Influence of thickness on properties of $Yb_xCo_4Sb_{12}$ layers prepared by laser ablation

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In this paper we contribute to the understanding of thickness dependence of thermoelectric properties of $Yb_xCo_4Sb_{12}$ layers. The $Yb_xCo_4Sb_{12}$ layers were prepared by Pulsed Laser Deposition at substrate temperature Ts=250 °C applying laser beam energy density Ds=3 J/cm^2. The thermoelectric properties such as the Seebeck coefficient, the electrical resistivity and the power factor of thin layers were studied at temperatures ranging from 300 K to 500 K. Depending on the layer thickness, an oscillatory behavior (with a period of about 10 nm) of the thermoelectric properties was observed. Room temperature measurements of carrier concentration and mobility show oscillations as well. The influence of a corundum cap layer (15 nm in thickness) on the thermoelectric properties is also reported. The aim of the presented work is to improve our knowledge and technology of future thermoelectric thin layer devices.

1. Introduction

Compounds with crystalline structure $CoAs_3$ are called skutterudites. This structure was first identified in 1928, the name skutteruditte coming from the small Norwegian town Skutterud, where the $CoAs_3$ based mineral had been mined extensively [1]. Skutterudites crystallize with body-centered-cubic symmetry of the spare group Im3 and have been of interest as a promising candidate for thermoelectric applications due to their possible high figure of merit ZT (ZT=1.2 at T=650 K for bulk hot pressed $Yb_{0.19}Co_4Sb_{12}$ [2]), an essential material property for thermoelectric energy conversion. ZT is proportional to the power factor and is inversely proportional to material thermal conductivity.

The low thermal conductivity of skutterudites is obtained due to filling the voids in the structure with small diameter, large-mass interstitials such as Yb in our case.

A great improvement of thermoelectric properties has been mathematically predicted as well as experimentally proven by preparing the material in a form of a low dimensional system [3]. The simplest example of such system is a single thin layer or a superlatice. Skutterudite layers and superlattice have been successfully prepared using several deposition methods: magnetron rf-sputtering [4, 5], simultaneous evaporation of elemental skutterudite components followed by temperature treatment in the ambient atmosphere or in vacuum [6-9], and Pulsed Laser Deposition (PLD) from a skutterudite target [6, 10, 11-

13]. The improvement of thermoelectrical properties in comparison to the bulk materials was published for thin layers of $CoSb_3$ skutterudite [4, 10] and for superlattices [11].

In our contribution we present results obtained on thin thermoelectric layers of different thickness ranging from 30 nm to 124 nm, prepared under the same deposition conditions (Ts=250 °C, Ds=3 J/cm^2) by the PLD method from an $Yb_xCo_4Sb_{12}$ target (x=0.19). Crystallinity and composition of layers were examined by X-ray Diffraction (XRD) and Wavelength Dispersive analysis (WDX). The electrical resistivity (R) and the Seebeck coefficient (S) were measured from 300 K up to 500 K and used to calculate the power factor. Room temperature measurements of the Hall mobility (μ_H) and of the concentration of carriers were also accomplished. For the 59 nm thick layer, temperature dependency of the Hall mobility is presented. After determining the transport properties, the layers were coated with a 15 nm thick corundum protective layer and their thermoelectric properties were re-measured.

All measured thermoelectric properties showed oscillatory behavior (with a period of approximately 10 nm) in dependence on layer thickness. The oscillatory behavior can be explained by a quantum size effect [14].

2. Sample preparation and measurements

Series of $Yb_xCo_4Sb_{12}$ thin layers with different thickness ranging from 30 nm to 124 nm were prepared by PLD on a quartz glass substrate 10 x 10 mm large. The basic scheme of the experimental apparatus for PLD is shown in Fig. 1. Conceptually and experimentally PLD is an extremely simple method, probably the simplest of all thin film growth techniques. A high power pulsed laser radiation (1) is utilized as an external energy source to vaporize material of a target (5) and to deposit thin films. A set of optical components is used to focus the laser beam on the target surface (2, 3). For all samples, during deposition the substrate temperature was held at 250 °C and the density of the laser beam (Ds) was set at 3 J/cm2. The substrate from the target was distanced 40 mm, deposition took place in an Ar atmosphere under 13 Pa of pressure. These deposition conditions had been proven by previous experiments to yield layers with favorable thermoelectric properties [15]. Layers prepared using the above described deposition conditions yielded stochiometry of $Yb_xCo_4Sb_{12}$ with x=0.14 +/- 0.015 and XRD determined skutterudite structure [15].
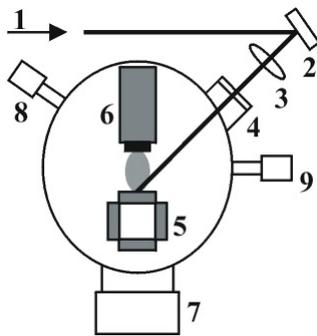

Fig. 1. The basic scheme of the experimental apparatus for PLD: (1) laser beam, (2) mirrors, (3) focusing lens, (4) quartz window, (5) target holder, (6) substrate holder, (7) vacuum pump, (8, 9) Pripani and Penning vacuum gauges, respectively.

