Cumhuriyet Science Journal
CSJ

e-ISSN: 2587-246X
ISSN: 2587-2680

Cumhuriyet Sci. J., Vol.38-4 (2017) 845-850

The Fluorescence Intensity Ratios of Superconducting $Fe_ySe_{1-X}Te_X$ Thin Films

Canan AKSOY[1]*, Engin TIRAŞOĞLU[2], Susannah SPELLER[3], Chris R.M. GROVENOR[3]

[1]*Engineering of Electronics and Communication, Karadeniz Technical University, Technology Faculty, 61830, Of, Trabzon / TURKEY*

[2]*Department of Physics, Faculty of Science, Karadeniz Technical University, 61080, Trabzon / TURKEY*

[3]*Centre for Applied Superconductivity, Materials Department, Oxford University / UK*

Received: 21.09.2017; Accepted: 04.10.2017 *http://dx.doi.org/10.17776/csj.363587*

Abstract: Superconducting thin films of FeySe1-xTex were grown on to the single crystal MgO substrates by RF sputtering and the effects of processing conditions on the microstructural development were investigated. Besides, the fluorescence intensity ratio $IK\beta/IK\alpha$ of Te in those films were examined by using the non-destructive EDXRF spectroscopy. The $Fe_ySe_{1-x}Te_x$ were irradiated with γ-photons at 59.5 keV from a 241-Am annular source and detected using an Ultra-LEGe detector with resolution of 150eV at 5.9 keV. The results showed that the heat treatment with vacuum and Ar pressure may be caused the change of the intensity ratios of Te in the thin films.

Keywords: FeSe (Te) Thin film, intensity ratio, EDXRF.

Süperiletken $Fe_ySe_{1-x}Te_x$ İnce Filmlerin Floresans Şiddet Oranları

Özet: Süperiletken $Fe_ySe_{1-x}Te_x$ ince filmleri MgO altlıklar üzerine Rf püskürtme yöntemi kullanılarak üretildi ve üretim koşullarının ince filmlerin mikroyapısı üzerindeki farklılıkları incelendi. Bunun yanısıra üretilen ince filmlerin Te $IK\beta/IK\alpha$ fluorescence şiddet oranları tahripsiz EDXRF spektroskopisi kullanılarak çalışıldı. $Fe_ySe_{1-x}Te_x$ ince filmleri 59,5 keV enerjili radyoaktif 241-Am kaynağından yayılan γ-fotonları ile uyarıldı ve 5.9 keV'ta rezülasyonu 150eV olan Ultra-LEGe dedektörü ile veriler tespit edildi. Elde edilern sonuçlar, vakum ve Ar atmosferi basıncının numunelerin Te şiddet oranlarınının değişimine sebep olabileceğini gösterdi.

Anahtar Kelimeler: FeSe (Te) ince film, şiddet oranı, EDXRF.

1. INTRODUCTION

Iron based high temperature superconductors offer new opportunities to establish the interplay between magnetism, composition and electronic properties [1]. Several structural families have now been established since the discovery of superconductivity at 26 K in $LaO_{1-x}F_xFeAs$ [2] The FeSe (Fe-11) phase has the simplest crystal structure of this series of compounds (tetragonal PbO-type structure), make it an interesting system for studying relationships between electromagnetic properties and structure. The superconducting transition temperature (Tc) can be increased from 8 K in FeSe to 14 K by partial substitution of Te for Se [3]. As a result of the application of hydrostatic pressure, there has been found a dramatical raise in Tc from about 8K to 37 K in FeSe, which might

* Corresponding author. *Email address:* *cananaksoy@ktu.edu.tr*
http://dergipark.gov.tr/csj ©2016 Faculty of Science, Cumhuriyet University

suggest that further increases may be achieved in Tc under atmospheric pressure by using chemical means.

