



Thermoelectric, Magnetic Properties and Re-entrant Spin-glass State in MBE Grown FeAs Film on LaAlO₃(100) Substrate

Duong Van Thiet,^{1,z} Dang Duc Dung,² Van Quang Nguyen,³ Anh Tuan Duong,⁴ Nguyen Xuan Chung,⁵ Nguyen Tuan Hong,¹ and Sunglae Cho^{6,z}

¹Center for High Technology Development, Vietnam Academy of Science and Technology, Hoang Quoc Viet 18, Hanoi 100000, Vietnam

²School of Engineering Physics, Hanoi University of Science and Technology, Dai Co Viet 1, Hanoi, 100000, Vietnam

³Neutron Science Division, Korea Atomic Energy Research Institute (KAERI), Daejeon, 34057, Republic of Korea

⁴Faculty of Materials Science and Engineering, Phenikaa University, Yen Nghia, Ha-Dong District, Hanoi, Vietnam

⁵Department of Physics, Hanoi University of Mining and Geology, Pho Vien 18, Hanoi, 100000, Vietnam

⁶Department of Physics, University of Ulsan, Ulsan 680-749, Republic of Korea

We report on the growth, thermoelectric, magnetic properties, and re-entrant spin-glass state in MnP-type orthorhombic FeAs thin film, grown on LaAlO₃ (100) substrate by using a molecular beam epitaxy. The film is polycrystalline with a grain size about 200 nm. Electrical resistivity as a function of temperature revealed a metallic behavior. A sign change of Seebeck coefficient was observed at 370 K, due to the contribution of multiple bands to charge transport. We found a re-entrant spin-glass state in the film, attributed to strain in the sample. As a result, a very sharp spin-glass magnetic transition at 50 K was observed in the temperature dependence of Seebeck coefficient, electrical resistivity, and magnetization curves. The bifurcation point between zero field cooled and field cooled magnetization occurred at 350 K. A ferromagnetic-type behavior was observed over a temperature range from 10 to 300 K, confirming the re-entrant spin-glass state. Where the determined magnetization and coercive field are small, around 7 emu cm⁻³ and 300 Oe at 10 K, respectively. Our work provided a study on thermoelectric and magnetic properties of re-entrant spin-glass FeAs in thin film form

© 2023 The Electrochemical Society ("ECS"). Published on behalf of ECS by IOP Publishing Limited. [DOI: [10.1149/2162-8777/acb96c](https://doi.org/10.1149/2162-8777/acb96c)]

Manuscript submitted November 29, 2022; revised manuscript received February 1, 2023. Published February 14, 2023.

In recent years, FeAs-based superconducting materials have attracted much attention. In the FeAs-based superconducting materials, FeAs layer acts as a two-dimensional conduction channel in different structures such as 1111-LnFeAsO (Ln = rare-Earth), 122-AFe₂As₂ (A = Ca, Sr, Ba), and 111-LFeAs (L = alkali metal).¹ These structures have a tetragonal coordination of iron by arsenic, forming a distorted FeAs₄-tetrahedron. Whereas in FeAs each iron atom is coordinated by six arsenic atoms, forming a distorted FeAs₆-octahedron.² Therefore, studying on transport properties of pure FeAs brings useful knowledge as comparing these properties of different superconductive materials based on FeAs. The structural properties, magnetic properties, the transport properties relating to the Seebeck coefficient (including its dependence on temperature, its value variation around the phase transition point, the inversion of its sign), the mechanism of electron-phonon interaction and the variation of thermal conductivity still need to be discovered, especially in form thin film. Efforts have been made to study the structural, magnetic, and transport properties of FeAs precursor materials in the bulk form.³⁻⁶ The FeAs has a MnP-type orthorhombic crystal structure (space group *Pnma*). It exhibits a metallic behavior in electrical transport. The magnetic phase transition of FeAs is approximate 70 K.³⁻⁷ Selte et al. reported the magnetic anisotropy of FeAs with a spin orientation in the *ac*-plane and the propagation vector along the *b*-axis, resulting in the collinear antiferromagnetic ordering (collinear spin-density wave) of iron atoms below 77 K.³ Rodriguez et al. reported the non-collinear spin-density wave antiferromagnetism, "helical" magnetic order, at $T_N \approx 77$ K.⁴ Segawa et al. reported that helical magnetic order is observed below $T_N \approx 70$ K and anisotropic antiferromagnetic domains are formed in the helical ordered phase.⁵ Zig et al. reported the spin-glass magnetic transitions and ferromagnetic-type behaviors over the temperature range of 5–300 K, observed in a self-flux grown single crystal. While single crystals, grown with iodine transport vapor, are non-magnetic, and associated with antiferromagnetic and spin wave characteristics.⁶ The bulk FeAs poses a complicated conductivity mechanism around phase transition temperature due to the contribution of multiband carrier.^{5,8} Recently, the study of Takeshita's group

