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A QUANTITATIVE STUDY ON THE GROWTH OF SILICON WHISKERS FROM SILANE AND GERMANIUM WHISKERS FROM GERMANE*

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The impurity-induced nucleation and the kinetics of the growth of filamentary crystals of silicon and germanium from silane and germane respectively have been studied in a closed system. Silicon whiskers were grown on heated substrates at temperatures between 550 and 900 °C, germanium whiskers at temperatures between 300 and 500 °C, both at hydride pressures between 5 and 100 Torr, and with Au as impurity. Whisker growth was also obtained with Ag, Cu, Ni and Pd, but not with In, Sn and Bi. The rates of growth of the whiskers in the length direction increase with increasing substrate temperature and hydride pressure, and are of the order of a hundred times higher than the rates of thickness growth of whiskers and substrate. As compared with the non-impurity aided deposition of Si and Ge from the hydrides, where there is an exponential relation between deposition rate and reciprocal temperature, the effect of the growth stimulus at the tip is reflected in a decrease of the activation energy and an increase in the pre-exponential factor. In terms of the VLS mechanism the catalyzed decomposition reaction at the V–L interface is the rate-controlling step.

1. Introduction

The pronounced non-equilibrium form of filamentary crystals, e.g. single-crystalline whiskers and polycrystalline fibres, is evidently caused by an enforced anisotropy in growth kinetics. In principle there are the following explanations for the difference in growth behaviour as compared with the growth of "normal" crystals. First the growth in directions perpendicular to the length direction of the filamentary crystals may be retarded or blocked, the growth in the length direction being "normal". Secondly, the growth in the length direction may be stimulated, with "normal" growth in the perpendicular directions. A combination of both may also occur: retardation or blocking in the perpendicular directions together with stimulation of growth in length. The word "normal" refers here to crystals and growth rates obtained in the absence of the retarding, blocking or stimulating effects.

The first possibility mentioned, in the form of retardation or blocking of growth by preferential adsorption of impurities on the side planes of the filamentary crystals^{1}), was introduced to explain whisker growth by electrolysis^{2}). One would then expect growth rates in the length direction of the whiskers of the same order as in normal conditions. For growth of whiskers from the vapour phase, however, this is generally not found.

Known examples of the second possibility, stimulation of growth at the tip, are enhancement by the presence of suitably oriented defects, especially axial screw dislocations^{3}), or by the presence of a foreign solid particle^{4}), a "Vapour–Solid–Solid" mechanism, or of a liquid layer, the Vapour–Liquid–Solid mechanism^{5}). The screw dislocation mechanism was assumed to be valid in a number of cases where filamentary metal crystals grow from their own vapour, e.g. mercury^{6}) and potassium^{7}). An additional feature of the growth of these whiskers is that the growth rates mostly exceed the direct impingement rates by orders of magnitude, which is explained by the supply of material to the tip by diffusion along the sides$^{6-8}$). The main objection to the general relevancy of the screw dislocation mechanism is that such defects could be detected as a rule only in a small percentage of the whiskers.

In whisker growth by chemical vapour deposition the rates are usually orders of magnitude smaller than those corresponding to the impingement, but much

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larger than for growth of normal crystals. Here the VLS mechanism is possibly of general relevancy. Mostly the processes of diffusion in the vapour phase V and through the liquid L may be excluded as rate-controlling, and the growth rate will be governed either by the crystallization at the L–S interface or by the reaction at the V–L interface. Mutaftschiev et al.[9]) ascribe the enhancement of the growth at the tip with respect to normal (Vapour–Solid) growth primarily to the lowering of the supersaturation required for crystallization at the L–S interface. However, if the chemical reaction or decomposition of vapours is rate-controlling, a catalyzing effect of the liquid alloy at the V–L interface could be the primary factor in the enhancement of growth.

With a VSS mechanism one can also explain locally stimulated growth by a catalytically enhanced chemical reaction, cf. the growth of carbon fibres from acetylene with nickel particles[10]).

Amongst the numerous papers on whisker growth (for reviews cf. ref. 11) the number of quantitative studies is relatively small. The reason for this is probably that systems permitting microscopic observation and measurement of relevant parameters during the growth are usually not suited for the production of perfect whiskers. This paper describes the growth of silicon and germanium whiskers, by decomposition of silane and germane respectively on impurity-seeded heated substrates. The growth of silicon whiskers by the reduction of silicon chloride with hydrogen at temperatures around 1000 °C, is the well-known example of VLS growth studied by Wagner et al.[5]), and also later on by James et al.[12]) and Filby et al.[13]). When hydrides are used simpler types of decomposition reactions take place at lower temperatures, facilitating microscopic observation and quantitative studies.

2. Experimental procedure

The experiments were performed in a closed pyrex glass system with a total volume of about 300 cm^3 (fig. 1). The substrates, mostly single crystals of the elements to be grown in whisker form or occasionally also tantalum strips, were placed in an optical cell to permit microscopic observation of the growth and pyrometric registration of the substrate temperature (Ircon Radiation Thermometer, Model 300 C). The silicon and germanium crystals (dimensions $10 \times 3 \times 1$ mm), mechanically polished and chemically cleaned, were clamped in tantalum clips connected to molybdenum leads. The substrates were heated by direct electric current. The pyrometric temperature measurements were calibrated with thermocouples attached to the substrate surface and by melting alloys with fixed melting points.

