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Preparation and Characterization of SnS_2

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Single crystals of SnS_2, crystallizing with the hexagonal CdI_2 structure, were grown by vapor transport and chemical vapor transport. Electronic, optical, and infrared properties were studied, as well as thermal stability in flowing oxygen. The impact on the electrical properties of slight deviations from stoichiometry and halogen impurity were investigated. Crystals free of halogen impurity can be grown by vapor transport. The sign of the majority carriers of crystals grown by vapor transport is dependent upon the growth conditions. If higher growth temperatures are used (750–700°C), vapor-grown crystals are *n*-type semiconductors and exhibit low resistivities (ρ = 4.5(5) Ω cm at 25°C). Annealing of vapor-grown crystals in sulfur at 600°C increases the resistivity to 2×10^5 Ω cm. When the charge-growth temperatures are lowered to 650–600°C and 5% excess sulfur is included in the charge, the crystals are *p*-type semiconductors with high resistivities ($\rho > 10^7$ Ω cm). Crystals grown in the presence of halogen (Cl_2) contain 22(6) ppm chlorine and are *n*-type semiconductors, ρ = 5 Ω cm at 25°C. The resistivity is not altered by annealing in sulfur. The chlorine impurity acts as donor states in this material. © 1988 Academic Press, Inc.

Introduction

SnS_2 is a semiconductor which crystallizes in the layered hexagonal CdI_2 structure (space group $C6$). The structural unit can be described as two layers of hexagonal, close-packed sulfur anions with a layer of tin cations sandwiched between them. The tin cations are octahedrally coordinated by six sulfur anions. Adjacent sulfur layers are bound by weak van der Waals interactions.

There have been numerous studies (*1–9*) of SnS_2 crystals prepared by chemical vapor transport, in which iodine was the predominant transport agent used. These included structural investigations (*6–9*) of polytypes formed from different stacking arrangements of the tin and sulfur layers, as well as electrical studies. The electrical resistivities of crystals from these reports varied several orders of magnitude from 10^2–10^{12} Ω cm, and the activation energies ranged from 0.1 to 0.05 eV. There are no reports of *p*-type SnS_2.

The incorporation of halogen during the growth process and nonstoichiometry in the crystal have not previously been studied and may have a pronounced effect on the electrical properties. Because of inconsistencies in the electrical data in these reports, this study addressed the possibilities

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of incorporation of transport agent and sulfur deficiency by comparing the electrical properties of crystals grown under various conditions. The impact of the growth temperature, the stoichiometry of the charge, and the presence of halogen transport agent were investigated.

The infrared transmission spectrum and thermal stability of SnS_2 were also determined in order to ascertain the suitability of this material as an infrared window.

Experimental

(1) Growth by Vapor Transport

The p-type single crystals of SnS_2 were grown by vapor transport. Freshly sublimed sulfur (Gallard and Schlesinger, 99.999%) and purified tin (Atomergic, 99.999%) were used. Charge compositions in the molar ratio 1 : 2.1 (5% excess sulfur) were introduced into silica tubes which were evacuated to 4 μm Hg. The transport tube was placed in a three-zone furnace and the charge was prereacted at 600°C for 24 hr with the growth zone maintained at 970°C in order to prevent transport. The furnace was then equilibrated to give a constant temperature zone across the reaction tube and was programmed to give, in 24 hr, the temperature gradient necessary for single-crystal growth to take place. A charge-growth gradient of 650–600°C was employed. Crystals grew at the cooler zone in 5–7 days. When the growth period was extended to 14 days, the crystals obtained were large plates measuring $10 \times 5 \times 0.1$ mm^3.

The n-type crystals were also prepared by vapor transport using a similar growth procedure. In this case, enough Sn and S to satisfy the stoichiometry of SnS_2 was used as a charge; no excess sulfur was added. Charge-growth gradients of 750–700°C and 640–590°C were used for a growth period of 7 days. Plates as large as $10 \times 5 \times 0.1$ mm^3 were obtained.

