

LOW-TEMPERATURE MAGNETORESISTANCE EFFECT AND THERMOELECTRIC PROPERTIES OF POLYCRYSTALLINE FeAs₂ THIN FILM ON LaAlO₃ (100) SUBSTRATE

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ABSTRACT

The polycrystalline FeAs₂ thin film grown on a LaAlO₃ (100) substrate by using molecular beam epitaxy (MBE) has been investigated. The origin of negative magnetoresistance (MR) is observed at 20K due to hopping conduction mechanism. The films exhibit semiconductor behavior with dominant charge-carrier being electron. Above room temperature, the electrical activation energy is estimated to be 0.20eV, that original from transport mechanism such as thermionic emission. The maximal Seebeck coefficient is, $S = -138\mu\text{V/K}$ at $T = 300\text{K}$.

Keywords: FeAs₂, MBE, magnetoresistance, thermoelectric, thin film

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NOMENCLATURE

S: Seebeck coefficient ($\mu\text{V/K}$)

PF: Power factor ($\mu\text{W/cmK}^2$)

MR: Magnetoresistance (%)

ρ : Electrical resistivity ($\Omega\cdot\text{cm}$)

T: Absolute temperature (K)

1. INTRODUCTION

Nowadays, using thermoelectric materials to convert thermal energies into electric energy and vice versa is a promising technique but it is still limited [1]. To evaluate efficiency of these materials, the thermoelectric dimensionless figure of merit $ZT = S^2T/\rho\kappa$ is often used, where S is the Seebeck coefficient, ρ is electrical resistivity, κ is thermal conductivity, and T is temperature [2]. The high value of ZT is achieved by either increasing S^2/ρ (called power factor) or reduction of κ .

FeAs₂ is also known as a candidate material with high Seebeck coefficient on both theory and experiment [3-7]. It

is a semiconductor with bandgap of 0.22eV, the crystal structure is orthorhombic Marcasite (space group Pnm) with the lattice parameters; $a = 5.299$, $b = 5.984$, and $c = 2.882\text{\AA}$. The iron atom is coordinated by six arsenic atoms forming distorted FeAs₆-octahedral that share corners along the c axis. Each anion is coordinated by three irons and another arsenic atom forming distorted tetrahedral site [3]. The peculiar band gap structure of FeAs₂ makes its unique thermoelectric properties [3-6]. In the early 1970s, Fan et al. reported the thermoelectric property of single crystal of FeAs₂ with Seebeck coefficient at room temperature approximately $-200\mu\text{V/K}$ [3]. A huge Seebeck coefficient of -7mV/K is obtained at the temperature of 12K [4, 5]. Recently, Usui et al. shown that electron-doped polycrystalline FeAs₂ exhibits metallic with a large Seebeck coefficient at 300K, about $-200\mu\text{V/K}$, for 1% selenium doping driven by quasi-one-dimensional pudding-mod-type band [6, 7]. However, the details of electrical conduction mechanism of polycrystalline FeAs₂ film, and magnetoresistance effect at low temperature are not still reported.

In this paper, we report on structural, transport and thermoelectric properties of polycrystalline FeAs₂ thin film grown on LaAlO₃ (100) substrate using molecular beam epitaxy (MBE). The film shows a negative magnetoresistance at the temperature of 20K. The maximal Seebeck coefficient of $-138\mu\text{V/K}$ is investigated around room temperature.

2. METHODS

A FeAs₂ film was grown on a (100) LaAlO₃ substrate by using MBE system (VG Semicon, Inc.). The substrate was chemically cleaned before loading the substrate into the growth chamber. The substrate was heated up to 700°C for 30 min to completely remove the residual impurities. The substrate was cooled down and stabilized at growth temperature of 300°C. The evaporation rate of Fe was 0.26\AA/s , and the As pressure was 1.8×10^{-6} Torr during the growth. For Fe evaporation, we used a high temperature effusion cell and for As, we used the As cracking cell. The evaporation rate was confirmed by quartz crystal microbalance and ion gauge beam flux monitor. The growth quality, we used reflection high - energy electron diffraction

(RHEED) for the in-situ observation of crystal structure and surface morphology. The crystal structures of the samples were characterized by X-ray diffraction (XRD). The surface morphology and roughness of FeAs₂ film were characterized by field emission scan electron microscopy (FE-SEM). The crystal structure of the sample was characterized by X-ray diffraction (XRD) investigation. The electrical resistivity was measured by using a four-probe van der Pauw configuration. The differential method was used to determine the Seebeck coefficient, where thermoelectric voltage was measured by maintaining small temperature difference constant across the sample by employing $\Delta V = S \nabla T$ and ignoring higher order ∇T terms. The Seebeck coefficient is determined from the slope in linear region of ΔV_i versus ∇T_i .

