

An Investigation of the Preparation and Properties of Some IIIa-Vb Compounds

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Previous work bearing on the techniques of preparation of the IIIa-Vb compounds is reviewed and the preparative problems systematically analysed. This study has resulted in the development of a simple low temperature method for preparing these compounds from their component elements with the minimum of contamination. It has been found that these very high melting point compounds can be sublimed and that sublimation techniques offer a convenient route for their purification and fabrication in thin film form.

Evidence that some of the IIIa-Vb compounds are semiconductors has been obtained from studies of the optical properties of thin films of PrAs, NdAs, SmAs, GdAs, DyAs, TmAs, YbAs, PrSb, SmSb, YbSb and SmP; their respective optical energy gaps were determined as $\sim 1, 1.04, 1.03, 0.63, 1, 1.18, 1.02, 0.66, 0.59, 1, \text{ and } 1.09$ eV respectively. A comparison is made between these measured values and those predicted by N. Sclar [1].

1. Introduction

The conventional III-V compounds such as GaAs, InSb, etc, formed between the elements of groups IIIb and Vb of the periodic table of elements are well-known semiconductors and find many useful applications. The analogous series of compounds formed between the elements of group IIIa, comprising Sc, Y, La, Ac, the Lanthanides (Rare Earths) and the Actinides, and the elements of group Vb are not so well known, although the IIIa group of elements represent 20% of the known elements. Like the IIIb elements the IIIa elements have a characteristic valency of three, and one might expect therefore, equivalent behaviour in the two groups of compounds. The present investigation offers new evidence on the properties and semiconducting status of the IIIa-Vb compounds.

The possibility of predicting semiconductivity or the energy gaps of these or other compounds on theoretical grounds from fundamental considerations remains a distant hope. However, it is possible to predict, or at least speculate about the energy gaps of new compounds by extrapolating or interpolating empirical models based on established data from known com-

pounds. Sclar [1] has developed such an empirical model in which a set of linear relationships between the energy gap of the IIIb-Vb compounds and the logarithm of the reciprocal ionic radius of the group IIIb element was obtained. Using these relationships he made a prediction of the energy gaps of the IIIa-Vb compounds from a knowledge of the ionic radii of the rare earth elements. Sclar predicted that the bismuthides and antimonides should be metallic along with the rare earth arsenides from La to Nd; the remaining arsenides should be low energy gap semiconductors (< 0.5 eV), and the phosphides and nitrides should have energy gaps ranging respectively from 0.5 to 1.3 eV and from 1.7 to 2.5 eV. The experimental evidence on the properties of the IIIa-Vb compounds which can be used to debate Sclar's empirical model is very scant and is discussed later. The experimental evidence for their structure is definitive; the AB compounds have the sodium chloride structure [2] whereas most of the conventional IIIb-Vb's have a zinc blende structure. This structural knowledge does not further theoretical prediction.

The development of the IIIa-Vb compounds

has followed no coherent trend due possibly to the low level of support and divided interest which has resulted in lack of contact between different groups of workers in the field. The principal fields of interest in the IIIa-Vb compounds involve fundamental studies of their magnetic, thermoelectric or possibly electrical properties. For most studies one would like good quality, preferably semiconductor quality, single crystal material. This ideal, however, has not yet been achieved.

The preparation of the IIIa-Vb compounds of semiconductor quality is beset with many difficulties. For example, their melting temperatures are very high; the few which have been measured or estimated are in the 2000 to 2500° C region. Also the exceptional reactivity of the rare earths results in their reaction at elevated temperatures, not only with the ubiquitous elements, oxygen, nitrogen, etc, and their compounds, but also with practically all container materials. The metals Ta, Mo and W, are less susceptible to attack and can be used to contain the compounds.

The most widely used method of preparing these compounds is by direct reaction between the elements. This can be achieved by a variety of techniques which involve heating intimate mixtures of the elements in powder, filing or in gaseous form. Some information – generally not very detailed – on these techniques can be found in some of the following studies of the nitrides [1, 5-11, 13, 16, 21] phosphides [1, 7, 8, 14, 15, 18], arsenides [1, 3, 7, 8, 13, 14, 15, 18, 19, 21], antimonides [1, 3, 4, 7, 8, 11, 12, 18, 19, 21, 25] and bismuthides [1, 19, 23]. A useful account is given by Carter [24] of some aspects of the preparation of rare earth chalcogenides.

One of the variants of the direct reaction method is the technique used by Reid *et al* [20] who distilled the group V element into the liquid metal as in the conventional IIIb-Vb compounds. However, only powders were obtained since it was not possible to reach a temperature at which the compound was significantly soluble.

A novel preparative technique of potential value for compounds having high heats of formation and offering the possibility of low contamination has been recently reported by Sato, Taylor and Calvert [25]. A small pellet of the mixed elements suspended by the tips of tungsten electrodes is ignited using a high current discharge. In a test on LaSb, ignition produced a molten blob which dropped and froze instantly

on contact with a large copper anvil. The application of the technique to arsenides and phosphides has yet to be tried. Alternative methods can be used for the nitrides. Sclar [6] and also Didchenko and Gortsema [5], reacted the metal hydrides with ammonia, but this also produced powders. The crystallisation of the nitrides from a metal-rich alloy has, however, been achieved by Gambino and Cuomo [22] using an interesting reactive arc melting technique. In this technique the rare earth metal or mixture of metals is arc melted on a cold copper hearth in pure argon which is then replaced with high purity nitrogen. The high concentration of nitride at the upper surface of the melt diffuses and convects to the colder bottom where it crystallises out as the dense polycrystalline nitride. The only other known example of the melting of the nitrides is that of O'Dell and Hensley [11] who briefly reported the melting point of CeN ($2572 \pm 20^\circ \text{C}$ at $5 \pm 1 \text{ atm}$).

