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TWO THERMOANALYTICAL METHODS FOR THE DETERMINATION OF GeO_2 ON GERMANIUM POWDERS

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Two thermoanalytical methods have been developed for determining GeO_2 on the surface of germanium. Possible errors and attainable accuracies are discussed. Both methods give the same results within the limits of error. The applicability of the determination is demonstrated in two ways:

1) in connection with the growth of the oxide layer in air,
2) in connection with the dissolution of the oxide layer in water.

The oxidation at room temperature proceeds at a practically constant velocity; the equilibrium thickness of the oxide layer on crystalline Ge powder in water proved to be about 5 Å.

Investigation of the physical and electrochemical properties of elementary germanium encounters difficulties due to the fact that the surface of germanium is oxidized fairly easily, and the oxide is not always uniform. An amorphous and two crystalline forms of the oxide of tetravalent germanium can be prepared (most easily the hexagonal form of the quartz type though this is thermodynamically stable only above 1033°) [1, 2], and there is also a germanium(II) oxide. All these oxides may be formed, in part as hydrates, on the surface of germanium in contact with moisture, liquid water or aqueous solutions. The complex and ill-defined character of the oxide layer affects the properties of germanium semiconductor materials.

It is therefore of importance to know the composition and structure of this layer to interpret the electric or electrochemical behaviour of oxide-coated germanium. The coating consists in most cases of hexagonal GeO_2.

There are various methods for establishing the composition or crystal structure of such layers (e.g. X-ray and low-energy electron diffraction). The results of these investigations can be advantageously supplemented by the quantitative determination of the oxide, using thermoanalytical methods. This determination also provides an independent method of following some processes, such as the oxidative corrosion in air, or oxidation and dissolution in aqueous solution.

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Experimental

Germanium powder was prepared from a Hoboken monocrystal by dry grinding in an agate mill, and was stored in ground-glass stoppered bottles. Characteristics of the original ingot:

type: n
specific resistance: 0.061 – 0.086 ohm · m
dislocation density: 3500 – 3600 cm^{-2}

The powder consisted of particles of 1 – 10 μm in diameter. The specific surface area was 0.6 ± 0.1 m^2/g, as measured by a dynamic nitrogen desorption method.

Gases. During the thermoanalytical experiments hydrogen was used as reducing agent, and nitrogen and argon as inert atmospheres. Argon was of purity "F", the two other gases "once purified". Their water contents were frozen out in two steps with liquid air. The oxygen contents of nitrogen and argon could not be completely removed by passing the gases over well-dispersed, red-hot copper. The small residual oxygen content was therefore determined separately with manganous oxide.

The thermobalance was a MOM derivatograph with scale reading and an accuracy of about ±0.1 mg. The error caused by gas expansion was corrected. The temperature scale was tested at the transition point of quartz in every case. A temperature accuracy of 10° was found sufficient. The furnace of the instrument was modified [3] in order to provide the possibility of using controlled atmospheres in the surroundings of the specimen.

Principle and sensitivity of the oxide determinations

For the determination of the dioxide the chemistry of germanium offers two reactions of unambiguous stoichiometry that yield gaseous products of measurable quantity in well-defined temperature intervals. The one is the reduction of the oxide by hydrogen:

$$\begin{array}{rcccc} & GeO_2(s) + & 2H_2(g) = & Ge(s) + & 2H_2O(g) \\ M = & 104.6 & 4.0 & 72.6 & 36.0 \end{array} \qquad (1)$$

while the other is the reaction:

$$\begin{array}{rccc} & Ge(s) + & GeO_2(s) = & 2GeO(g) \\ M = & 72.6 & 104.6 & 177.2 \end{array} \qquad (2)$$

being carried out in inert atmospheres. The latter is known as gas etching in semi-conductor technology.

In reaction (1), occurring in the interval 400 – 600°, the oxygen content of the dioxide leaves the sample in the form of water vapour. In reaction (2) monoxide molecules are evolved at about 700 – 900°, two GeO corresponding to one GeO_2 in the sample. Both reactions take place quantitatively in gas streaming at a flow rate of 100 – 200 cm^3/min and at heating rates of 2 – 5°/min.