has showed that polycrystalline FeAs in bulk form does not perform superconductive statement under a pressure of 11 GPa.⁹ To the best of our knowledge, there has been no research on thermoelectric and magnetic properties and re-entrant spin-glass state in FeAs thin film form.

In this work, we focused on the fabrication of FeAs polycrystalline thin film on LaAlO₃ (100) substrate using molecular beam epitaxy and investigated its thermoelectric, magnetic properties, and re-entrant spin-glass state. The film showed a grain structure with an average grain size of 200 nm. Metallic behavior and a sign change in Seebeck coefficient were observed. The re-entrant spin-glass transitions were observed in thermoelectric and magnetic measurements with a freezing temperature and bifurcation point at 50 and 350 K, respectively. The results were thoroughly discussed.

Experimental

FeAs thin film was grown on LaAlO₃(100) substrate by a molecular beam epitaxy (MBE, VG Semicon. Inc.). The LaAlO₃ substrate (MTI Crystals, Inc. (USA)) was first chemically cleaned with methanol before loading into the growth chamber. The substrate was then heated to 600 °C for 30 min to completely remove the residual impurities on the surface. After that, the substrate was cooled down to 500 °C for the growth of FeAs thin film. During the growth process of FeAs film, the evaporation rate of Fe and As pressure was set at 0.26 Å s⁻¹ and 1.8 × 10⁻⁶ Torr, respectively. A high temperature effusion cell was used for Fe evaporation and an As cracking cell was used for As. The evaporation rate of Fe and As was monitored by a quartz crystal microbalance and an ion gauge beam flux monitor, respectively. The quality of the film was monitored by in situ reflection high energy electron diffraction (RHEED). The crystal structure was characterized by X-ray diffraction (XRD) EQUINOX 5000 Thermo Scientific, France with Cu-K_α radiation, $\lambda = 1.54056$ Å. The composition of the sample was determined by electron probe microanalysis (Shimadzu EPMA-1600). The film's thickness, surface morphology, and roughness were characterized by field emission scan electron microscopy (FE-SEM) and atomic force microscopy (AFM) Veeco, Dimension 3100. The electrical resistivity and Seebeck coefficient were measured using a commercial equipment

^zE-mail: duongthiet86@gmail.com; slcho@ulsan.ac.kr

Ulvac ZEM-3 (ULVAC, Methuen, MA, USA) with temperature differential mode and four-probe configuration inside a chamber filled with helium gas at the low pressure. The differential method was used to determine the Seebeck coefficient, where the thermoelectric voltage was measured by maintaining a small temperature difference constant across the sample, employing $\Delta V = S\Delta T$ and ignoring the higher order ΔT terms. Seebeck coefficient is determined from the slope in the linear region of ΔV_i vs ΔT_i . The magnetic properties were characterized using a Superconducting Quantum Interference Device (SQUID) magnetometer (Quantum Design Inc.).

Results and Discussion

Figure 1a shows the RHEED pattern of the film taken after the growth. The film shows a dark RHEED pattern, revealing a sign of polycrystalline FeAs film with a rough surface on the LaAlO_3 substrate. FE-SEM and AFM images of the sample are displayed in Figs. 1b and 1c. The FE-SEM image shows FeAs grain structure with an even shape. The grains are coalescent with an average grain size of 200 nm. On the other hand, some nano-pores are observed on the sample's surface. The formation of pores may be due to the re-evaporation of volatile As elements during the growth at a high substrate temperature, 500 °C. The AFM image shows a root mean square (RMS) of about 10.65 nm, indicating a rough surface, consistent with the RHEED pattern. Cross-section FE-SEM image shows a layer thickness of about 100 nm, as expected.