3. RESULTS AND DISCUSSION

The ratio of Fe and As concentrations determined from electron probe microanalyzer (EPMA) measurement system is 1:2. Fig. 1(a) shows ring-shape RHEED pattern, a characterization was polycrystalline of FeAs₂ film. Fig. 1(b) shows the secondary electron image (SEI) characterized by arrangement of like-particles with the root mean square (RMS) of 4.33 nm. Furthermore, the compositional image produced by backscattered electron (BEI-COMPO) indicates homology surface, and an evident of no cluster is found as shown in Fig. 1 (c). The inset in Fig. 1 (b) is the cross-section SEM image, indicating the layer thickness approximately 100nm.

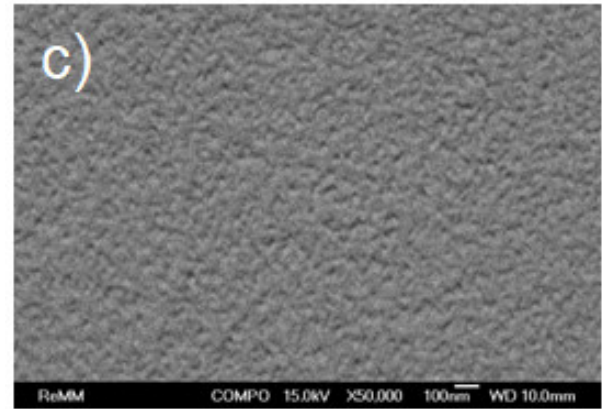
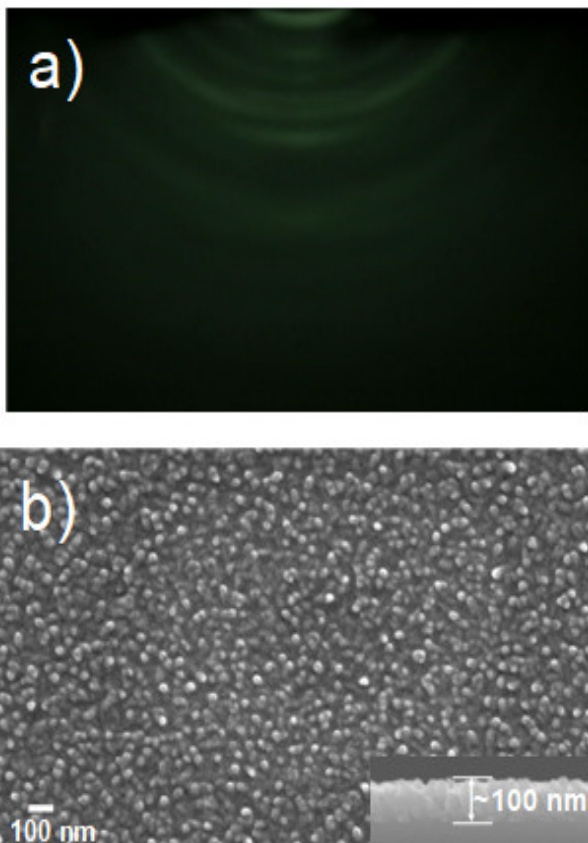


Fig. 1. RHEED patterns (a), SEM (b) and COMPO (c) images of the FeAs₂ film on (100) LaAlO₃ substrate using MBE. The inset in Fig. 1 (b) shows the cross-section.

