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Low-temperature fabrication of superconducting FeSe thin films by pulsed laser deposition

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ABSTRACT

Superconducting FeSe thin films were prepared at a substrate temperature of 320 °C by pulsed laser deposition. X-ray diffraction and transmission electron microscopic analyses showed that highly *c*-axisorientated and high-quality films were obtained on various substrate materials, including single-crystal MgO, LaAlO₃, SrTiO₃ and (100)-Si, and amorphous-SiO_x, at such low temperature. From transport measurements all the films showed low-temperature structural phase transition at ~60–90 K and superconducting transition at onset temperature varies from ~7 K to <2 K, depending on the substrate used. The transport property of FeSe film on Si was found most different from all the others, in spite of their similarity in structural analysis. Chemical analysis demonstrated that Fe and Se homogeneously distributed in the film and the stoichiometry of FeSe and the bonding states of Fe and Se are as well uniform along the film growth direction.

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1. Introduction

Recent discovery of high-transition-temperature (T_c) superconductivity in iron-based quaternary-layered compounds LnFePnO (Ln: La, Ce, Sm; Pn: P, As) has drawn considerable attention [1–3]. Closely followed by the first report of superconductivity with $T_c = 26$ K in LaFeAsO_{1-x} F_x [4], several similar but simpler ternary- and binarylayered compounds, Ba_{1-x}K_xFe₂As₂ (122-family) [5], LiFeAs (111family) [6], and FeSe (11-family) [7], were found showing superconductivity that might have the same origin as the 1111-family. The parent compounds (undoped) of the 1111- and 122-families undergo a phase transition (structural distortion) at low temperature (T_s) followed by an antiferromagnetic (AFM) state developed at equal or somewhat lower temperatures, where the high- T_c superconductivity emerges only when this magnetic state was suppressed together with the phase transition by doping or applying external pressure [8,9]. However, this distortion seemed to be indispensable to the superconductivity in FeSe compounds [7,10]. To date, no static magnetic order was clearly identified in FeSe at ambient pressure below the phase transition temperature (T_s) and beyond T_c [11]. However, Mössbauer [10,12] and ⁷⁷Se nuclear magnetic resonance (NMR) [13] measurements suggested that AFM spin fluctuations are strongly enhanced near T_c . Using muon-spin rotation (μ SR) technique [14], Bendele et al. demonstrated that a static magnetic order might emerge above at applied pressure > 0.8 GPa.

Unlike the 122-family [15,16], high-quality single-crystals of 1111-family and FeSe are small (usually plate-like measuring a few hundreds of micrometer across and tens of micrometer thick) [17-19]. In this respect, preparing high-quality thin-film samples not only satisfies the demands for some basic physical properties measurements but also provides suitable bases for making tunneling junctions, which determines several important superconducting parameters such as gap value and paring symmetry. Moreover, epitaxial thin films are also appropriate for studying the uniaxial pressure dependence of superconducting properties by introducing interfacial stress between thin films and the substrates underneath. Recently we showed that the strain induced by the film/substrate interface suppresses the low-temperature phase transition along with the superconductivity for FeSe thin film with certain preferred orientation [20]. In the mean time, Hiramatsu et al. [21] and Iida et al. [22] reported superconducting thin films of $Sr(Fe_{1-x}Co_x)_2As_2$ and $Ba(Fe_{1-x}Co_{x})_{2}As_{2}$, respectively, while thin films of FeSe, FeTe and FeSe1-xTex were also demonstrated to have superconductivity [20,23,24]. Very recently, Kidszun et al. showed the first superconducting epitaxial LaFeAsO_{1 - x} F_x thin film with comparable T_c (to that of bulk) [25], by growing at room temperature followed with 7 h post-annealing at 960 °C in vacuum.

In this article, we present the structural, chemical, and superconducting properties of high-quality FeSe thin films deposited on various kinds of substrates at relative low temperature, 320 °C. This is



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much lower than the superconducting 122- and 1111-films, 600–700 $^{\circ}$ C [21,22] and 960 $^{\circ}$ C [25], respectively. The lower deposition temperature allows many kinds of substrate including soft materials to be used that may find applications in the future.