Room temperature XRD pattern of the FeAs film is shown in Fig. 2. By excluding the diffraction peaks from the substrate, the main distinct peaks are assigned to MnP-type orthorhombic structure FeAs phase, indicating a polycrystalline FeAs film on the LAO substrate. The peaks of XRD pattern of FeAs film clearly match to that of bulk FeAs in card PDF#891911. On the other hand, no other peak is observed within the detection limit of XRD technique, indicating a single-phase thin film. This observation is further confirmed by EPMA composition analysis, showing indeed a Fe:As ratio of 1:1. The determined lattice constants, *a*, *b*, and *c*, using XRD data, are 5.401, 3.380, and 5.988 Å, respectively. Compared to those of bulk FeAs, 5.44, 3.371, and 6.026 Å [3], our film exhibits 0.72 and 0.63% compressive strain along *a* and *c*-axes and a 0.27% tensile strain along *b*-axis.

Electrical resistivity and Seebeck coefficient measurements are performed on the film to obtain information on the transport property, as shown in Fig. 3. As can be seen in Fig. 3a, the electrical resistivity increases with temperature, indicating a metallic behavior as in bulk FeAs.⁷ Initially, the electrical resistivity increases with temperature then undergoes a sharp increase with temperature below 100 K, after that it gradually increases again. The increase in electrical resistivity with temperature is attributed to the increase in electron-phonon scattering. Figure 3b shows the temperature dependence of the Seebeck coefficient, *S* for the temperatures between 30 and 410 K, *S* is negative and positive for the temperature below and above 370 K, respectively. At 100 K, *S* reaches a negative broad peak of $-11 \mu\text{V K}^{-1}$ which is higher than that of bulk material.⁸ The Seebeck coefficient is a sensitive probe for the phenomenon associated with changes in the Fermi surfaces such as structural distortion, contribution multiband effect. For magnetic materials, the Seebeck coefficient is an ensemble of many factors, such as carrier diffusion, phonon drag and magnon drag effect.¹⁰ However, this effect is not considerably evaluated and investigated in the scope of this report. To explain the role of multiband for Seebeck coefficient, it is hypothesized to be described as $S = (p\mu_p|S_p| - n\mu_n|S_n|)/(n\mu_n + p\mu_p)$, where S_n and μ_n represent the Seebeck coefficients and carrier mobility for the *n*- and *p*-type carriers, respectively.¹⁰ It is clear that negative *S* relates to electrical conduction by electrons of which mobility is higher than that of holes. For higher temperature, the competition between the contribution of electrons and holes changes, and then the sign of *S* inverts. The inversion of *S* due to the contribution of multiband