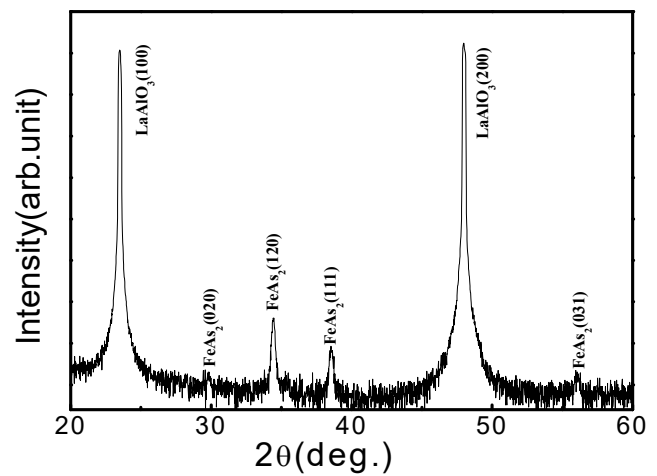
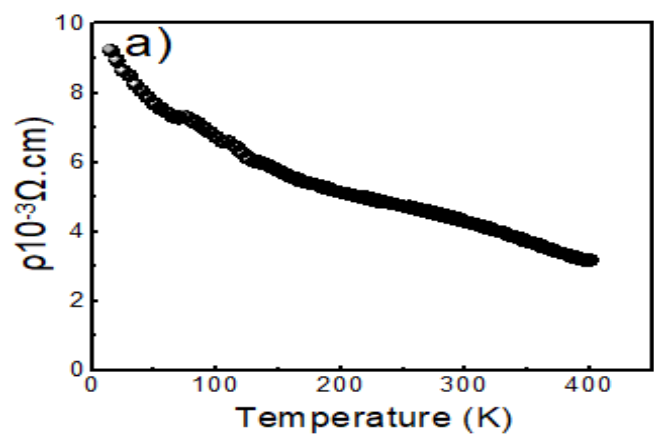


Fig. 2. The θ - 2θ X-ray diffraction patterns of the FeAs₂ films on LaAlO₃ substrate

The crystal structure of FeAs₂ thin film was investigated by using XRD measurements, as shown in Fig. 2. There are four distinct peaks at 29.82, 34.42, 38.54, and 56.05°, which indexed (020), (120), (111), and (031), respectively. All XRD patterns can be indexed to a pure orthorhombic phase consistent with the reported data (JCPDS: 79-0251). The result shows that the film is polycrystalline with the lattice constants $a = 5.276 \text{ \AA}$, $b = 5.991 \text{ \AA}$ and $c = 2.892 \text{ \AA}$.