2. Experimental

Polycrystalline FeSe target was synthesized by solid-state-reaction in vacuum [7]. Tetragonal phase FeSe films were grown on singlecrystal (100)-MgO, (100)-LAO (LaAlO₃), (100)-STO (SrTiO₃), (100)-Si, and amorphous-SiO_x (\sim 400-nm thick formed by thermal oxidation of (100)-Si) substrates by pulsed laser deposition (PLD) using a KrF $(\lambda = 248 \text{ nm})$ excimer laser source (Lambda Physik LPX Pro). The substrate temperature was 320 °C during film growth and the laser energy density was ~5-6 J/cm² at 2 Hz. No additional working gas was introduced in the vacuum chamber. Film thickness was kept ~400 nm by controlling numbers of shot. X-ray diffraction (XRD) for structural analysis was performed on a Philips PW3040/60 X-ray diffractometer. Film surfaces were observed by a Hitachi S-4200 fieldemission scanning electron microscopy (FESEM) equipped with an energy dispersive spectroscopy (EDS). Film/substrate interface was analyzed by a JEOL JEM-2100F 200-kV field-emission scanning transmission electron microscope (STEM), which provided a <0.2nm electron probe for local chemical analysis, accompanied with an EDS analyzer. Transport measurements were made using 4-probe method in a Quantum Design physical property measurement system (PPMS). Additional chemical information was obtained by a Thermo K-Alpha X-ray photoelectron spectroscopy (XPS) using monochromated Al K α radiation at 54.7°. The contamination carbon C 1s was taken at 285.0 eV.

3. Results and discussion

Recent studies have shown that the tetragonal phase FeSe (space group P4/nmm) undergoes a structural phase transformation at ~90 K (T_s) , to orthorhombic phase (space group *Cmma*), involving mainly a slight distortion in a-b plane, i.e., $\gamma_{tetragoal}$ angle slightly enlarged from 90°, as it becomes superconducting at ~8 K (T_c) [7,10,26]. By altering the stoichiometry of FeSe, such as adding extra iron [10,12], or doping with foreign atoms, like substitution of iron with copper [27], the lowtemperature structural distortion could be suppressed along with the superconductivity of polycrystalline samples. For thin-film samples, we have shown that by depositing at lower temperature, e.g. 320 °C, the *a*-*b* plane of tetragonal FeSe sits well at MgO substrate and the constraint to low-temperature structural distortion becomes stronger as the film grown thinner [20]. If the films deposited at higher temperature, like 500 °C, the film preferred orientation changes from [001] to [101] and the film/substrate interface broadens, resulting in more thickness-independent superconductivity. Therefore, it is necessary to deposit thicker films, as the deposition temperature is low, for obtaining superconducting films. All the data present in this article are from ~400-nm thick FeSe films, which are expected to be able to overcome the strain from film/substrate interface [20].

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Properties of FeSe films deposited on various substrates.

Substrate	Lattice misfit ^a	<i>c</i> -Axis lattice constant (nm)	(001) Bragg peak FWHM (°)	<i>T</i> _c (K) ^b
MgO	11.9%	0.5514	0.07	4.8
LAO	0.66%	0.5521	0.08	5.8
STO	3.7%	0.5529	0.09	6.8
Si	44%	0.5511	0.05	3.0 ^c
a-SiO _x	-	0.5500	0.06	<2.0 ^c

^a Assuming (001)FeSe//(001)substrate:[100]FeSe//[100]substrate.

^b The onset of superconducting transition (95% of normal resistivity).

^c The sample showed only a transition but no zero resistivity above 2 K.

