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Growth of High-Quality Superconducting $\text{FeSe}_{0.5}\text{Te}_{0.5}$ Thin Films Suitable for Angle-Resolved Photoemission Spectroscopy Measurements via Pulsed Laser Deposition *

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High-quality superconducting $\text{FeSe}_{0.5}\text{Te}_{0.5}$ films are epitaxially grown on different substrates by using the pulsed laser deposition method. By measuring the transport properties and surface morphology of films grown on single-crystal substrates of Al_2O_3 (0001), SrTiO_3 (001), and MgO (001), as well as monitoring the real-time growth process on MgO substrates with reflection high energy electron diffraction, we find the appropriate parameters for epitaxial growth of high-quality $\text{FeSe}_{0.5}\text{Te}_{0.5}$ thin films suitable for angle-resolved photoemission spectroscopy measurements. We further report the angle-resolved photoemission spectroscopy characterization of the superconducting films. The clearly resolved Fermi surfaces and the band structure suggest a sample quality that is as good as that of high-quality single-crystals, demonstrating that the pulsed laser deposition method can serve as a promising technique for in situ preparation and manipulation of iron-based superconducting thin films, which may bring new prosperity to angle-resolved photoemission spectroscopy research on iron-based superconductors.

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The discovery of superconductivity in F-doped LaFeAsO ^[1] in 2008 has attracted intensive research attention, and many families of iron-based superconductors (IBSCs) have been discovered.^[2–4] Among those families of IBSCs, FeSe (and also $\text{FeSe}_{1-x}\text{Te}_x$, the so-called ‘11’ system) has the simplest form of crystal structure. The simple quasi-two dimensional stacking of FeSe layers are of the same structure as that of the FeAs layers in the iron pnictide superconductors. Many properties, including the Fermi surface topology and the phase diagram of the 11 system, are similar to those of the FeAs -based SCs.^[5] Therefore, it is quite likely that they share the same pairing mechanism.^[6] Consequently, the 11 system is an ideal platform to study the relationship between electronic structure and superconducting mechanism.

On the other hand, the pulsed laser deposition (PLD) technique has achieved great progress^[7] in the fabrication of super high-quality complex perovskite structure oxides during the last two decades,^[8] which brings up interesting exotic physics in strongly correlated electron systems as well as new electronic devices.^[9] While single-crystals of some materials are not easy to synthesize with high quality or suffer from a polar cleavage plane problem^[10] preventing the access by angle-resolved photoemission spectroscopy (ARPES) to the three-dimensionality of the electronic band structure, the thin film approach possesses all

the corresponding advantages.^[8] Thus the fabrication of high-quality superconducting $\text{FeSe}_{0.5}\text{Te}_{0.5}$ thin films via the PLD method and its combinatorial research with ARPES to quantitatively study the electronic structure of superconducting films emerges to be a promising approach to tackle unsolved problems in iron-based superconductivity.

In this Letter, we try to find appropriate parameters for epitaxial growth of superconducting $\text{FeSe}_{0.5}\text{Te}_{0.5}$ films on different substrates. For the thin films with highest T_C grown on MgO substrates, we investigate the growth mode in detail and report the T_C dependence on thickness. We further characterize the electronic structure of annealed $\text{FeSe}_{0.5}\text{Te}_{0.5}$ thin films grown on MgO substrates with ARPES. The distinct Fermi surfaces and the band structure demonstrate that the superconducting $\text{FeSe}_{0.5}\text{Te}_{0.5}$ film is of high quality and suitable for ARPES measurements.

Thin films of $\text{FeSe}_{0.5}\text{Te}_{0.5}$ were prepared by the PLD method in an ultra-high vacuum (with a base vacuum of 8.2×10^{-7} Pa) on Al_2O_3 (0001) single-crystals, SrTiO_3 (001), and MgO (001) substrates. A KrF excimer laser source ($\lambda = 248$ nm, pulse width=20 ns) with a power density of 3 J/cm^2 and a pulse repetition rate of 10 Hz was directed at a 45° incident angle onto the $\text{FeSe}_{0.5}\text{Te}_{0.5}$ target. The distance between the target and the substrate was maintained at 60 mm during the deposition. The substrates

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were physically cleaned with acetone and alcohol in an ultrasonic bath before being transferred to the deposition chamber. The substrates were heated to and maintained at 500°C for 3 h before deposition, and the target rotated at a rate of 3 rpm to avoid excessive heating and erosion of the target surface. At the end of the depositions, the films were cooled down to room temperature at a rate of 3°C/min. The structural characteristics of the deposited films were studied by x-ray diffraction (XRD) with a θ - 2θ geometry by using a Cu K α radiation source ($\lambda = 1.5406 \text{ \AA}$). The deposition process of the film on MgO substrate was *in situ* monitored by reflection high electron energy diffraction (RHEED). Scanning electron microscopy (SEM) and atomic force microscopy (AFM) were used to determine the thickness of the films and their surface roughness, respectively. The temperature dependence of the resistivity (RT) was obtained from a quantum-design physical property measurement system (QD-PPMS), by using the standard four-point probe method.