According to the indicated stoichiometric weight ratios, the measurable weight loss in reaction (1) is 0.306 times and in reaction (2) 1.70 times the weight of the dioxide content, that is the sensitivity of the second method is 5.55 times greater.

The absolute sensitivity of either method is determined by the sensitivity of the balance. With the given balance sensitivity of 0.1 mg it was possible to observe at best 0.33 mg dioxide in method (1) and 0.06 mg dioxide in method (2).

The relative sensitivity also depends on the GeO_2/Ge ratio of the sample.

An oxide content of 1 % of the usual sample quantity of 1.0 g can be determined with a sensitivity of 0.33 mg (3.3 %) by the first method, and with a sensitivity of 0.06 mg (0.6 %) by the second one. The sensitivity and the accuracy can be increased, of course, by improving the balance properties.

Possible errors of the determinations

In the following only those errors will be dealt with which can occur specifically during the determination of germanium dioxide.

Evaporation of germanium. According to the literature the sublimation pressure of solid germanium [4] at 900° is $2.2 \cdot 10^{-7}$ torr, and the vapour tension of the liquid at 1000° is $4.2 \cdot 10^{-6}$ torr. Accordingly, under the present conditions at 1000° a maximum weight loss of $5 \cdot 10^{-10}$ g germanium per minute can occur, which is negligible.

Formation of germanes by reduction. All necessary data for the calculation of the chemical equilibria were found only for monogermane, GeH_4 [4–9]. The equilibrium constants of the formation:

$$Ge(s) + 2\,H_2(g) = GeH_4(g) \qquad (3)$$

are given in Table 1.

Table 1

Temperature, °K	*Equilibrium constant*
298	$1.0 \cdot 10^{-20}$
1173	$9.5 \cdot 10^{-11}$

The increase of temperature favours the formation of monogermane (the formation being exothermic with a standard heat of reaction of 21.7 kcal/mole [5]). At the relatively favourable temperature of 900° the equilibrium pressure of the germane formed (at the prevailing hydrogen partial pressure of 0.75 atm.) is $5.35 \cdot 10^{-11}$ atm.

Accordingly, in the event of 130 cm^3 of gas passing over the sample per min, only $4.5 \cdot 10^{-8}$ mg germanium can depart as monogermane per hour.

As the germane homologues containing more hydrogen are still less stable, it can be stated that germanes are not formed in measurable quantities at the temperatures in question.

In the presence of nitrogen *the formation of a germanium–nitrogen compound* might also be assumed. A compound of composition Ge_3N_4 is known, and two references were found in the literature. One of these concerns the standard heat of formation of solid Ge_3H_4 [4]:

$$\Delta H^{*}_{f,298} = -15.1 \text{ kcal/mole}$$

The standard free enthalpy of formation is probably also negative.

The other reference is in the compilation of Samsonov [10]. Ge_3N_4 is formed from germanium powder and ammonia at 700–850°, or from germanium dioxide and ammonia at 750–850°, and the product is stable in air or water. The formation from the elements is not mentioned, though otherwise fairly complete particulars are given.

The authors of the present paper have not observed any specific weight change in nitrogen. In their opinion, the formation of germanium nitride is thermodynamically possible in the interval 0–1000°, but the reaction is kinetically hindered in the case of elementary germanium and molecular nitrogen as starting components.

The oxidation of germanium. The undesirable oxidation of germanium can be caused by

1. the oxygen content of the gases
2. the water content of the gases, and
3. the water content of the sample.

The water content can oxidize germanium in the reaction:

$$Ge\ (s) + 2\,H_2O = GeO\begin{pmatrix} s \\ g \end{pmatrix} + H_2\ (g) \tag{4}$$

As observed earlier, reaction (4) causes a measurable weight increase from about 200 to 300°. A weight loss is recorded at about 750–800°, due to the sublimation of the monoxide, if the ratio oxygen/water vapour is not great enough.

