"Nanotechnology and nanomaterials"

Sublimation of Sb in formation nanosized thermoelectric films Co-Sb

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One of the ways to increase the thermoelectric coefficient efficiency (ZT) is the application of $CoSb_3$ antimony (conception the G. Slack). The transition to nanoscale materials can further increase ZT due to increasing of the structure defectiveness. In this work we investigated the laws of the thermo induced phase and composition formation of 30 nm thick Co-Sb nanoscaled films with concentration of Sb in the range of 65 at.% – 81 at.%, obtained by molecular beam deposition onto SiO_2(100 nm)/Si(001) substrates. It established, deposition onto the substrate at room temperature, followed by heating after the crystallization, leads to the formation of x-ray-amorphous state. At heating temperature above 150^{o}C it is occurred crystallization of amorphous state of the films and expands the region of homogeneity $CoSb_3$ phase (75-80) atm.% Sb. After the increasing of the substrate temperature to 200°C in the Co-Sb films, the crystal state is formed, and the laws of phase formation are determined by the sequence that is analogical to the diagram of phase equilibrium for the bulk state of Co-Sb system with the formation of the homogenous $CoSb_3$ phase under the ~75 at.% of Sb.

That the $CoSb_3$ based are thermally stable up to ~300°C. Heat treatment of the Co-Sb films with Sb concentration of 65 at.% to 81% as in vacuum and in nitrogen atmosphere under the temperatures, higher than 300°C, leads to the passing of the phase transition and structural change via the next schemes: $CoSb_3 + Sb \xrightarrow{>300^o C(Sb\uparrow)} CoSb_3 \xrightarrow{>400-500^o C(Sb\uparrow)} CoSb_3 + CoSb_2$, $CoSb_2 \xrightarrow{>500-600^o C(Sb\uparrow)} CoSb_2 + CoSb$, because of increasing ability of the Sb atoms to sublimation. The activation energy of the Sb sublimation process was determined on the rate of the Sb sublimation at the different annealing temperatures according to the Arrhenius equality. It is found that a more intensive process sublimation Sb upon annealing above 300°C of amorphous films is reflected in lower (2-3 times) the activation energy sublimation Sb compared to films with crystalline state, wherein the chemical bonds are already formed. The change of phase composition by sublimation in films affects the level of stress. Shown, that after deposition in the films it is observed a slight level of tensile stress ~1 GPa, which raises after thermal annealing up to ~5 GPa and is accompanied by appearing of pores and cracks in the film.