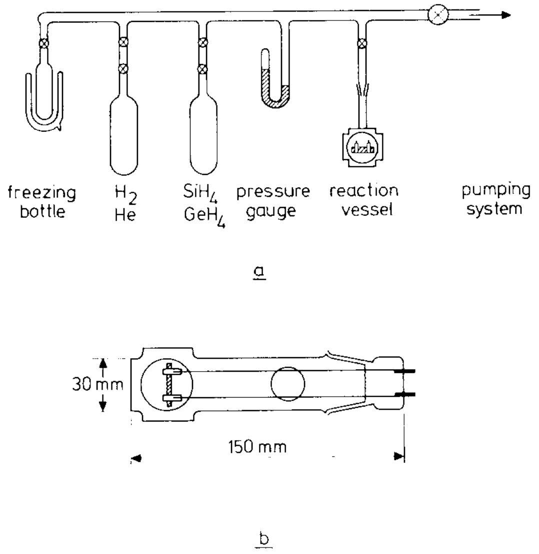


Fig. 1. Diagram of the experimental arrangement (a) and top view of reaction vessel (b).

Prior to each growth experiment the system was evacuated by means of a mercury diffusion pump to a pressure of about 10^{-6} Torr. The substrates were heated to the desired temperature in hydrogen or helium, usually at a pressure of 10 Torr, in order to avoid rapid cooling upon addition of the hydrides. The total vapour pressure of ambient and hydrides in the system was measured with a mercury manometer or with a MacLeod. The system was provided with a freezing bottle in which the hydrides were preserved prior to the addition, and which was also used to determine the amount of unconsumed hydride after an experiment.

3. Experimental results

3.1. SILICON FROM SILANE

3.1.1. *Nucleation of filamentary crystals*

On the substrates impurities were placed, mostly in the form of particles (diameter 10–100 μm, purity

99.99%) or clusters of particles, and occasionally in the form of evaporated spots or films. As in Wagner's study of the growth of silicon whiskers from $SiCl_4$ and H_2[5]), by far the best results were obtained with Au as agent, in our case at temperatures between 550 and 900 °C. At lower temperatures the gold becomes overgrown by silicon, at higher temperatures the growth takes place "explosively", in the form of sheets, spirals and other forms of a rather spongy appearance. In the intermediate temperature range below a partial silane pressure, p_{min}, only overgrowth takes place, and above a pressure, p_{max}, the growth is again explosive. The values of p_{min} and p_{max} at 600 °C are about 5 and 100 Torr, and at 800 °C about 20 and 50 Torr respectively. Though the eutectic temperature in the Au–Si system is as low as 370 °C, probably owing to the presence of oxide layers on the silicon substrate, liquid formation mostly does not occur with Si from the substrate but only by reaction with the silane. Occasionally, at temperatures above 900 °C, the gold particles transform completely into a liquid droplet by alloying with the substrate.

The observations made after addition of the silane to the reaction vessel are further essentially the same for tantalum or silicon substrates with solid gold particles, spots or films, or silicon substrates with liquid alloy droplets. At the surface of the solid particles decomposition takes place accompanied by the formation of a liquid phase, which later on gets covered by a solid porous crust of silicon. After a time, which is shorter for higher temperature and higher silane pressure, filamentary crystals grow, most of them with the same diameter, independent of the size of the gold particles. The diameter, d_0, as measured at the tip of whiskers stopped in their growth shortly after the start (total length $\leq$ 100 μm), increases with increasing substrate temperature, T_s, and initial silane pressure, p_0. For p_0 varying from 20 to 60 Torr and for T_s = 650 °C, the diameter d_0 increases from 0.5 to 1.0 μm, and for T_s = 850 °C from 0.7 to 1.6 μm respectively.

In the case of liquid alloy droplets (diameter $\geq$ 50 μm) an increase in droplet size is observed upon addition of the silane; the outer layer of the droplets gets enriched in silicon and a solid porous crust is formed. Thereafter a bunch of whiskers sprouts out, the diameters of which are similar to those found for the growth on the solid particles.

Filamentary growth was also obtained with Ag, Cu, Ni and Pd, at substrate temperatures of about 800 °C. At substrate temperatures up to about 800 °C no filamentary growth was observed with In, Sn and Bi. Apparently some deposition of Si takes place on the surface of the liquid droplets, in the form of separated solid particles, but, in the same conditions of T_s and p_0, at a rate much lower than with Au. For a discussion of the impurity influence see section 4.1.

3.1.2. *Growth rates of filamentary crystals*

The quantitative measurements during the growth of the whiskers comprised the length, l, of the whiskers as a function of the silane pressure, p, and substrate temperature, T_s. Given identical conditions of p and T_s reproducible growth curves, l versus time t, were obtained. In our system changes in the growth direction, such as bending and kinking, often occur. As is illustrated for a whisker in fig. 2, the discontinuities in growth direction are not reflected in discontinuities in the growth curves.

