1989, 40, 6591.
- 19 S. Leyer, S. Heck, A. Kaiser, E. Dormann and R. G. Barnes, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2005, 72, 125115.

- 20 H. Kim, I. Park, J. H. Shim and D. Y. Kim, npj Comput. Mater., 2024, 10, 173.
- 21 Y. Shi, N. Jia, J. Cai, Z. Lyu and Z. Liu, J. Phys.: Condens. Matter, 2022, 34, 475303.
- 22 J. Shinar, B. Dehner, B. l. Beaudry and D. T. Peterson, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1988, 37, 2066.
- 23 R. G. Barnes, C. T. Chang, M. Belhoul, D. R. Torgeson, B. J. Beaudry and D. T. Peterson, *J. Less-Common Met.*, 1991, 411, 172.
- 24 N. Ishimatsu, R. Sasada, H. Maruyama, T. Ichikawa, H. Miyaoka, T. Kimura, M. Tsubota, Y. Kojima, T. Tsumuraya, T. Oguchi, N. Kawamura and A. Machida, *J. Phys.: Conf. Ser.*, 2009, **190**, 012070.
- 25 H. Mizoguchi, M. Okunaka, M. Kitano, S. Matsuishi, T. Yokoyama and H. Hosono, *Inorg. Chem.*, 2016, 55, 8833.
- 26 S. Herbirowo, A. W. Pramono, H. Hendrik, H. Nugraha, V. Puspasari, A. Imaduddin, M. C. Fatah, E. Sulistiyo and A. H. Yuwono, S. Afr. J. Chem. Eng., 2023, 46, 182.
- 27 C. Zhang, Z.-J. Li, H. Jiang, X.-N. Hua, G.-H. Zhong and Y.-H. Su, *et al.*, *J. Alloys Compd.*, 2014, **616**, 42.
- 28 H. Zogg, S. Blunier, A. Fach, C. Maissen, P. Müller, S. Teodoropol, V. Meyer, G. Kostorz, A. Dommann and T. Richmond, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1994, 50, 10801.
- 29 E. Boroch, K. Conder, C. R. Xiu and E. Kaldis, *J. Less Common Met*, 1989, **156**, 259.
- 30 J. Narayan and B. C. Larson, J. Appl. Phys., 2003, 93, 278.
- 31 C. E. Holley Jr., R. N. R. Mulford, F. H. Ellinger, W. C. Koehier and W. H. Zachariasen, *J. Phys. Chem.*, 1955, **59**(12), 1226.
- 32 W. L. Korst and J. C. Warf, Inorg. Chem., 1966, 5, 1719.
- 33 A. T. M. van Gogh, D. G. Nagengast, E. S. Kooij, N. J. Koeman, J. H. Rector, R. Griessen, C. F. J. Flipse and R. J. J. G. A. M. Smeets, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2001, 63, 195105.
- 34 P. Y. Yu and M. Cardona, *Fundamentals of Semiconductors: Physics and Materials Properties*, Springer, Heidelberg, 4th edn, 2010.