Evolution of Tetragonal Phase in the FeSe Wire Fabricated by a Novel Chemical-Transformation Powder-in-Tube Process

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We fabricated superconducting FeSe wires by the chemical-transformation powder-in-tube (PIT) process. The obvious correlation between annealing temperature and phase transformation was observed. Annealing above 500 °C produced wire-core transformation from hexagonal to tetragonal phase. Furthermore the hexagonal phase completely transformed into the tetragonal phase by annealing at 1000 °C. With increasing annealing temperature, the superconducting property was dramatically improved, associated with the evolution of the tetragonal phase.

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1. Introduction

Fe-based superconductor is one of the candidate materials for superconducting applications, owing to the high transition temperature (Tc) and high upper critical field (Hc2).1-10 Several kinds of Fe-based superconducting wires have been fabricated using the superconducting materials of BaFe2As2, SmFeAsO, and FeSe systems.11-18 To date, the highest record of critical current density (Jc) over 10⁴ A/cm² at 4.2 K was achieved in the Ba1-xKxFe2As2 wire.12

Among the Fe-based superconducting materials, FeSe has several advantages for application because of the simplest crystal structure and composition.10,19-22 Low anisotropy23-25 and relatively low toxicity compared to the FeAs-based compounds are also advantageous for applications. Furthermore, the Tc of FeSe was enhanced up to 37 K under high pressure of 4-6 GPa, while the ambient Tc is only ~10 K.26-29 Large enhancements of Tc have been observed in strain-stressed Fe-chalcogenide thin films, bulk poly crystals, and wires as well.30,31 In these respects, Fe-chalcogenide superconductor is a great candidate material used in superconducting application. However, the present record of the highest Jc in Fe-chalcogenide wires is 1027 A/cm² at 4.2 K,35 10 times as low as that of FeAs-based wires. To achieve higher Jc using Fe-chalcogenide superconductors, a new wire fabrication process should be created.

Recently we reported a successful fabrication of FeSe superconducting wire by an unconventional powder-in-tube (PIT) method based on chemical transformation of the wire core using an Fe sheath. Via a wire fabrication process, the wire core transformed from hexagonal FeSe₁₋₄ (non-superconducting) to tetragonal FeSe (superconducting) upon a diffusion of Fe from the pure Fe sheath by annealing.32 In this article, we report a systematic study on the annealing temperature dependences of structural changes and transport properties of the FeSe superconducting wires fabricated by the chemical-transformation PIT process.

2. Experimental Methods

FeSe superconducting wires were fabricated by the chemical-transformation PIT process. Figure 1 shows a schematic chart for wire fabrication process. Firstly, we synthesized precursor powders of hexagonal FeSe₁₋₂ by solid state reaction. Pure Fe powder (99.9%) and pure Se chips (99.9999%) were used as starting materials. These materials were sealed into an evacuated quartz tube, and heated at 700 °C for 10 h. The obtained precursor was packed into a pure Fe tube with outer and inner diameters of 6.2 and 4.0 mm, respectively. The tube sealed with two edge caps of pure Fe was groove-rolled into a rectangular wire with a size of ~2 mm. The obtained wire was cut into several pieces, sealed into an evacuated quartz tube, and then annealed at various annealing temperature (Ta) of 400-1000 °C. The cross section of the wire was observed using an optical microscope. The crystal structure was characterized by X-ray diffraction (XRD) using a Cu Kα radiation. Temperature dependence of total resistivity down to 2 K was measured using a four-terminal method, where the total resistivity was estimated using the total cross-sectional area including Fe sheath.

3. Results and Discussion

Figure 2 shows the optical-microscope images of the obtained cross section for Ta = (a) 400, (b) 800, and (c) 1000 °C, respectively. Dense core without voids was observed for all specimens.

Figure 3 shows the XRD patterns for the FeSe₁₋₂ precursor and wire core annealed at 400-1000 °C. The peaks of FeSe₁₋₂ precursor was well indexed using the hexagonal space group of P6₃/mmc. The estimated lattice parameters were a = 3.602(2) Å and c = 5.894(6) Å. With increasing Ta, peaks of the hexagonal phase were suppressed, in contrast the peaks of tetragonal phase were appeared. For Ta > 500 °C, the ratio of the tetragonal phase to the hexagonal phase was over 70%. Finally, the peaks of the hexagonal phase disappeared at Ta = 1000 °C, while a small peak of Fe was detected. The lattice constants of the tetragonal phase were estimated to be a = 3.777(2) Å and c = 5.535(7) Å. To discuss the evolution of the hexagonal-tetragonal transformation by annealing, we plotted the Ta dependence of the existence ratio of the hexagonal phase in Fig. 4. The ratio of the hexagonal phase was defined as Ihex/(Ihex + Itet), where Ihex and Itet were the first peak intensities for the hexagonal and tetragonal phase, respectively. Dramatic changes were observed at two critical points. The first critical Ta exists between 400 and 500 °C. The second critical Ta is between 900 and 1000 °C. This shows that the annealing temperature would be a key parameter of FeSe wire fabrication process.

Figure 5 shows the temperature dependence of total resistivity from 50 to 2 K for Ta = 400-1000 °C. With increasing Ta, the drop of resistivity corresponding to...
superconducting transition became larger and transition became sharper. Figure 6 shows the annealing temperature dependence of $T_{\text{onset}}$ and $T_{\text{offset}}$, where the resistivity was 90 and 10% of normal-state resistivity just above $T_c$, respectively. Both $T_{\text{onset}}$ and $T_{\text{offset}}$ were enhanced with increasing $T_a$. A dramatic enhance of $T_{\text{onset}}$ was observed around $T_a = 400{\pm}500 \degree C$, at which the hexagonal-tetragonal transformation was activated. For $T_a > 600 \degree C$, $T_{\text{offset}}$ was observed and strongly enhanced with increasing $T_a$, while the XRD patterns showed almost no differences. This indicates annealing at a higher temperature enhances connectivity of boundary between the sheath and the superconducting core. For $T_a = 1000 \degree C$, a large enhance of $T_{\text{onset}}$ and $T_{\text{offset}}$ were observed, and the highest critical current density of 218 A/cm$^2$ (at 4.2 K and 0 T) was obtained for this wire as reported in ref. 16. These tendencies seem to correspond with that in Fig. 4, indicating that the annealing temperature is one of the most important parameter to enhance transport properties of FeSe wire as well. By optimization of annealing conditions, the transport properties of FeSe wire will be greatly enhanced.

4. Summary

We fabricated superconducting FeSe wires by the novel chemical-transformation PIT process, and investigated annealing temperature dependence of structural and superconducting properties. The obvious correlation between annealing temperature and phase transformation was observed. Annealing above 500 $\degree C$ produced the wire-core transformation from hexagonal to tetragonal phase. Furthermore the hexagonal phase completely transformed into the tetragonal phase by annealing at 1000 $\degree C$. With increasing...
annealing temperature, the superconducting property was improved, associated with the evolution of tetragonal phase.

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