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Superconductivity and magnetism in FeSe thin films grown by metal–organic chemical vapor deposition

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Abstract

High quality FeSe thin films with different ratios of Fe to Se have been grown on GaAs and Si substrates by changing the flow rate of Fe(CO)₅ in a low-pressure metal–organic chemical vapor deposition (MOCVD) system. For both substrates, the films grown at a low flow rate of Fe(CO)₅ are non-ferromagnetic and exhibit superconductivity at low temperature, while those grown at a high flow rate of Fe(CO)₅ display ferromagnetic and semiconducting behaviors. Our results suggest that the superconducting phase does exist in a narrow range of Fe and Se concentration near stoichiometry. The introduction of excess Fe favors ferromagnetism and leads to the suppression of superconductivity.

(Some figures in this article are in colour only in the electronic version)

Motivated by the recent discovery of superconductivity in F-doped LaOFeAs with a transition temperature T_c of 26 K [1], other iron-based planar compounds have been revisited, leading to the discovery of new families of superconductors [2–4]. Among them, the finding of superconductivity in FeSe is surprising [4], because it has been well studied before as a ferromagnetic semiconductor [5–8]. The investigation of FeSe thin films, prepared by low-pressure metal–organic chemical vapor deposition (MOCVD), showed that the stoichiometric FeSe is non-ferromagnetic and the ferromagnetism can be induced by changing the Se/Fe atomic ratios [8]. It is still unclear if these FeSe films grown by MOCVD were superconducting.

After the discovery of superconductivity in FeSe with $T_c \sim 8$ K, several groups prepared superconducting FeSe films by the pulsed laser deposition (PLD) method [9–12]. It was shown that superconductivity of the prepared films can be tuned by tensile strain [10, 11]. However, the relation between

superconductivity and the Se/Fe atomic ratios or magnetism was not touched.

For the superconducting FeSe compounds, the initial understanding was that the Se deficiency is crucial for superconductivity [4]. Recent experiments suggested that the superconductivity in single-phase samples of FeSe can only occur in nearly stoichiometric compositions [13–15]. When preparing superconducting FeSe, whether the nominal composition is stoichiometric or not, the final synthesized samples always contain the superconducting FeSe phase with composition near stoichiometry as well as impurity phases, such as metallic Fe and iron oxides [14, 15]. It seems that it is difficult to control the ratio of Fe to Se for bulk samples synthesized by the solid-state reaction method and films grown by the PLD technique (the targets are bulk polycrystalline). Therefore, it is not strange why the FeSe samples prepared by different groups with different nominal compositions have almost the same $T_c \sim 8$ K [4, 13–15].

In this paper, FeSe thin films with different ratios of Fe to Se have been prepared on GaAs and Si substrates by

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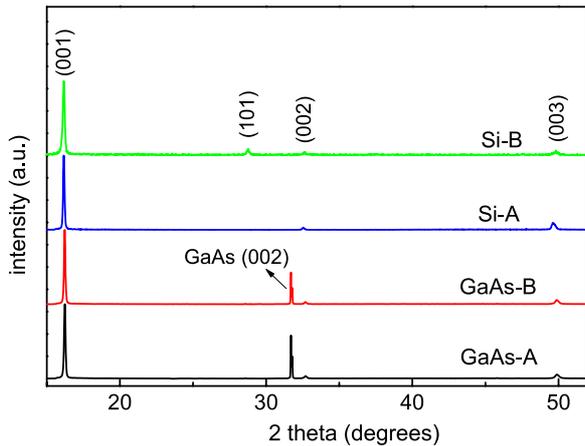


Figure 1. X-ray diffraction pattern of FeSe films on GaAs and Si substrates with different flow rates of $\text{Fe}(\text{CO})_5$. Samples with flow rate of $5 \times 10^{-6} \text{ mol min}^{-1}$ are labeled as GaAs-A and Si-A; samples with flow rate of $8 \times 10^{-6} \text{ mol min}^{-1}$ are labeled as GaAs-B and Si-B.

low-pressure MOCVD. The ratio of Fe to Se in the films is controlled by changing the flow rate of $\text{Fe}(\text{CO})_5$. For both substrates, the films grown with low flow rate of $\text{Fe}(\text{CO})_5$ are non-ferromagnetic and superconducting, while the films grown with high flow rate of $\text{Fe}(\text{CO})_5$ are ferromagnetic and display semiconducting behavior.