(2) Growth by Chemical Vapor Transport

Single crystals (n-type) of SnS_2 were synthesized by chemical vapor transport using chlorine as the transport agent. The procedure is similar to that described for vapor transport; however, 100 Torr of chlorine was added to the transport tube prior to sealing. Charge-growth gradients of 640–590°C and 730–680°C were used. Crystal growth was considerably faster; 80% of the charge was transported during a 5-day experiment using chlorine as the transport agent, whereas only 10% of the charge was transported by vapor transport under the same conditions. Flat, yellow-orange crystals of the size $10 \times 5 \times 0.1$ mm^3 were grown in this manner.

X-ray diffraction analysis. X-ray diffraction patterns of ground crystals were obtained using a Philips diffractometer and monochromated high intensity Cu$K\alpha_1$ radiation (λ = 1.5405 Å). The diffraction patterns were taken in the range $12° < 2\theta < 80°$ with a scan rate of 0.25 2θ/min and a chart speed of 30 in./hr. In order to avoid preferred orientation in the diffraction patterns of this layered material, Pyrex was introduced before grinding the single crystals. The X-ray patterns could always be indexed on the basis of a simple ($2H$) hexagonal unit cell.

Annealing experiments in sulfur. Crystals were loaded into a silica tube which contained excess sulfur and evacuated to 3 μm prior to sealing. The tube was heated isothermally at 500 and 600°C for 5 days and then cooled at a rate of 50°C/hr to room temperature. The amount of sulfur added was sufficient to produce a pressure of 2 atm at 500°C and 3 atm at 600°C.

Thermal stability. Temperature-programmed oxidation of ground crystals was performed using a Cahn System 113 thermal balance. The temperature was in-

creased to 1000°C at a rate of 60°C/hr in 60 sccm of oxygen.

Infrared, optical, and electronic measurements. Infrared measurements were performed at room temperature on a Perkin–Elmer 580 single-beam scanning infrared spectrophotometer. The measurements were performed in the transmission mode over the range 2.5–25 μm. Transmission through the sample was normalized to the signal obtained in the absence of sample.

Measurements of the absorption coefficient were made with an Oriel Model 1724 monochromator, an Oriel 6672-5400 long pass filter, and a calibrated silicon diode detector. Absorption values were calculated from the response with and without the crystal in the beam.

Resistivity from 77 to 330 K and dc Hall effect were measured in the basal plane of single crystals using the van der Pauw techniqiue (*10*). Contacts were made by painting a colloidal mixture of graphite and isopropanol (Electrodag 154, Port Huron, MI) to the edge of the crystal. Ohmic behavior was established by measuring the current–voltage characteristics. A qualitative Seebeck voltage measurement was made to determine carrier type.

Results and Discussion

Single crystals were grown in this study by vapor transport and by chemical vapor transport using chlorine as the transport agent. Chemical vapor transport was the procedure predominantly used in previous reports on the preparation of SnS_2 crystals. There are large discrepancies in the electrical properties of crystals in those studies. Two important factors which may cause these discrepancies are (1) the inclusion of halogen impurity in the SnS_2 crystal and (2) slight departures from stoichiometry, i.e., a metal to sulfur ratio greater than 1 : 2. This comparative study examines the impact of these two factors on the properties of SnS_2.

TABLE I

X-RAY AND PREPARATIVE DATA FOR SnS_2

Process	Gradient (°C)	Cell parameters	
		a (Å)	*c* (Å)
CVT (chlorine)	730–680	3.649(2)	5.902(2)
CVT (chlorine)	640–590	3.649(2)	5.900(2)
Vapor transport (5% excess sulfur)	650–600	3.652(2)	5.902(2)
Vapor transport	750–700	3.651(2)	5.904(2)
CVT (Ref. (*1*))	800–700	3.639(5)	5.884(5)
CVT (Ref. (*2*))	700–600	3.644(4)	5.884(4)
CVT (Ref. (*3*))	690–650	Not reported	Not reported

Crystals prepared by both vapor transport and chemical vapor transport can be indexed on a simple hexagonal unit cell, with a = 3.649(2), c = 5.902(2) or 5.900(2) Å, as shown in Table I. These values are in close agreement with those of Mikkelsen (*11*) (a = 3.649, c = 5.899 Å) and Whitehouse and Balchin (*6*) (a = 3.643(2), c = 5.894(5) Å). However, they differ from those reported by Greenway and Nitsche (*1*) (a = 3.639(5), c = 5.884(5) Å) and Conroy and Park (*2*) (a = 3.644(4), c = 5.884(4) Å).