Of these three factors only the first need be taken into consideration. The possible water content of the gases can be decreased sufficiently by freezing out with liquid air in two steps. The quantity of water bound to the oxidized germanium surface can be only of the magnitude of 0.1% even when the oxide content amounts to 10%. By elevating the temperature the major part of this water content goes off below the temperatures used for the oxide determinations.

The oxygen content of the hydrogen was negligible. The reaction of germanium with oxygen is a process accelerating characteristically at about 500°. Such a disturbing effect was never observed. It can therefore be concluded that the reductive oxide determination was not disturbed by any oxygen content in the gases used.

The other method of determination requires an inert gas. In general nitrogen, and occasionally argon, were used. Both gases (even the argon of grade "F") contained oxygen. Unfortunately, it was not possible to remove the oxygen traces sufficiently in the usual manner by passing the gases through heated, finely-dispersed copper. The outcoming gases contained oxygen amounting to about 0.01%.

The traces of oxygen were determined by the oxidation of manganous oxide prepared in situ in the crucible of the furnace from manganese carbonate. The manganous oxide formed at about 400° yields manganic oxide at approx. 600° with a yield of practically 100%. In one of the nitrogen charges an oxygen content of $2.4 \cdot 10^{-3}\%$ by volume was found after oxygen "removal" by copper.

Let us examine the effect of the oxygen impurity on the weight of the sample, taking as worst an oxygen content of 0.01% in the gas of 1 atm, which corresponds to a partial pressure of 10^{-4} atm.

The germanium sample can be partially oxidized in the reactions:

$$Ge\,(s) + 1/2\,O_2\,(g) = GeO\,(g) \tag{5}$$

$$Ge\,(s) + O_2\,(g) = GeO_2(g) \tag{6}$$

at the usual temperature of 860° of the oxide determinations (2).

At this temperature the equilibrium constant of reaction (6) is

$$K_{1133}^{(6)} = 1.25 \cdot 10^{15} \text{ [4, 11]}$$

and it is possible to give the equilibrium oxygen pressure, too:

$$p_{O_2} = 0.8 \cdot 10^{-15} \text{ atm.}$$

This means that if the pressure of oxygen rises above the given value and the attainment of equilibrium is not hindered, oxidation advances until the partial pressure of oxygen decreases below $0.8 \cdot 10^{-15}$ atm.

As the formation of monoxide is also favoured in the vicinity of 860°, it is reasonable to consider the equilibrium of the reaction:

$$1/2\,GeO_2 + 1/2\,Ge = GeO \tag{2/b}$$

which is the combination of reactions (5) and (6). The resulting equilibrium can be calculated in different ways, the present one being the simplest. The equilibrium constant of reaction (2/b) is:

$$K_{1133}^{(2/b)} = 3.1 \cdot 10^{-2} \text{ atm} = p_{GeO}$$

and does not depend on the pressure of oxygen. It can be concluded that

if Ge and GeO_2 are present simultaneously, or

if, in the absence of GeO_2, there is in the gas an oxygen partial pressure of at least $0.8 \cdot 10^{-15}$ atm, and

if there is no kinetic hindrance, the formation of gaseous monoxide will continue until the pressure of the monoxide reaches $3.1 \cdot 10^{-2}$ atm. If the monoxide is removed continuously, the reaction proceeds as long as germanium is present in the system.

To summarize these conclusions, the whole of the oxygen contamination reacts with germanium and leaves as gaseous monoxide. Under our usual experimental conditions an oxygen content of 0.01% may cause a perceptible weight loss of 0.02 mg/min. In one case the results had to be corrected for this reason.

Identification of the main reactions

Reductive oxide determination

The equilibrium constants of the reduction:

$$GeO_2 + 2\,H_2 = Ge + 2\,H_2O \qquad (1)$$

according to [4, 5, 10, 12] are tabulated in Table 2.

Table 2

Temperature, °C	Equilibrium constant $K^{(1)}$
25	10^{-7}
430	$8 \cdot 10^{-2}$
630	0.69

On raising the temperature, the equilibrium shifts more and more to the right hand side of Eq. (1). Under our gas stream conditions at 550° a maximum, of about 5 mg, and at 630° 6.5 mg water vapour may leave the crucible per minute for the limiting case of chemical equilibrium conditions at all times, and of complete exchange between the gas and the solid.