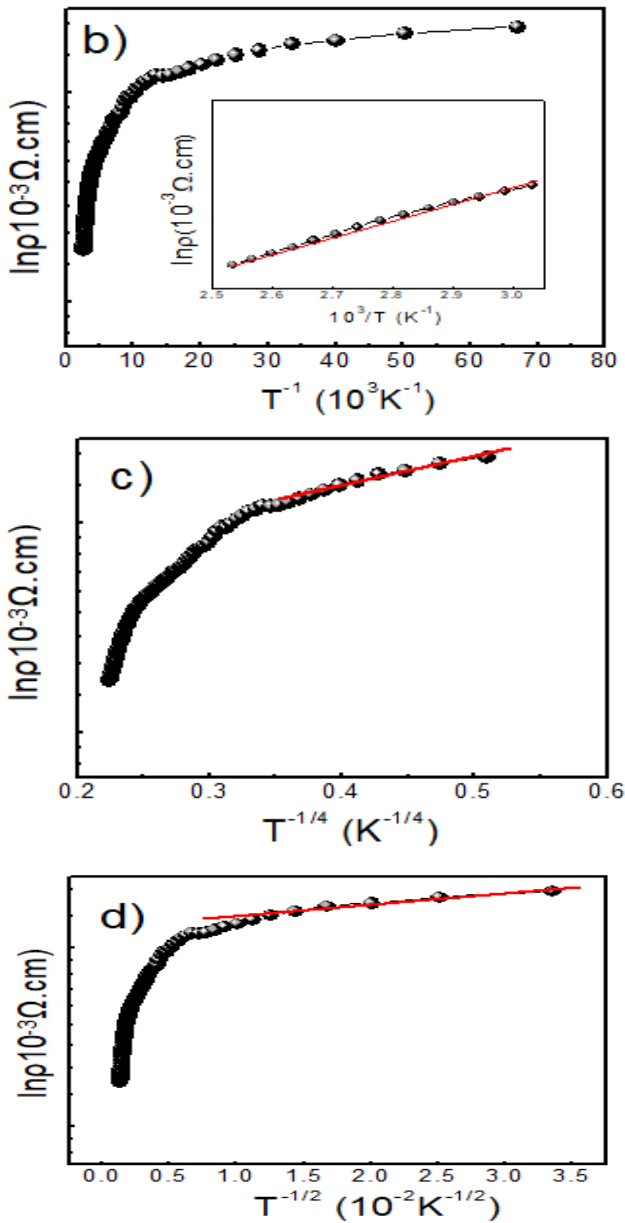


Fig. 3. The temperature dependent of resistivity of FeAs₂ film (a), the natural logarithm of electrical resistivity vs. reciprocal temperature (Arrhenius plot) (b), the plot the logarithmic of ρ vs. $T^{-1/4}$, $T^{-1/2}$ (c) and (d), respectively. The inset of Fig. 3 (b) shows linear fitting theory compare to experiment, the variation of the resistivity from 330 to 400K.

A variation of the resistivity of FeAs₂ film vs. temperature is given in Fig. 3 (a). The increase of the resistivity with decrease of the temperature presents a semiconductor behavior in the film. The explanation about conduction mechanism in polycrystalline materials, especially semiconductor, is much complicated. In this work, to better understand the mechanism of conduction of film, we use Arrhenius equation: $\rho = \rho_0 \exp(\Delta/k_B T)$ [8], where ρ_0 is a preexponential factor, Δ is the activation energy, and k_B is the Boltzmann constant. A natural logarithm of electrical resistivity vs. reciprocal temperature (Arrhenius plot) is shown in Fig. 3 (b). In the range of temperature from 330 to

400K, the variation of the resistivity vs. $(1000/T)$ is like-linear inset in Fig. 3 (b). The electrical activation energy is estimated about 0.20eV, these results suggest that the mechanism of conduction such as thermionic emission. This mechanism was also reported on polycrystalline CdTe, and GaSe, FeS₂ films before [9-11]. While at low temperature, the electrical conduction is provided by the so-called variable-range hopping (VRH), that can be expressed by formula: $\rho = \rho_0 \exp[(\Delta/k_B T)^\beta]$ [8], where β is determined by the shape of energy-dependent distribution of impurity (DOI) atoms. For $\beta = 1/4$ corresponding to the Mott VRH regime, $\beta = 2$ corresponding to the Efros and Schklovskii (ES) VRH regime. Fig. 3 (c) and Fig. 3 (d) present the logarithmic plot of ρ vs. $T^{-1/4}$, $T^{-1/2}$ for Mott's and ES VRH, respectively. Using linear fitting function on both cases in range of temperature below 60K, we conclude that the mechanism of conduction is described as variable range hopping cause of imperfection associated in the film.

Fig. 4 (a) shows negative magnetoresistances at 20K caused from hopping conduction mechanism at low temperature. The result is quite similar to polycrystalline β -FeSi₂ film and n-type InP semiconductor [12-13]. The negative MR is plotted versus $H^{1/2}$, and using fitting function in Fig. 4 (b), it is identified that $H^{1/2}$ dependence of negative magnetoresistance is linear. The result from hopping conduction under applied magnetic field. This behavior is consistent with theoretical predictions and experiments [14-18].

