Electrodeposition of nano-dimensioned FeSe

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A R T I C L E   I N F O

Keywords:
FeSe
Tetragonal
Superconductor
Electrochemical deposition

A B S T R A C T

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 FeSO4 and SeO2. The deposition mechanism was inferred that the Se4+ ions are reduced to Se and successively oxidized to Se2−, which was immediately involved with Fe2+ to form the tetragonal structure. This new approach promises to be of strong significance for succeeding fabrication of iron-based superconductor.

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1. Introduction

Over the past 20 years, the astonishing discovery of the high-Tc cuprate superconductors and noncuprate superconductors such as MgB2 with Tc of 39 K [1–3], and the iron-based superconductor was first found in 2008 in LaFeAsO1−xFx (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 NdFeAsO1−xFx and SmFeAsO1−xFx [5,6]. The second serious type of superconductors is A1−xFeAs (A = Ba, Sr, Ca, Eu) [7] (known as “122 system”) and the third serious type of superconductors is Li1−xFeAs [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 FeSO4·7H2O and SeO2 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 spectrometry (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 FeSO4·7H2O and 0.01 M SeO2. On scanning, the
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 SeO₂ dissolved in the DI water and formed H₂SeO₃ in the solution. FeSO₄·7H₂O 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 Fe²⁺ to Fe and the second peak is due to the reaction of the Se to Se²⁻. The reactions formula and the theoretical potential are as follow:

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

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

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 grains was dissolved more clearly 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 V, the morphology and the composition are changed compared with the potential −0.8 V and −0.9 V, it can be speculated...
that one or more chemical reactions occurred and promote the growth of the iron component and this evidence is useful to help us to understand the mechanism of FeSe with tetragonal structure by electrochemical deposition.

The crystal structure of FeSe film with different reduction potential was characterized by X-ray powder diffraction and because oxidation will happen easily on the material of FeSe, the samples will be kept in the vacuum to avoid contact with oxygen until the measurement. Fig. 3 shows the XRD pattern of FeSe films with different reduction potential in the 2θ region between 15° and 60° and comparison with the standard diffraction peaks of the corresponding constituent materials. At the potential −0.8 V, reflection peaks are found at 31.19°, 34.98°, 36.5°, 37.56°, 48.4°, 51.02° and 54.37°, corresponding to the (002), (111), (012), (020), (121), (200) and (103) facets of FeSe. It indicates that the crystallography of the film as the potential −0.8 V is of orthorhombic crystal structure, this result also almost matches with the elements ratio of Fe/Se equal to 0.44 and the grain size of FeSe2 was calculated by Scherrer equation, the grain sizes, as determined from the full width at half-maximum exceed approximately 15 nm. At the potential −0.9 V, the reflection peak of FeSe2 was observed decreased and it means that the crystalline structure was destroyed and according to the results of morphology and elements ratio, it seems like the grain is going through the transformation in crystalline structure, from orthorhombic structure of FeSe2 to Se grains preferably and the evidence of increasing the quantity of selenium and grains growth can be proved. At the potential −1 V, reflection peaks are found at 16.05°, 28.68°, 37.49°, 47.42°, 48.31°, 51.23° and 57.15°, corresponding to the (001), (101), (111), (112), (200), (201) and (211) facets of FeSe and in comparison with the standard diffraction peaks of the corresponding constituent materials of tetragonal structure in FeSe (JCPDS nos. 85–0735). The grain sizes that are determined from the full width at half-maximum exceed approximately 30 nm. As the reduction potential is decreased, the crystal structure of FeSe is still kept as tetragonal but there is a little change in the grain size, which slightly decreased to 25 nm at potential −1.2 V and this can be explained by the observation of the FeSe grains dissolved.

Based on the above observations, we propose a model of the growth mechanism of FeSe film with tetragonal structure that includes a phase transition. The detailed reactions of mechanism will be described in Fig. 4 and the iron and selenium will form the alloy compound, and will be deposited on the ITO substrate by electrochemical deposition. The precursor of SeO2 dissolved in the water will transform to the SeO2− existing in the solution. At below reduction potential −0.9 V, the ratio of Fe/Se decreases as the potential decreases from −0.8 V to −0.9 V and the quantity of the selenium is almost larger than iron two times or over. The two kinds of grains appear on the substrate, the smaller one is around 200 nm and distributes homogeneous on the big area and the bigger one is around 3 μm and is like an irregular ball on the substrate. The result of XRD also indicates that below the potential −0.9 V the crystal structure is dominated by FeSe2 with orthorhombic phase and the crystal structure will be destructed as the potential decreases to −0.9 V. Above the potential −1 V, the quantity of iron increase acutely and the change in morphology is observed, the silk shape grains grow from the edge and the sheet shape grains will be decomposed as the potential increases. The ratios of Fe/Se are almost equal to 1 or over and the crystal structure is dominated by FeSe with tetragonal phase. According to above this, we conjecture that at high potential the FeSe2 is the stable structure to form and as the potential decreases, the reaction of the reduction of the selenium happened. From potential equal to −1 V, the reactions will be surmised that first the selenium oxide was dissolved in the water and exist this form of SeO32− with tetravalent of selenium in the solution. Applying the potential, the tetravalent of selenium was reduced to selenium element and immediately got the two electrons to form the Se2− ion which will attract the Fe2+ ion in the solution and the FeSe alloy compound with tetragonal structure will be formed.

4. Conclusions

In direct synthesis the FeSe with tetragonal crystal structure by electrochemical deposition is successful to develop and the relationship between the reduction potential and the crystalline is also discussed. The crystal transition of iron and selenium alloy compounds is from FeSe2 with orthorhombic phase to FeSe with tetragonal phase and we also propose the model to explain the mechanism of phase transition and tetragonal phase forming process. The FeSe with tetragonal structure is the new type of the iron-based superconductors and the mechanism in superconductivity is not explored completely. This novel method will be a tool to study the
nanoscale superconductors and also can offer an easier and quicker fabrication process.

Acknowledgments

The authors would like to thank the National Science Council of the Republic of China, Taiwan (Contract nos. NSC 98-2112-M-003-007-MY3 and NSC 98-2113-M-002-012-MY3) and the Ministry of Economic Affairs of the Republic of China, Taiwan (Contract nos. MOEA 98-EC-17-A-01-S1-026 and 98-EC-17-A-08-S1-006) for financially supporting this research.

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