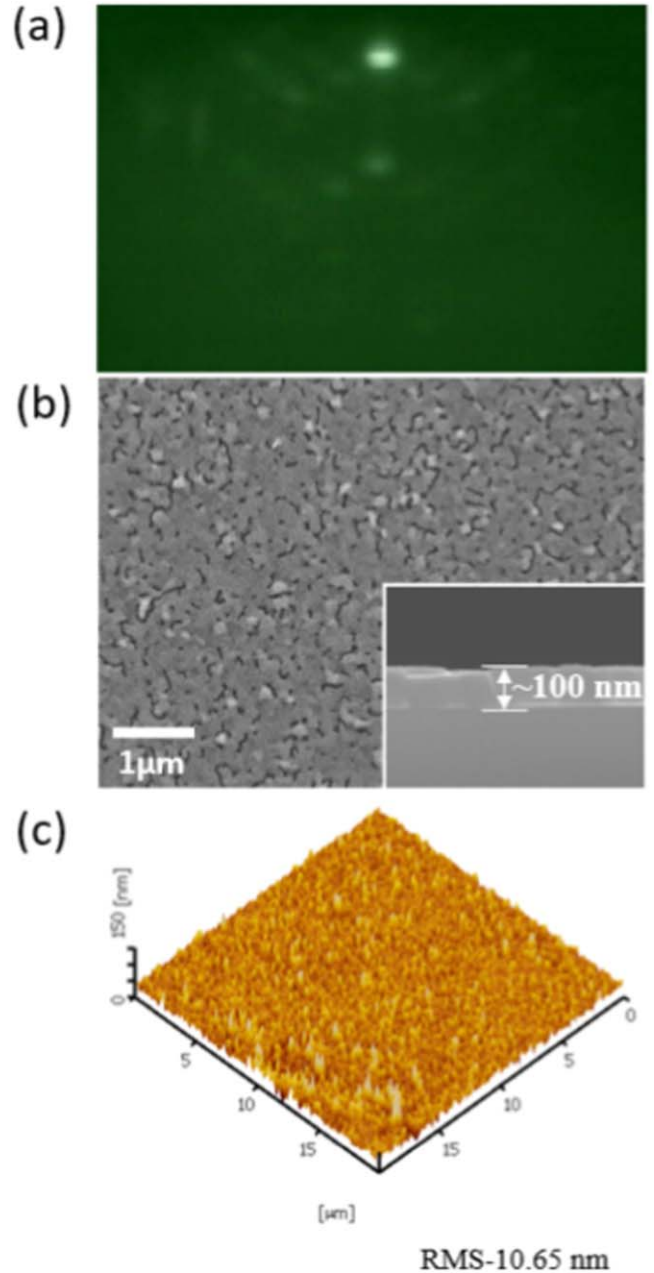


Figure 1. (a) RHEED pattern, (b) SEM, and (c) AFM images of FeAs film grown on $\text{LaAlO}_3(100)$ substrate. The inset in Fig. 1c shows the cross-section of the film.

carrier was studied in both bulk FeAs and FeAs-based superconductive materials.^{11,12} Nevertheless, comparing to FeAs bulk, Saparov et al. reported that *S* is negative above antiferromagnetic ordering ($T_N \sim 70$ K), positive below this temperature and *S* reaches a negative peak around 150 K.⁸

The determined power-factor, PF, value is shown in Fig. 3c. Small values of PF are obtained, as expected for metallic materials. The PF also sharply increases with temperature below 100 K, reaches a maximum value of $27 \mu\text{W m-K}^{-2}$ at 100 K, and then decreases with temperature. The sharp increase in ρ , *S*, and PF with a temperature below 100 K reveals a change in the scattering mechanism. This sharp change is confirmed by a sharp peak in the temperature dependent first derivative of electrical resistivity with a small enough measured temperature interval (inset of Fig. 3a). The change in temperature dependent transport parameters will be clarified below.

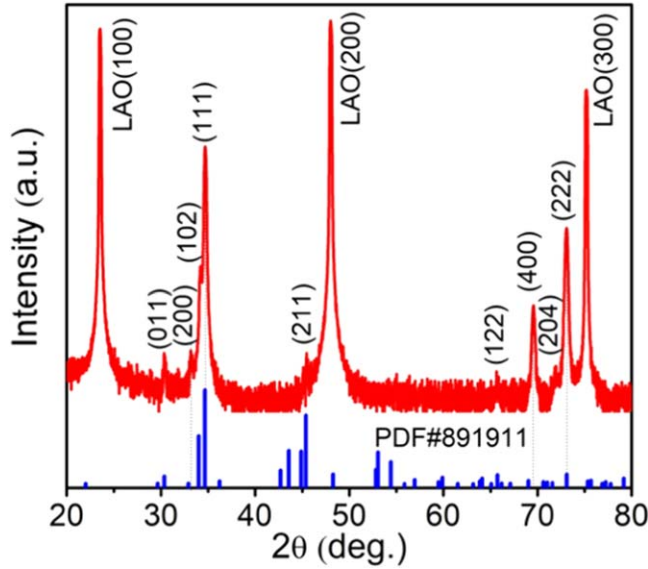


Figure 2. θ - 2θ X-ray diffraction pattern of the FeAs film on the LaAlO₃ substrate.

Figure 4a presents the magnetic field dependent Hall resistance for the temperatures between 20 and 320 K. The result proves that the dominant carrier contribution is n-type electron which matches with the above experimental result of $S(T)$. For bulk material, Segawa et al. presented that the contribution of hole is dominant for the temperatures above 170 K and below 50 K, while the conduction is mainly contributed by electron for temperature between 50 K and 170 K.⁵ As can be seen from the measurement of $S(T)$ and of Hall effect, the mechanism of conduction in our sample is different from that of bulk material.^{5,8} This result is probably the effect of many factors on the transport property of this material. However, in the scope of this research, the variation of band structure may originate from the lattice mismatch between FeAs and substrate, and the competition of crystal growth on two different directions.^{13,14} Figure 4b shows the carrier concentration, conductivity, and mobility measured at different temperatures, from 20 K to 320 K. The carrier concentration is calculated from the slope of R_H vs H curves using the formula, $R_H = (1/ne)dH$, where $R_H = V_H/I$, where R_H is Hall resistance, V_H is Hall voltage, I is applied current, n is carrier concentration, d is sample's thickness, and e is electrical charge. Negative slope of R_H vs H curves indicated the n-type characteristic of our samples. The carrier mobility is calculated by the formula $\mu = \sigma/ne$. As can be seen, the variation of carrier concentration is similar to that of Seebeck, while the mobility and conductivity degrade around the phase-transition temperature as showed in Fig. 4b.

