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STUDIES ON THE THERMAL DECOMPOSITION OF PHOSPHIDES AND ARSENIDES OF SILICON AND OF GERMANIUM

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ABSTRACT

The thermal decomposition in vacuum of phosphides and arsenides of silicon and germanium has been investigated using a simple set-up designed to resist the attack of the corrosive decomposition products. The phases GeP, GeAs, $SiAs_2$ and $GeAs_2$ disintegrate directly to the elements. X-ray amorphous intermediary products $Si_{\sim 5}P$ and Si_6As are formed when SiP and SiAs are heated to 940 and 930°C, respectively. The electron diffraction pattern of Si_6As is reported.

INTRODUCTION

Some vacuum decomposition experiments have been done with binary compounds from groups IV and V in the periodic system. This paper will show findings concerning the stepwise degradation. For comparison, the behaviour of elemental red phosphorus and metallic arsenic is included.

The phase diagrams of the systems Si–P, Si–As, Ge–P and Ge–As have been obtained by thermal analysis, microscopic observations and X-ray techniques. Many workers have contributed to the present appearance of these diagrams. The X-ray crystalline phases identified are: SiP, SiAs, GeP, GeAs, SiP_2, $SiAs_2$ and $GeAs_2$. Their structures are known; there are three types, all of them with a pronounced layer-like character, which form if the syntheses are carried out at not too high temperatures and under not too high pressures, i.e., below 1100°C and a few bars.

EXPERIMENTAL

The starting chemicals used were silicon, germanium and arsenic (3 N Koch-Light) and red phosphorus (99.5%), washed in boiling water and dried with acetone and ether.

The IV–V compounds to be investigated were prepared by direct combination of the elements in sealed evacuated silica tubes. In two cases, SiP and SiAs, samples

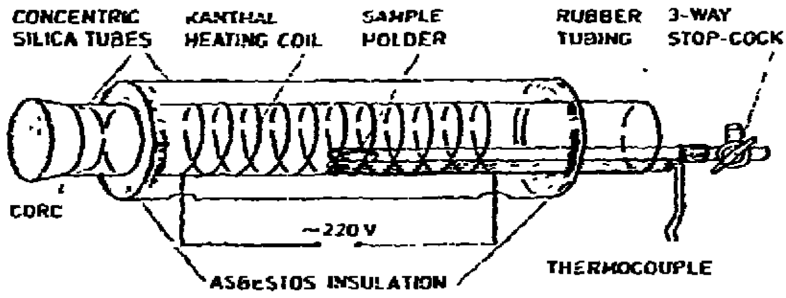

Fig. 1. Schematic silica tube furnace for experiments up to 1000°C.

were also obtained by transport reaction techniques. The reaction parameters are described in ref. 1.

The test samples as well as the decomposition products were characterized by their X-ray powder patterns obtained with a Guinier–Hägg camera using strictly monochromatized $CuK\alpha_1$ radiation. Potassium chloride ($a = 6.2930$ Å) was added to the specimens as an internal standard. Powder patterns of the IV–V compounds are listed in a previous publication[1].

An electron microscope, Philips 300 M, was used to produce electron diffraction patterns of some samples. These were internally calibrated with molybdenum trioxide and externally with polycrystalline thallium(I) chloride. The morphology of some materials was studied by scanning electron microscopy techniques.

Because of the evolution of corrosive phosphorus and arsenic vapours the present studies could not be performed in the TG instrument available. Instead, the following rather simple and resistance set-up, mainly built of transparent silica tubes (cf. Fig. 1), was used for the decomposition experiments:

A small silica tube, 10 mm long and 3 mm wide, weighing about 100 mg, is charged with a known amount of sample and plugged with silica wool. It is then placed inside a horizontal tube, 400 mm long and of 9 mm inner diameter, which is connected to a vacuum pump via a 3-way stopcock. The sample holder can thus be easily removed for weighing. The temperature of the sample is measured by means of a Pt–PtRh thermocouple enclosed in another silica tube with the same dimensions which is attached to the one previously mentioned. The position of this assembly can be adjusted inside a fourth silica tube, of 20 mm inner diameter, fitted with a Kanthal heating coil which is wound so as to give a fairly constant temperature zone of about 20 cm length. Another, wider, silica tube surrounds the whole set-up; it serves as protection and stabilizes the temperature. The construction allows a maximum temperature of around 1000°C. Its heat capacity is so small that constant temperature is attained within a few minutes.

