Synthesizing and Studying the Crystal Structure of ZnSb thin films

H.S.Al-Selman and A.K.Al-Qazzaz
Dept.of Physics, College of Science, University of Basrah, Iraq.
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Abstract:

Zinc antimonide was prepared by melt-quenching method, then the pre-synthesized powder evaporated on different substrates (glass, Si (001) and KBr) at room temperature (R.T) and (473K) by using thermal evaporation technique.The ZnSb powder and thin films were analyzed by X-ray diffraction (XRD) pattern, were we note two phases (ZnSb and Zn_4Sb_3) in all samples except the $(2.1\mu m)$ film that deposited on glass substrate at (R.T) which has exposed a single phase (ZnSb phase) in comparison with the other films which have a small volume fraction of Zn_4Sb_3 phase .

Introduction:

The Zn-Sb mixture has three intermetallic compounds;
ZnSb, Zn_4Sb_3 and Zn_3Sb_2.The latter two have various polymorphic modifications, therefore the characteristic features of this system have many different crystal structures [1,2]. Zinc antimonide has two structures of orthorhombic and hexagonal [3,4]. The ZnSb compound is classified as thermoelectric material. Such materials are used in many applications of thermoelectric devices such as electrochemical energy storage (Lithium batteries, Supercapacitors/Asymmetric Supercapacitors), engines (Miniature Internal Combustion Engine, Micro turbine jet engine), and direct energy Conversion (Thermoelectric Generators, Solar Power/Photovoltaics/Beam, Direct Nuclear Conversion, Chemical Muscle Generation, Micro Fuel Cell) depends primarily on increasing the figure of merit [5-7].

The figure of merit, Z, of a thermoelectric material is defined by the relation[7]:

$$Z = \alpha^2 \sigma / \lambda \quad \text{.....(1)}$$

where α : the Seebeck coefficient, σ : the electrical conductivity and λ : the thermal conductivity. Since Z has a unit of per degree of temperature, a more useful dimensionless figure of merit can be defined as ZT, where T is the average operating temperature[6].Thin film of ZnSb, has a potentially high ZT for power generation application and it is always p-type with Seebeck Coefficient as high as $(600\mu V/K)$ at (500K), and $ZT \approx 3.2$ and 0.4 at (423K) , (R.T) respectively[8,9]. In the present work, we examined the crystal structure of ZnSb thin films deposited on various substrates (glass, Si (001) and KBr) at (R.T) and (423K).

Experimental:

ZnSb polycrystalline with a stoichiometry of Zn:Sb=1:1 were prepared by the melt-quenched method. Zinc (99.99% pure) and antimony shots (99.99% pure) were put into quartz ampoule, which subsequently evacuated and sealed at (10^{-5} torr),then placed in a single zone vertical Lindbergh furnace.

The quartz ampoule was heated to (950K) by rate of (323K/h) and held at this temperature for about 5h for homogenization and quenched in water. The Resulting ingots were ground in a gate mortar and analyzed by X-ray diffractometr (XRD), which showed that the powder has a multi-phase after quenching.The pre-synthesized powders evaporated on different substrates (glass, Si (001) and KBr) at (R.T) and (473K) by using thermal evaporation technique under vacuum up to (10^{-5} torr). The prepared thin films were analyzed by (XRD) in order to compare the results with the results which were obtained from the powder of the same material.

Results and Discussion:

The (XRD) pattern of ZnSb powder is shown in Fig.(1),which agrees with the data reported by Dobryden [3].The powder seems to be multi-phase and it's structure is in agreement with that of orthorhombic ZnSb.The inter-planer spacing (d_{hkl}) was calculated for all planes by using the Bragg's relation[10]:

$$2d\sin\theta = n\lambda \quad \ldots\ldots(2)$$

where λ: wavelength, d: lattice spacing, n: order number and θ: Bragg's angle.

From the values of d_{hkl} of each plane, lattice dimensions were calculated by using the relation[11]:

$$\frac{1}{d^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2} \qquad \ldots. (3)$$

where (a, b, c) are the lattice parameters and (h, k, l) are miller's indices.