Figure 5a shows the magnetization (M) vs temperature (T) in a temperature range from 10 to 350 K under an applied magnetic field of 500 Oe. The zero-field cooled (ZFC) magnetization initially increases sharply with temperature, revealing a peak at around 50 K. The magnetization drops to a plateau until 130 K then decreases gradually with temperature up to 300 K and finally slightly increases again up to 350 K. In contrast to the ZFC magnetization, the field cooled (FC) magnetization initially decreases with temperature and then increases, showing a sharp peak at 50 K, finally it gradually decreases with temperature up to 350 K. As result, the magnetic transition was detected at a temperature of 50 K on both ZFC and FC curves. This sharp peak can be relative to some possibility such as i) the influence of oxygen contamination content due to leak system measurement or oxygen outgassing from the sample so appear the paramagnetism to antiferromagnetism transition,¹⁵ ii) the distribution is not uniform of defects lead to affect the movement of domain wall, which is known as magnetic

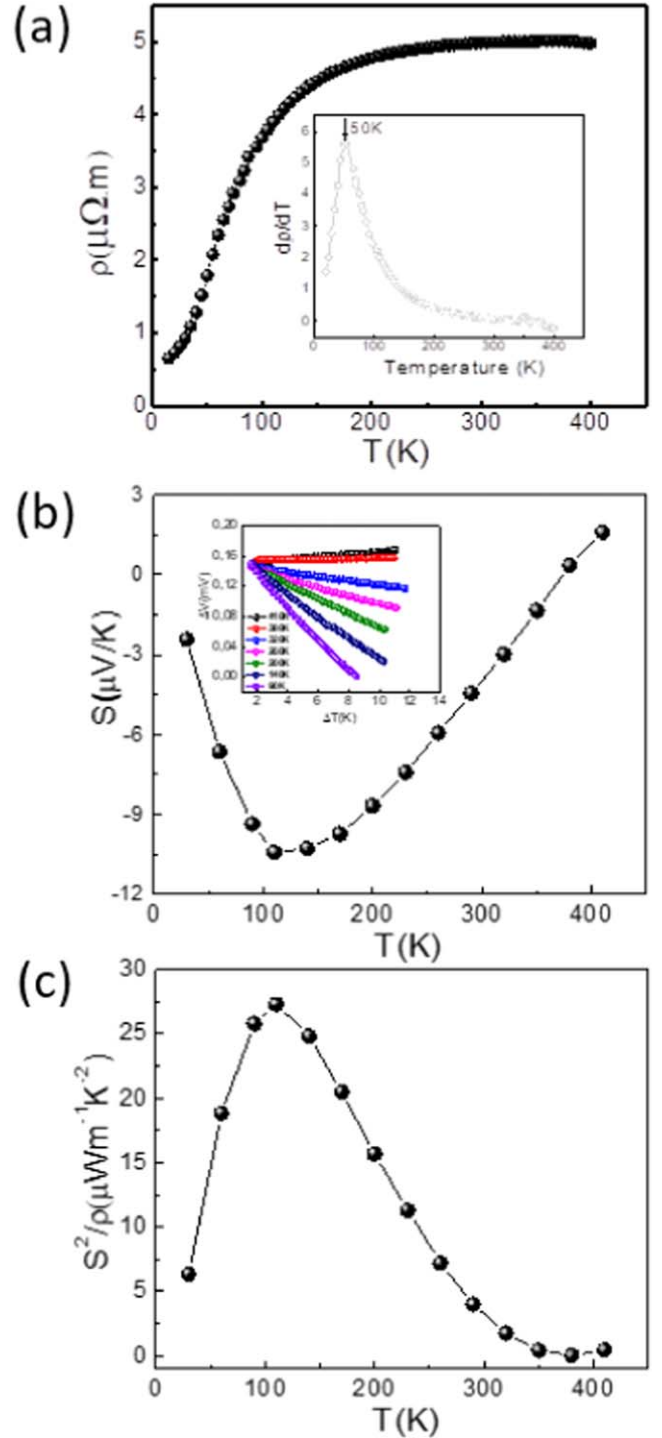


Figure 3. (a) Temperature dependent electrical resistivity of FeAs film. The inset is the first derivative of the electrical resistivity as a function of temperature. (b) Temperature dependence of Seebeck coefficient $S(T)$. (c) Temperature dependence of Power factor (S^2/ρ).