Thin films grown on to substrates have many useful applications, especially in the production of electronic and optical materials and devices. The physical properties of thin films are determined by their elemental composition, impurities, structure and thickness. Quantitative methods can be carried out for the measurement of these characteristics, which requires available non-destructive methods such as X-ray fluorescence Quantitative measurement of elemental composition, electronic transition, fluorescence yield and fluorescence intensity ratios, etc. may be performed, for instance, using X-ray fluorescence (XRF) or MeV ion beam analysis (IBA) [5]. X-ray emission spectroscopy has been applied to investigate the electron structure of high-Tc, superconducting materials as well as other condensed matter with the help of the tenability, polarization and high flux of synchotron radiation [6-10]

Precise knowledge of IK_β/IK_α X-ray intensity ratios are quite important in applied and basic researches, including elemental analysis by X-ray emission techniques and for studies of physical processes in plasmas. Furthermore, the measurement of IK_β/IK_α X-ray intensity ratios is based on atomic models in order to test the validity of these models. The K_α X-rays arise from transitions from the L- to the K-shell. The K_β X-rays arise from transitions from M, N, O, etc to K-shell [11].

In this research, thin films of FeySe1-xTex (FST) have been grown by RF sputtering onto single crystal MgO substrates. The IK_β/IK_α X-ray intensity ratios of Te have been reported and compared to the theoretical values.

2. EXPERIMENTAL

The insitu FST films were grown onto the MgO single crystal substrate by sputtering onto substrates heated to temperatures of 315◦C – 350◦C for 30 min-1hour in 2×10^{-2} mbar Ar atmosphere. The post heat treatment were carried out to investigate phase stability. FST 5,7, 9 thin films were vacuumed in a quartz tube and heated at the temperature 350-450◦C for 18 min and FST 6,8 were heated to 350-450◦C in Ar atmosphere for 198 min. The all the experimental procedure of preparing and analysing FST thin films were explained at our previous work [12]. The crystal structure and phases were investigated by using Cu Kα radiation in a Philips θ–2θ diffractometer and EDX was carried out to study local variations in chemical composition using an Oxford Instruments INCA system in a JEOL JSM 6300 scanning electron microscope (SEM). The elemental compositions of the FST thin films and the Kβ/Kα X-ray intensity ratios were measured by using the geometry of the experimental set-up for an annular source which can be seen in Fig.1 including an Ultra-LEGe (ultra low energy germanium detector; FWHM 150 eV at 5.9 keV, active area 13 mm2, thickness 5 mm and Be window thickness 30 μm). The out preamplifier, with a pulse pile-up rejection capability, was fed to a multi-channel analyzer interfaced with a private computer provided with suitable software for data acquisition and peak analysis. In this experimental set-up, 59.5 keV photons emitted by an annular 50mCi Am-241 radioactive sources were utilized.

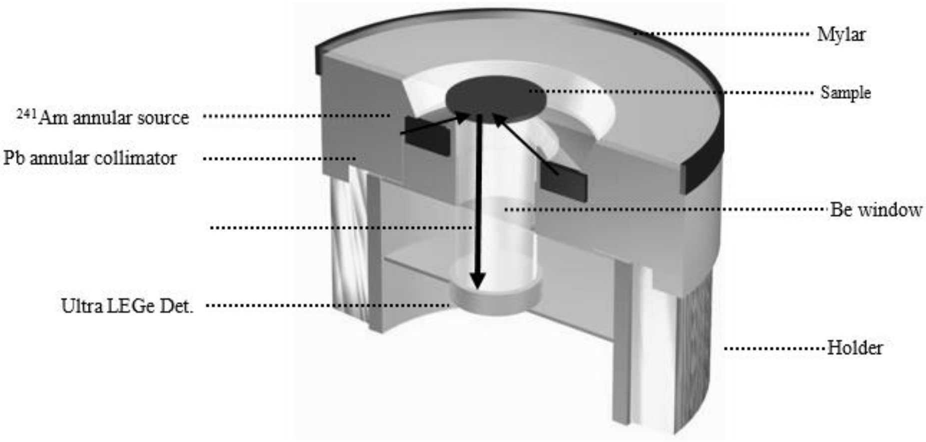

Figure 1. Geometry of the experimental set-up.