The $Yb_xCo_4Sb_{12}$ (x=0.19) target material compound was prepared by cold-pressing described e.g. in [16] until only peaks of a skutterudite structure were detected by XRD. The final target for PLD deposition with a diameter of 20 mm and height of 2 mm was prepared by hot pressing (temperature 500 °C, pressure 500 MPa for 30 minutes). The measured density of the pressed samples was within 96-98 % of the theoretical density.

The crystalline structure of the deposited layers was examined using XRD described in [15]. The composition of the layers was studied by WXD analysis using the JXA 733 instrument and the Strata program.

Transport properties, such as the electric resistivity and the Seebeck coefficient, were measured within the temperature range 300 K to 500 K. A room temperature measurement of the Hall carrier mobility was performed as well. For the 59 nm thick layer the temperature dependency of the Hall mobility was measured within the range 300 K to 400 K. Contacts for the measurements were obtained by evaporation of Ti on which Pt/PtRh thermocouples (d=0.07 mm) were pressed as leads. The electrical resistivity and the Hall mobility were measured by the van der Pauw's method using a magnetic field of 0.6 T, the Seebeck coefficient was determined from different temperature gradients.

After the first measurement of the transport properties the layers were covered by a 15 nm thick corundum layer using the PLD technique. This protective layer is necessary for our future experiment, measuring thermal conductivity on a thermal microscope. The transport properties were re-measured in order to explore the possible influence of the corundum cap layer on thermoelectric properties.

The thickness of the layers was determined by Alpha Step 500 profilometer.

3. Results and discussion

The electrical resistivity and the Seebeck coefficient were studied for all prepared layers at different ambient temperature ranging from 300 K to 500 K. Fig. 2 and Fig. 3 display the dependence of the measured results on layer thickness for the different ambient temperatures. Obvious oscillatory behavior of both transport properties was observed at all measured ambient temperatures in dependence on layer thickness. The oscillation period was determined around 10 nm. Such oscillations caused by the quantum size effect had been previously observed in semi-metallic and semiconducting thin layers [14, 17, 18].
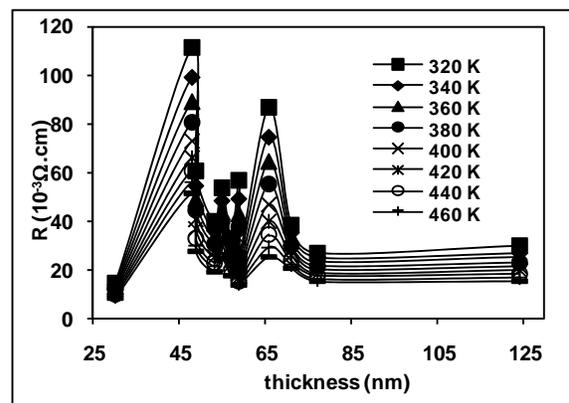

Fig. 2. Electrical resistivity versus layer thickness for ambient temperature ranging from 300 K to 500 K.
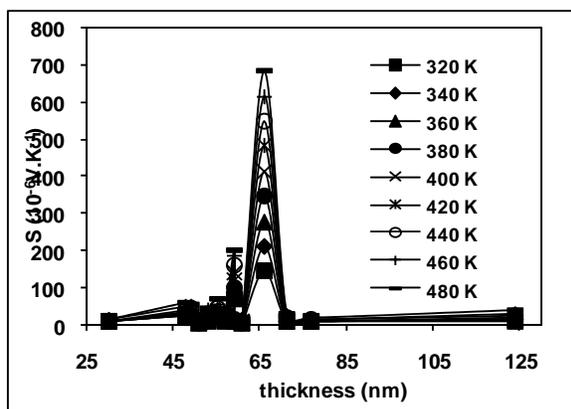
Fig. 3. The absolute value of Seebeck coefficient versus layer thickness for ambient temperature ranging from 300 K to 500 K.

In case of the resistivity variation, the two significant maxima occur for 48 nm and 66 nm layer thicknesses. The amplitude of oscillations decreases with the increasing ambient temperature.

Dependency of the Seebeck coefficient on layer thickness showed the same period oscillations, the Seebeck coefficient maximum was observed in a 66 nm thick sample. The absolute value of oscillation magnitude for the Seebeck coefficient increases with increasing ambient temperature.