The electrical properties of crystals grown by vapor transport under different conditions were investigated initially, since crystals grown by this method are free of halogen impurities. Therefore, any anomalies in the electrical properties can be directly attributed to slight deviations from stoichiometry. SnS_2 is a low resistivity n-type crystal when grown with charge-growth temperatures of 750–700°C, as indicated in Table II. In these reactions, stoichiometric amounts of sulfur and tin were used as the charge. The material exhibits a resistivity ρ = 4.5(5) Ω cm at 25°C. When the charge and growth temperatures are lowered to 640 and 590°C, respectively, the resistivity increases to $\rho = 10^4$ Ω cm. Crystals can be prepared in which the majority of carriers are p-type when grown at 650–

TABLE II

ELECTRICAL AND OPTICAL PROPERTIES

Process	Gradient (°C)	ρ (25°C) (Ω cm)	Ea (eV)	Carrier type	Eg (eV)
Vapor transport	750–700	4.5		*n*	2.28(5)
Vapor transport	640–590	10^4	—	*n*	—
Vapor transport (5% excess sulfur)	650–600	$>10^7$	—	*p*	2.28(5)
CVT, Cl_2	730–680	3	0.06(1)	*n*	2.22(5)
	640–590	5	0.06(1)	*n*	2.22(5)
CVT (Ref. (*1*))	800–700	—	—	—	2.21
CVT (Ref. (*2*))	700–600	10^9	—	*n*	2.20
CVT (Ref. (*3*))	690–650	10^2–10^{12}	0.05–0.4	*n*	—

600°C with 5% excess sulfur added to the charge. The *p*-type crystals showed high resistivity ($\rho > 10^7$ Ω cm) at 25°C. The high resistivity of *p*-type SnS_2 indicates that this material is stoichiometric, whereas the lower resistivity of *n*-type SnS_2 samples shows that the tin to sulfur ratio deviates from 1 : 2. As shown in Table III, the *n*-type crystals were annealed at 500 and 600°C in a sulfur atmosphere in order to produce a more stoichiometric material. The resistivity was shown, in fact, to increase from 4.5 to 2×10^5 Ω cm, demonstrating that nonstoichiometry is predominantly responsible for the low resistivity of SnS_2 prepared at higher temperatures. This shows that both the temperature used in the growth and the stoichiometry of the charge affect the degree of nonstoichiometry in SnS_2.

The electrical properties of crystals grown by chemical vapor transport were also measured in order to determine the ef-

TABLE III

ELECTRICAL PROPERTIES OF ANNEALED SnS_2 VAPOR-GROWN CRYSTALS

Process	Anneal	Resistivity ρ (25°C) (Ω cm)	Mobility μ (25°C) (cm^2/volt sec)	Carrier type
Vapor transport (750–700°C)	As grown	4.5(5)	26(5)	*n*
	500°C (<1 atm sulfur)	6.9(5)	46(5)	*n*
	500°C (2 atm sulfur)	8×10^4	—	*n*
	600°C (3 atm sulfur)	2×10^5	—	*n*
CVT, Cl_2 (640–590°C)	As grown	5.0	21(1)	*n*
	500°C (<1 atm sulfur)	4.5(5)	19(1)	*n*
	500°C (2 atm sulfur)	6.9(5)	9.0(1)	*n*

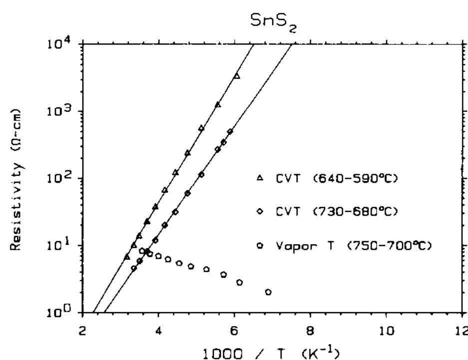

FIG. 1. Resistivity as a function of temperature for SnS_2 crystals as grown by vapor transport and by chemical vapor transport with the indicated charge-growth gradients.

fect of the halogen transport agent (Cl_2) (Table II). Crystals grown by CVT are *n*-type semiconductors with $\rho = 5\ \Omega$ cm at 25°C and are not appreciably affected by the growth temperature. Neutron activation analysis shows 22(6) ppm chlorine is present in crystals grown where the charge-growth temperatures are 640–590°C. Crystals grown by this method, when annealed under the same conditions as those used for vapor transport crystals, show no significant change in resistivity (Table III). This indicates that nonstoichiometry does not contribute appreciably to the magnitude of electrical resistivity. Instead, the presence of halogen impurity must account for the low resistivity of this material.