The ARPES measurements were performed in our lab-based system equipped with a VG-Scienta R4000 analyzer and a microwave-driven helium discharge source. To measure the electronic structure of the thin films, we first capped the $\text{FeSe}_{0.5}\text{Te}_{0.5}$ thin films with amorphous Se (deposited via the PLD method at a substrate temperature of 100°C for 10 min) and then transferred them into the ARPES annealing chamber, where we annealed the samples *in situ* at 450°C for 7 h in a base vacuum of $5 \times 10^{-7} \text{ Pa}$ to evaporate the protective Se layer and to achieve well-ordered surfaces suitable for ARPES measurements. The annealed thin films are then transferred into the ARPES measurement chamber with a working vacuum better than $5 \times 10^{-9} \text{ Pa}$ and cooled down to low temperature to measure the Fermi surface and the band structure.

$\text{FeSe}_{0.5}\text{Te}_{0.5}$ thin films were prepared in the same procedure on Al_2O_3 ($a = 4.758 \text{ \AA}$), SrTiO_3 ($a = 3.905 \text{ \AA}$), and MgO ($a = 4.212 \text{ \AA}$) substrates, respectively. The a -axis lattice constant of $\text{FeSe}_{1-x}\text{Te}_x$ varies from 3.76 \AA to 3.82 \AA . Figure 1(a) shows the XRD patterns of these films. Only the (00 l) reflections of a tetragonal PbO-structure are observed, indicating a pure phase and an optimum c -axis alignment of the desired films. The c axis lattice constants of the films deposited on Al_2O_3 , SrTiO_3 , and MgO are 5.87 \AA , 5.94 \AA and 5.91 \AA , respectively. These values are slightly smaller than that of bulk single-crystal (6.03 \AA), while are in agreement with the values reported previously.^[11]

Figure 1(b) shows the resistivity measurements of $\text{FeSe}_{0.5}\text{Te}_{0.5}$ films with a thickness of around 80 nm grown on Al_2O_3 , SrTiO_3 , and MgO substrates, respectively. A T_C^{onset} (the temperature when the electrical resistivity deviates from the normal state) of 17.6 K is

observed on MgO , which is consistent with the bulk value. Films on Al_2O_3 , SrTiO_3 , and MgO substrates show zero resistivity at 2.5 K, 8.5 K and 13.3 K, respectively. According to the lattice match and the c axis lattice constant principle,^[12,13] the better the lattice constant between the film and the substrate matches, the higher the T_C will be, and the value of T_C increases monotonically with the lattice constant c in the range of 5.80 \AA – 6.00 \AA . Obviously, neither principle can give a satisfactory explanation for our results.

