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Growth and characterization of superconducting $\beta$-FeSe type iron chalcogenide nanowires

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Abstract
We have grown highly crystalline $\beta$-FeSe type iron chalcogenide nanowires (NWs) by annealing thin film that is prepared by a pulsed laser deposition method. Three kinds of NWs with compositions of Fe$_{0.8}$Se, Fe$_{0.88}$Se$_{0.32}$Te$_{0.68}$ and Fe$_{0.88}$Te$_{0.91}$S$_{0.09}$ have been prepared and carefully characterized by a high-resolution transmission electron microscope (HRTEM). The NWs reveal ideal tetragonal structure with crystal growth along the [100] direction. Energy dispersive spectroscopy (EDS) studies and HRTEM images show the NWs to have good compositional uniformity, except for the existence of a thin layer of oxide on the surface. No superconducting transition was observed in the FeSe$_x$NWs, which is possibly caused by Fe deficiency. The other two types of NWs show relatively higher and sharper superconducting transitions than their bulk counterparts. Interestingly, a resistive transition tail is observed in the NWs with diameter smaller than 100 nm, which might originate from a phase slip process in the quasi-one-dimensional system. The success in producing these high quality NWs provides a new avenue for better understanding the origin of superconductivity in $\beta$-FeSe type iron chalcogenides.

Keywords: nanowires, iron chalcogenide, superconductivity

1. Introduction
Iron chalcogenides have received renewed attention following the unexpected discovery of superconductivity in anti-PbO type FeSe with critical temperature ($T_c$) at 8 K [1]. The superconducting transition temperature can be enhanced to 15 K and 10 K by partially substituting the selenium by tellurium and sulfur, respectively [2, 3]. Application of high pressure was found to enhance the superconducting transition temperature up to 37 K [4]. More recently, Xue et al reported a zero resistance at 30 K and an onset temperature of over 55 K in one unit cell FeSe film on SrTiO$_3$ substrate [5]. More striking is the observation of a superconducting-like gap of about 15–20 meV by both STM (scanning tunneling microscopy) and ARPES (angle-resolved photoemission spectroscopy) on this one unit cell film [5, 6]. We have also reported the observation of a clear diamagnetic signal around 40 K observed in fresh FeSe nano-particles [7]. These results strongly suggest that iron chalcogenide superconductors in nanometer scale may reveal interesting properties.

High quality crystalline superconducting NWs have been used to study low dimensional effects such as supercon-
Targets with nominal compositions of FeSe$_0$ tubes and annealed at 400$^\circ$C for 120 h for NW growth. Hereafter, we will denote these three kinds of NWs as Fe$_0$Se, Fe$_{0.88}$Se$_{0.32}$Te$_{0.68}$ and Fe$_{0.88}$Te$_{0.91}$S$_{0.09}$. The contact electrodes were patterned with an E-beam lithography and Ti/Au layer lift-off process. In situ Ar$^+$ plasma cleaning was used to remove the surface oxide layer of the NWs before metal deposition. The transport measurements were performed with a conventional lock-in technique with a constant applied current of 0.1–15 nA. Comparison of four-probe and two-probe measurements shows that the contact resistances are small (several Ohms) and not responsible for the temperature dependence of the transport data.

3. Results and discussion

Figures 1(a)–(c) show the SEM images of the as-grown $\beta$-FeSe type iron chalcogenide NWs on the substrates. The NWs are tens to hundreds of nanometers in diameter and of the order of 10 $\mu$m in length. In general, the number density and size of Fe$_0$Se NWs are lower and smaller than what is found for Fe$_{0.88}$Se$_{0.32}$Te$_{0.68}$ and Fe$_{0.88}$Te$_{0.91}$S$_{0.09}$ NWs on their respective substrates. High-resolution transmission electron microscope (HRTEM) images show excellent crystalline tetragonal structure in these NWs, figures 1(d)–(f). The growth of NWs is along the [100] direction, as indicated in the insets. The x-ray diffraction patterns reveal a good square lattice in the $ab$-plane.

It has been reported that the surface of $\beta$-FeSe type iron chalcogenide can easily form a thin layer of oxide [19, 20]. It is important to know the thickness and growth rate of the oxide layer after the NWs are prepared because this oxide layer...
needs to be removed before Ohmic contacts can be made on the NWs. HRTEM images of the NWs show an amorphous layer a few nanometers thick at the NW edge, which is identified as the surface oxide, figures 2(a)–(c). After storing in vacuum desiccator for around three weeks, the oxide layer increases to ~10 nm thick. The growth rate of surface oxide is similar for Fe$_{0.8}$Se, Fe$_{0.88}$Se$_{0.32}$Te$_{0.68}$ and Fe$_{0.88}$Te$_{0.91}$S$_{0.09}$ NWs. Figure 2(d) shows the back field TEM image and line profile of energy dispersive spectroscopy (EDS) of a 170 nm Fe$_{0.8}$Se NW six months later. The amorphous layer increases to 40 nm thick. The EDS line profile demonstrates high oxygen and iron concentration except in the core area, as shown in figure 2(e), indicating that this amorphous layer is indeed iron oxide.