The inability to achieve slow controlled crystallisation of these compounds is one basic reason for the poor quality of the product. In the case of the nitrides the departure from stoichiometry is sufficiently significant to be measured. The nitrides prepared by Sclar [6] – Dy, Er, Ho as well as Sc and Y – never contained more than 90% of their theoretical stoichiometric nitrogen content. The corresponding nitrogen contents of the nitrides – Tb, Dy, Ho, Er and Tm – analysed by Child *et al* [7] and by Wilkinson *et al* [8] were 94 to 97%. Didchenko and Gortsema [5] heated two of their compounds LaN and GdN, under extreme conditions, 1500° C, at 3000 atm of N₂ for 1 h, and found no change in the properties of the materials. Their inference that their nitrides were stoichiometric must be treated with caution, however, since in the cases of Dy, Er, Ho, La, Pr and Nd the nitrides exhibited semimetallic behaviour and the resistivities were almost the same as the equivalent non-stoichiometric compounds of Sclar.

The work of Wilkinson *et al* [8] included a study of the magnetic properties of the phosphides, arsenides and antimonides, as well as the nitrides of the rare earths. They state that they were not able to obtain single crystals of these compounds and also found it impossible to achieve complete stoichiometry in any case. This they attribute to the lack of purity of the rare earth starting materials and to the formation of other compounds such as carbides and oxides

during preparation.

Specific evidence pertaining to semiconductivity in the IIIa-Vb compounds is limited. Prior to Sclar's work the most extensive investigation of these compounds appears to be that of Brixner [3] who prepared the AB type arsenides, antimonides and tellurides of all the rare earths (excepting Eu and Lu) and the elements Sc and Y. Brixner made resistivity and Seebeck coefficient measurements on specimens of the majority of these compounds. Most of the specimens were reported to show a negative coefficient of resistivity indicating semiconducting behaviour.

Sclar [6], in addition to the resistivity measurements mentioned, also obtained optical transmission data and found optical absorption edges in films of DyN, ErN and HoN which were consistent with their having energy gaps in the 2 to 3 eV range. He concluded that the nitrides were high energy gap defect type degenerate semiconductors with a large concentration of carriers due to a deficiency of nitrogen.

A considerable amount of work involving studies of the semiconducting and thermoelectric properties of the chalcogenides (selenides and tellurides) has been carried out by a group working at Battelle [21]. In addition, the same workers prepared NdAs, GdAs, SmAs, and NdSb. The specimens had low resistivities, of the order of 10^{-4} ohm cm, carrier concentrations of 10^{20} to 10^{21} /cc and mobilities of 50 to 100 $\text{cm}^2 \text{ volt}^{-1} \text{ sec}^{-1}$ at room temperature. The temperature dependence of their electrical conductivity did not indicate semiconductor behaviour. The specimens contained large quantities of impurities - 2000, 2000 and 400 ppm (atomic) respectively of Si, Cu and Ta - due probably to system contamination at the very high (2500°C) sintering temperatures used. Films of GdAs, SmAs, and NdAs which were prepared by evaporating metal films and reacting them with arsenic vapour were found to have the same electrical properties as the bulk material. Attempts were made to vapour transport SmAs using iodine as a transporting agent. No transport was observed at temperatures in the range 700 to 900°C in closed tubes over a period of 48 h. Busch, Vogt and Hulliger [17, 26] on the other hand, have noted the preparation of single crystals of various IIIa-Vb compounds using an iodine vapour transport method by using higher

temperatures (1000 to 1100°C) for much longer periods. The transport apparently takes place from cold to hot. Crystals with typical dimensions 1 to 2 mm, were prepared of Er, Gd, Tb, Ho and Dy arsenides. The crystals were homogeneous and were reported as a result of microprobe analysis to contain less than 0.1% of impurities except TbAs which contained 1% Si. In addition, very small crystals of Tb, Dy, Ho and Er phosphides [15] were also prepared. The electrical measurements on these compounds, particularly the temperature dependence of resistivity, revealed that they had metallic characteristics and were probably cation deficient [26].

It is evident, therefore, that due to the preparation difficulties, the IIIa-Vb compounds so far prepared are very impure, certainly by semiconductor standards, and the electrical measurements are not a reliable guide to their intrinsic character. Consequently, the present investigation has been primarily aimed at elucidating the optical properties of these compounds where the rôle of impurities is not quite so critical.

2. Preparation of the IIIa-Vb Compounds

The rare earth metals used were obtained from New Metals and Chemicals Ltd, Koch Light Ltd, and Johnson Matthey Ltd, with quoted purities of 99.8 to 99.9% with respect to other metals. Phosphorus was supplied in the red form by Koch Light Ltd, with a quoted purity of 5N (99.999%); arsenic with a quoted purity of 99.999% was supplied by Hoboken-Belgique in the β (non-oxidizing) form, and the bismuth and antimony were zone-refined at RRE.