FeSe thin films with thickness about 200 nm were grown on GaAs and Si substrates with [001] orientation by low-pressure MOCVD at 330 °C with a chamber pressure at about $2 \times 10^4 \text{ Pa}$. Ironpentacarbonyl ($\text{Fe}(\text{CO})_5$) and hydrogen selenide (H_2Se) were used as the precursors. The gas flow rate of H_2Se was fixed at $4 \times 10^{-5} \text{ mol min}^{-1}$, and the gas flow rates of $\text{Fe}(\text{CO})_5$ were fixed at $5 \times 10^{-6} \text{ mol min}^{-1}$ and $8 \times 10^{-6} \text{ mol min}^{-1}$, respectively. High purity hydrogen was used as carrier gas to carry the reactants into the reaction chamber with a horizontal rectangular quartz reactor and the total gas flow rate was kept at 2 l min^{-1} .

Structure and crystalline quality of the prepared thin films were examined by x-ray diffraction (XRD) with $\text{Cu K}\alpha$ radiation at room temperature. The resistivity was measured by using a standard four-probe method in a Quantum Design Physical Properties Measurement System (PPMS). Magnetic properties were investigated using a superconducting quantum interference device (SQUID) magnetometer; the magnetic field H is applied perpendicular to the films.

Figure 1 shows the XRD patterns of FeSe films grown on GaAs and Si substrates with different flow rates of $\text{Fe}(\text{CO})_5$. Samples prepared with flow rate of $5 \times 10^{-6} \text{ mol min}^{-1}$ are labeled as GaAs-A and Si-A, and samples prepared with flow rate of $8 \times 10^{-6} \text{ mol min}^{-1}$ are labeled as GaAs-B and Si-B. For GaAs-A, GaAs-B and Si-A, three peaks located at about 16.22°, 32.68° and 49.86° can be observed, which are in good agreement with (001), (002) and (003) diffraction peaks of tetragonal FeSe (PbO type). Only (00 l) diffraction peaks appear, indicating that the films are preferentially oriented along the c -axis. For film Si-B, besides the (00 l) diffraction peaks, the (101) peak is also observed. No impurity phase is

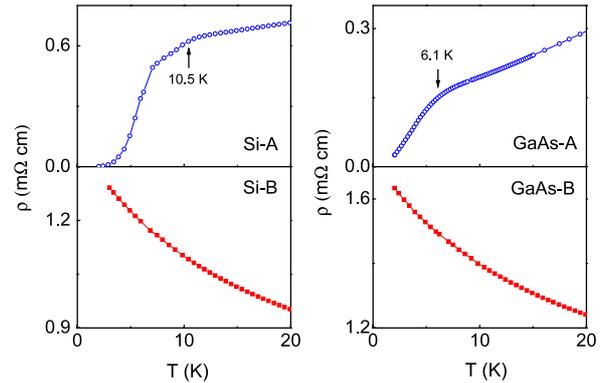


Figure 2. Resistivity as a function of temperature of GaAs-A, GaAs-B, Si-A and Si-B films.

observed for all the films. The c -axis lattice constants derived from the XRD patterns ($c = 5.48 \text{ \AA}$ for films on GaAs and $c = 5.49 \text{ \AA}$ for films on Si) are found to be close to the values of the bulk samples.

The resistivity as a function of temperature for the FeSe films is shown in figure 2. For sample Si-A, the resistivity exhibits a metallic behavior above $T_c^{\text{onset}} \sim 10.5 \text{ K}$, and reaches zero at $T_c^{\text{zero}} \sim 2.4 \text{ K}$. For sample GaAs-A, an abrupt decrease in the resistivity at temperature near 6.1 K is also observed. According to the similarity of the resistivity curves between GaAs-A and Si-A, it can be expected that sample GaAs-A would reach zero resistance when the temperature drops low enough. In contrast, both samples GaAs-B and Si-B, prepared at higher flow rate of $\text{Fe}(\text{CO})_5$, display semiconducting behavior with no sign of superconducting transition down to 2 K.