The experimental K-shell X-ray intensity ratios IK_{β}/IK_{α} were evaluated using the following equation:

$$\frac{I_{K\beta}}{I_{K\alpha}} = \frac{N_{k\alpha}}{N_{K\beta}} \frac{I_0 G\varepsilon_{K\beta}}{I_0 G\varepsilon_{k\alpha}} \frac{\beta_{K\beta}}{\beta_{K\alpha}} \quad (1)$$

where N_{Ki}/N_{Kj} represents the ratio of the counting rates under the K_i and K_j peaks, $\beta_{K\beta}/\beta_{K\alpha}$ is the ratio of self-absorption correction factors of the target that accounts for the absorption of incident photons and emitted K X-ray photons, and $I_0G\varepsilon_{K\beta}/I_0G\varepsilon_{K\alpha}$ is the ratio of the detector efficiency values for K_{α} and K_{β} X-rays [13] given by the following equation

$$I_0 G\varepsilon_{Ki} = \frac{N_{Ki}}{\sigma_{Ki}\beta_{Ki} m_i} \quad (\text{i}=\alpha, \beta) \quad (2)$$

The self-absorption correction was calculated using the equation

$$\beta_{Xi} = \frac{1-\exp\{[-(\mu_{inc}\csc\theta_1 + \mu_{emt}\csc\theta_2)m_i]\}}{(\mu_{inc}\csc\theta_1 + \mu_{emt}\csc\theta_2)m_i} \quad (3)$$

where μ_{inc} and μ_{emt} are the mass attenuation coefficients from XCOM (Berger and Hubbell, 1999) of incident photons and emitted characteristic X-rays; the angles of the incident photons and the emitted X-rays with respect to the surface of samples, θ_1 and θ_2, were equal to 45^0 and 90^0 in the present experimental set-up, respectively.

The compositions of the thin films (gr/cm^2) have been determined by using the following equation:

$$m = \frac{N_{K\alpha}}{\sigma_{K\alpha}\beta_{K\alpha} I_0 G\varepsilon_{K\alpha}} \quad (4)$$

where $N_{K\alpha}$ is the measured intensity (area under the photo peak) corresponding to the K_{α} group of X-rays, I_0 is the intensity of the incident radiation, G is a geometrical factor, $\varepsilon_{K\alpha}$ is the detection efficiency for the K_{α} group of X-rays.

3. RESULTS AND DISCUSSIONS

The FST films were grown by RF sputtering and analysed by XRD, SEM and EDXRF. Fabricated superconducting thin films have been irradiated by an Ultra LeGe detector to determine the experimental IK_{α}/IK_{β} X-ray intensity ratios.

The values of the intensity ratios IK_{α}/IK_{β} for Te in FST films, determined experimentally using Eq 1, are listed in Table 1 and compared with theoretical values of pure Te [14]. There are deviations between the theoretical and experimental values within range 2–27%. However, it is important to mention that the intensity ratios of IK_{α}/IK_{β} are in good agreement with the theoretical values.

Table 1 The intensity ratios of the FST thin films.

Te	*I Kβ/I Kα*	*Theoretical*	*Sputtering Temperature (ºC) /Time*	*Heat Treatment Temperature (ºC) /Time*
FST1	0.20±0.01	0.21	315 ºC / 1 hour	
FST 2	0.20±0.01		315 ºC /1 hour	350 ºC in-situ / 18 min
FST3	0.15±0.01		315 ºC /15 min	350 ºC Vac/ 18 min
FST4	0.16±0.01		315 ºC /30 min	350 ºC Ar /18 min
FST5	0.22±0.01		315 ºC /30 min	350 ºC Vac/18 min
FST6	0.18±0.01		315 ºC /30 min	450 ºC Ar /18 min
FST7	0.24±0.01		315 ºC /30 min	450 ºC Vac/18 min

Vac: in vacuum atmosphere, Ar: in Argon atmosphere

The overall error in this study is estimated to be ~6 % .This error is the quadrature sum of uncertainties in the different parameters used to evaluate sub-shell fluorescence yield and cross sections, i.e. target thickness (1%), the evaluation of the peak area, (1.5%), $I_o G\varepsilon$ product (~2%) and the absorption correction factor (~1.5%).