Four kinds of single-crystal substrates, MgO, LAO, STO, and Si, and one amorphous substrate, a-SiO_x, were chosen in this study, for the sake of introducing variant lattice misfits between FeSe films and the substrates (Table 1). Unexpectedly, all FeSe films deposited at 320 °C show very good crystallinity with *c*-axis preferred orientation, illustrated by the XRD patterns in Fig. 1. No additional impurity phases could be identified from both Lab X-ray (Fig. 1) and synchrotron radiation (see Ref. [20]), which are commonly found in polycrystalline samples such as α -Fe, Fe₇Se₈, and δ -FeSe (nonsuperconducting hexagonal phase) [7,12,28]. However, the *c*-axis lattice constants are somewhat different from each other, as shown in the inset of Fig. 1 and Table 1. The FWHM (full-width at half maximum) of (001) Bragg peaks are about the same, indicating no significant difference in crystallinity for FeSe films on these substrates, no matter how high their lattice misfits are.

The XRD analysis seems to suggest that the strain from film/ substrate lattice misfit has nothing to do with the FeSe film. However, the temperature dependence of resistivity $(\rho - T)$ in Fig. 2 shows that these films have different transport properties, even though their XRD profiles are so similar. The ρ -T curves of FeSe films grown on MgO, LAO, and STO are about the same, showing a gradual concave at around 60–90 K where the tetragonal-to-orthorhombic structural phase transition takes place [10,20]. Below 7 K, the films become superconducting at distinct temperatures (T_c) , as shown in the inset of Fig. 2. These T_c values are lower than that of FeSe bulk (polycrystalline samples, onset of $T_c \sim 10-11$ K). We reported earlier that full recovery of T_c may need a film thickness of >1 µm on MgO [20]. The ρ -T curve of FeSe film deposited on a-SiO_x shows similar behavior above phase transition temperature (T_s) . Below T_s , the resistivity increases exhibiting a semiconductor-like behavior. However, the resistivity tends to decrease before reaching the lowest measuring temperature, 2 K, indicating a superconducting transition with very low $T_{\rm c}$. Particularly, the resistivity of FeSe film grown on Si is about an order higher at all temperature ranges than those deposited on other substrates, and its behavior is more complicated than all others. At least three transitions could be observed evidently, one at ~250 K, changing the film from semiconducting-like to metal-like, followed by phase transition at $T_{\rm s}$ ~60 K, showing a concave similar to the transition observed in the FeSe film on a-SiO_x, and finally a sharp decrease indicating the superconducting transition at $T_c \sim 3$ K.



Fig. 1. XRD patterns of FeSe thin films deposited on MgO, LAO, STO, Si and a-SiO_x. Only (001) Bragg peaks were observed for all films indicating well out-of-plane (*c*-axis) preferred orientation. Stars represent Bragg reflections from substrates. Inset shows a closer look at the 001 peak, revealing the variation of *c*-axis lattice constant for films on different substrates.



Fig. 2. Temperature dependent resistivity of FeSe films on MgO, LAO, STO, Si and a-SiO_x. The netted area is the temperature range (T_s) where tetragonal FeSe distorts to orthorhombic crystal structure. The slopes of resistivity somewhat change below this temperature. Inset shows the superconducting transition of FeSe films on MgO, LAO, and STO at low-temperature region.