In fig. 3 we have plotted average growth curves for T_s = 650 °C and for initial silane pressures, p_0, varying from 10 to 80 Torr. The decrease in the growth rate with time may be caused by two effects, namely the decrease in temperature with increasing distance of the tip to the heated substrate, and the decrease of the silane pressure in the closed system by the decomposition. As the decrease in silane pressure during an experiment is relatively small, the first effect is dominant. Estimates of the temperature gradient in the neighbourhood of the substrate are given in section 3.3. To determine the influence of temperature and silane pressure, values of $\dot{l}_0$, defined as the growth rate, $\dot{l}$, at $t = 0$ or $l = 0$, were derived from the growth curves by plotting ln $\dot{l}$ versus t or l, both results being the same within the limits of experimental accuracy (± 20%). In fig. 4a the results for two temperatures are plotted as a function of initial silane pressure p_0, added to a hydrogen ambient of 10 Torr pressure. The growth rate of the whiskers increases with increasing temperature and with increasing silane pressure. At a given substrate temperature, the rates appear to be proportional to the silane pressure up to pressures of about 30 Torr; at higher pressures the rate increases relatively more, ending up in the explosive growth mentioned in section 3.1.1.

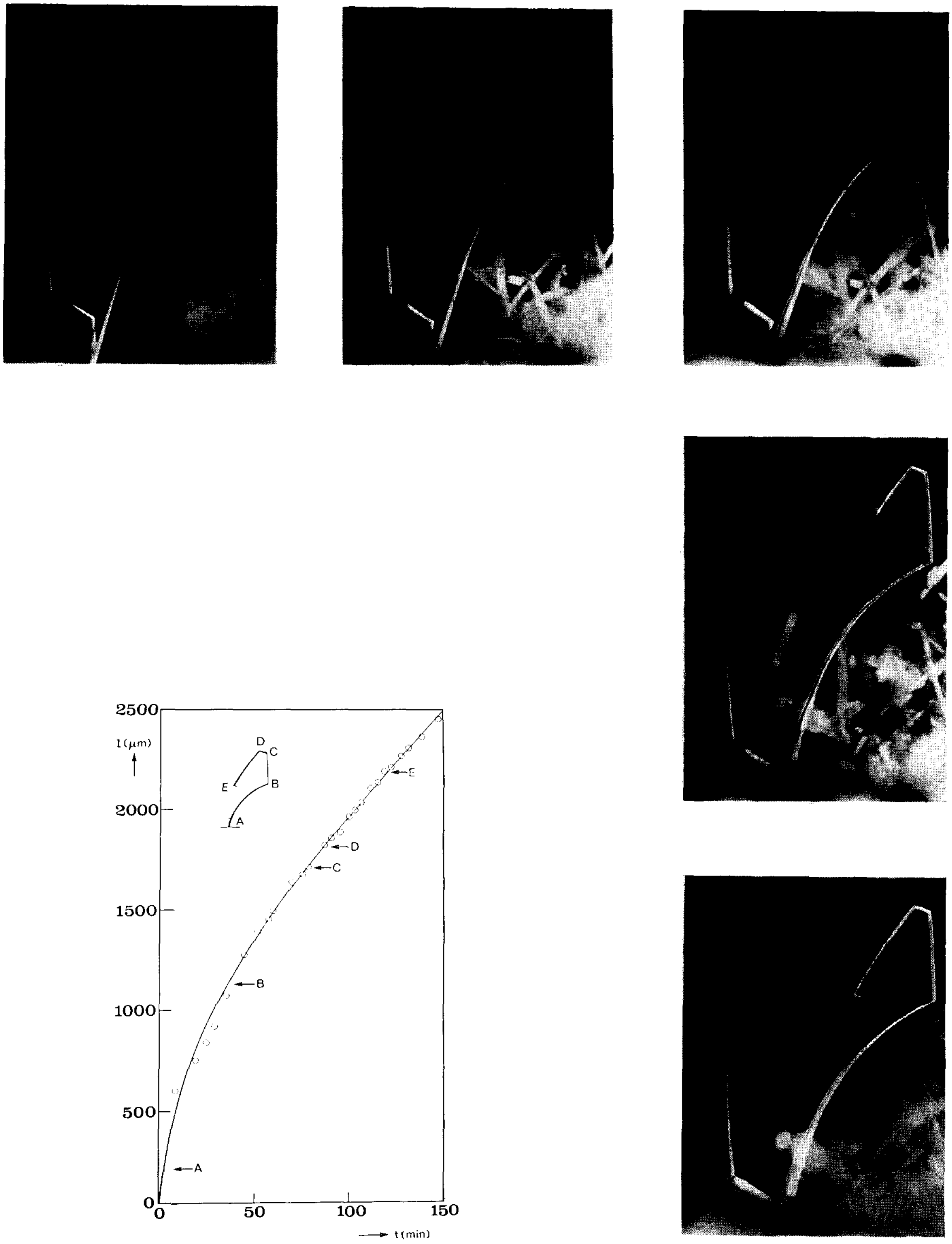


Fig. 2. Photographs and growth curve of silicon whiskers, with bending and kinking.