The reduction started at about 400° and 0.6 mg of water per minute was found to leave at 550°. The difference between the observed and calculated equilibrium values can be easily accounted for by assuming non-equilibrium conditions, caused mainly by the insufficient exchange between the streaming gas and the fine powder layer which had a thickness of several millimeters.

Oxide determination in inert gas

For the reaction:

$$GeO\,(g) = 1/2\,Ge\,(s) + 1/2\,GeO_2\,(s) \qquad (2/c)$$

which is the reverse of (2/b), the following polynomial expression can be found in the book of Kubashewsky [4]:

$$\Delta G_T^* = -54600 - 6.9\,T \log T + 62.0\,T \pm 4 \cdot 10^3 \text{ cal}$$

The calculated equilibrium data for reaction (2/b) are listed in Table 3.

Table 3

Temperature, °K	ΔG_T^*, kcal/mole	Equilibrium constant $K_T^{(2/b)}$
850	19.3 ± 4	about $1.1 \cdot 10^{-5}$
950	15.2 ± 4	about $3.2 \cdot 10^{-4}$
1150	7.6 ± 4	about $3.6 \cdot 10^{-2}$

The given limit error of the polynomial expression is rather high. For example the variation of the equilibrium constant at 1150 K is more than two orders of magnitude, as can be seen in Table 4. It must be added that the authors of the original paper [11] give the polynomial function only for the interval of 298–860 K. Thus, the extrapolation to higher temperatures can cause an additional error. This latter is probably not too considerable because the plot $\Delta G_T^* - T$ in the given interval is reasonably linear.

Table 4

	$K_T^{(2/b)}$	if ΔG_T^*
minimum value	$6.3 \cdot 10^{-3}$	11.6 kcal/mole
mean value	$3.6 \cdot 10^{-2}$	7.6 kcal/mole
maximum value	$2.1 \cdot 10^{-1}$	3.6 kcal/mole

The process of the oxide determination on the basis of reaction (2) starts in general at about 920 K and becomes markedly faster in the vicinity of 970 K.

With the use of the mean equilibrium values at 1150 K an evolution of monoxide of 4.4 mg/min can be derived, if the velocity of the gas stream at 1 atm is 130 cm^3/min. The measured value is about 0.3 mg/min, the deviation again being ascribed to non-equilibrium conditions.

Results. Calibration and application of the oxide determination

Calibration

The methods were checked by oxidizing oxide-free germanium samples in a controlled manner. The oxide-coated germanium powder placed in the sample holder of the thermobalance was reduced in hydrogen at 500° until free of oxide.

By passing dry air at about 640° through the system for a period established in preliminary experiments, dioxide was formed at the surface, and its quantity, was measured exactly by the oxidation step on the chart. The oxide determination using method (1) or (2) followed immediately afterwards. The three operation steps performed one after the other were recorded on the same chart (Fig. 1). In this way both the weight of the oxide-free sample and the oxide content of

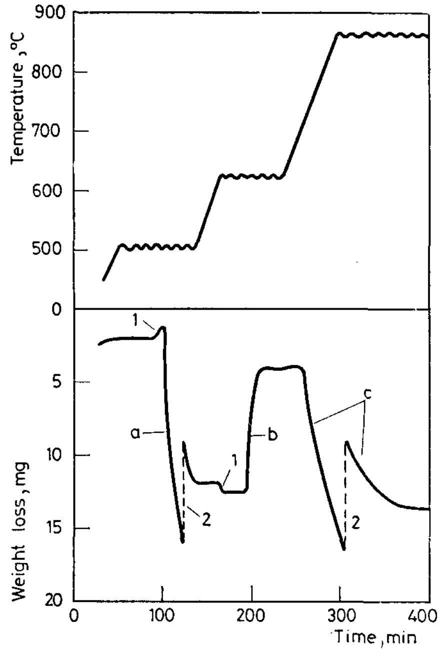

Fig. 1. Thermal curve of a GeO_2 analysis. a: reduction of the original GeO_2 content of the sample by H_2; b: oxidation by O_2; c: reaction $Ge + GeO_2 \rightarrow 2\,GeO$ in inert gas. 1: change of the gas stream, 2: change of weight on the balance. Sample: 0.5 g Ge powder with an original GeO_2 content of 13.0%

