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PRODUCTION OF NANOSIZE FILMS ON THE BASE OF SCUTTERUDITE $CoSb_3$ FOR THERMOELECTRIC DEVICES

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The work is concerned with ascertainment of the regularities for thermostimulated formation of the phase composition and structure of $CoSb_3$-scutterudite-based films deposited by the vacuum condensation method.

Introduction

The solution to energy security by improving the efficiency of alternative energy generation, the search for new, clean and renewable energy sources is a key objective of both science and the economy. One of the ways to increase the efficiency of thermoelectric coefficient (ZT) – use skutterudite $CoSb_3$, which corresponds to the concept G. Slack "phonon glass – electron crystal". In addition, the transition from bulk materials to the nanoscale allows to further increase ZT due to increased defects in the structure [1-4].

The goal of the paper is to ascertain the behaviour characteristics for the processes of thermally stimulated formation of the phase composition and structure in the 30 nm $CoSb_x$ films ($1.8 \leq x \leq 4.2$; Sb concentration belongs to the range of 65-81 at.%) obtained by molecular beam deposition on a SiO_2 substrate (100 nm)/Si(001).

Experimental Part

The $CoSb_x$ ($1.8 \leq x \leq 4.2$) (65-81 at.% Sb) films with thickness of 30 nm were obtained by molecular beam deposition under ultrahigh vacuum ($\approx 7 \cdot 10^{-9}$ Pa) on the substrates of single-crystal Si (001) with a 100 nm thick layer of SiO_2 dioxide.

To study the phase composition and structure of the films, we applied a set of methods of the physical materials science. They are X-ray diffraction phase analysis, the Debye-Scherrer method with photographic X-ray registration on the URS-55 equipment, survey on the DRON UM-1 diffractometer, and Rigaku Ultima IV. The chemical composition was determined by the Rutherford backscattering methods with an accuracy of ±1 at.%, using He+ ions accelerated by an energy of 1.7 MeV. The layer-

by-layer chemical analysis was performed by the method of mass spectrometry of secondary neutrals (MSSN) on the Specs INA-X device. Electroconductivity properties were measured by a four-probe method. To study the morphology of the surface of nanosized films, we used both scanning electron microscopy (SEM, REMMA-106I) and atomic force microscopy (AFM, Dimension 3000).

Results and Discussions

The CoSb*x* films (30 nm; $1.8 \leq x \leq 4.2$; 65-81 at.% of Sb) deposited on the substrate at room temperature are in the X-ray amorphous state since it is confirmed by X-ray diffraction analysis data, namely, there no diffraction maxima on the diffractograms (Fig. 1). The heating of X-ray amorphous films in the temperature range of ≈140-200 °C results to their crystallization (Fig. 2).

The process of transformation into a crystal state in the CoSb*x* ($2.6 \leq x \leq 4.1$) 30 nm films is accompanied with an abrupt (jump) increase in electrical conductivity.

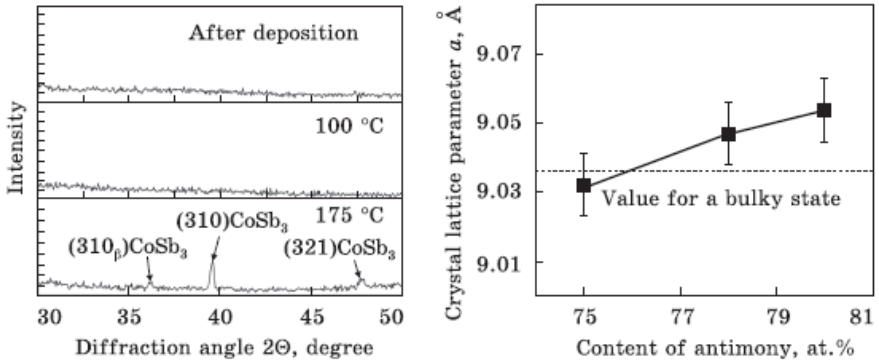

Fig. 1. X-ray patterns of as-deposited $CoSb_{3.5}$ film on substrate at a room temperature and after heating (λ*K*αβ-Fe)