Liu et al. reported back in year 2007 that highly c-axis preferentially oriented FeSe thin film grown on GaAs (001) substrate showed a ferromagnetic property in nature, which was not expected to be superconducting [29], even though they only measured the resistivity above liquid nitrogen temperature. One thing worth to note is that their films grown above 260 °C showed a Se-rich composition (Se/Fe>1) with a c-axis lattice constant smaller than 0.5518 nm (value from FeSe powder in JCPDS Card No. 85-0735). This is consistent with our results that T_c decreases with *c*-axis lattice constant (see Table 1). However, it is supposed to be not so straightforward since a-axis lattice constant should be also considered, which involves the Se-Fe-Se bond lengths and bond angles that directly vary the electronic structure of FeSe. For example, it was shown that under high pressure, where *c*-axis lattice constant was compressed (along with *a*-constant), T_c could be raised to 37 K [11,30]. On the other hand, the chemical composition is also a very important parameter. McQueen et al. suggested that Fe_{1.01}Se exhibits the best superconductivity (highest T_c and superconducting volume) while Fe_{1.03}Se shows no superconductivity [10]. In the mean time, Pomjakushina et al. reported that a stable phase exhibiting superconductivity at $T_c \sim 8$ K exists in a narrow range of selenium deficiency, $FeSe_{0.974\pm0.005}$ [28]. Unfortunately, the stoichiometries of FeSe in the aforementioned reports were determined by neutron powder diffraction, which required significant amount of sample (typically several grams at least). This is difficult to obtain for thinfilm samples. Using EDS or XPS technique for accurate quantitative analysis might be achieved if applying standard sample. Yet no FeSe standard is available because in the first place, no big high-quality crystal has ever been made as mentioned in the introduction section, and second, tetragonal phase FeSe exists in a wide range of composition in the phase diagram [31] (yet exhibiting superconductivity within a narrow composition range [12,28]), which makes it hard to control the stoichiometry. Nevertheless, we performed both EDS and XPS analyses that would be discussed in the later section.

Fig. 3 shows the plan-view SEM images of FeSe films deposited on MgO and Si substrates. The FeSe film on MgO shows smooth surface while cracks are clearly seen on the surface of FeSe film on (100)-Si. Those on other substrates, i.e., LAO, STO, and a-SiO_x, are as smooth as that on MgO. The cracks on the surface of FeSe film on Si substrate were found only if the film thickness is over 400 nm. This means that the formation of these cracks is mainly from release of strain, resulting



Fig. 3. SEM images and the corresponding EDX spectra of the top surface of FeSe films grown on (a) MgO and (b) Si. Semi-quantitative chemical analysis results of the EDX spectra are also shown in the figure. The error in (a) is higher due to the overlap of Mg K and Se L lines. Particles on the surfaces show similar composition to the matrix underneath, indicating that they are most likely tetragonal phase FeSe.

from film/substrate interface and/or from grain boundaries, which is reasonable because of the high lattice misfit (44%) between FeSe and silicon. On the other hand, the difference of linear thermal expansion coefficient (LTEC, α) between FeSe film and substrates is also considered. The LTEC of FeSe is 14.8 10^{-6} /K estimated by extrapolating the temperature dependent synchrotron X-ray diffraction data to room temperature. The LTEC of MgO, STO, Si, and a-SiO₂ (fused silica) are 12.4, 10.2, 2.5, and 0.4 10⁻⁶/K at room temperature [32,33]. Using the formula $\frac{\Delta A}{A} = 2\alpha\Delta T$ (assuming that the thermal expansion in *a*-*b* plane of FeSe is isotropic), there are approximately 0.89%, 0.74%, 0.15% and 0.02% shrinkages in area for FeSe, MgO, Si, and a-SiO₂, cooling from the deposition temperature (320 °C) to room temperature (20 °C). Indeed the LTEC value for Si is much smaller than those of MgO and STO oxide-single-crystals, yet they are all insignificant as compared to the values of lattice mismatch. It is worthy to note that the FeSe film deposited on a-SiO_x (with smallest LTEC) shows no severe cracks. Thus the thermal expansion during cooling must not be the main reason that causes the observed cracks on FeSe/(100)-Si. Nevertheless, these cracks may affect the transport property to a certain extent. It is, however, confusing that the film on Si substrate exhibits smallest FWHM of (001) Bragg peak and its c-axis lattice constant is not the nearest one to that of FeSe bulk. Since we do not know the exact stoichiometry of FeSe in the database (JCPDS Card No. 85-0735), which affects the lattice constants, perhaps it is improper to use the value from the database as a standard to estimate the film stress.