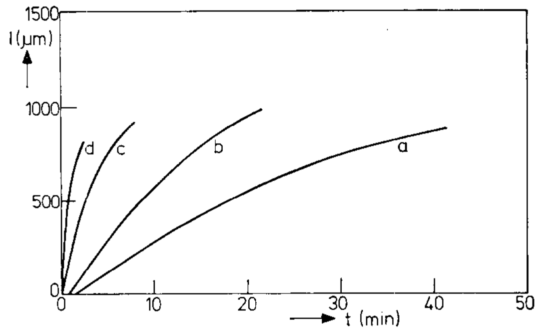


Fig. 3. Growth curves of silicon whiskers. $T_s = 650$ °C, p_0 (in Torr): 10 (a), 20 (b), 40 (c) and 80 (d).

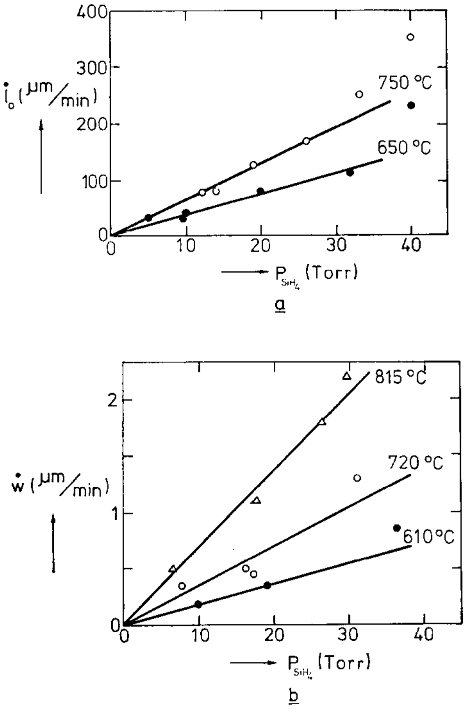


Fig. 4. Growth rates of silicon whiskers in length for $T_s = 650$ and 750 °C (a), in width for $T_z = 610$, 720 and 815 °C (b).

3.1.3. *Rates of decomposition of silane*

In order to compare the growth of the whiskers in the length direction with growth in "normal" conditions, rates of silicon deposition, viz. silane decomposition, on substrates without deliberately added impurities, were also determined. The substrate temperatures varied between 600 and 1000 °C and the starting partial pressures of silane from 10 to 50 Torr.

The decomposition rates were determined by measuring changes in total pressure, p^m. According to the overall reaction scheme

$$SiH_4 \rightarrow Si_s + 2H_2, \tag{1}$$

the silane pressure, p_t, at a time t after addition, is given by

$$p_t = 2p_0 - p_t^m + p_0^{H_2}, \tag{2}$$

where $p_0^{H_2}$ is the initial hydrogen pressure.

The validity of (2) was confirmed by recuperating the silane in the freezing bottle. The logarithmic dependence of p_t on t, following from the first-order reaction scheme (1), could also be confirmed (fig. 5). A more rapid decrease in the silane pressure of the order of 10–20% in p_0 was observed within the first minute.

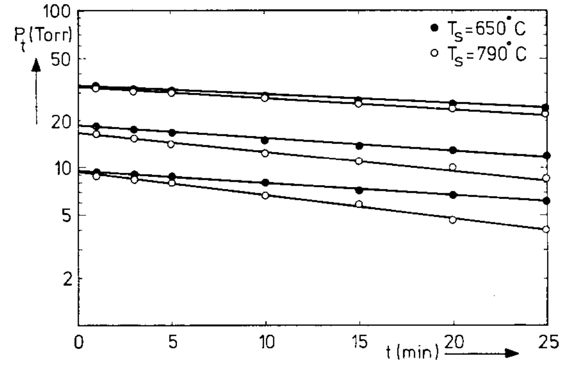


Fig. 5. Decomposition of silane. $T_s = 650$ and 790 °C, and $p_0 =$ 10, 20 and 40 Torr.

From the slope of the ln p_t versus t plots rate constants, k, were derived, defined by

$$\ln \frac{p_{t=0}}{p_t} = k \frac{A}{V} t, \tag{3}$$

where A is the area of the substrate surface at which the decomposition takes place, and V the volume of the closed system. In these experiments A/V was about 10^{-2} cm^{-1}. In the investigated pressure range the k-values showed no significant dependence on the silane pressure. Increase of $p_0^{H_2}$ to pressures up to 100 Torr caused a decrease in k of the form $k \propto (p_0^{H_2})^{-n}$ with n varying from 0.7 to 1.0. As experiments with helium instead of hydrogen showed the same kind of pressure influence on k, the retarding influence is not so much an effect of a shift in the chemical equilibrium but is probably due to changes in the gas density and temperature distribution in the reaction vessel. For comparison with the growth rates of whiskers the k-values obtained by extrapolation to $p_0^{\mathrm{H}_2} = 10$ Torr were transformed into rates of thickness growth of the substrate (cf. section 4.2 and fig. 9).