Fig. 2. Changing of a lattice parameter *a* for $CoSb_3$ phase after heating of Co-Sb films up to 200°C

As established using the X-ray structural phase analysis and resistometry, if the Sb concentration increases, the temperature range of crystallization of the investigated films shifts toward higher temperatures and amounts 140-200 °C. Electrophysical properties of the films depend on their chemical and phase compositions. Phase composition affects a temperature dependence of the resistivity $R=f(T)$. After crystallization from X-ray amorphous state in $CoSb_{3.0}$ film, the dependence $R=f(T)$ has a

semiconductor character with ionic conductivity type. In $CoSb_{3.5}$ film with an abundant Sb concentration (more than 75 at.%), the temperature dependence of conductivity has a metallic behaviour.

X-ray structural phase analysis showed that after crystallization of X-ray amorphous films, a single-phase composition corresponding to $CoSb_3$ scutterudite was observed in a wide concentration range of 75-80 at.% Sb. The large values of the lattice parameter a for the $CoSb_3$ phase as compared to those for a bulk state of the material indicate that atoms of abundant antimony occupy voids in the unite crystal cell (Fig. 2). These results indicate that region of existence of scutterudite $CoSb_3$ (75-80 at.% Sb) broadens by 5%.

After deposition on a substrate at a temperature of 200°C, the $CoSb_x$ ($1.8 \leq x \leq 4.2$) films had a crystal structure. The diffraction maximum intensities for the films coincide with those values for the bulky material; this fact indicates that films are in a non-textured polycrystalline state. In the film containing 75 at.% Sb, the scutterudite $CoSb_3$ crystallizes during the deposition. In the films with Sb concentration less than 75 at.%, the $CoSb_2$ antimonide is formed additionally to the $CoSb_3$. In the samples with abundant Sb concentration (more than 75 at.%), two phases appear: $CoSb_3$ and Sb.

The change in the phase composition of the films results to the change in the resistivity. The Sb-concentration-dependence of resistivity has a parabolic behaviour for the films with a maximum at 75 at.% of Sb. The $CoSb_3$ scutterudite is a more high-resistant phase as compared with both $CoSb_2$ and Sb (Fig. 3).

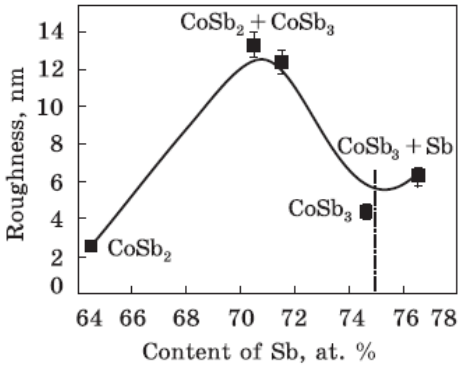

Fig. 3. Effect of antimony content on electrical resistance of Co-Sb films

When the Sb-rich films $CoSb_{3.6}$ and $CoSb_{4.2}$ with a two-phase composition (scutterudite $CoSb_3$ and crystalline antimony Sb) are subjected to annealing in a vacuum above 500°C, the ratio of the intensities of the diffraction reflections $I(210)Sb/I(310)CoSb_3$ decreases. This is due to the sublimation of antimony during annealing.

The annealing of films, where the concentration of Sb is close to its content in a scutterudite in vacuum above 300°C, results in the change of the phase composition. One can see the appearance of the $CoSb_2$ reflexes in the diffraction pattern and growth of the intensity ratio $I(210)CoSb_2/I(310)$ $CoSb_3$ in the absence of texture (Fig. 4, *a*). This indicates that $CoSb_2$ phase grows, while $CoSb_3$ one reduces. Therewith, the parameter *a* of the cubic crystal lattice of scutterudite decreases (Fig. 4, *b*), and for the most part *a* decreases in the films after crystallization from the X-ray-amorphous state.