domain pinning effect,^{16,17} iii) the large difference of ZFC and FC curves exhibit competition between ferromagnetism and antiferromagnetism phases, which called reentrant spin-glass systems. It undergoes a magnetic ordering transition and has a spin freezing transition at lower temperatures.^{18,19} Note that a peak at approximately 50 K also was observed from the first derivative of the resistivity with temperature, as shown in the inset in Fig. 3a above. This temperature matches the magnetic ordering transition temperature in the magnetization vs temperature. It suggested that the peak

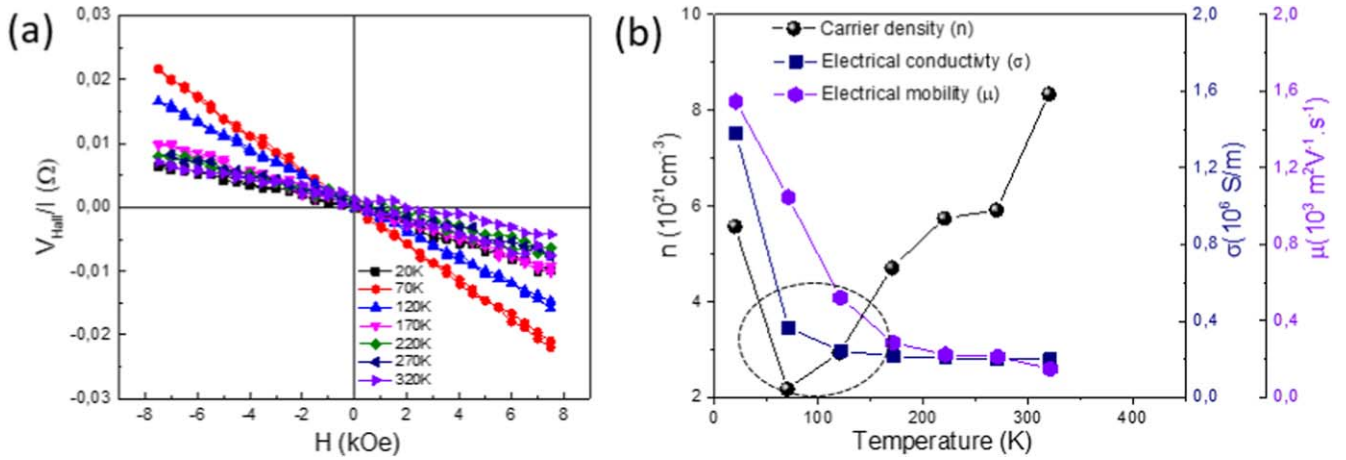


Figure 4. (a) The magnetic field dependent Hall resistance for the temperatures between 20 and 320 K. (b) Temperature dependence of carrier density, electrical conductivity, electrical mobility.

