KAPL-P-000153

(K97022)

CONF-9704192--

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April 1997

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Thermoelectric Properties of ZnSb Films Grown by MOCVD

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Abstract

The thermoelectric properties of metallorganic chemical vapor deposited (MOCVD) ZnSb films are reported. The growth conditions necessary to obtain stoichiometric ZnSb films and the effects of various growth parameters on the electrical conductivity and Seebeck coefficients of the films are described. The as-grown ZnSb films are p-type. It was observed that the growth of thicker ZnSb films lead to improved carrier mobilities and lower free-carrier concentrations. The Seebeck coefficient of ZnSb films was found to rise rapidly at approximately 160 to 170°C, with peak Seebeck coefficients as high as 470 $\mu\text{V/K}$ at 220°C. The various growth conditions, including the use of intentional dopants, to improve the Seebeck coefficients at room temperature and above, are discussed. A short annealing of the ZnSb films at temperatures of $\sim 200^\circ\text{C}$ resulted in reduced free-carrier levels and higher Seebeck coefficients at 300K. Finally, ZT values based on preliminary thermal conductivity measurements using the 3- ω method are reported.

Introduction

Thin film ZnSb, with a stoichiometry of Zn:Sb=1:1, could be a material with a potentially high ZT for power generation applications. ZnSb, an intermetallic compound, tends to offer a high Seebeck coefficient compared to other phases of the alloy probably due to the ionic character of the compound. Thin films of ZnSb grown by the ionized cluster beam (ICB) process have indicated Seebeck coefficients as high as 600 $\mu\text{V/K}$ at 550K [1]. These ZnSb films had appreciable electrical conductivity, as high as $5 \times 10^2 \text{ ohm}^{-1} \text{ cm}^{-1}$. The ZnSb thin-films were always p-type with modest carrier mobilities $\sim 22 \text{ cm}^2/\text{V sec}$. Even so, assuming that the thermal conductivity of the ZnSb thin films are comparable to bulk polycrystalline samples, a ZT of ~ 5 was estimated at 520K [1]. In this paper we report that ZnSb films grown by MOCVD, with a stoichiometry of Zn:Sb=1:1, offer high Seebeck coefficients and also provide some experimental justification of the assumption that the thermal conductivity of the thin-films are indeed comparable to bulk ZnSb crystals.

MOCVD Growth of ZnSb

We chose to grow the ZnSb thin films on semi-insulating GaAs substrates using diethylzinc (DEZn) and trisdimethylaminoantimony (TDMASb). The semi-insulating GaAs substrates were chosen to enable the measurement of resistivity by the van der Pauw Hall method and the determination of the in-plane Seebeck coefficients of the ZnSb epitaxial layers. We found that the stoichiometry was reproducible for a given set of flow rates of DEZn and TDMASb and also preferably over a wide ratio of the flow rates of these precursors. There was considerable variation of the Zn:Sb ratio in $\text{Zn}_x\text{Sb}_{1-x}$ films with flow-rates of DEZn and TDMASb depending on the growth temperature. The stoichiometry values were determined by energy dispersive X-Ray analysis (EDAX) and where results are accurate to within a few percent.

Properties of ZnSb Films

Here, we first discuss the electrical transport properties of ZnSb films measured by Hall-effect. Next the Seebeck coefficient (α) measured in the films at 300K, the variation of α with temperature and the effect of various growth conditions on α are discussed. Then we discuss the thermal conductivity values in a select set of films, measured by the 3- ω method. Finally, the potential ZT values in some thick ZnSb films are indicated at $\sim 175^\circ\text{C}$.

Electrical Transport Properties

The as-grown ZnSb films on GaAs were found to be always p-type, similar to the ZnSb films [1] grown by the ICB process. Shown in Table I is the effect of increased layer thickness of the epitaxial ZnSb film on lower residual p-doping level and higher hole mobility. The fairly significant reduction in residual doping level in conjunction with increase in mobility, up to $\sim 0.75 \mu\text{m}$, is probably a result of decreasing lattice-mismatch (with respect to GaAs substrate) related defects in the ZnSb films. Growth of films with thickness greater than $\sim 1.35 \mu\text{m}$ was hampered by the limited growth rates of these films, with not-yet-fully-optimized growth conditions. We note that the best carrier mobility ($\sim 23.5 \text{ cm}^2/\text{V sec}$) of the

micron-thick film is comparable to the value of $22.8 \text{ cm}^2/\text{V}\cdot\text{sec}$, reported in ZnSb films grown by the ICB process. The electrical conductivities of the films are in the range of $1\text{E}3 \text{ ohm}^{-1} \text{ cm}^{-1}$, about a factor of two higher than those reported in ZnSb films by the ICB process [1].