Reliable techniques for preparing the compounds were developed following a detailed investigation of the reaction between samarium and arsenic. This reaction in principle is very simple, but in practice, deceptively dangerous; at 500°C it proceeds with explosive violence. However, at lower temperatures a safe controlled reaction can be achieved. The basic preparation procedure involved sealing the mixed samarium (or other rare earth) filings and arsenic powder in an evacuated silica tube - 8 to 12 mm internal diameter, 7 to 10 cm in length - and placing it in a furnace either cold or at any temperature up to 250°C^* . It was found critically important to raise the temperature of the mixed powders the

*This temperature could be 300°C in the case of SmAs, but for safety with the less thoroughly investigated compounds 250°C was considered an upper limit.

last 100° C up to 350° C slowly, i.e. no more than 1° C min⁻¹. After 4 h the reaction was virtually complete, but the silica ampoule containing the compound was generally left overnight (12 h) in the furnace at 350° C whence the temperature could be safely taken up to 1000° C in order to obtain complete homogeneity. A free-flowing powdered compound was obtained leaving a clean silica ampoule with no evidence of attack or deposit whatsoever.

The evidence from the initial experiments that the solid state reaction between the elements went to completion at relatively low temperatures clearly indicated that a direct reaction technique could be used to measure the heats of formation of the compound. Dr Faktor and Mr Hanks of the Post Office research group at Dollis Hill, London, kindly undertook a fundamental study of the heat of formation of the arsenides [27]. Using a dynamic differential calorimetric technique they found that the reaction between the elements started, depending on the metal, in the temperature range 295 to 420° and was complete within 50 to 100° C. Further, both the initial temperature and temperature ranges were dependent upon the rate of heating. A heating rate of 5° Cmin⁻¹ caused a 100° C increase in the initial temperature of reaction over that produced by a 1° Cmin⁻¹ heating rate.

Using the standard reaction conditions ten rare earth arsenides, three antimonides, three phosphides and one bismuthide have been successfully prepared and are listed in table I. The reaction between Eu and As did not, however, produce a compound EuAs with a NaCl structure. The reaction product was not investigated further.

2.1. Limitations of Melt-Growth

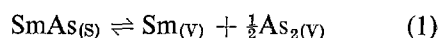
A number of attempts were made to melt SmAs. They were not very successful although evidence was obtained on one occasion of partial melting of a charge. In this case it was noted that the Mo crucible containing the SmAs also partially melted; since Nb can be melted in the presence of solid SmAs it was concluded that the melting point of SmAs is between that of Nb and Mo i.e. 2468 and 2628° C and probably nearer the latter.

In view of these difficulties attempts were made to crystallise SmAs from alloys (or solutions) at lower temperatures. After a number of unsuccessful attempts using Ag, In, Cd₃As₂ and Zn₃As₂ as solvents, liquid Sm was tried. The two main problems with Sm are the extreme

reactivity of the liquid metal and its tendency to wet containers to such an extent that molten metal creeps out and attacks other parts of the system. The only materials which were in any way compatible with liquid Sm were Ta, Mo or W. In an effort to avoid the creep problem protective coverings or liquid encapsulants were used on top of the Sm alloy. BaCl₂ and CaCl₂ appeared to be stable. They did not stop the creep of liquid Sm, however, since the latter wets the crucible more effectively than the liquid encapsulant. The volatility of the chlorides decreased their usefulness since even at 1500° C there appeared to be virtually no solubility of SmAs in Sm. The vapour pressure of Sm (bpt 1900° C) is about 10 cm Hg at 1500° C, hence growth at higher temperatures would present an additional vapour pressure problem. The solution growth of SmAs was therefore considered too formidable a task.

2.2. Vapour Growth

Theory: a thermodynamic assessment of the potentialities of sublimation as a method of vapour growth has been made using standard techniques. The basic assumption is that at elevated temperatures (~2000° C) the rare earth arsenide, for example, SmAs sublimes according to equation 1



The heat of formation of the arsenides have been measured by Hanks and Faktor [27] at relatively low temperatures, i.e. around 300 to 450° C. Their results for the heats of formation can be taken for the purpose of this assessment as equivalent to ΔH_{298}° for the solid compound. The thermochemical data for the rare earth vapour and arsenic (As₂) vapour was taken from the papers of Habermann and Daane [28] and Thurmond [29] respectively. The standard free energy change ΔG_T° for reaction 1 can be written as:

$$\Delta G_T^\circ = \Delta H_{298}^\circ - T\Delta S_{298}^\circ + \int_{298}^T \Delta C_p dT - T \int_{298}^T \frac{\Delta C_p}{T} dT \quad (2)$$

Estimates of the specific heat change ΔC_p between the vapour components and the solid were made using data of Stull and Sinke [30]; an estimated value of 14.5 cal deg⁻¹ mole⁻¹ was used for C_p for the rare earth arsenide [31]. Since the equilibrium constant K_p is related to ΔG_T° by

$$\Delta G_T^\circ = -RT \ln K_p, \quad (3)$$

(where $K_p = p_{\text{Sm}} p_{\text{As}_2}^{\frac{1}{2}}$ and $p_{\text{Sm}} = 2/3P$ and $p_{\text{As}_2} = \frac{1}{3}P$, $p_{\text{Sm}} p_{\text{As}_2}$ and P are partial pressure of Sm vapour, As_2 vapour, and the total pressure respectively) the value of P can be readily calculated.

