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Electrodeposition of nano-dimensioned FeSe

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ABSTRACT

Herein we report a direct synthesis of FeSe nanostructure with tetragonal phase by electrochemical deposition. The FeSe thin films have been successfully deposited onto indium doped tin oxide coated conducting glass (ITO) in the aqueous electrolytic bath containing $FeSO_4$ and SeO_2. The deposition mechanism was inferred that the Se^{4+} ions are reduced to Se and successively oxidized to Se^{2-}, which was immediately involved with Fe^{2+} to form the tetragonal structure. This new approach promises to be of strong significance for succeeding fabrication of iron-based superconductor.

1. Introduction

Over the past 20 years, the astonishing discovery of the high-Tc cuprate superconductors and noncuprate superconductors such as MgB_2 with Tc of 39 K [1–3], and the iron-based superconductor was first found in 2008 in $LaFeAsO_{1-x}F_x$ (known as “1111 system”) with Tc of 26 K [4]. The superconducting transitions were obtained by F doping to the O site or the deficiencies of O ion in this system and the same serious type superconductors with tetragonal structure were obtained by superconductivity such as $NdFeAsO_{1-x}F_x$ and $SmFeAsO_{1-x}F_x$ [5,6]. The second serious type of superconductors is AFe_2As_2 (A = Ba, Sr, Ca, Eu) [7] (known as “122 system”) and the third serious type of superconductors is $Li_{1-x}FeAs$ [8,9] (known as “111 system”), conferring on among the iron-based superconductor may should more understand the mechanism of the superconductivity. The recent discovery of the new type iron-based superconductors, FeSe with tetragonal structure (known as “11 system”) [10], was reported and the structural phase transitions around 70 K and the occurrence of superconductivity at 8 K. The phenomenon of enhancement in critical temperature of FeSe superconductors was obtained, with a Tc of 27 K under 1.48 GPa high pressure [11]. The crystal structure of tetragonal FeSe is actually simple compared to other iron-based superconductors and it plays an important role in the mechanism of superconductivity due to this uncomplicated structure and the relative easiness of theoretical calculation. Until now most using synthesis of FeSe superconductor is solid-state reaction method, but the process is time-consuming and difficult. The FeSe superconductor with tetragonal structure is considered as a slightly Se-deficient phase (45 to 49.4% at Se) [12], the composition range of FeSe with superconductivity is very narrow and the reaction must be placed in an evacuated quartz tube under high temperature. Herein, we report a novel method to directly synthesize the nano-dimensional FeSe with tetragonal structure. The FeSe films with tetragonal structure were successfully obtained by electrochemical deposition on indium doped tin oxide coated conducting glass (ITO) and the reduction potential is an important factor for the formation of pure phase tetragonal structure. This simple synthesis process may be a useful tool to guide us to study the superconductivity in nano-scale dimension and clearly understand the mechanism.

2. Experimental

Herein we use the ITO glass to be the substrates and the ITO glass with sheet resistance of around 30 Ω is commercial. Electrochemical deposition process was carried out at high temperature by three-electrode potentiostatic control, the Ag/AgCl as the reference electrode, the platinum sheet as the counter electrode and the ITO or AAO template as the working electrode. The sources of Fe and Se are $FeSO_4 \cdot 7H_2O$ and SeO_2 and the concentration of Fe and Se are 0.01 M and 0.001 M to 0.01 M respectively. The reduction potential was tried from −0.8 V to −1.2 V and the optimal value is −1 V.

The morphology of FeSe film was characterized by field-emission scanning electron microscopy (FE-SEM, JEOL JSM-6700F) and the element ratio with various reduction potential was measured by energy dispersive X-ray spectroscopy (EDS). The FeSe film observed by X-ray powder diffraction (XRD; X'Pert PRO diffractometer) was performed to obtain the crystallographic structures.

3. Results and discussion

Fig. 1 shows the cyclic voltammogram for gold wire in the solution composed of 0.01 M $FeSO_4 \cdot 7H_2O$ and 0.01 M SeO_2. On scanning, the

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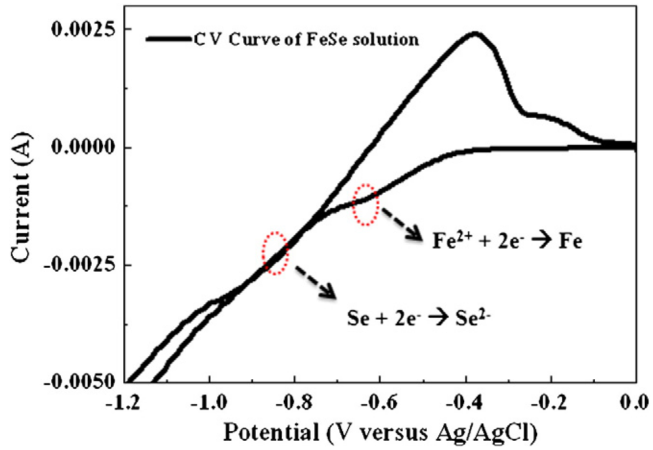

Fig. 1. Cyclic voltammogram of gold wire as the working electrode in 0.01 M $FeSO_4$ and 0.01 M SeO_2 and the scan rate is set as 0.05 V/s.