The experiments have been carried out with a combination of visual and gravimetric observations. The onset of a pyrolysis process is simply observed if products such as phosphorus or arsenic condense in the cooler part outside the heated area, as in the classical "arsenic mirror" test by Marsh. In this way, however,

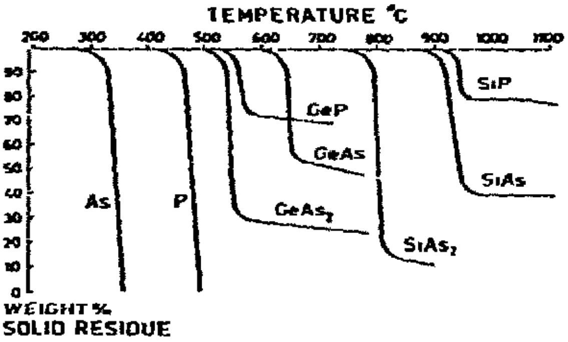

Fig. 2. Vacuum decomposition and sublimation curves for some compounds and elements from group IV and V.

at the beginning of the decomposition amounts too small to be weighed, are observed. In other words, the visual detection limit is considerably lower than the gravimetric limit. Because of this all curves in Fig. 2 start with a tail. The curves summarize the results of series of measurements performed in the following way:

The silica tube containing the sample holder, which is filled with a known amount of a compound, is evacuated and placed close to the thermocouple tube in the furnace. The temperature is slowly raised until the first sign of a condensed material is observed. Then the temperature is raised stepwise by three to five degrees. At each step the sample is kept at constant temperature for about 10 min. At the end of a run, before the sample holder is taken out for weighing, the evacuated tube is pushed some 10 cm further into the furnace, so that the deposit mirror will be transferred outwards and the tube cleaned for the next run.

Thermal analysis experiments performed in this way do not give very accurate and reproducible results. The curves in Fig. 2 typically correspond to series of some twenty measurements for each particular material studied. The shape of the curves is influenced by the heating rate (height of temperature steps) and the heating time. Thus, the temperatures of decomposition or sublimation derived from the curves are not very accurate. On the other hand, by adjusting the heating rate and heating temperatures in a suitable way, one may follow the decrease of weight rather closely.

RESULTS AND DISCUSSION

In the germanium–phosphorus system the monophosphide is the only compound reported. When heated to about 560°C this phase rapidly decomposes into the elements. The melting temperature reported[2] for germanium monophosphide heated in a closed tube is substantially higher, viz., 713°C. When the temperature is further increased above the decomposition point, there is a continuous slow decrease in weight due to evaporation of germanium. This is also obvious from the formation of a germanium mirror outside the hot region of the reaction tube.

TABLE 1

DECOMPOSITION (SUBLIMATION) TEMPERATURES (°C) OBTAINED FROM THERMAL DECOMPOSITION CURVES DETERMINED IN VACUUM

SiP	SiAs	GeP	GeAs	SiP_2	$SiAs_2$	$GeAs_2$	P	As
940	930	560	650	*	805	550	485	340

* Prepared so far single-phased in too small amounts to be decomposed.

Germanium monoarsenide behaves in a way similar as the phosphide, its decomposition temperature is 650°C. Germanium diarsenide also decomposes into the elements, at 550°C, without showing any sign of formation of an intermediary phase. Silicon diarsenide decomposes at a considerably higher temperature, 805°C, directly into the elements. The melting points observed for these compounds in sealed tubes all have higher values. For GeAs it is reported to be 737°C, for $GeAs_2$ 732°C[3] and for $SiAs_2$ 944°C[4].