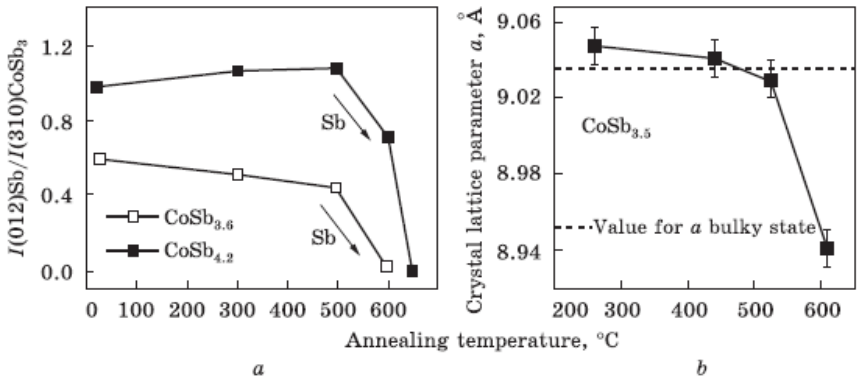

Fig. 4. Influence of annealing temperature for $CoSb_{3.6}$ and $CoSb_{4.2}$ films (in vacuum) on the change of (*a*) ratio of intensities *I* (012) Sb/*I* (310) $CoSb_3$ of diffraction reflections and (*b*) the lattice parameter a for $CoSb_3$ phase

Such a change in the phase composition is attributed to the partial sublimation of Sb atoms out of $CoSb_2$ and $CoSb_3$ crystal lattices during annealing in the nitrogen atmosphere as well as vacuum due to the phase transformations according to the schemes:

$$CoSb_3 + Sb \xrightarrow{>300^\circ C(Sb\uparrow)} CoSb_3 \xrightarrow{>400-500^\circ C(Sb\uparrow)} CoSb_3 + CoSb_2, \quad CoSb_2 \xrightarrow{>500-600^\circ C(Sb\uparrow)} CoSb_2 + CoSb \cdot$$

We revealed that a thermal stability of the $CoSb_3$-based nanosize films is conserved up to ≈300°C, which is evidenced by the fact that the ratio of the most intense diffraction maxima for the $CoSb_3$ and Sb phases remains unchanged during the long-time annealing (Fig. 5) [5].

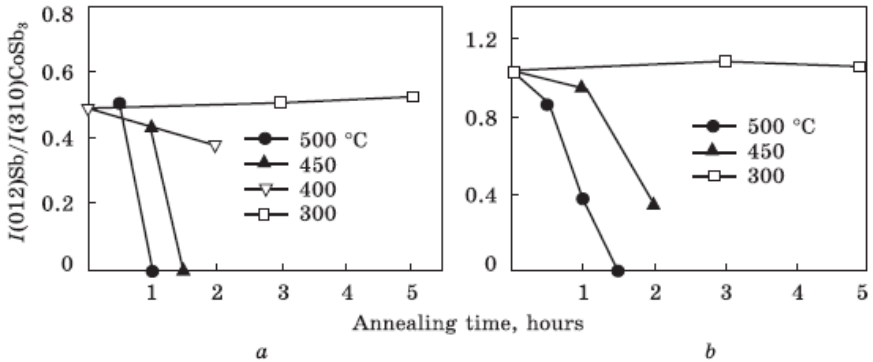

Fig. 5. Dependence of the intensity ratio of the *I* (012) Sb/*I* (310) $CoSb_3$ diffraction peaks for $CoSb_{3.6}$ (*a*) and $CoSb_{4.2}$ (*b*) films on the annealing time in vacuum within the temperature range of 300–500 °C