Atomic-resolution TEM image of the FeSe/MgO interface is shown in Fig. 4a, revealing an atomically sharp interface, with a transition layer of about 1–1.5 nm (2–3 layers of FeSe). Along with the FFT power spectrum (see insert image), the epitaxial geometry could be confirmed as (001)FeSe//(001)MgO:[100]FeSe//[100]MgO, which



means that the a-b plane of tetragonal FeSe sits well on the a-b plane of MgO substrate. This explains why the low-temperature structural phase transition is substantially affected for these *c*-axis-oriented films since the transition involves mainly a slight distortion of the a-b plan. However, the reason that FeSe film on a-SiO_x shows smallest *c*-axis lattice constant and lowest T_c is still unclear.

STEM/EDS elemental mappings of the FeSe film on MgO are shown in Fig. 4b. The size of electron probe was controlled to be less than 0.2 nm, i.e., smaller than one unit cell of tetragonal FeSe, allowing to show atomic level elemental distribution. From several mappings (one shown in Fig. 4b and one shown in the supplementary information of Ref. [20]) we found that the Fe and Se are uniformly distributed in the film. There is no clustering of Fe or Se in nanometer scale. Despite checking Fe and Se distribution, the Fe/Se ratio (stoichiometry of FeSe) is also concerned over the entire film and over films on different substrates. Since these FeSe films were deposited on different substrates at the same run, we believed that the stoichiometry of FeSe should be close to each other and it was confirmed by SEM/EDS, STEM/EDS, and XPS techniques. In Fig. 4b, the semi-quantitative chemical analyses of the four points indicated by black crosses (aligned along the growth direction) are comparable to each other and to those obtained from SEM/EDS analysis (Fig. 3), i.e., within the equipment error.

We employed high-resolution XPS analysis to reveal the bonding states of iron, selenium, and oxygen, and to verify the depth profiles as a double check of cross-sectional STEM/EDS analysis. Fig. 5 shows four series of Fe 2p, Se 3d, and O 1s spectra recorded from (a) film surface, (b) 50-nm below surface, (c) 100 nm below surface, and (d) FeSe/Si interface, for a FeSe film deposited on Si substrate. The Fe 2p spectrum from film surface reveals a clear multiplet splitting of $2p_{3/2} = 710.4$ eV and $2p_{1/2} = 723.4$ eV and an embedded weak satellite peak, indicating a mix of Fe^{2+} and Fe^{3+} species, i.e., more like a spectrum of Fe_3O_4 [34– 36]. The surface oxidation of iron in FeSe-related superconductors has been addressed many times [28,37], and this is in very good agreement with the Se 3d and O 1s spectra from film surface. The broad Se 3d spectrum on the surface could be deconvoluted into two splits $(3d_{5/2} \text{ and } 3d_{3/2})$: one split at binding energy 54–55 eV attributed to selenides (Se^I) and the other at binding energy 55.6-56.5 eV assigned as metallic selenium (Se⁰) [29,38,39], with a peak- $\left(\frac{A_{Se^{0}3d_{5/2}} + A_{Se^{0}3d_{3/2}}}{A_{Se^{0}3d_{3/2}}}\right) \text{ of } 0.82. \text{ The O 1s spectrum from film}$ area ratio ($A_{Se^{1}3d_{5/2}} + A_{Se^{1}3d_{3/2}}$ surface shows two main peaks situated at binding energy of 529.9 eV and 531.4 eV. The former is consistent with the reported iron oxides [34,35] and the latter is most likely to be the oxygen atoms in the hydroxyl groups, trapped nitrate ions, or adsorbed carbonates [40], which was not presented within the film, i.e., removed by argon sputtering (see O 1s curves b and c in Fig. 5). Nevertheless, the surface oxidation of iron accompanied with reduction of selenium was adequately demonstrated.

XPS curves b and c in Fig. 5 are acquired ~50 nm and ~100 nm beneath the film surface, respectively. These spectra, Fe 2p and Se 3d core-levels, are nearly identical in both peak position and peak area, suggesting not only a homogeneous chemical composition as discussed in STEM/EDS analysis, but also uniform bonding states for both Fe and Se. However, semi-quantitative analysis gives a composition of FeSe_{0.75} by applying only the atomic sensitivity factors. Thus, standard sample must be prepared and used for accurate quantitative analysis in FeSe compound.