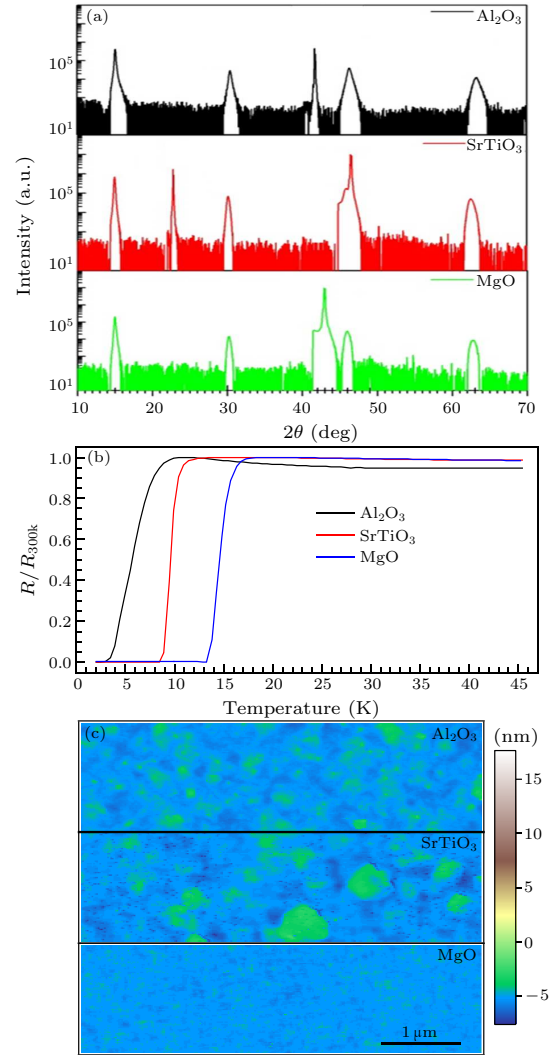


Fig. 1. (a) XRD patterns at room temperature for films deposited on Al_2O_3 , SrTiO_3 and MgO substrates. (b) Normalized resistance as a function of temperature for $\text{FeSe}_{0.5}\text{Te}_{0.5}$ films grown on Al_2O_3 , SrTiO_3 and MgO substrates, respectively. (c) AFM scanning images of $5 \mu\text{m} \times 5 \mu\text{m}$ $\text{FeSe}_{0.5}\text{Te}_{0.5}$ films deposited on Al_2O_3 , SrTiO_3 and MgO substrates, respectively. Only an area of size $1.7 \mu\text{m} \times 5 \mu\text{m}$ is shown.

To further explore the difference among these films on three different substrates, AFM scans of the surface morphology were recorded, as shown in Fig. 1(c). The surface roughness of these films is estimated at room temperature. The rms values for the samples grown on Al_2O_3 , STO and MgO substrates are 0.97, 1.42 and

0.56 nm, respectively. Hence, the films grown on the MgO substrate with the flattest surface possess the highest T_C value. Generally, the flatness of the film is attributed to the good crystallinity during epitaxial growth. Here we propose that the core factor affecting T_C is the crystallinity during thin film deposition.

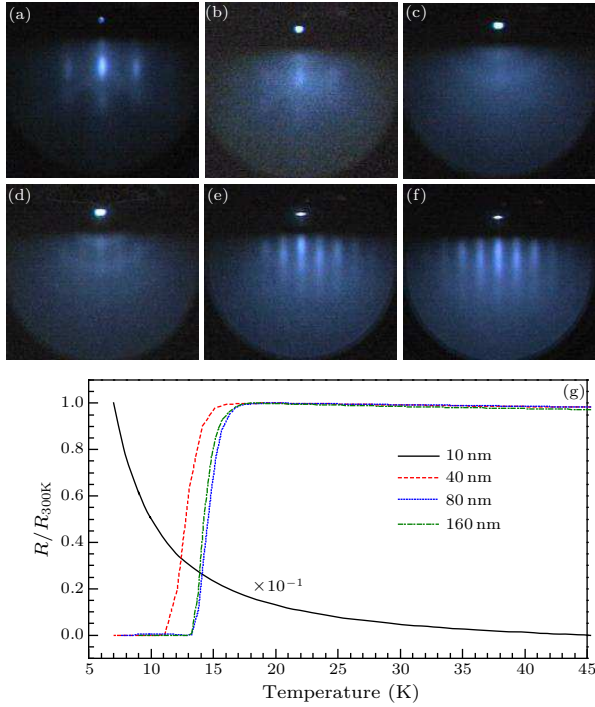


Fig. 2. (a) RHEED image of a MgO substrate. (b)–(f) RHEED images after 2, 4, 16, 30 and 40 unit cells growth of FeSe_{0.5}Te_{0.5}, respectively. (b) Amorphous layer. (c) Polycrystalline layer. (d) Single-crystal layer emerges. (e)–(f) Persistent single-crystal layer. (g) Normalized resistance as a function of temperature for FeSe_{0.5}Te_{0.5} films grown on MgO substrates, with thicknesses ranging from 10 nm to 160 nm.

To better understand the procedure that the FeSe_{0.5}Te_{0.5} thin films crystallize on MgO substrates, we monitored the film growth process *in situ* with RHEED. After the initial growth of amorphous and polycrystalline layers, we did observe the good layer-by-layer epitaxial growth mode starting from roughly 16 unit cells, judging from the persistent RHEED pattern after growth of 16 unit cells. The RHEED pattern evolution corresponding to different unit cells of growth is shown in Figs. 2(a)–2(f). The in-plane lattice constant of MgO is approximately 10% larger than that of FeSe_{1-x}Te_x and the lattice mismatch is so large that the epitaxial-strain effect should not be expected for the FeSe_{0.5}Te_{0.5} films. The thin films are relaxed within a few layers from the substrate surface, and the resultant layer-by-layer epitaxially grown film has a T_C value similar to that of the single-crystal samples.^[13,14]