The results for the total pressure, P over various IIIa-Vb compounds at 2300°K are shown in table I. The accuracy of the thermochemical data is limited by the accuracy of the estimation procedures used [31]. The absolute value of P will therefore be subject to some uncertainty; an error of 5 kcal in ΔG° at 2300°K can change P by about a factor of two. Nevertheless, relative values of P for different compounds form a useful guide to their differences in volatility. The predictions indicate that at 2300°K YbAs and SmAs should sublime readily but YAs, TbAs and GdAs should show poor volatility. This was the case in practice; the experimental results for SmAs were in rough quantitative agreement with theory.

2.3. Flash Evaporation

The initial vapour growth experiments were carried out using a flash evaporation apparatus similar to that used by Richards [32] for the study of the conventional III-V compounds. In this technique a fine stream of SmAs powder was dropped continuously on to a very hot –

1800 to 2000°C – molybdenum filament in vacuum. The spontaneous evaporation of the powder produced a near stoichiometric vapour which was condensed on to a glass or silicon substrate held at temperatures between 20 and 450°C . Although the films generally had a good overall appearance they were optically opaque in the range 0.8 to $15 \mu\text{m}$. A disadvantage of the technique was that it frequently produced films spotted with sputtered powder. They could remain bright for a period of months but generally tended to tarnish rapidly in air. Powder diffraction photographs even of the poor films, showed SmAs lines, but the high angle lines in all films were diffused due to poor stoichiometry or possibly high strain in the film. It was found that the films having the most perfect SmAs patterns occurred when too rapid delivery of powder produced an accumulation of solid SmAs in the boat during evaporation. The potentialities of sublimation were therefore investigated.

2.4. Sublimation

Two sublimation procedures – bulk transport and thin film deposition – were attempted. In the former procedure SmAs was transported from one end of a tantalum tube ($\sim 40 \text{ mm}$ in length $\times 12 \text{ mm}$ in diameter) to the other under the influence of a temperature gradient. The tube

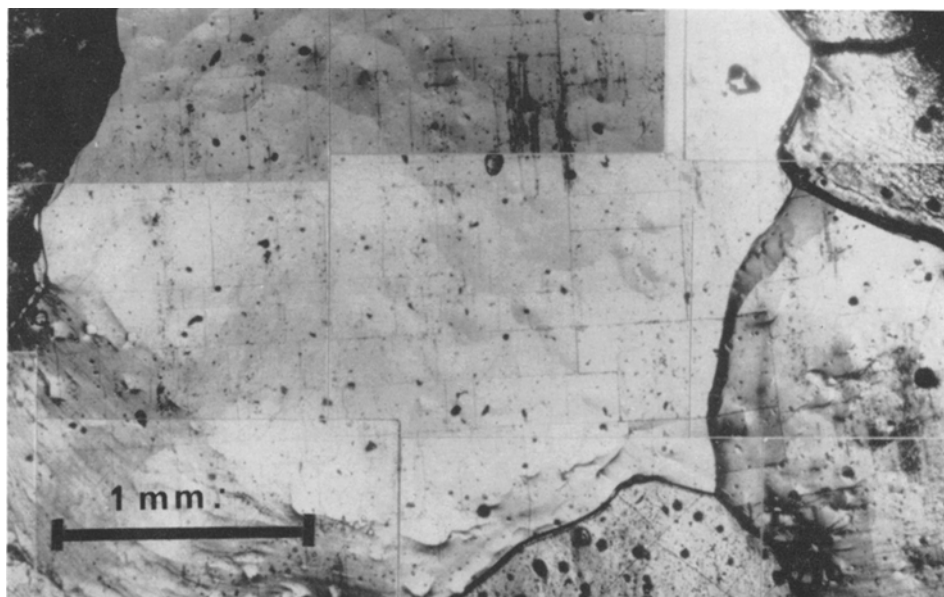


Figure 1 Composite photograph of the surface of a crystal of SmAs prepared by vapour transport: note the square symmetry of the cleavages in the film surface.

which was encased in thermally insulating graphite felt was heated by RF induction so that the hottest region was around 2500° C. Although the tube was sealed at both ends a small hole (~ 1 mm in diameter) in its wall allowed it to be continuously outgassed; this was achieved by fixing the tube in its graphite surround in a silica chamber connected to a backing pump. The removal of the foreign gases from the tube permitted transport of the SmAs at a rapid rate which could be as high as 10 g/h; additionally the vacuum assisted in the removal of volatile impurities and improved the thermal insulation of the tube.

The transported SmAs possessed a polycrystalline columnar structure and showed highly anisotropic electrical properties. Whiskers of SmAs 1 to 2 mm in length by 0.1 to 0.2 mm in diameter were also produced on the graphite felt opposite

the evacuation hole. The lack of suitable apparatus which would allow precise reproducible temperature control precluded serious investigation but a crystal 2.5 mm across and 1 mm thick (fig. 1) was obtained in this way. A potential disadvantage of the process as used was the cleavage strain cracks induced in the deposited compound due to expansion mismatch between the compound and the Ta.

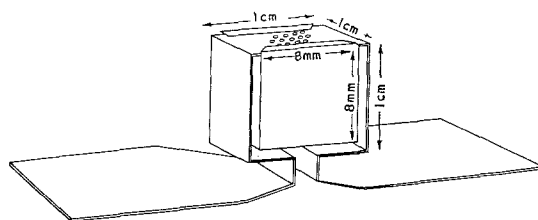


Figure 2 Construction of Ta-boat used for sublimation experiment.