Fig.(2),Fig.(3) and Fig.(4) show the (XRD) pattern of ZnSb thin films deposited on glass, Si (001) and KBr substrates respectively, at different temperatures. The peaks in these patterns indicate that, the ZnSb thin films also have orthorhombic structure.The ZnSb films deposited on glass substrate at (R.T) have single phase (ZnSb phase only), this may be due to the increase in thickness $(2.1\mu m)$ in comparison with the other samples which have thicknesses about $(0.6 \mp 0.05\mu m)$.

A small volume fraction of Zn_4Sb_3 phase was noticed in most samples but it is very small in comparison with ZnSb phase in the films deposited on (KBr) substrate. However this phase seems to be larger in films deposited on Si (001).

The existing of the Zn_4Sb_3 phase is in agreement with the results of V.E.Antonov and T.Caillat[2,5].

In general, it is difficult to obtain single phase of ZnSb, because the transition between the thermodynamically equilibrium two-phase state and single phase has a complex multi-step process[2].

The existing of the Zn_4Sb_3 phase in as grown compound and thin films can be attributed to the present method to preparation ZnSb compound as well as the unstability of this phase between (263-765)K[5,8].Another technique can be used to obtained single phase compound such as metallorganic chemical vapor deposition (MOCVD) and ionization cluster beam (ICB)[8].The grain size (D) of films and powder were calculated from the Debye Scherrer's formula, from the full-width at half-maximum (FWHM),B, of the peaks expressed in radians[11]:

$$D = \frac{0.9\lambda}{B\cos\theta} \qquad \ldots\ldots\ldots (4)$$

The calculated lattice parameters and grain size of the present work were illustrated in table (1).Our results has a good agreement with Komiya et. al.[12]

Table (1): lattice parameters and grain size of ZnSb compound

Prepared compound	Substrate	Substrate temperature (K)	Lattice parameters			Grain size (Å)	Ref.
			a (Å)	b (Å)	c (Å)		
Powder	----	300	6.32	7.74	8.08	367.26	Present work
Thin film	glass	300	6.13	7.66	8.3	518.24	Present work
		473	6.13	7.63	8.29	366.75	
	Si(001)	300	6.17	7.66	8.3	307.82	Present work
		473	6.22	7.66	8.11	307.82	
	KBr	300	6.32	7.72	8.3	220.65	Present work
		473	6.2	7.72	8.05	171.65	
Single crystal	----	300	6.218	7.741	8.115	----	[12]

It has been noticed that the grain size of ZnSb thin film deposited on glass at (R.T) is larger than in the other samples, this is due to the increase in the thickness of this film $(2.1\mu m)$ in comparison with the other samples which have $(0.6 \pm 0.05\mu m)$ thick.

Conclusion:

The ZnSb powder was found to be multi-phase, similar to the ZnSb films deposited on various substrates (glass, Si (001) and KBr), this indicates that it is difficult to prepare a single phase samples.The existing of Zn_4Sb_3 phase can be attributed to the present method to preparation ZnSb compound as well as the unstability of this phase between (263-765)K.

We also found that the grain size increases with increasing film thickness and we noticed no significant effect for substrate on the structure. The ZnSb film which deposited on glass at (R.T) was found to be a single phase, this is may be due to the increase of it's thickness $(2.1\mu m)$ in comparison with the other samples which have a thickness about $(0.6 \pm 0.05\mu m)$.

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المستخلص:

حضر المركب ZnSb من صهر عناصره الأولية حسب النسبة الوزنية Zn:Sb=1:1 بتقنية صهر المواد–التبريد السريع للمنصهر،ثم حضرت أغشية رقيقة من المركب على قواعد مختلفة (glass, Si (001) and KBr) في درجة حرارة الغرفة .R.T و 473K باستخدام تقنية التبخير الحراري في الفراغ وبعدها تم دراسة وتحليل التركيب البلوري للمركب المحضر و الأغشية المرسبة باستخدام تقنية حيود الأشعة السينية (XRD) حيث لوحظ وجود طورين وهما (ZnSb) و (Zn_4Sb_3) في جميع النماذج ماعدا الأغشية المرسبة على قواعد من الزجاج ($2.1\mu m$) بدرجة حرارة الغرفة (R.T) حيث تظهر طور منفرد (ZnSb phase) مقارنة بالنماذج الأخرى التي تحتوي على نسبة حجمية صغيرة من الطور Zn_4Sb_3.