Only one significant Seebeck coefficient maximum was observed in a 66 nm thick layer, and thus only one dominant maximum is present in the calculated power factor versus layer thickness dependency in Fig. 4. The power factor equals S^2/R, where S is the Seebeck coefficient and R is the electrical resistivity. The calculated power factor is less than previously published for bulk materials [2].
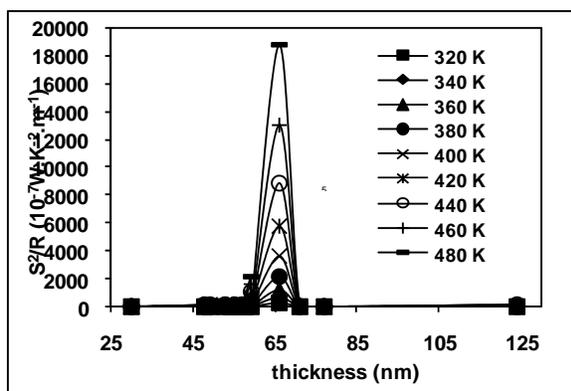

Fig. 4. Calculated power factors versus layer thickness for ambient temperature ranging from 300 K to 500 K.

Room temperature measurements of the Hall mobility and concentration of carriers showed oscillatory behavior as well. The dependency of the Hall mobility on layer thickness is presented in Fig. 5. The carrier concentration oscillates for all studied layers in the range 4.57e18 cm^{-3} to 3.07e20 cm^{-3}. Measurements of temperature dependency of the Hall mobility for the 59 nm thick layer is presented in Fig. 6, yielded very low values in comparison to values typically observed for different bulk skutterudites [19].
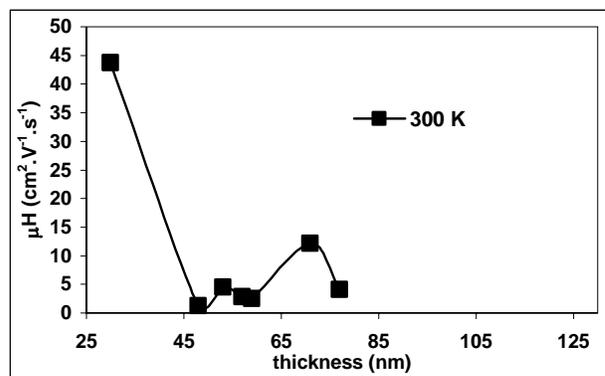

Fig. 5. The Hall carrier mobility (average values) versus layer thickness for ambient temperature.

After PLD deposition of the protective 15 nm thick corundum layer, the electrical conductivity and the Seebeck coefficient were measured again on all samples. The corundum layer, which must not significantly affect the thermoelectric properties of the layer, is necessary for thermal conductivity measurements using a thermal microscope. Values of the measured transport properties changed within +/-10-20%, thus within the precision limit of the applied methods. The periods of oscillation remained unaffected and the corundum cap layer does not influence the layer's electrical resistivity and the Seebeck coefficient. The influence of the corundum layer on the thermal conductivity measurements has not been verified on a thermal microscope yet.
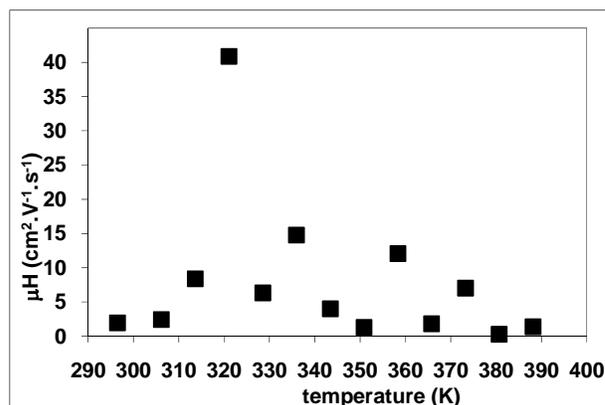
A WDX study of layer composition was accomplished on all prepared layers. The average stochiometry of the layers was determined to be Yb$_x$Co$_4$Sb$_{12}$, with x=0.14+/-0.015 thus indicating less Yb in the layer than observed in the PLD target. Such phenomenon was described on previously prepared layers [15]. XRD results on thicker layers prepared at Ts=250 C and Ds= 3 J/cm^2 confirmed the skutterudite structure as reported earlier [15].

4. Conclusions

PLD layers with different thickness ranging from 30 nm to 124 nm were prepared from a Yb$_{0.19}$Co$_4$Sb$_{12}$ target under the same deposition conditions, Ts=250°C and Ds=3 J/cm^2. The thickness dependencies of the measured Seebeck coefficient, electrical resistivity, Hall mobility and the calculated power factor of the PLD layers showed oscillatory behavior with a oscillation period of approximately 10 nm. One significant power factor maximum, lower than for published bulk material data, was observed in the 66 nm thick layer. Assuming that the thermal conductivity of thin layers will be lower than that of hot pressed bulk material, the most favorable thermoelectric properties are expected for approximately 66 nm thick layers. Because of its low homogeneity, the influence of Yb on thermal conductivity of thinner layers than those prepared by us is relatively uncertain. For the final conclusion on thermoelectric efficiency of future thin layer devices based on Yb$_x$CoSb$_3$ materials further research focused on direct measurements of thermoelectric figure of merit and thermal conductivity of PLD layers is necessary.

Acknowledgments

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