By using MOCVD, either superconducting or semiconducting films can be prepared. For the films prepared by PLD, it is reported that the superconductivity is modulated by the strain effect of the substrates [10, 11]. Considering (001) orientated FeSe thin film on single crystalline GaAs(001) ($a = 0.5653 \text{ nm}$) and Si(001) ($a = 0.5430 \text{ nm}$), the lattice mismatch between the film and substrate is 5.79% and 1.94%, respectively. For such a big mismatch, the strain effect dominates mainly for thinner film and should be almost relaxed for film with thickness of 200 nm. For example, the 100 nm FeSe film on SrTiO_3 and 200 nm FeSe film on MgO and LaAlO_3 are all unstrained because 100 and 200 nm are above the relaxation critical thickness [10]. Even if the strain is not relaxed fully, the strain effect can be ignored here because the superconductivity mainly relies on the gas flow rates of $\text{Fe}(\text{CO})_5$ as prepared, regardless of what kind of substrate they use. Totally different conducting behavior in these films suggests that the ratio of Fe to Se is modulated by changing the gas flow rates of $\text{Fe}(\text{CO})_5$.

In order to examine if the prepared films display ferromagnetism as reported previously, we further performed magnetic measurements. Figure 3 shows the M - H curves measured at 10 K for all the samples. For semiconducting samples GaAs-B and Si-B, both magnetization curves show typical ferromagnetic features, similar to the results reported by Wu *et al* [8]. In contrast, for superconducting sample Si-A, the M - H curve is almost linear, suggesting that the sample is

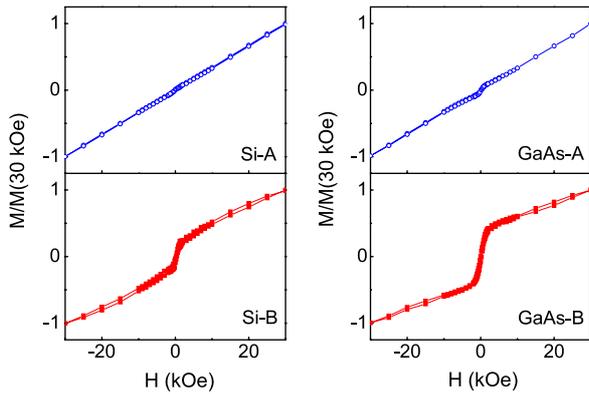


Figure 3. $M-H$ curves of GaAs-A, GaAs-B, Si-A and Si-B films at 10 K. The external magnetic field H is applied perpendicular to the substrates.

non-ferromagnetic. For sample GaAs-A, which only displays superconducting transition tendency, the $M-H$ curve is not strictly linear in the lower field range, implying that trace amounts of magnetic phases coexist with the superconducting phase.

Clearly the appearance of superconductivity in the prepared films is closely correlated to magnetism. As mentioned above, stoichiometric FeSe is believed to be non-ferromagnetic while nonstoichiometric FeSe samples show distinct ferromagnetism [8]. Recent investigations on polycrystalline FeSe indicate that the superconducting FeSe is non-magnetic and the chemical composition is nearly stoichiometric [13–15]. By comparing our results with these works, it can be deduced that film Si-A, which displays superconductivity and non-ferromagnetism, might be nearly stoichiometric. On increasing the gas flow rate of $\text{Fe}(\text{CO})_5$, excess Fe will be introduced into FeSe films either at interstitial sites or entering the lattice at the expense of the Se vacancy, resulting in ferromagnetism and thereby suppressing superconductivity.

The coexistence and competition between superconductivity and magnetism is a hot topic in $\text{Fe}_{1+y}\text{Te}(\text{Se})$ [16–19]. Density functional study on Fe_{1+y}Te showed that the excess Fe at the interstitial sites acts as a magnetic electron donor and is strongly magnetic [20]. In the non-superconducting Fe_{1+y}Te , the excess Fe modulates the magnetic order from incommensurate to commensurate [16]. For Se substituted Fe_{1+y}Te , the excess Fe is believed to be essential for short-range magnetic order; the latter not only suppresses superconductivity but also leads to charge carrier localization [17]. Our recent investigations on $\text{Fe}_{1+y}\text{Te}(\text{Se})$ imply that the superconducting and magnetic phases coexist in the form of phase separation [18]. Since the superconducting FeSe does not show static magnetism, it is still controversial whether excess Fe in FeSe can induce magnetism [8, 13, 21, 22]. However, Bendele *et al* reported that at a pressure near 0.8 GPa the non-magnetic and superconducting FeSe enters a region where static magnetic order is realized above T_c and bulk superconductivity coexists and competes on short length scales with the magnetic order below T_c [23].