After the insitu at 350 ºC annealing process of FST1, there was not any crucial change of the intensity ratios. However, it can be seen that heat treatment process in different atmosphere clearly effected the intensity ratios of the samples. In FST4 were annealed at 18 min-350 ºC in to the argon pressured a quartz tube and FST 5 were annealed in 10^{-6} mbar a quartz tube vacuum and similar process for FST 6 and FST 7 were applied and it is observed from the results that the vacuum annealing is much more effective than the vacuum annealing as the vacuum process increased the intensity ratios for FST 5 and FST 7. Probably, the atoms might be rearranged after annealing in the high vacuum as closing together and increasing the intensity. The XRD results showed that the intensity of the (001) peak increased due to the Ar effect, different phases (*) appeared and Te rich dendrites occurred (see Figure 3). If the correct phase changes (mean the crystal structures alter), the atom content in a unit cell can change as well. It may be caused of the intensity ratio changing. Furthermore, the correct phase disappeared after the annealing in vacuum, it may be caused, the melting point of elements decreased during the vacuum annealing and the Se was vapoured. It may be changed the crystal structure of the FST.

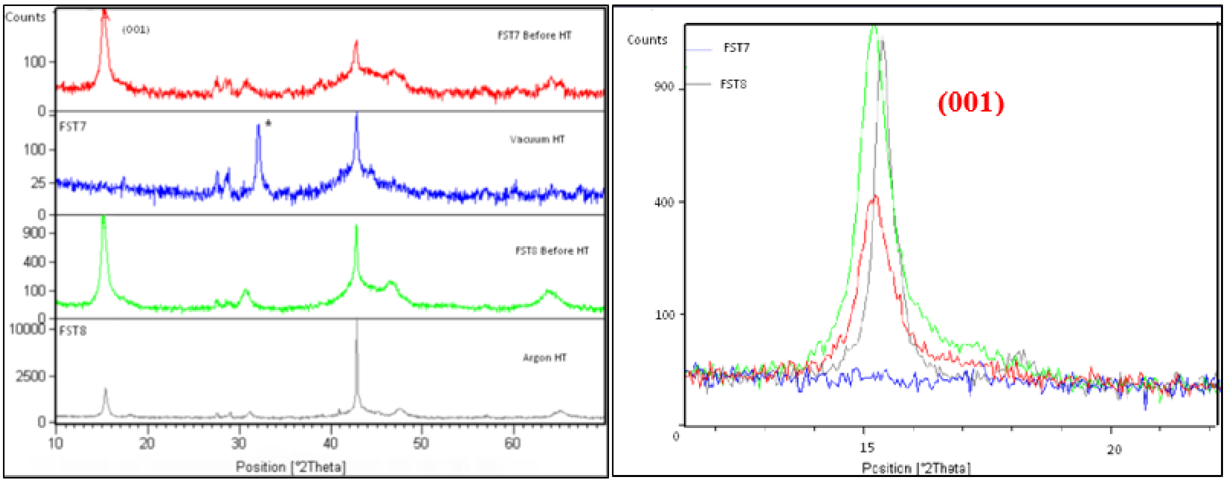

Figure 2. a) (θ-2θ) XRD scans for the FST films show the heat treatment affect b) The peak difference of (001) phase [11].

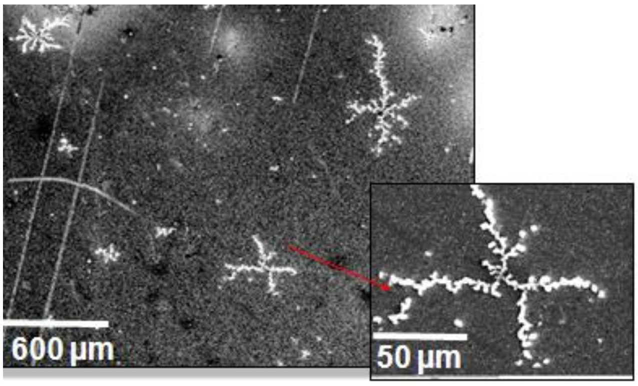

Figure 3. SEM image show Te rich dendrites on the FST 6 film surface after the Argon heat-treatment.