Further differences between the electrical properties of crystals grown by CVT and vapor transport are shown by the temperature dependence of the resistivity (Fig. 1). Crystals grown by vapor transport, 750–700°C (Fig. 1), show resistivities which decrease with decreasing temperature, indicative of a degenerate semiconductor. Such resistivities are due to scattering rather than carrier activation. The donor states introduced by slight deviations in stoichiometry lie close to the conduction band edge and are ionized. In contrast, crystals grown by chemical vapor transport show classical semiconductive behavior; i.e., the resistivity increases with decreasing temperature (Fig. 1). It has already been noted that these materials are not sulfur deficient, since their resistivities are unaffected by annealing experiments in sulfur. This is further borne out by the graph of log ρ vs $1/T$ (Fig. 1), which shows no deviation from the ideally linear case of a classic semiconductor. If donor states arising from nonstoichiometry were also present in this material, then the linearity of this plot would be affected. The activation energy obtained from these plots for crystals grown by CVT is 0.06(1) eV. This suggests that the chlorine impurity is solely responsible for the donor states, and these states lie slightly below the conduction band. These results, therefore, explain the discrepancies in the electrical properties which were reported in the literature.

Figure 2 shows the decomposition (weight loss) curve of SnS_2 in flowing oxygen as a function of temperature. The onset occurs at 400°C and oxidation is complete by 800°C. The final oxidation product is SnO_2, as determined by X-ray diffraction. The programmed oxidation was stopped before and after the plateau region and the

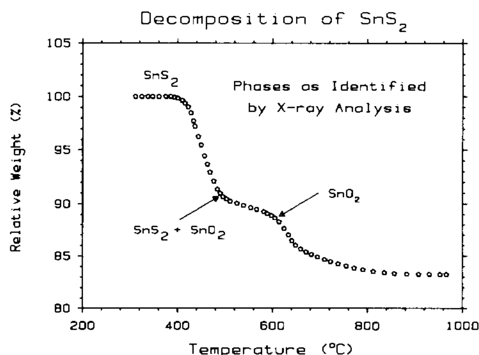

FIG. 2. Variation with temperature of the relative weight of coarsely ground crystals of SnS_2 (grown by CVT) when heated in flowing oxygen. The phases identified by X-ray analysis at various stages of the decomposition are indicated.

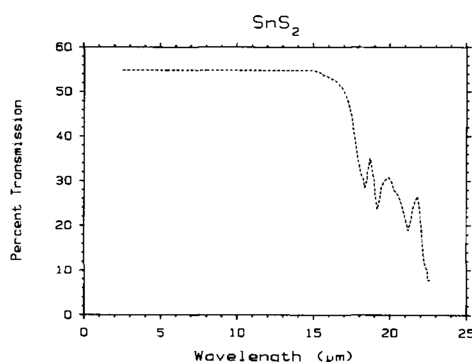

FIG. 3. Infrared spectrum of a typical crystal of SnS_2 as grown by CVT.

materials obtained were analyzed by X-ray diffraction. Prior to the plateau, sharp (001) reflections were observed for SnS_2, showing order in the *c*-direction. Immediately following the plateau, only the SnO_2 phase was visible, indicating that the remaining SnS_2 is present as an amorphous phase with no long-range order in the *c*-direction. This demonstrates that the plateau is due to a kinetic effect related to the layered structure, a phenomenon previously observed for MoS_2 (*12*).

The optical band gaps obtained are given in Table II. The value of 2.22 eV measured for crystals grown by chemical vapor transport is in agreement with the reported values of 2.21 and 2.20 eV for an indirect gap (*1*, *2*). The crystals grown by vapor transport, in the absence of halogen, show a similar optical gap of 2.28 eV. The infrared spectrum of SnS_2 is displayed in Fig. 3, showing infrared transparency to 16 μm. The absorption bands are centered at 16.5, 18.2, and 23 μm. Despite the high transmission in the infrared, the lack of thermal stability restricts the usefulness of this material.

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