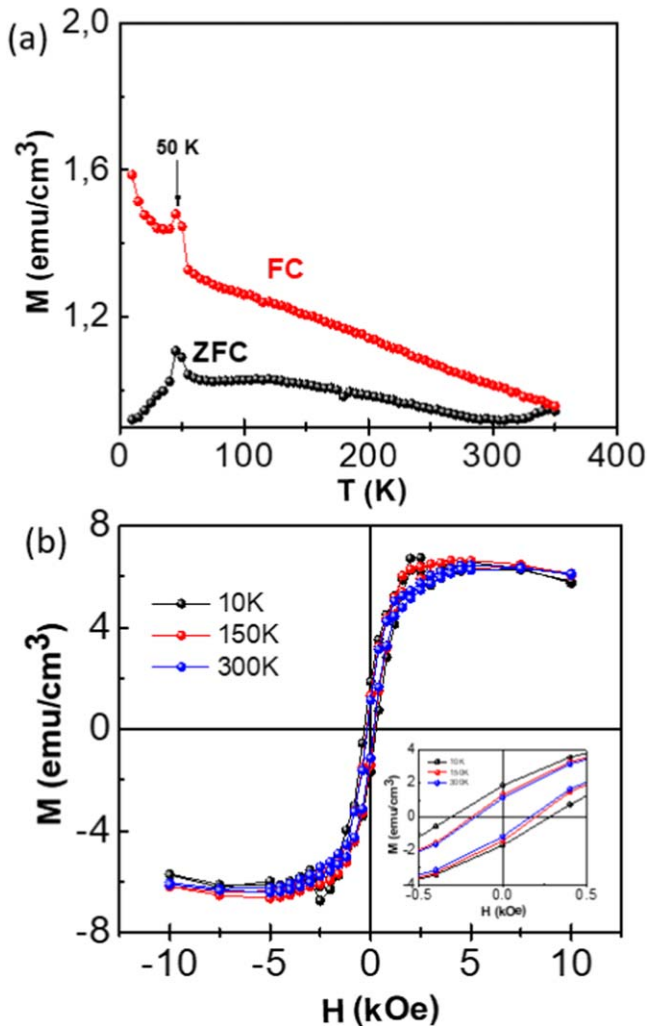


Figure 5. (a) Zero-field cooled (ZFC) and field cooled (FC) curves of the magnetization as a function of temperature in an applied magnetic field of 500 Oe. (b) The out-of-plane magnetization hysteresis loop (M - H) of FeAs films, taken at 10, 110, 150, 200, and 300 K.

around 50 K must come from natural material. It can be a re-entrant spin-glass state or magnetic domain pinning effect. The bifurcation point is observed at 350 K which is a sign of spin-glass behavior.⁶

The peak at 50 K indicates the freezing temperature of spin-glass state, T_f . Similar results have been reported for ball-milled FeAs powders with coarse-grain.⁷ Apparently, the bifurcation point is much higher, while the T_f is much lower than those reported for flux-grown FeAs single crystal, 150 and 110 K, respectively.⁶ We attribute this phenomenon to the strain of the film and the effects of grains boundary in polycrystalline film, mentioned above. The plateau behavior in the temperature dependent magnetization usually indicates ferromagnetic ordering. These observations reveal the re-entrant spin-glass state in our sample. Now, the changes in the temperature dependent transport parameters (Fig. 3), as mentioned above, can be understood, due to the frozen spin, which alters the electron scattering mechanism. Figure 5b shows the out-of-plane magnetization hysteresis loop (M - H) of FeAs film at 10, 150, and 300 K. Well defined square shape M - H curves indicate a ferromagnetic property of FeAs film from low to room temperature, as expected above. The determined magnetization (M_s) and coercive field (H_c) values were around 7 emu cm⁻³ and 300 Oe at 10 K, respectively. These values of M_s and H_c are comparable to those of FeAs single crystal.⁶

Conclusions

In conclusion, we have grown polycrystalline FeAs thin film on LaAlO₃ (100) substrate using MBE. The film exhibited a uniform grain structure with coarse grain and an average grain size of 250 nm. Metallic and ferromagnetic behaviors were observed from low to room temperature. A sign change in temperature dependent Seebeck coefficient was observed, attributed to the contribution of multiple bands to the charge transport. We observed a re-entrant spin-glass state in our sample, which can be attributed to the strain of the thin film. The frozen temperature was determined from temperature dependent transport and magnetic measurements to be 50 K. The bifurcation point between zero field cooled and field cooled magnetization curves occurred at 350 K. This work provided the first study on thermoelectric and magnetic properties of FeAs thin film with a re-entrant spin-glass state.

Acknowledgments

This work was supported by the National Research Foundation of Korea [NRF-2019R1A6A1A11053838, NRF-2020K1A4A7A02095438, and NRF-2022R1A2C1091734]. The authors also would like to acknowledge the financial support by the Vietnam Academy of Science and Technology (VAST) under grant number DL0000.04/20-21.