3.1.4. *Rates of thickness growth of filamentary crystals*

Simultaneously with the growth in the length direction the whiskers show thickening at a rate which increases with increasing temperature and pressure. Rates of thickness growth, w, were measured microscopically for thicker whiskers at small distances, z, from the substrates ($z \sim 100$ μm), at substrate temperatures T_s of 650, 750 and 850 °C. In contrast with the growth rate in length, the rate in width was hardly time dependent, evidently due to the isothermal condition parallel to the substrate. The temperature T_z at the measuring points was estimated by

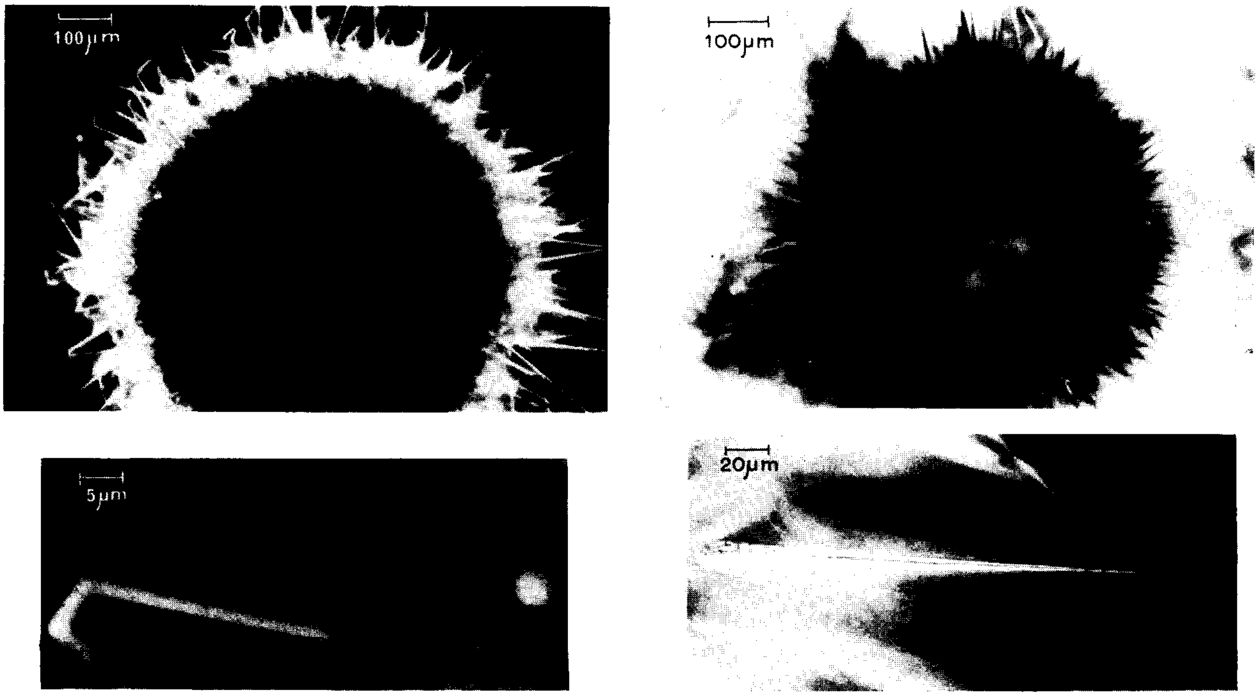
$$T_z = T_s - az, \tag{4}$$

with $a = 0.2$ deg/μm (cf. section 3.3). The results are plotted in fig. 4b. Up to pressures of about 30 Torr a linear dependence of the thickness-growth rate on the silane pressure is found.

3.1.5. *Structure, morphology and growth mechanism of the filamentary crystals*

The straightness of most of the filamentary crystals as well as the fact that the pronounced kinking (cf. fig. 6a) often occurs at an angle equal to the angle between two different [111]-directions – the preferred directions for Si-whisker growth by VLS[5]) –, suggests that the filamentary crystals are single crystalline. Indeed in the electron microscope the thinnest whiskers with a diameter ≈ 0.1 μm, produced clear diffraction patterns. However, X-ray rotation photographs of thick filamentary crystals, with a diameter of about 10 μm, showed no distinct diffraction spots and indicated a polycrystalline character. The cross-section of most of the filamentary crystals is circular.

During the growth no liquid droplet could be observed on the tips of whiskers with diameter d_0 (section 3.1.1) and attempts, by electron microprobe analysis, to detect gold on the tips of whiskers for which the



(a) (b)

Fig. 6. Top view of silicon (a) and germanium (b) whisker growth with gold nucleation. Details showing kinking and circular cross-section (Si) and conical shape (Ge).