The thermoelectrical efficiency coefficient *ZT* for $CoSb_{3.0}$ film is ≈1 at 500°C [6], this is ≈8 times higher as compared with the material in a bulky state when *ZT*≈0.12 [7,8]. $CoSb_{4.1}$ film with excess of Sb has lower values of *ZT*≈0.2. The effect of increasing of thermoelectric efficiency coefficient is caused by the nanosize factor: the presence of single-phase crystal structure of $CoSb_3$ scutterudite with an extended existence region (75-80 at.% Sb) in the film, and enhanced structural imperfection due to antimony sublimation – decrease in grain sizes and increase in extent of grain boundaries.

Conclusions

It is shown that deposition of Co-Sb films (with 65-81% of Sb) on the substrates at a room temperature results to the formation of X-ray amorphous state of condensed material with an extended region for existence of the $CoSb_3$ (75-80 at.% Sb) phase at a further heating after crystallization.

In case of a deposition of Co-Sb films (65-81 at.% Sb) on the substrates at 200°C, the crystal state of condensed material forms in accordance with the phase equilibrium diagram for a bulky state of the Co-Sb system.

The nanosize $CoSb_3$ films are stable up to ≈300°C. Increase of the temperature of annealing in both vacuum and nitrogen atmosphere results to the sublimation of abundant antimony in the crystal or X-ray amorphous state and from $CoSb_2$ and $CoSb_3$ phases, which is reflected in the changing of phase composition and structure accordingly.

There is a nanosize factor – a single-phase crystal structure of $CoSb_3$ scutterudite with extended existence region (75-80 at.% Sb) in the film with high structural defectiveness due to nanosize grains that decrease as annealing temperature increases during antimony sublimation. This nanosize effect causes increase in thermoelectric efficiency coefficient at 500°C ($ZT \approx 1$) as compared with that for material in a bulky state ($ZT \approx 0.12$).

This has a practical importance when these materials are used for providing the autonomous power supply for low-power electronic devices and creating film coolers in the elemental base of the nanoscale range for computer equipment and infrared sensors.

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References

1. A.F. Ioffe, *Ehnergeticheskie Osnovy Termoelektricheskikh Batarey iz Poluprovodnikov* [Energy Basis of Thermoelectric Semiconductor Batteries] (Moscow-Leningrad: AN SSSR.: 1950) (in Russian).

2. G.A. Slack, New Materials and Performance Limits for Thermoelectric Cooling, *CRC Handbook of Thermoelectrics* (Ed. D.M. Rowe) (Boca Raton: CRC Press: 1995), p. 407.

3. A.O. Epreman, V.M. Arutyunyan, and A.I. Vaganyan, *Alternative Energy and Ecology (ISJAEE)*, **25**, No. 5: 7 (2005) (in Russian).

4. D.M. Freik, M.O. Galuschak, O.S. Krunutcky, and O.M. Matkivskiy, *Physics and Chemistry of Solid State*, **14**, No. 2: 300 (2013) (in Ukrainian).

5. Yu. M. Makogon, S. I. Sidorenko, and R. A. Shkarban, *Metallofiz. Noveishie Tekhnol.*, **39**, No. 5: 677 (2017) (in Russian).

6. D. Zhao, Ch. Tian, Y. Liu, Ch. Zhan, and L. Chen, *J. Alloys and Compounds*, **509**: 3166 (2011).

7. Daniel M. Herstellung und Charakterisierung thermoelektrischer $CoSb_3$-Schichten: Diplomarbeit / M. Daniel // Technische Universität, Chemnitz. – 2009. – 98 p.

8. M.V. Daniel, C. Brombacher, G. Beddies, N. Jöhrmann, M. Hietschold, D.C. Johnson, Z. Aabdin, N. Peranio, O. Eibl, and M. Albrecht, *J. Alloys and Compounds*, **624**: 216 (2015).