Most Fe$_{0.8}$Se NWs measured show insulating temperature dependence (defined as dρ/dT < 1) or high resistivity. Figure 3(a) presents the normalized resistance versus temperature curves of two Fe$_{0.8}$Se NWs, with resistivity of about a few tens of mΩ cm, which is relatively low among all the Fe$_{0.8}$Se NWs measured. We took resistivity $\rho = \frac{R \cdot d^2}{l}$, where $d$ is the NW diameter (including oxide) and $l$ is the length. No superconducting transition is observed in these Fe$_{0.8}$Se NWs, as shown in figure 3(a). Furthermore, we observe no trend suggesting that the metallic or insulating temperature dependence of resistance depends on NW diameter. We are able to extract an Fe/Se ratio of 0.8 from EDS, and the results of HRTEM and x-ray diffraction demonstrate a tetragonal crystal structure with lattice constants of $a = 3.728$ Å and $c = 5.363$ Å, which are much smaller than those of the $\beta$-FeSe$_x$ (x = 1) bulk sample ($a = 3.7734$ Å and $c = 5.5258$ Å) [21]. Based on these results, we can conclude that our Fe$_{0.8}$Se NWs are tetragonal FeSe phase with Fe vacancies. Recently, de Souza et al [22] reported that Fe vacancies are introduced in the $\delta'$-phase of FeSe$_{1-x-y}$ samples synthesized under high pressure and only spurious superconductivity is observed. It is noted that our recent high-resolution TEM investigation on a high pressure synthesized single crystal suggests the possible existence of a new phase with tetragonal symmetry and ordered Fe-vacancy [23]. Such a new phase with ordered Fe-vacancy is not superconducting, instead it exhibits magnetic order at low temperature.

A sharp superconducting transition at 14.5 K and 10.3 K is observed in Fe$_{0.88}$Se$_{0.32}$Te$_{0.68}$ and Fe$_{0.88}$Te$_{0.91}$S$_{0.09}$ NWs with diameters of 335 nm and 220 nm respectively, as shown in figures 3(b) and (c). The estimated normal state resistivity is around a few mΩ cm for Fe$_{0.88}$Se$_{0.32}$Te$_{0.68}$ and Fe$_{0.88}$Te$_{0.91}$S$_{0.09}$ NWs. The EDS data show that the ratios of Se/Te and S/Te are 0.33/0.67 and 0.09/0.91, respectively. Compared with bulk/film/crystal samples with similar composition [2, 24–26], these NWs have slightly higher transition temperature and much narrower transition width. In addition
to superconductivity, most reports on Te rich FeSe_{1-x}Te_{x} show samples with semiconducting-like temperature dependence at low temperature. Chang et al [27] reported that such temperature dependence is attributed to a weak localization effect which results from the high scattering rate of carriers by impurities. The NWs show metallic-like temperature dependence, indicating a lower impurity concentration or better crystalline quality. It is interesting to note the normal state resistivity behavior of the Fe_{0.88}Se_{0.32}Te_{0.68} and Fe_{0.88}Te_{0.91}S_{0.09} NWs. There appears to be a broad resistive bump on cooling with a total resistivity drop of about 50% before the onset of superconducting transition temperature. The onset of the resistive bump, or the maximum resistivity as a function of temperature, is at about 200 K for Fe_{0.88}Se_{0.32}Te_{0.68} and 100 K for Fe_{0.88}Te_{0.91}S_{0.09}. On the other hand, a similar resistive bump onset at about 200 K was also observed in the superconducting β-FeSe. It has been proposed that an orbital modification exists in the Fe-chalcogenides prior to the occurrence of structural distortion [28]. Whether the observed resistive bump at normal state in these nanowires is related to the proposed orbital modification is a subject of current intensive investigation.

**Figure 3.** The temperature dependence of the normalized resistance of NWs with different diameters and lengths of around 10 µm. (a) Fe_{0.8}Se NWs with diameters of 115 and 80 nm, which have resistivity of about a few tens of Ω cm. (b) Fe_{0.88}Se_{0.32}Te_{0.68} NWs with diameters of 335 and 79 nm. (c) Fe_{0.88}Te_{0.91}S_{0.09} NWs with diameters of 220 and 90 nm. The estimated normal state resistivity is around a few mΩ cm for Fe_{0.88}Se_{0.32}Te_{0.68} and Fe_{0.88}Te_{0.91}S_{0.09} NWs. A long resistive transition tail is observed in both Fe_{0.88}Se_{0.32}Te_{0.68} and Fe_{0.88}Te_{0.91}S_{0.09} NWs with smaller diameter.