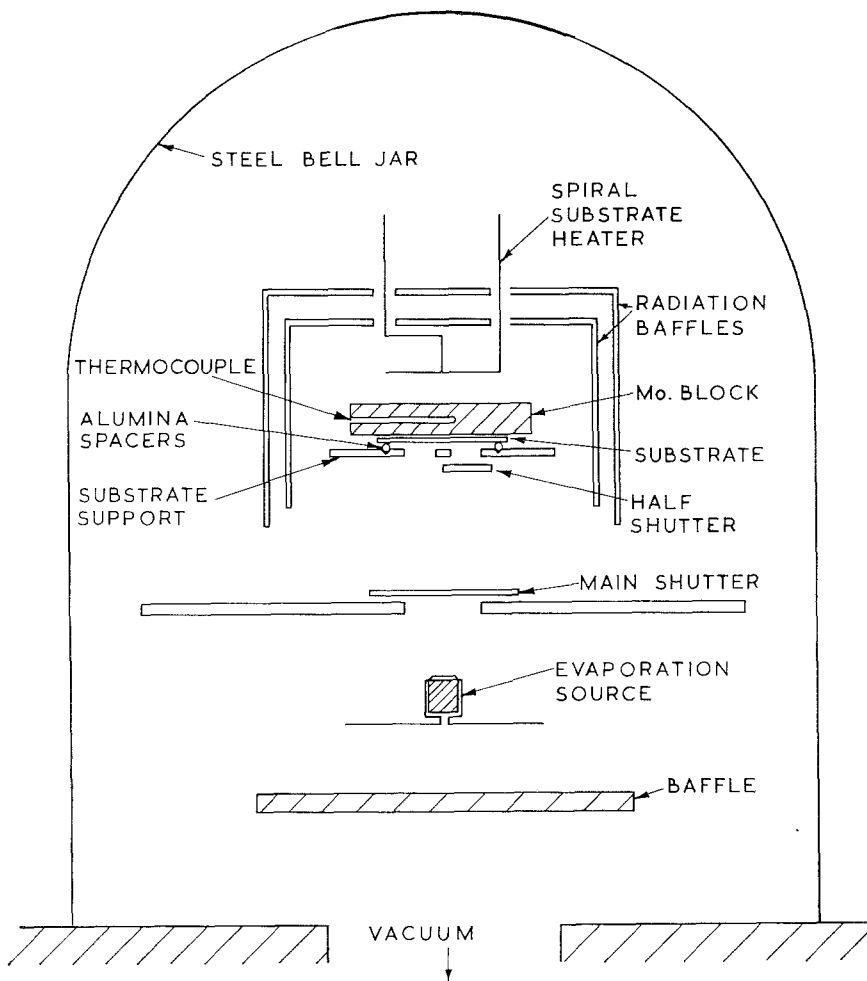


Figure 3 Sublimation apparatus.

The development of a procedure for depositing high quality thin films involved a systematic investigation of the optimum conditions of sublimation and deposition. The initial attempts at controlled sublimation from a simple boat-shaped heater were frustrated by the SmAs jumping out due to the rapid pressure build up on the hotter underside of the charge. This problem was eliminated by the specially designed boat shown in fig. 2. In this boat the charge was primarily heated from the sides and the top; perforations in the top tantalum strip permitted the escape of vapour. Very high temperatures were possible with these tantalum crucibles. Vapour transport within the box structure of the boat produced cube-shaped SmAs crystals 1 to 2 mm on edge, but they invariably tarnished rapidly in air indicating, probably, an arsenic deficiency.

It was found that the source temperature was critical only in so far as it was necessary to get a

reasonable rate of deposition – typically $0.2 \text{ mg cm}^{-2} \text{ min}^{-1}$. A mechanically controlled main shutter was used to sample an intermediate fraction of the subliming material. A “half shutter” was used to prepare adjacent sections of film of different thicknesses (fig 3). The temperature of the substrate during deposition was critical as has been found with the conventional IIIb-Vb compounds [33]. The minimum temperature for successful deposition was 500°C but the best results were obtained between 650 and 800°C depending on the compound. The most consistently successful substrate was silica although silicon, calcium fluoride, and glass (at lower temperatures) were tried. Thick films on silicon ($\sim 5 \mu\text{m}$) tended to peel off; but films sublimed on to silica under optimum conditions were bright, smooth, free from tarnish, and maintained stable optical characteristics. Films of all the compounds have been prepared in this way and many have kept their bright tarnish-free con-