The high residual p-doping level in the ZnSb films, even with thicker films, is thought to be related to

native Sb vacancies. Te, a Group-VI atom, is expected to occupy the Sb site and reduce the residual p-doping level. In fact, there has been a published work on the use of Te doping in bulk CdSb to improve the thermoelectric properties [4]. So we investigated the use of Te doping in ZnSb films. The initial results are shown in Table 2.

Table 1 Effect of ZnSb Layer Thickness on Residual Doping Level and Hole Mobility at 25°C.

Sample #	Thickness (t) (μm)	Doping Level (cm^{-3})	300K Carrier Mobility ($\text{cm}^2/\text{V}\cdot\text{sec}$)
7-125	0.13	8.5E20	13.4
7-127	0.5	5.4E20	15.5
7-234	0.55	4.8E20	17.1
7-235	0.50	4.5E20	18.6
7-236	0.75	3.3E20	20.4
7-237	0.75	3.4E20	20.6
7-239	1.1	2.7E20	20.8
7-242	1.2	2.9E20	19.0
7-247	1.05	2.7E20	23.5
7-248	0.9	4.0E20	17.7

Table.2 Effect of Te Doping on Properties of ZnSb Films.

Sample #	Thickness t(μm)	Te-Doping (Torr)	X-Ray Data	p (cm^{-3})	μ ($\text{cm}^2/\text{V}\cdot\text{sec}$)
7-235	0.5	---	Single	4.5E20	18.6
7-244	0.5	3.5×10^{-4}	Crystalline Single	3.6E20	20.0
7-240	0.33	5.5×10^{-3}	Crystalline Poly	2.0E18	0.76
7-245	0.47	7.0×10^{-4}	Single Crystalline	3.1E20	16.2

For layer thickness of $\sim 0.5 \mu\text{m}$, we noticed a fairly small drop in residual doping level with small partial pressures of the Te dopant during growth. At high concentrations of the Te dopant, we observed that the ZnSb films become polycrystalline (from x-ray data) and even though the residual doping falls dramatically over two orders of magnitude, the hole

mobility becomes very low from the polycrystalline nature of the film.

Seebeck Coefficients in ZnSb Films

The Seebeck coefficients (α) in the ZnSb films were typically measured between 25°C to 200°C. Shown in Figure 1 is the variation of α with temperature, for

two ZnSb samples of different thickness (see Table 1). We noted that the thicker film, due to the lower residual doping level, offers a significantly higher α from 25°C through 200°C.

We also noted the rather sharp rise in α near 175°C, for both samples. This is very similar to the observed α vs. T behavior of ZnSb films grown by the ICB process [1]. The near-constant Seebeck coefficients between 25°C to ~175°C is indicative of near-constant electrical conductivity and absence of any chemical changes, as experimentally noted in the work of ZnSb films by ICB. We believe that the ZnSb films are stable till ~175°C; above this temperature some chemical changes may occur in the films leading to a sharp increase in α . This was confirmed partly by the significant reduction in carrier concentration and increase in resistivity of ZnSb films at 25°C, after an exposure to ~200°C. This data is summarized in Table 3.

Thus, the ZnSb films are stable up to ~175°C and apparently offer significantly high Seebeck coefficients between 25°C to ~175°C, in spite of the free-carrier levels considered here.

Thermal Conductivity of ZnSb Films

Some preliminary measurements of the thermal conductivity (K) of ZnSb films were carried out using the 3- ω method [2,3]. Shown in Table 4 are the K values at 300K for ZnSb films, as a function of layer thickness (or carrier concentration) and the effect of Te doping. It is interesting to note that, for as-grown films, the thermal conductivity decreases at lower carrier levels suggesting that a significant portion of the thermal conductivity could be from transport of heat by carriers. It is worth noting that the Sample 7-240, which had the lowest free-carrier level and turned polycrystalline from excessive Te-doping, offers the lowest thermal conductivity at 25°C. This is consistent with the polycrystalline grain-boundary scattering of phonons as well as lower contribution of carrier transport of heat to thermal conductivity.

As noted in the previous section, the Seebeck coefficient of ZnSb films remains fairly stable up to 175°C and so it was important to measure thermal conductivity of the films at ~175°C, to estimate ZT values. Hence, we carried out 3- ω measurements on a set of samples and the data is shown in Table 5.

Figure 1 Effect of layer thickness and temperature on Seebeck coefficients of ZnSb films.

Table 3 Hall-Data of ZnSb Samples Before and After 200°C Exposure During Seebeck Coefficient Measurement.