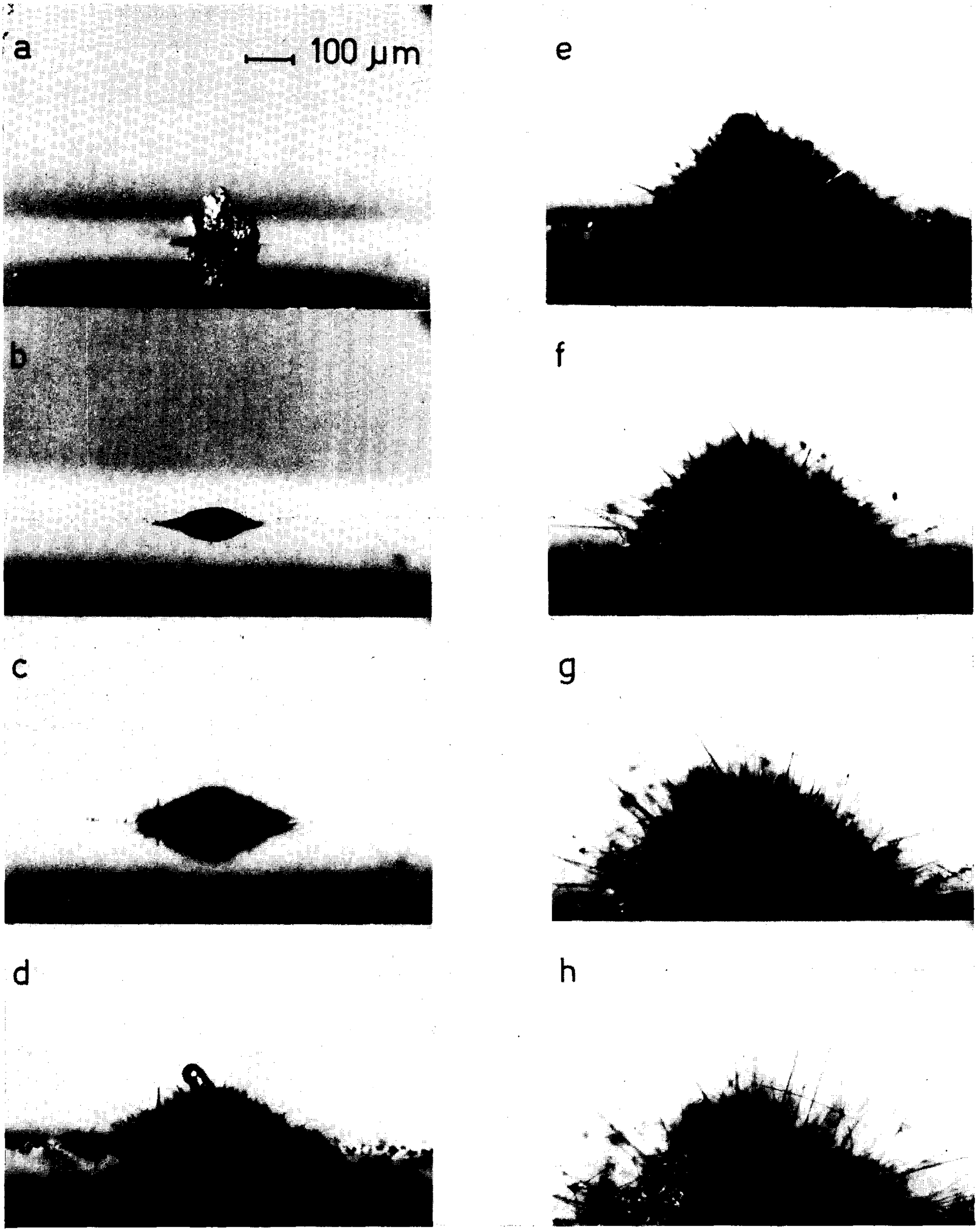


Fig. 7. Photographs of growth of germanium whiskers from a Au-Ge droplet. $T_s = 400$ °C, $p_0 = 60$ Torr.

growth had been intentionally interrupted also failed. A liquid phase was only observed on tips or part of tips of very thick filamentary crystals (diameter 20–50 μm), which occasionally grow (cf. fig. 7d). The presence of a corresponding amount of liquid alloy on the tips of the thinner whiskers cannot of course be excluded.

From the above we assume that the thicker filamentary crystals as well, at least the straight ones and those kinked at tetrahedral angles, are composed of thin single-crystalline cores, probably growing by a VLS mechanism, on which polycrystalline silicon may be deposited.

3.2. GERMANIUM FROM GERMANE

The results of experiments on nucleation and growth of germanium whiskers from germane were similar to those obtained for silicon, the main difference being the lower temperatures at which the processes take place. Therefore this study was carried out in less detail than for silicon.