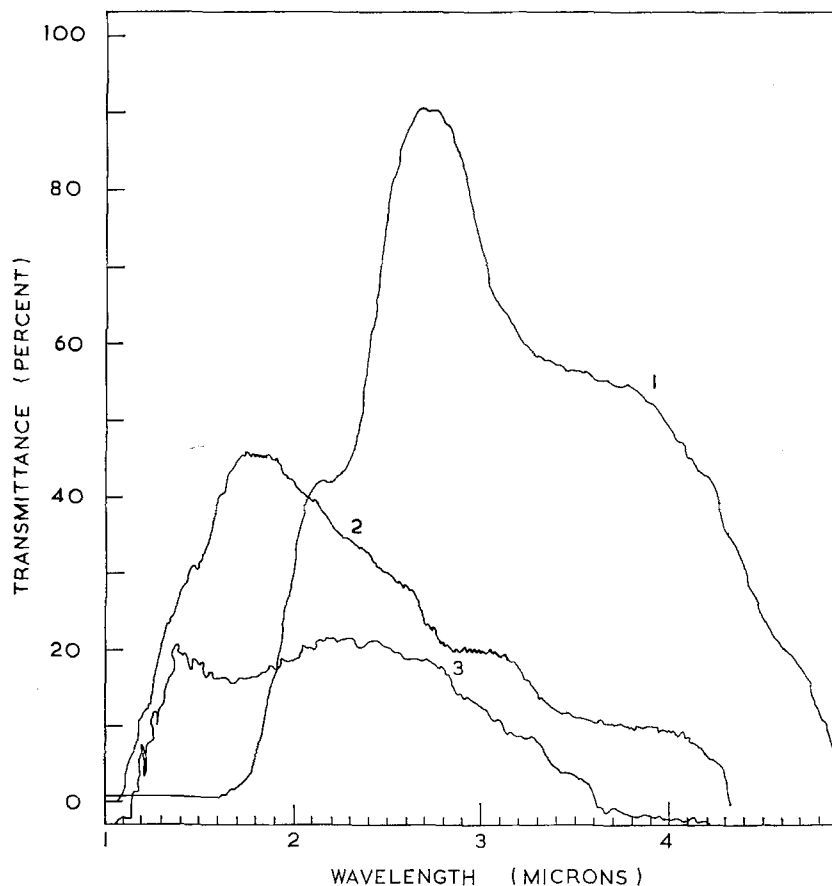


Figure 4 Relative optical transmission for different thicknesses of the same film on silica: 1, GdAs 2, TmAs and 3, YbAs. (Note, in case 3 only, comparison film was a blank silica substrate.)

dition for over a year.

3. Properties of Films

3.1. Optical Properties

The optical transmission characteristics of a number of IIIa-Vb compounds have been examined using a Perkin Elmer spectrometer. The compounds which included the arsenides of Pr, Nd, Sm, Gd, Dy, Tm and Yb, the antimonides of Pr, Sm and Yb and the phosphide of samarium were deposited on to silica substrates by the sublimation technique described. Initially the optical transmission of the film on its silica substrate was measured relative to the optical transmission of an equivalent uncoated silica substrate. Subsequently, a slightly more sophisticated technique was adopted with the majority of the films. This involved blanking off part of the substrate during the deposition of the film so as to produce two areas of differing film thickness. By comparing the transmission of the two thicknesses of film on different parts

of the same substrate, errors due to reflection differences were minimised and a more representative measure of the transmission of the film of the IIIa-Va compound itself was obtained.

The transmission curve obtained on some of the compounds are reproduced in figs. 4 and 5. The curves all show an enhanced transmission in the infra-red, compared with the visible, and an absorption edge around 1 to 2 μm . These absorption edges have been analysed using the current theory of photon absorption in solids; a review of this subject with particular reference to III-V compounds has recently been published by Johnson [34].

The absorption coefficient (α) in solids is predicted to show an inherent inverse dependence on the photon energy ($h\nu$). But, in the region of the band edge where the photon energy is approximately equal to the energy gap (ΔE) the absorption coefficient is proportional to $(h\nu - \Delta E)^\gamma$. Since γ is $\frac{1}{2}$ for an allowed direct transition and 2 for an allowed indirect transition

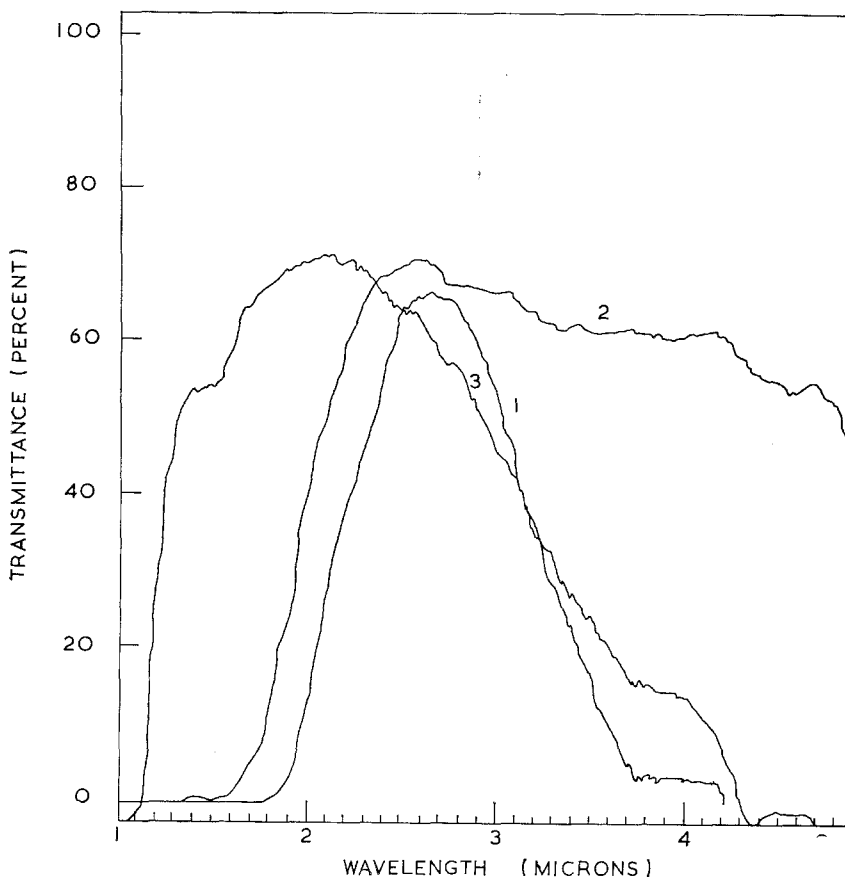


Figure 5 Relative optical transmission for different thicknesses of the same film on silica, 1, SmSb 2, PrSb and 3, SmP.

it is possible from a plot of $[(\log_{10} (I_0/I))^2$ or $[\log_{10}(I_0/I)]^{\frac{1}{2}}$ versus $h\nu$ to obtain a value for ΔE . (Note $\alpha \propto [\log_{10}(I_0/I)]$).