Then we study the T_C dependence on thickness, films with different thicknesses were prepared on the MgO substrates (corresponding to different crys-

tallinities as seen in the previous RHEED patterns). Figure 2(g) shows that T_C increases with the film thickness until T_C equals that of the bulk, which is consistent with our RHEED observation. With the thickness of films increasing, the films' surface growth mode changes from amorphous state to polycrystalline state, and then to single-crystalline state, resulting in the increase of T_C . When the surface of the films becomes single-crystalline, thin films grow further in layer-by-layer mode on the single-crystal surface, keeping the single-crystal surface reproduction to a thicker and better surface, and thus T_C increases and saturates at the bulk value.

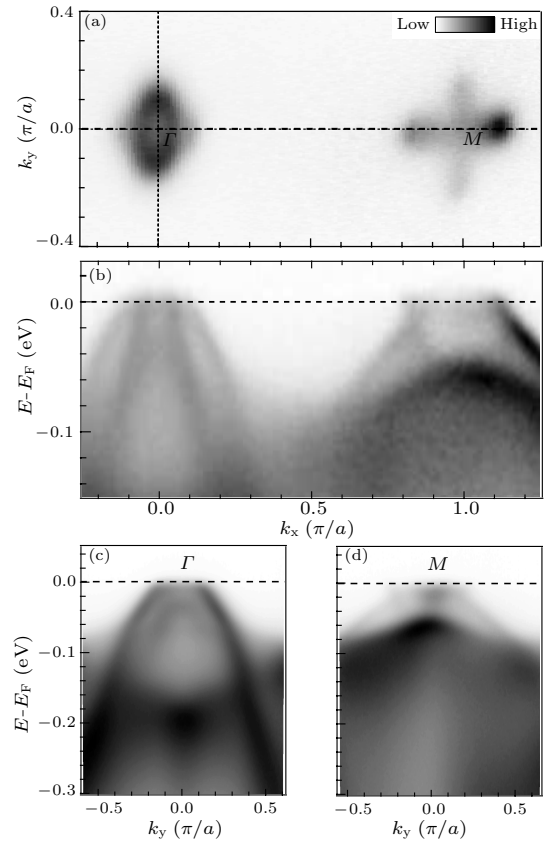


Fig. 3. Fermi surface and band structure measured at 30 K of FeSe_{0.5}Te_{0.5} films grown on a MgO substrate obtained after being capped with Se and annealed in vacuum at 450°C for 7 h. (a) Fermi surface. (b) Band structure along the Γ –M direction. (c) and (d) High-resolution cut of band structures at the Γ point and the M point, respectively.

With the AFM and RHEED pattern results we find the appropriate parameters for epitaxial growth of high-quality superconducting FeSe_{0.5}Te_{0.5} films and we choose to fabricate 100-nm-thick FeSe_{0.5}Te_{0.5} films and further characterize their electronic structure. We measure the Fermi surface (Fig. 3(a)) and the band structure along the Γ –M direction (Fig. 3(b)). Figure 3(c) shows the high-resolution band structure at the Brillouin zone center (the Γ point) and Brillouin zone boundary (the M point). Both hole pockets

at the Γ point and electron pockets at the M point can be distinctly resolved. These results demonstrate that the quality of the annealed thin films is good enough to be electronically imaged by ARPES. Actually, the ARPES spectra obtained on the thin films is as good as the data acquired from available single crystals.^[5,15,16]

In conclusion, we have explored the appropriate growth parameters for epitaxial growth of high-quality superconducting $\text{FeSe}_{0.5}\text{Te}_{0.5}$ thin films. The T_C of the films grown on the MgO substrates increases with the film thickness and eventually saturates at the bulk T_C , which is attributed to the epitaxial layer-by-layer growth mode resulting in good crystallinity. We also present the high-quality ARPES data on annealed $\text{FeSe}_{0.5}\text{Te}_{0.5}$ superconducting thin film grown on MgO substrates by the PLD method. The clear results of Fermi surface and band structure indicate that the PLD method is capable of fabricating high-quality thin film samples suitable for ARPES measurements, which hopefully will help in providing new information on the relationship between the electronic structure and the superconducting mechanism in the iron-based superconductors. With the combinatorial system of ARPES, STM and PLD completed in the future, we will be able to further monitor and manipulate the thin film and to study the novel electronic state in different quantum materials.

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