applied potential ranged from 0 V to −1.5 V and then back from −1.5 V to 0 V, the scan rate is 0.05 V/s and the step will be set as 0.1 V. The SeO_2 dissolved in the DI water and formed H_2SeO_3 in the solution. $FeSO_4 \cdot 7H_2O$ dissociated in the solution as the iron ions. The two peaks can be observed clearly at −0.63 V and −0.86 V in Fig. 1. The first peak is due to the reaction of the Fe^{2+} to Fe and the second peak is due to the reaction of the Se to Se^{2+}. The reactions formula and the theoretical potential are as follow:

$$Fe^{2+} + 2e^- \rightarrow Fe(-0.44V \text{ vs NHE})$$

$$Se + 2e^- \rightarrow Se^{2-}(-0.67V \text{ vs NHE})$$

Considering the Ag/AgCl as reference electrode, the potential will shift to −0.637 for Fe and −0.867 for Se, respectively and match with the result of cyclic voltammogram curve. The reduction peak of Fe is slightly unclear. It caused by with no associate conducting salts in the electrolyte and will limit the ability of Fe reduction deposition on the substrates. The reduction peak of Se is more unobvious than the iron reduction peak and the reason is that the concentration of Se in the electrolyte is much lower. Herein, according to the result, the FeSe film with tetragonal crystal was not deposited on the substrate directly and the grains could be formed in the solution near the surface of the substrate and then deposited.

The applied potential determines which elements can be deposited and the composition ratio in the alloy compounds. The forming process of FeSe with tetragonal crystal structure is necessary to be discussed as we know that the composition range of FeSe with tetragonal crystal is very narrow. Fig. 2 shows that the morphology and elements ratio of FeSe film on ITO substrates with various applied potentials from −0.8 V to −1.2 V and the deposition time are all the same in one hour. At starting potential −0.8 V, the less spherical particles were observed on the substrate. The particle size is around 150 nm to 200 nm and the composition is mainly dominated by selenium. The iron content is much less and the elements ratio of Fe/Se is 0.44. At the potential −0.9 V, it can be clearly seen that various particle sizes exhibit on the substrate. The smallest one is around 200 nm, while the biggest one is around 3 μm. As the potential is decreasing, the composition of selenium is also increasing. The selenium still much easily deposited on the substrate than iron and there is more occupation and domination in the structure. It also can be proved by the ratio of Fe/Se of 0.27. The potential −1 V has the distinguishing observation in morphology in FeSe film, the grain of FeSe in growth transforms from spherical particle to sheet shape and disorderly distributes on the substrates. The composition of FeSe film also has distinguishing change, the distribution of selenium element is still uniform and with the great quantity as the potential decreased on the substrate, but the quantity of iron rapidly increases and the distribution is uniform and almost the same with selenium. The element ratio of Fe/Se is almost 1 and it indicates that the ratio of composition is suit for synthesis of FeSe with tetragonal crystal structure. At the potential −1.1 V, the morphology of FeSe film changes, it seems like the sheet of FeSe grains was dissolved slightly and the grains like silk shape grow along the edge of the sheet like dendritic. The composition ratio of Fe/Se just slightly increases to 1.4 and the distribution of iron and selenium are both uniform. At the potential −1.2 V, the silk shape of FeSe is more on the irregular shape of FeSe sheet which is dissolved more clearly and the composition ratio of Fe/Se the same as potential −1.1 V is equal to 1.4. At the potential −1 V, the morphology and the composition are changed compared with the potential −0.8 V and −0.9 V, it can be speculated

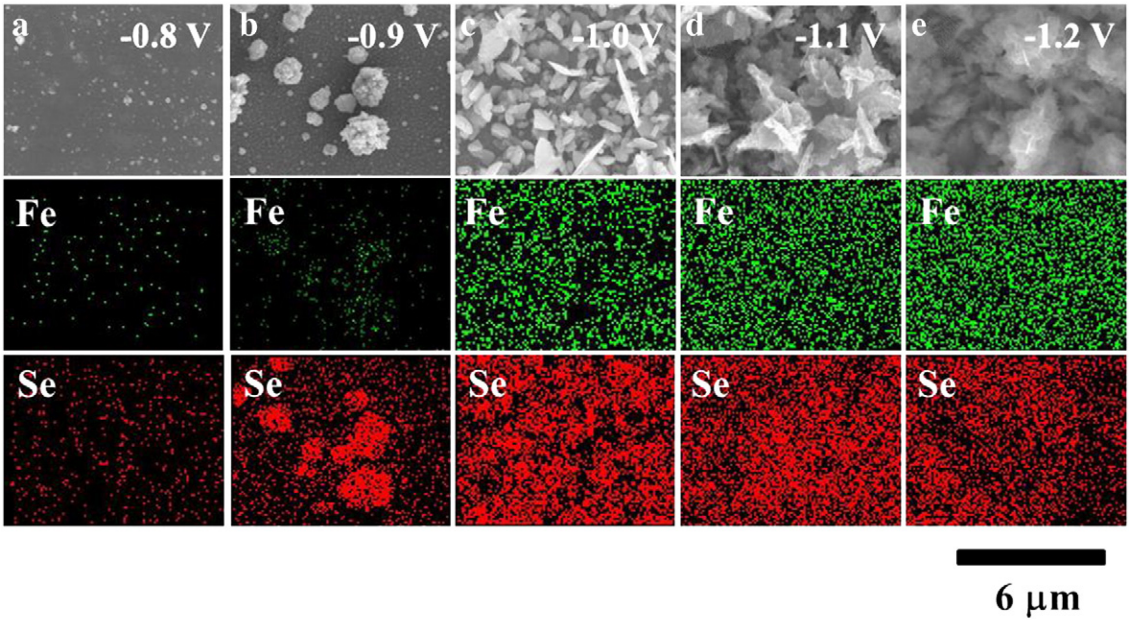

Fig. 2. The morphology and EDS mapping images of as-deposited FeSe thin film with variation of reduction potential.