The $[\log_{10}(I_0/I)]^2$ versus $h\nu$ relationships obtained by plotting data from the absorption curves are reproduced in figs. 6 and 7. Extrapolation of the linear portions of the curves to $[\log_{10}(I_0/I)]^2 = 0$ was used to obtain a measure of ΔE . The $[\log_{10}(I_0/I)]^{\frac{1}{2}}$ versus $h\nu$ curves – not reproduced – did not show linear regions except in a few cases when α was very small. The values of ΔE are recorded in table I; they represent upper estimates of the energy gap of the pure compound, since impurities – and probably non-stoichiometric defects – could be expected to increase the optical energy gap (the Burstein shift).

The individual values of ΔE from this work would not be expected to show a close identity with the predictions of Sclar, but there are some interesting trends to the results worthy of comparison. The basic prediction that many of these IIIa-Vb compounds should show semiconducting characteristics is borne out. But, the antimonides which were examined also showed semiconducting characteristics contrary to the prediction of metallic character. Further, the predicted increase in the ΔE values of the energy gap with atomic number of the rare earth element in the arsenide series is not apparent. On the contrary, with the exception of GdAs,* all the arsenides showed approximately the same values of ΔE , 1 eV.

The optical studies did not reveal any evidence

TABLE I Properties of some IIIa-Vb compounds

Compound	Thermochemical data*				Vapour pressure of compound <i>P</i> atm. at 2300° K	Compound	Transmission edge μm	ΔE , energy gap in eV	
	$-\Delta H_{298}^{\circ}$ † (solid compound)	ΔH_{298}° †	$T\Delta S_{298}^{\circ}$ †	ΔG_{2300}° †				from optical measurements	predicted by Sclar [1]
CeAs	68.9	207	111	102	7×10^{-7}	ScAs‡			0.63
YAs	77.4	206	120	98.9	1×10^{-6}	YAs			0.35
LaAs	73.0	203	115	94.8	2×10^{-6}	LaAs			metallic
LuAs	75.2	204	121	93.5	2×10^{-6}	CeAs			metallic
GdAs	74.4	197	117	91.6	3×10^{-6}	PrAs‡	0.9-1.1¶	~1.0	metallic
TbAs	75.0	196	113	89	5×10^{-6}	NdAs‡	~1.1	1.04	metallic
PrAs	73.4	189	111	84	9×10^{-6}	SmAs‡	~1.1	1.03	0.5
ErAs	75.6	184	111	79.4	2×10^{-5}	(EuAs)§			
NdAs	72.9	178	110	76.4	4×10^{-5}	GdAs‡	~2.0	0.63	0.15
ScAs	65.2	183	122	74.8	4×10^{-5}	TbAs‡			0.20
DyAs	78.1	175	109	73	5×10^{-5}	DyAs‡	0.9-1.1¶	~1.0	0.25
HoAs	72.3	170	108	67.9	1×10^{-4}	HoAs‡			0.30
TmAs	72.8	159	104	62	2×10^{-4}	ErAs‡			0.35
SmAs	72.0	147	110	45.5	3×10^{-3}	TmAs‡	~1.0	1.18	0.40
YbAs	61.8	125	107	31.7	2×10^{-2}	YbAs‡	~1.1	1.02	0.45
						LuAs‡			0.50
						PrSb‡	~1.8	0.66	metallic
						SmSb‡	~2.0	0.59	metallic
						YbSb‡	~0.9¶	~1	metallic
						ScP‡			1.45
						SmP‡	~1.1	1.09	0.85
						EuP‡			0.91
						SmBi‡			metallic

*in kcal

†refers to reaction 1

‡prepared in this investigation

§found to be polyphase from X-ray studies

¶data from [27]

*estimated from absorption curves.

*Gadolinium has a complete half shell and is known to show anomalies in comparative studies of the properties of the rare earth elements and their compounds.