As with silicon, gold appeared to be the most suitable impurity; filamentary growth occurred at substrate temperatures between 300 and 500 °C. At the lower temperatures thin, often bent filamentary crystals grow, at the higher temperatures the whiskers are conically shaped (fig. 6b). An example of growth from a liquid alloy droplet is shown in fig. 7; kinking again occurs preferentially at the tetrahedral angle. From the thinnest filamentary crystals clear electron diffraction patterns were obtained. At temperatures up to 650 °C no filamentary growth was observed with In, Sn and Bi, whereas with Cu short germanium fibres were grown at about 450 °C. Rates of whisker growth in the length direction and of thickness growth, both of substrates and whiskers, were determined at various temperatures and for various pressures up to 60 Torr. As with silicon, a linear dependence of the growth rates on pressure was observed (up to pressures of about 40 Torr). The increase of the rates with the temperature is shown in fig. 9, for conditions where germane and hydrogen are both at a pressure of 10 Torr.

3.3. TEMPERATURE GRADIENTS AND GAS-DENSITY DISTRIBUTION IN THE REACTION VESSEL

In contrast with the situation in the hot-wall furnaces in which long and straight whiskers are usually grown, the gas density and the temperature of the gas and of the whiskers in our cold-wall reaction vessel vary considerably with the distance to the heated substrate. In this section we present some rough measurements of these gradients.

In section 3.1.2 we assumed that the decrease in growth rate of the whiskers with increasing distance to the heated substrate is primarily due to a decrease in temperature of the tip of the growing whisker. It was also observed that the maximum height of the whisker growth increases with increasing substrate temperature T_s. For silicon at $T_s = 650$ °C this height amounts to about 1300 μm, at 750 °C to about 1600 μm. When a heater element was placed in front of the growing whiskers the decrease in growth rate was much smaller and the maximum length of the whiskers considerably longer. Within the scope of the VLS mechanism a possible explanation for the cessation of growth is that the growth stops if the tip temperature becomes lower than the eutectic temperature ($T_z = 370$ °C). Assuming a linear dependence of the temperature on the distance to the substrate, as given by eq. (4), one gets from the above-mentioned maximum lengths: $a \sim 0.2$ deg/μm. This value was substantiated by an estimate of the temperature gradient along thicker whiskers from photographs taken with an I.R. image converter (Wild, Bildwandler Röhre), yielding $a \sim 0.2 \pm 0.05$ deg/μm.

An impression of the gas-density distribution in the reaction vessel was obtained by holographic interferometry[14]). Fig. 8 shows double exposure holograms of the reaction vessel filled with xenon at various pressures, the two exposures taken at $T_s = 25$ °C and $T_s = 970$ °C. For the same pressures fringe patterns obtained with silane were almost identical with those obtained for xenon, the refractive index for both gases being almost equal. The fringes correspond to regions of equal gas density, or equal p/T. For low substrate temperatures and/or low xenon pressures the number of fringes decreases and the contrast in the patterns fades. The contrast was improved by using phase amplification methods. At low T_s and p fringe patterns were obtained[15]), which show the same type of gas-density distribution around the heated substrates as those for higher T_s and p. If we assume that the pressure in the reaction vessel with a heated substrate is uniform, and equal to or slightly higher than with a cold substrate, and that the temperature near the sub-