Sample #	Thickness (μm)	Before 200°C Exposure			After 200°C Exposure		
		μ (cm ² /vs)	P (cm ⁻³)	Resistivity (ohm-cm)	μ (cm ² /vs)	P (cm ⁻³)	Resistivity (ohm-cm)
7-125-b	0.03	13.4	8.5E20	5.5E-4	13.1	4.2E20	1.1E-3
7-127	0.5	15.5	5.4E20	7.4E-4	15.7	3.0E20	1.3E-3
7-127-a	0.5	9.0	4.8E20	1.45E-3	9.3	2.5E20	2.7E-3

Table 4 Thermal Conductivity of ZnSb Films at 25°C Determined by the 3-ω Method.

Sample #	Thickness (μm)	Carrier Concentration (cm ⁻³)	Te Doping	K (W/cm-K)
7-248	0.9	4.0E20	--	0.033
7-247	1.05	2.4E20	--	0.011
7-244	0.5	3.6E20	Yes	0.083
7-246	1.1	3.3E20	Yes	0.010
7-240	0.33	2.0E18	Yes; Polycrystalline	0.008

Table 5 Thermal Conductivity of ZnSb Films at 150°C, Determined by the 3-ω Method.

Sample #	Thickness (μm)	Te Doping	K ₃₀₀ (W/cmK)	K ₄₂₃ (W/cmK)
7-248	0.9	--	0.033	0.021
7-247	1.05	--	0.011	0.009
7-244	0.5	Yes	0.083	0.034
7-240	0.33	Yes; Polycrystalline	0.008	0.020

For as-grown films, the thermal conductivity (K) falls slowly in going from 25°C to 150°C. This is consistent with the observed variation of K with temperature in CdSb bulk crystals [4]. However, in the case of Te-doped ZnSb films, we noticed a significant drop in thermal conductivity in going from 25°C to 150°C. This is a potentially useful

result for higher ZT values of Te-doped ZnSb films at higher temperatures, considering that Te-doped ZnSb films also show near constancy of α with temperatures between 25°C to 175°C. We also noted that the polycrystalline ZnSb film shows an increasing K with temperature and this is consistent with reduced phonon-scattering by grain boundaries

at higher temperatures. It is important to note that typical K values of ZnSb films at $\sim 150^\circ\text{C}$ are ~ 0.01 to 0.03 W/cm K , in reasonable agreement with $\sim 0.01 \text{ W/cm K}$ seen in bulk ZnSb crystals at $\sim 250^\circ\text{C}$ [1]. This is indicative of the validity of the K values determined by the 3- ω method in thin-films of well-known materials.

ZT values of ZnSb films

With the measurement of the Seebeck coefficient and thermal conductivity of ZnSb films at $\sim 150^\circ\text{C}$, well below the possible onset of dissociation and with the assumption that the electrical conductivity of ZnSb films do not change appreciably between 25°C and 150°C , we have indicated the ZT value of the best ZnSb film at 150°C in Table 6.

Sample 7-248 indicates a ZT of ~ 3.2 at 150°C . At 25°C , this sample has a ZT of ~ 0.4 . This represents an important milestone for the potential performance of thin-film ZnSb, with a well-controlled stoichiometry of Zn:Sb=1:1, grown by MOCVD.

Summary

We have demonstrated that ZnSb single-crystalline films with a stoichiometry of Zn:Sb=1:1 can be grown by MOCVD. The residual doping level in these films was rather high, although decreasing monotonically from $8.5\text{E}20 \text{ cm}^{-3}$ for layer thickness of $0.13\mu\text{m}$ to $2.7\text{E}20 \text{ cm}^{-3}$ for layer thickness of 1.1

μm . The preliminary values of Seebeck coefficients of these films were found to be as high as $372 \mu\text{V/K}$ at $\sim 150^\circ\text{C}$. With the evaluation of the Seebeck coefficient of ZnSb thin films, the measurement of thermal conductivity by the 3- ω method and assuming that the electrical resistivity at 150°C remains about the same as that measured at 25°C , we estimate a ZT of ~ 3.2 at 150°C for a ZnSb film of $\sim 1.0 \mu\text{m}$ -thickness. These results are of interest to efficient low-temperature, low-grade-heat, thermoelectric power generation.

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Table 6 Property of best ZnSb Film at 150°C .

SAMPLE #	THICKNESS (μm)	Te DOPING	α_{423} ($\mu\text{V/K}$)	POWER FACTOR ⁺ ($\mu\text{W/cm-K}^2$)	THERMAL CONDUCTIVITY K_{423} (mW/cmK)	ZT ⁺
7-248	0.9	--	372.4	159.4	20.5	3.28

+ Power factor and ZT are calculated assuming resistivity value at 423K is about the same as at 300K.