From this point, static magnetism induced by the excess Fe might be expected. We hope that our results will stimulate further theoretical investigation in this field.

In summary, we have successfully deposited tetragonal FeSe films on GaAs and Si substrates by the low-pressure MOCVD technique. The prepared films are found to be either superconducting (non-ferromagnetic) or semiconducting (ferromagnetic) depending on the ratio of Fe to Se.

Acknowledgments

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References

- [1] Kamihara Y, Watanabe T, Hirano M and Hosono H 2008 *J. Am. Chem. Soc.* **130** 3296
- [2] Rotter M, Tegel M and Johrendt D 2008 *Phys. Rev. Lett.* **101** 107006
- [3] Wang X C, Liu Q Q, Lv Y X, Gao W B, Yang L X, Yu R C, Li F Y and Jin C Q 2008 *Solid State Commun.* **148** 538
- [4] Hsu F-C *et al* 2008 *Proc. Natl Acad. Sci. USA* **105** 14262
- [5] Feng Q J, Shen D Z, Zhang J Y, Li B S, Li B H, Lu Y M, Fan X W and Liang H W 2006 *Appl. Phys. Lett.* **88** 012505
- [6] Wu X J *et al* 2007 *Appl. Phys. Lett.* **90** 112105
- [7] Liu K W, Zhang J Y, Shen D Z, Shan C X, Li B H, Lu Y M and Fan X W 2007 *Appl. Phys. Lett.* **90** 262503
- [8] Wu X J, Zhang Z Z, Zhang J Y, Li B H, Ju Z G, Lu Y M, Li B S and Shen D Z 2008 *J. Appl. Phys.* **103** 113501
- [9] Han Y, Li W Y, Cao L X, Zhang S, Xu B and Zhao B R 2009 *J. Phys.: Condens. Matter* **21** 235702
- [10] Nie Y F, Brahimi E, Budnick J I, Hines W A, Jain M and Wells B O 2009 *Appl. Phys. Lett.* **94** 242505
- [11] Wang M J, Luo J Y, Huang T W, Chang H H, Chen T K, Hsu F C, Wu C T, Wu P M, Chang A M and Wu M K 2009 *Phys. Rev. Lett.* **103** 117002
- [12] Jung S-G, Lee N H, Choi E-M, Kang W N, Lee S-I, Hwang T-J and Kim D H 2010 arXiv:1005.0192 [cond-mat.supr-con]
- [13] McQueen T M *et al* 2009 *Phys. Rev. B* **79** 014522
- [14] Pomjakushina E, Conder K, Pomjakushin V, Bendele M and Khasanov R 2009 *Phys. Rev. B* **80** 024517
- [15] Young B-L, Wu J, Huang T-W, Yeh K-W and Wu M-K 2010 *Phys. Rev. B* **81** 144513
- [16] Bao W *et al* 2009 *Phys. Rev. Lett.* **102** 247001
- [17] Liu T J *et al* 2009 *Phys. Rev. B* **80** 174509
- [18] Li L, Yang Z R, Zhang Z T, Pi L, Tan S and Zhang Y H 2010 *New J. Phys.* **12** 063019
- [19] Khasanov R *et al* 2009 *Phys. Rev. B* **80** 140511(R)
- [20] Zhang L J, Singh D J and Du M H 2009 *Phys. Rev. B* **79** 012506
- [21] Lee K-W, Pardo V and Pickett W E 2008 *Phys. Rev. B* **78** 174502
- [22] de Souza M, Haghghirad A-A, Tutsch U, Assmus W and Lang M 2010 arXiv:1006.0073
- [23] Bendele M, Amato A, Conder K, Elender M, Keller H, Klauss H-H, Luetkens H, Pomjakushina E, Raselli A and Khasanov R 2010 *Phys. Rev. Lett.* **104** 087003