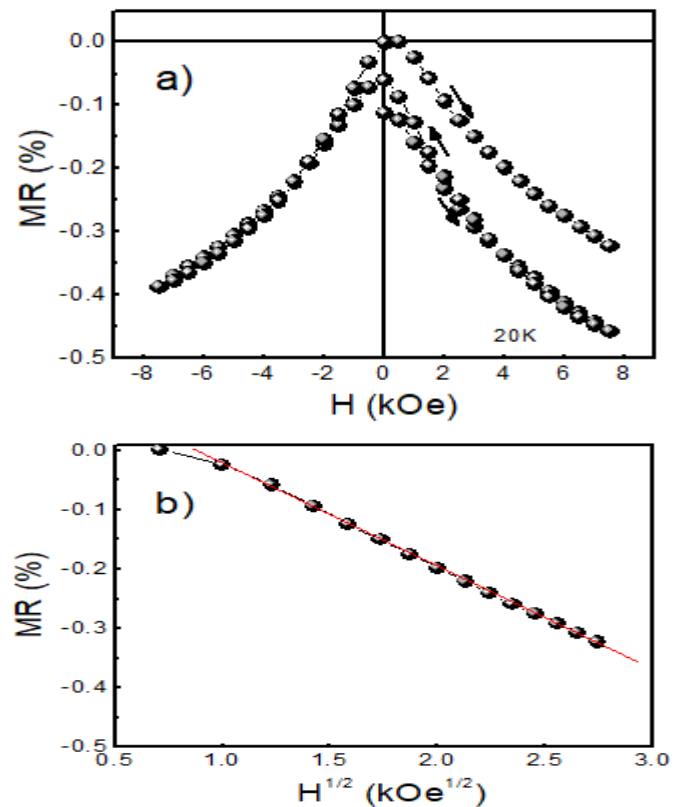


Fig. 4. Magnetoresistance vs. magnetic field at 20K (a), the negative MR is plotted versus $H^{1/2}$ (b)

The Seebeck coefficient (S) value of the film is negative, indicating electron is dominant charge carriers in the whole temperature range as showed in Fig. 5(a). The temperature dependence of S is expressed by increasing value from 400 to about 300K. The variation of S value above-below room temperature originates from the change of conduction mechanism. The maximum of S is $-138\mu\text{V/K}$ at $T = 300\text{K}$, that is smaller than typical bulk sample [3-6]. The temperature dependence of thermoelectric power factor (PF) is shown in Fig. 5 (b). Highest PF value is $4.31\mu\text{W/cmK}^2$ near room temperature.

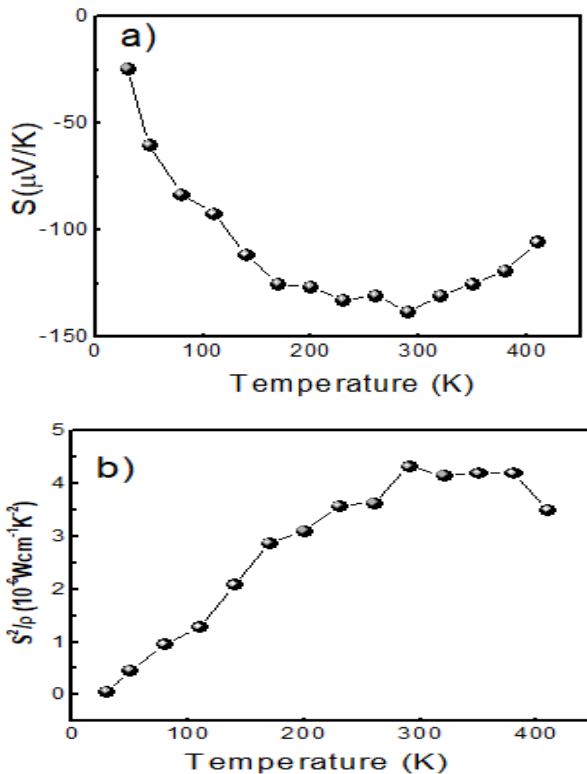


Fig. 5. The temperature dependence of Seebeck coefficient $S(T)$ (a), temperature dependence of thermoelectric power factor (b)

4. CONCLUSIONS

The polycrystalline FeAs_2 thin film was grown on a LaAlO_3 (100) substrate with orthorhombic phase. The effect of the conduction mechanism to observation of negative magnetoresistance (MR) at low-temperature of 20K is due to hopping conduction mechanism. The film exhibit semiconductor behavior is found with dominant charge-carrier being electron. Above room temperature, the electrical activation energy is estimated to be 0.20eV, that originates from transport mechanism such as thermionic emission. The maximum of Seebeck coefficient is $S = -138\mu\text{V/K}$ at $T = 300\text{K}$ that smaller than bulk typical material.

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