Table 5

Oxide formed in the crucible, mg	Oxide found, mg	Error, mg	Method
50.0	45.5	−4.5	inert gas (2)
26.6	26.6	<0.05	inert gas (2)
18.6	18.2	−0.4	inert gas (2)
15.0	15.2	+0.2	inert gas (2)
9.65	9.45	−0.2	inert gas (2)
34.8	35.1	+0.3	H_2 (1)
15.2	15.2	<0.05	H_2 (1)

Comments on Table 5:

1. The error of the data "oxide formed in the crucible" is at most ±0.3 mg.
2. When the reduction was not complete, the "oxide formed in the crucible" includes the residual part of the original oxide quantity too.
3. It can be seen that both methods give correct and equal results, when the amount of oxide does not exceed 35 mg.

the powder prepared for the analysis were known with a small error, which was given on the whole only by the balance reproducibility. External circumstances could certainly not alter the quantity of oxide before the analysis.

Samples of about 1.0 g each, with dioxide contents of 3 – 45 wt.% were prepared and analysed. Typical results of the determinations are shown in Table 5.

The surface oxidation of germanium during storage

It follows from the given sensitivity of the balance used that the method can be applied only in the case of finely powdered samples bearing a fairly thick oxide layer. The first germanium charge, the results of which could be evaluated, was produced by moist grinding. It contained particles 1 – 10 μm in diameter and had an oxide content of 1 – 2%. It was found impossible to increase the amount of oxide beyond this value by either dry or moist treatments below 100°.

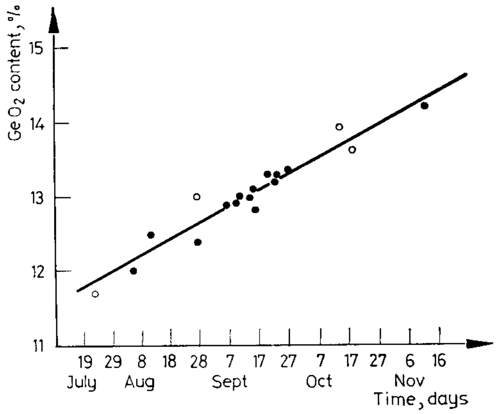

Fig. 2. The change of the GeO$_2$ content of a germanium powder during storage. ● by reduction; ○ by the inert gas method

A germanium powder examined later was produced by dry grinding (one year before analysis). It contained similar particles in the range of 1 – 10 μm. It was assumed to have an oxide content of 1 – 2%, similarly to the first portion, shortly after preparation, but the analysis gave an oxide content of about 12%. This was surprising at first, but it was then found that the oxide layer increases in thickness with time, slowly but continuously.

The change in the oxide content of this germanium powder (stored in air at room temperature) is demonstrated in Fig. 2. The oxide content was generally determined by the reduction method, but in some cases by the inert gas method. Fig. 2 shows that the oxide content related to the sample weight increased by

0.6% per month under the given conditions. This rate of increase was constant in the time interval investigated and was obviously characteristic of the specific surface area and the storage conditions.

In the literature no reference was found relating to such a spontaneous, constant-rate room-temperature oxidation of germanium.

The assumption of a nearly constant oxidation rate for longer periods needs further examination, of course. The fact that the oxidation does not slow down can be explained in the following manner. Under given external conditions the rate of growth of the oxide layer can be influenced by two factors, namely the change in binding strength of the oxygen atoms and the change of rate of diffusion (of Ge, O_2 or Ge and O_2 in the solid oxide phase) as a function of the thickness of the oxide layer.

The properties of the oxide interface, which may be assumed to have a thickness of 1 or 2 atomic layers, surely differ from those of the bulk of the oxide. The results of Fig. 2, however, point to the growth of a layer which has a considerable thickness.* The rate of diffusion, which controls the oxidation, may decrease at most proportionally to the thickness of the surface layer, but as the plot shows the decrease proves quite infinitesimal.