**Figure 4.** The temperature dependence of the resistance at different external magnetic fields for (a) Fe_{0.88}Se_{0.32}Te_{0.68} and (b) Fe_{0.88}Te_{0.91}S_{0.09} NWs. The phase diagrams are shown in the insets. The upper critical field is estimated to be 85 ± 7 and 94 ± 7 T for Fe_{0.88}Se_{0.32}Te_{0.68} and Fe_{0.88}Te_{0.91}S_{0.09} NWs respectively, using the WHH formula [32] and the initial slope of the phase diagram in the inset.

For NWs with smaller diameters, also shown in figures 3(b) and (c), the superconducting temperature is slightly lower and with a longer transition tail. We rule out the possibility of quality degradation in small diameter NWs as TEM results show that the NWs have similar crystalline quality. Due to the existence of surface oxide, the dimensions of actual superconducting area can be smaller than the outer dimensions of the NWs. Moreover, we expect the oxide thickness to increase with prolonged exposure to air during the electrical contact fabrication process, as evidenced in figure 2(d). The dimensions of the superconducting area would be reduced and the phase slip effect might become important as the NW approaches the quasi-1D limit, resulting in a long transition tail [29–31].

Figure 4 shows the temperature dependence of the resistance at different external magnetic fields for (a) Fe_{0.88}Se_{0.32}Te_{0.68} and (b) Fe_{0.88}Te_{0.91}S_{0.09} NWs. The superconducting transition tail is slightly broadened in Fe_{0.88}Se_{0.32}Te_{0.68} NW as external magnetic field is applied, similarly to the results for bulk [33] and single crystals [24]. For Fe_{0.88}Te_{0.91}S_{0.09} NW, the superconducting transition shifts to low temperature similarly to earlier reports [3, 26]. The insets display the phase diagrams of the NWs. Here, $T_c$ is defined as the temperature of $R(H, T) = 50\% R_n$, where
$R_c$ is the resistance of the NW before the superconducting transition. Following the Werthamer–Helfand–Hohenberg (WHH) theory [32], we can estimate the critical magnetic field at zero temperature from the initial slope of the phase diagram, $H_c2(0) = 0.693$ |d$H_c2$/d$H$|, where $t$ is the reduced temperature, $T_c(H)/T_c(0)$. The estimated $H_c2(0)$ values for 335 nm Fe$_{0.88}$Se$_{0.3}$Te$_{0.68}$ and 220 nm Fe$_{0.88}$Te$_{0.91}$S$_{0.09}$ NWs are 85 ± 7 and 94 ± 7 T, respectively. These values are close to the reported values of FeSe$_{0.3}$Te$_{0.7}$ and FeTe$_{0.8}$S$_{0.2}$ bulk samples [3, 33].

4. Conclusion

In conclusion, we have presented a simple two-step method to synthesize high crystalline quality β-FeSe type superconducting and non-superconducting iron chalcogenide NWs. Three kinds of NWs with compositions of Fe$_{0.8}$Se, Fe$_{0.88}$Se$_{0.32}$Te$_{0.68}$ and Fe$_{0.88}$Te$_{0.91}$S$_{0.09}$ have been prepared and carefully characterized by TEM. The NWs show good crystallinity along the (100) crystal direction. An amorphous oxide is observed on the surface of fresh NWs and becomes thicker with prolonged air exposure. The Fe$_{0.8}$Se NWs have tetragonal structure with smaller lattice constant than found in bulk samples, are Fe deficient, and display a high resistivity of a few tens of $\mu$mΩ. We conclude that the as-grown Fe$_{0.8}$Se NWs are tetragonal FeSe phase with many Fe vacancies, resulting in no superconductivity. On the other hand, compared with bulk samples, Fe$_{0.88}$Se$_{0.32}$Te$_{0.68}$ and Fe$_{0.88}$Te$_{0.91}$S$_{0.09}$ NWs show a higher and sharper superconducting transition, although the Fe/chalcogen ratio is still smaller than 1. Combining with the results of normal state resistance behavior and upper magnetic critical field, we conclude that these Fe$_{0.88}$Se$_{0.32}$Te$_{0.68}$ and Fe$_{0.88}$Te$_{0.91}$S$_{0.09}$ NWs have excellent quality. Interestingly, Fe$_{0.88}$Se$_{0.32}$Te$_{0.68}$ and Fe$_{0.88}$Te$_{0.91}$S$_{0.09}$ NWs with diameters smaller than 100 nm always show a long resistive transition tail. This characteristic could be associated with a phase slip process in the quasi-one-dimensional feature of the NWs.

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