ORCID

Duong Van Thiet  <https://orcid.org/0000-0002-6302-8129>

References

1. Y. Kamihara, T. Watanabe, M. Hirano, and H. Hosono, "Iron-based layered superconductor $\text{LaO}_{1-x}\text{F}_x\text{FeAs}$ ($x = 0.05\text{--}0.12$) with $T_c = 26\text{ K}$." *J. Am. Chem. Soc.*, **130**, 3296 (2008).
2. H. H. Le, K. Kihou, A. Lyo, H. Kito, P. M. Shirage, and H. Eisaki, "Relationship between crystal structure and superconductivity in iron-based superconductors." *Solid State Commun.*, **152**, 644 (2012).
3. K. Selte, A. Kjekshus, and A. F. Andresen, "Magnetic structure and properties of FeAs." *Acta Chem. Scand.*, **26**, 3101 (1972).
4. E. E. Rodriguez, C. Stock, K. L. Krycka, C. F. Majkrzak, P. Zajdel, K. Kirshenbaum, N. P. Butch, S. R. Saha, J. Paglione, and M. A. Green, "Noncollinear spin-density-wave antiferromagnetism in FeAs." *Phys. Rev. B*, **83**, 134438 (2011).
5. K. Segawa and Y. Ando, "Magnetic and transport properties of FeAs single crystals." *J. Phys. Soc. Japan*, **78**, 104720 (2009).
6. K. A. Ziq and A. F. Salem, "Magnetic properties of FeAs single crystal." *Journal of superconductivity and novel magnetism.*, *J. Supercond. Nov. Magn.*, **26**, 1185 (2013).
7. Y. Zhou, Y. Wang, Y. Liang, Y. Zhou, Z. Liu, C. Peng, Y. Ke, and X. Min, "Microstructure and magnetic properties of FeAs with coarse-grain and nanocrystalline structure." *Trans. Nonferrous Met. Soc. China*, **32**, 972 (2022).
8. B. Saparov, J. E. Mitchell, and A. S. Sefat, "Properties of binary transition-metal arsenides (TAs)." *Supercond. Sci. Technol.*, **25**, 084016 (2012).
9. N. Takeshita, A. Iyo, S. Ishida, H. Eisaki, and Y. Yoshida, "Electrical resistivity of FeAs, FeAs₂ and Fe₂As at homogeneous high pressures." *IOP Conf. Series: Journal of Physics: Conf. Series*, **950**, 042024 (2017).
10. P. D. Lodhi, N. Kaurav, K. K. Choudhary, and Y. K. Kuo, "Measurement and analysis of normal-state transport properties of FeSe superconductor." *J. Low Temp. Phys.*, **196**, 494 (2019).
11. I. Pallecchi, G. Lamura, M. Tropeano, and M. Putti, "Seebeck effect in $\text{Fe}_{1+x}\text{Te}_{1-y}\text{Se}_y$ single crystals." *Phys. Rev. B*, **80**, 214511 (2009).
12. F. Cagliaris et al., "Magnetoelectric effect in REFeAsO (RE = rare Earth) compounds: probing the magnon drag scenario." *Phys. Rev. B*, **90**, 134421 (2014).
13. D. D. Dung, D. Odkhue, L. T. Vinh, S. C. Hong, and S. Cho, "Strain-induced modification in the magnetic properties of Mn_5Ge_3 thin films." *J. Appl. Phys.*, **114**, 073906 (2013).
14. W. Feng, D. Van Thiet, D. D. Dung, Y. Shin, and S. Cho, "Substrate-modified ferrimagnetism in MnGa films." *J. Appl. Phys.*, **108**, 113903 (2010).
15. T. Dubroca, J. Hack, and R. Hummel, "Comment on 'Unusual magnetic transitions and nature of magnetic resonance spectra in oxide glasses containing gadolinium.'" *Phys. Rev. B*, **74**, 026403 (2006).
16. F. Huang et al., "Peculiar magnetism of BiFeO_3 nanoparticles with size approaching the period of the spiral spin structure." *Sci. Rep.*, **3**, 1 (2013).
17. M. Malik, Y. Sun, Ying, L. Wang, S. Deng, K. Shi, P. Hu, H. Lu, and C. Wang, "Competition between ferromagnetic and antiferromagnetic interactions by Cr doping at Mn sites in antiperovskite $\text{Mn}_{3-x}\text{Cr}_x\text{ZnN}$ ($0 \leq x \leq 0.5$) compounds." *Phys. B: Condens. Matter.*, **488**, 19 (2016).
18. S. Wang, J. Zhang, G. Cao, C. Jing, and S. Cao, "Distinguishable reentrant spin-glass behavior induced by the frustration of exchange interaction in phase-separated $\text{Sm}_{0.5}(\text{Ca}, \text{Sr})_{0.5}\text{MnO}_3$ systems." *Phys. Rev. B*, **76**, 054415 (2007).
19. S. Chattopadhyay, S. Giri, and S. Majumdar, "Glassy magnetic ground state in $\text{La}_4/3\text{Sr}_5/3\text{Mn}_2\text{O}_7$: Role of first order phase transition and short range antiferromagnetic correlations." *J. Appl. Phys.*, **112**, 083915 (2012).