For the studies of the decomposition of silicon monophosphide two different samples were used. When prepared by direct synthesis from the elements in a sealed silica tube at 1100°C, the phosphide was obtained as fairly thick platelets, while the product resulting from a reaction in a temperature gradient and with a small amount of iodine added as a transport agent gave large but extremely thin crystal flakes deposited at about 900°C. The crystals obtained by direct synthesis were found to decompose at about 880°C whereas the thin flakes did so at 940°C. In both cases the residue was found to have a composition of about Si_5P or Si_6P. The product was found to be X-ray amorphous and gave very poor electron diffraction patterns. Fritz and Berkenhoff[5] have previously reported the possible existence of a silicon phosphide phase of approximate Si_5P stoichiometry.

In a previous paper[6] the author has reported on the deterioration in air of silicon monophosphide and monoarsenide, which both undergo reactions leading to formation of elementary silicon while phosphorus and arsenic are oxidized. This effect was strikingly demonstrated by thermal degradation experiments with silicon monophosphide which had been exposed to laboratory air for some time.

Also for the silicon monoarsenide experiments two samples of different origin were used. Material synthesized from the elements at 1100°C in a sealed silica tube was found to decompose at 900°C, while the much thinner crystals obtained in a 1000 to 600°C gradient by a transport reaction with iodine disintegrated at 930°C. The residue was, however, in both cases found to have Si_6As stoichiometry. The product was found to be amorphous in the X-ray powder camera but gave a characteristic electron diffraction pattern (Table 2).

A crystalline compound with a composition of Si_6As was prepared in 1864 by Winkler[7]. He obtained needle-shaped crystals by a tedious and complex procedure. The existence of that compound has been questioned by several investigators, and attempts by the present author to repeat Winkler's experiments have been unsuccessful.

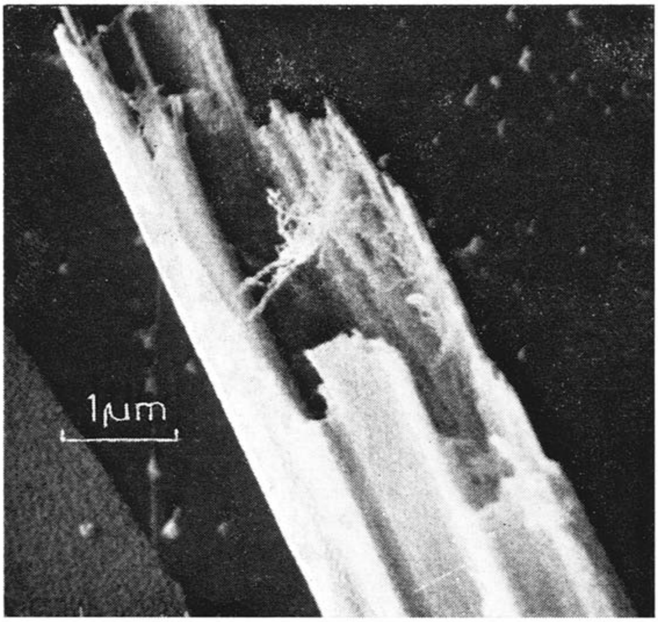

Fig. 3. A SEM-photo of an X-ray amorphous tube with a composition Si_6As.

TABLE 2

ELECTRON DIFFRACTION POWDER PATTERN OF Si_6As

Externally calibrated with TlCl and internally with MoO_3.

d_{obs}(Å)	I_{obs}	d_{obs}(Å)	I_{obs}
3.047	v st	1.211	m
2.490	v w	1.190	v w
2.071	v w	1.078	m
1.896	st	1.018	w
1.594	st	0.935	v w
1.524	m	0.899	v w
1.323	w		

However, it is highly doubtful whether it is possible to reproduce the conditions of the experiment performed more than a century ago.

Transmission electron microscope pictures of the decomposition product (Si_6As) could be interpreted as arising from tube-shaped material. This habitus has been confirmed by pictures taken in a scanning electron microscope. These show long, thin-walled tubes with diameters up to a few microns (Fig. 3). In this connection it is of interest to observe that the starting material of the decomposition experiment, silicon monoarsenide, has a pronounced layer structure, which may be described as composed of a central silicon network covered on both sides with arsenic. This is a fact which invites speculation, but any serious attempt to explain the habitus of Si_6As would require additional experimental evidence.

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