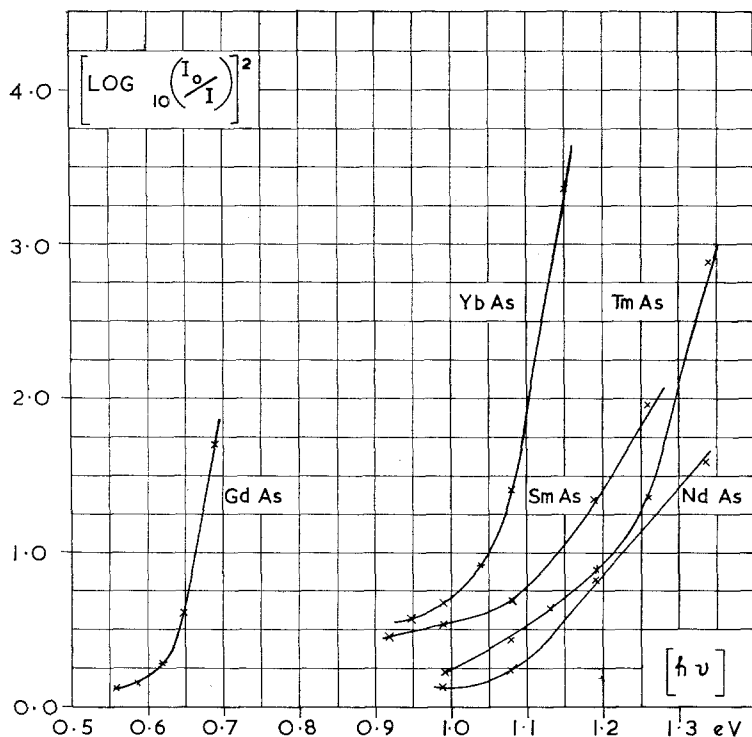


Figure 6 (Optical density)² vs. photon energy curves for NdAs, SmAs, GdAs, YbAs, TmAs.

on the intrinsic stability of the compounds. The resistance of the films to oxidation, for example, was primarily dependent on their formation conditions. Thus films of SmAs would tarnish within a few hours or not after two years depending on the sublimation or deposition conditions during preparation. It is interesting that the absorption edge of the arsenides, notably Sm, Tm and Nd, are less steep than the absorption edge of antimonides or the phosphide. This may or may not be a reflection of the non-stoichiometric aspect of the arsenide films; certainly good transmitting films of the arsenides were less readily prepared than those of the antimonides and phosphide.

3.2. Electrical Properties

The electrical properties, resistivity, Hall coefficient and mobility, were made on Van de Pauw specimens in order to establish the general characteristics of the films. These results are shown in table II. They indicate that the films have a low resistivity and high carrier concentration and are generally similar to the results obtained by Brixner on bulk samples of the arsenides, and antimonides. In view of this, detailed electrical measurements were not undertaken.

4. Conclusions

The optical properties of the IIIa-Vb compounds

TABLE II Electrical characteristics of IIIa-Vb compounds at 20° C

Sample	Compound	Resistivity ohm cm	Free electrons cm ⁻³	Mobility cm ² volt ⁻¹ sec ⁻¹
E135I	SmP	3.2×10^{-4}	7×10^{20}	27
E200	SmAs	6.8×10^{-3}	1×10^{21}	0.9
E205I	SmAs	1.8	3×10^{17}	10
E1371B	SmBi	1.2×10^{-3}	3×10^{19}	177
E137II	SmBi	1.5×10^{-3}	9×10^{18}	468
E139	PrSb	1.9×10^{-2}	4×10^{18}	9
E139II	PrSb	1.4×10^{-1}	9×10^{19}	5

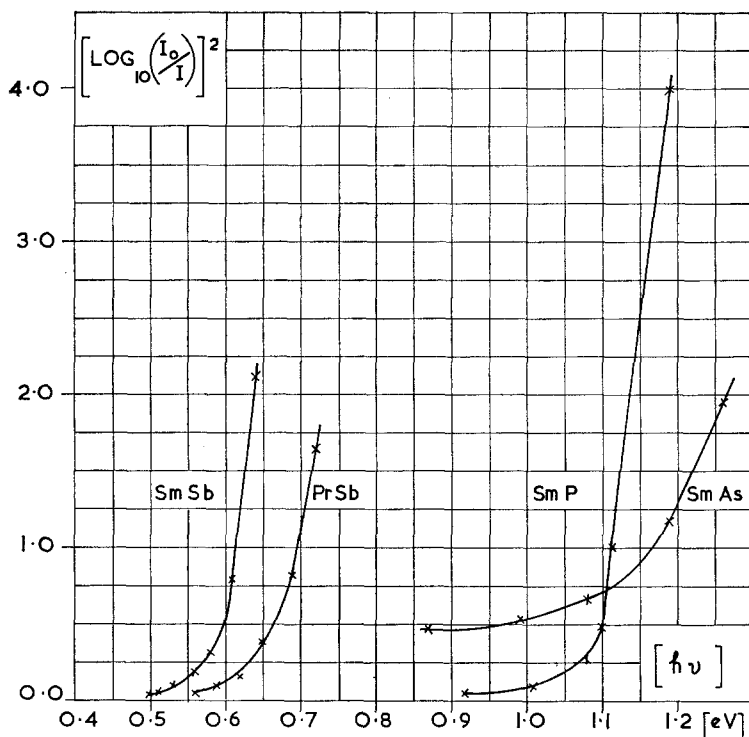


Figure 7 (Optical density)² vs. photon energy curves for SmP, SmAs, SmSb and PrSb.

which have been investigated in thin film form are characterised by an infra-red absorption edge which can be taken as evidence that the compounds are semiconductors. The arsenides antimonides and phosphide examined had relatively low energy gaps (~ 1 eV or less) the values showing no correlation with Sclar's predictions. It will require considerably more effort to establish more precise values for the energy gaps of these materials since the preparation of the IIIa-Vb compounds in a high state of purity is very difficult. However, present evidence indicates that sublimation techniques offer considerable scope as purification techniques and by better control of purity and stoichiometry it should be possible to prepare materials whose intrinsic electrical properties can be established. Since these materials have very high melting points their device applications could become important.

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