In order to explain this phenomenon it must be assumed that the outer layers are porous or their defect density is greater, when the diffusion coefficient can be much greater than in the inner, more regular and more compact layers.

Dissolution of the oxide layer

It has been a long-standing problem of the authors as to how the surface layer of germanium is altered when in contact with aqueous solutions. The effect of storage in distilled water and electrochemical polarization in several solutions have been investigated previously [13].

According to this work the thickness of the oxide layer on germanium plates after 0.5 + 2 minutes of etching in CP−4 A at 70° was 23 Å (by ellipsometry). This thickness increased to about 60 Å in the first three days but afterwards did not alter considerably.

The surprisingly thick oxide layer found on a germanium powder after 1 year of storage (see the previous section) raised the question of solubility. In order to settle the question, 10 g of a germanium powder with an oxide content of 14%

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* Knowing the specific surface area, the thickness of the oxide layer can be estimated. The surface area of the germanium powder was $0.6\ m^2/g$. The oxide content of the sample at the end of October, 1971, for example, was 14%. From the normal density of hexagonal germanium dioxide ($4.2\ g/cm^3$), assuming cubic particles of the same size, an average thickness of 550 Å can be derived. The change in thickness per month in this run was about 2.0 Å. If the thickness of one GeO_2 molecule is taken as roughly 3 Å [14], the thickness of 550 Å given above corresponds to 180 molecules of GeO_2 perpendicular to the surface, with the uncertainty of the specific surface area determination and the assumptions made above. This uncertainty can be estimated as ±25%.

was stirred in 500 cm^3 of distilled water for 4 hours, the liquid was centrifuged for 5 minutes at 7000 rpm, and after decantation the wet powder was dried. Its oxide content measured by method (2) proved to be 0.26%.

The specific surface area of the powder undoubtedly increased during the aqueous treatment. By microscopic study the degree of dispersion was found rather homogeneous, and the particle size was around 1 μm. From the specific surface area of 1.2 m^2/g thus estimated, a thickness of about 5 Å was derived.

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Résumé — Deux méthodes d'analyse thermique ont été développées pour déterminer les quantités de GeO_2 présentes à la surface du germanium. Les erreurs possibles et la précision que l'on peut atteindre sont discutées. Les deux méthodes donnent les mêmes résultats dans les limites d'erreur. Leur applicabilité est illustrée par des études sur l'épaississement de la couche d'oxyde dans l'air et sur la dissolution de la couche d'oxyde dans l'eau.

A la température ambiante, l'oxydation progresse à une vitesse pratiquement constante. L'épaisseur stationnaire de la couche d'oxyde est de 5 Å environ, d'après les mesures.

Zusammenfassung — Zwei Methoden der Thermoanalyse wurden zur Bestimmung der Mengen von GeO_2 an der Oberfläche von Germanium entwickelt. Die möglichen Fehler und die zu erreichende Genauigkeit werden erörtert. Die beiden Methoden ergeben innerhalb der Fehlergrenzen dieselben Resultate. Die Anwendbarkeit der Methoden wird an Hand von Studien betreffs

1. der Verbreitung der Oxidschicht in Luft und
2. der Lösung der Oxidschicht in Wasser veranschaulicht.

Bei Zimmertemperatur erfolgt das Fortschreiten der Oxidierung bei praktisch gleichbleibender Geschwindigkeit. Nach den Messungen beträgt die stationäre Stärke der Oxidschicht etwa 5 Å.

Резюме — Разработано два термоаналитических метода для определения количества GeO_2 на поверхности германия. Оба метода дали одинаковые результаты в пределах ошибки. Применимость определения показана в двух направлениях:

1. в связи с увеличением окиси на воздухе
2. в связи с растворением слоя окиси в воде.

Окисление при комнатной темпеpетуре происходит практически с постоянной скоростью. Найдено, что в воде равновесная толщина окиси на поверхности кристаллического порошка германия около 5 Å.