4. CONCLUSIONS

Superconducting thin films of $Fe_ySe_{1-x}Te_x$ were grown on to the single crystal MgO substrates by RF sputtering and the effects of processing conditions on the microstructural development were investigated. The fluorescence intensity ratio IK_β/IK_α of Te in those films were examined by using the non-destructive EDXRF spectroscopy. The annealing process on vacuum and argon atmosphere effected the fluorescence intensity ratios. The vacuum annealing is more effective than the vacuum annealing.

Acknowledgement

The FST thin film samples were fabricated at Superconductivity lab at Oxford Materials in The University of Oxford and EDXRF measurements were carried out at Spectroscopy lab at the Department of Physics in Karadeniz Technical University. As authors, we would like to thank to all staff of Oxford Materials for their supports on this research.

REFERENCES

[1]. Paglione J., and Greene R.L. High-temperature superconductivity in iron-based materials. Nature Physics 2010; 6, 645.

[2]. Kamihara Y., et al. Iron-Based Layered Superconductor La[O1-xFx]FeAs (x = 0.05-0.12) with Tc = 26 K. J. Am. Chem. Soc. 2008 :130, 3296.

[3]. Fang M.H., Pham H.M., Qian B., Liu T.J., Vehstedt E.K., Liu Y., Spinu L., and Mao Z.Q. Superconductivity close to magnetic instability in Fe(Se1−xTex)0.82. Phys Rev. 2008; 8, 224503.

[4]. Medvedev S., McQueen T.M., Trojan I., Palasyuk T., Eremets M.I., Cava R.J., Naghavi S., Casper F., Ksenofontov V., Wortmann G., and Felser C. Superconductivity at 36 K in beta-Fe1.01Se with the compression of the interlayer separation under pressure. 2009; 8: 630.

[5]. Moore J. A. and Elsahlli T. Measurement of composition of thin films obtained by sputtering using radioisotope excited X-ray fluorescence. *X-ray Spectrom.* 1994; 23: 155

[6]. Bajat J.B., Miskovic-Stankovic V.B., Maksimovic M.D., Drazic D.M. and Zec S. Electrochemical deposition and characterization of Zn-Fe alloys. J. Serb. Chem. Soc. 2004; 69: 807.

[7]. Wassdahl N. et al., Soft x-ray emission studies of adsorbates Phys. Rev. Lett.1992; 69 812.

[8]. Guo J.H., Butorin S.M., Wassdahl N., Skytt P. and Nordgren J., Electronic structure of La2-xSrxCuO4 studied by soft-x-ray-fluorescence spectroscopy with tunable excitation. Phys. Rev. B 1994; 49: 1376-80.

[9]. Butorin S.M, Guo J-H., Wassdahl N., Skytt P., Nordgren J., Ma Y., Ström C., Johansson L-G. and Qvarford M. Physical Review B-Condensed Matter, 1995; Vol. 51, no 17, 11915-11923 p.

[10]. Söğüt Ö., Bütün H., Karahan I.H., Tırasoğlu E., Apaydın G. Investigation by XRF and XRD of Zn and Fe in Fex Zn1− x thin films. Phys. 2008; Scr. 78, 065701.

[11]. Speller S, C, Aksoy C, Saydam M, Taylor H, Burnell G, Boothroyd A T and Grovenor C R M, Analysis of FeySe1− xTex thin films grown by radio frequency sputtering Supercond. Sci. Technol. 2011; 24, 075023.

[12]. Aksoy C., Tıraşoğlu E., Cengiz E., Apaydın G., Saydam M., Aylıkçı V., Aylıkçı N.K. Chemical effects on the L-shell X-ray fluorescence parameters of Ta and W compounds Journal of Electron Spectroscopy and Related Phonemena, 2012; 184, 1-12, pp.556-560.

[13]. Scofield J.H. Exchange corrections of K x-ray emission rates Phys. Rev. A,1974b; 9: 1041.