Fig. 4. (a) Cross-sectional HRTEM image of FeSe film on MgO substrate, revealing an atomically sharp interface with a transition layer of only 1–1.5 nm. Inset shows the fast Fourier transform (FFT) from the FeSe lattice, indicating high quality of the film. (b) STEM/EDS elemental mapping of the FeSe/MgO interface. Four spectra were acquired from the black crosses in the image using an electron probe of <0.2 nm. The stoichiometries estimated from the four spectra were S1 = FeSe_{1.09}, S2 = FeSe_{1.09}, S3 = FeSe_{1.02}, and S4 = FeSe_{1.08}. The Fe K_{ccl} and Se L_{ccl.2} maps show no particular feature (random distribution) at an atomic level.



Fig. 5. XPS depth profiles of Fe 2p, Se 3d, and O 1s core-levels for FeSe film grown on Si substrate. Curves were recorded from (a) film surface, (b) \sim 50 nm and (c) \sim 100 nm below the surface, and (d) the FeSe/Si interface. Peak positions are assigned by performing peak deconvolution. Some results of peak deconvolution are shown together with the raw experimental data.

The Fe 2p spectra obtained in the FeSe film (curves b and c) show a highly asymmetric $2p_{3/2}$ peak at binding energy 706.8 eV, about 3.6 eV lower than that of iron oxides. This value is close to the reported FeS (707.2 eV) [36] and FeBr₂ (707.1 eV) [35], but far away

from the reported FeSe film (710.75 eV) [29] and FeSe bulk (~712 eV obtained by EELS, electron energy loss spectroscopy) [12]. With only few references available, we still have confidence with our data since the reported binding energy 710.75 eV for FeSe film is too close to that for Fe₂O₃ [35,38] and EELS often suffers time-dependent shifting of energy (while 712 eV is too high for Fe $2p_{3/2}$). Yet small amount of bonded oxygen (~529.9 eV) was detected in curves b and c. Because there seems to be no metallic Se in Se 3d spectra b and c, we believe that the oxygen is from thin oxidized layer on the very top surface during argon sputtering. Note that the pre-edge-like peak at 52.3 eV in Se 3d spectra comes from Fe 3p core-level.

At FeSe/Si interface, the Fe 2p and Se 3d spectra show only slight changes (curve d in Fig. 5). An additional shoulder appears in Fe 2p spectrum at binding energy ~710 eV and a broad tail arises in Se 3d spectrum at ~56 eV, indicating certain degree of iron oxidation and selenium reduction. By looking at the O 1s profile d, a new peak comes up at binding energy 532.3 eV which is coincident with 532.5 eV of SiO₂ [38]. This must be the native oxide on Si substrate formed before film growth (even though it was cleaned by HF solution before loading into the vacuum chamber). Therefore, the variations of Fe 2p and Se 3d spectra at interface should mainly attribute to the reaction between native oxide and FeSe deposited.

5. Conclusions

We successfully grew high-quality tetragonal phase FeSe thin films on MgO, LAO, STO, Si, and amorphous-SiO_x substrates at 320 °C by pulsed laser deposition. These films showed highly *c*-axis preferred orientation and similar crystallinity on various substrates. From transport measurements all the films showed low-temperature structural phase transition at ~60–90 K and superconducting transition at onset temperature varies from ~7 K to <2 K. The transport property of FeSe film on Si was found most different from all the others, in spite of their similarity in structural analysis. Chemical analysis employed using STEM/EDS and XPS depth profiles demonstrated that Fe and Se homogeneously distributed in the film and the stoichiometry of FeSe and the bonding states of Fe and Se are as well uniform along the film growth direction. The successful growth of superconducting FeSe films at low temperature may find future applications for academic studies and commercial uses.

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