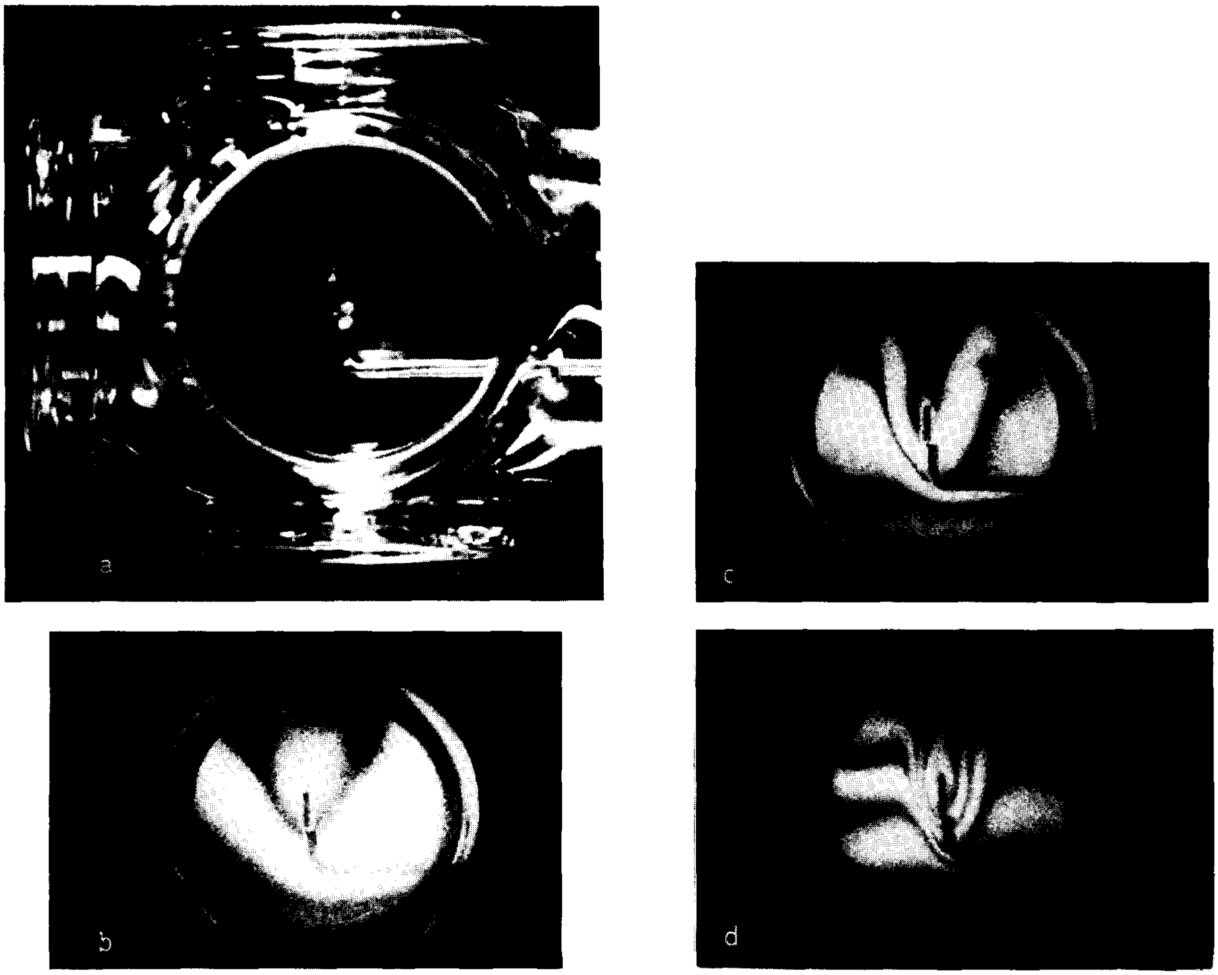


Fig. 8. Reaction vessel (a) and double exposure holograms showing the gas density distribution for T_s = 970 °C and various xenon pressures: 96 Torr (b), 210 Torr (c) and 460 Torr (d).

strate changes only in the direction perpendicular to the substrate, we get for the conditions of T_s and p during the growth experiments a mean temperature gradient of the order of 0.1 deg/µm in the neighbourhood of the substrate ($z < 3$ mm), followed by a less steep decrease in temperature to the wall with glass windows. The temperature of the windows, as measured directly with thermocouples, is higher for the top window than for the front, side and bottom windows, for instance at T_s = 800 °C and with xenon at a pressure of 50 Torr these temperatures are 85 and 60 °C respectively.

4. Discussion and conclusions

4.1. NUCLEATION OF THE FILAMENTARY GROWTH

A prerequisite of the VLS mechanism is the existence of a liquid alloy composed by the whisker material (S) and an impurity substance (I); the binary system S–I is characterized by miscibility in the liquid phase and immiscibility in the solid phase, i.e. by a eutectic phase diagram. In table 1 the following data are presented for some Si–I and Ge–I eutectic systems: the eutectic temperature T_E and composition X_E, and the type of phase diagram. Type A represents the simple systems with two liquidi, type B systems with one or more intermediate compounds, where the compound S_xI ($x = 3$ for Cu and $x = 1$ for Ni and Pd) forms the

TABLE I

Phase-diagram data for S–I systems, collected from ref. 16

I		S–I	S = Si		S = Ge	
Element	Group periodic table	type	T_E (°C)	X_E (at% Si)	T_E (°C)	X_E (at% Ge)
Ag	IB	A	840	11	651	26
Au	IB	A	370	19	356	27
Cu	IB	B	802	30	640	36
Ni	VIII	B	966	56	775	62
Pd	VIII	B	870	57		
In	III	C	156	2×10^{-8}	156	–
Sn	IV	C	232	10^{-5}	231	0.3
Bi	V	C	271	10^{-8}	271	2×10^{-2}

eutectic with S, and type C systems with the eutectic composition practically at 0% of component S.

One explanation for the observation of filamentary growth with elements of the IB and VIII group of the Periodic Table at substrate temperatures below the eutectic temperature (cf. sections 3.1.1 and 3.2) could be local liquid formation caused by heating due to the decomposition reaction. In fact pyrometric measurement of the substrate temperature, as well as direct measurement with thermocouples fixed in frozen Au–Ge alloys, revealed a rise in temperature after addition of germane, at temperatures below the eutectic temperature of the order of 50 °C. It is probable that at the surface of the alloy, the bulk of which remains solid, as well as at the tip of the growing filamentary crystals, the temperature is above the eutectic temperature. Another explanation would imply a mechanism other than VLS, e.g. "VSS" or "VAdS" in which instead of a liquid a solid particle or adsorbed layer plays the role of growth stimulus. At the low temperatures concerned, by the lack of a single well-defined interface between agent and filamentary crystal, one expects for a VSS mechanism fibrous growth rather than whisker growth, which, however, was not found for the Ge–Au system.

The negative results obtained with In, Sn and Bi show that the presence of a liquid phase as such is not a sufficient condition for filamentary growth. A possible explanation could be that at the temperatures of growth the content of S in the liquid phase is too low, or the slope $\Delta T/\Delta X$ of the liquidus too high. This could be the case for S = Si, where even at 900 °C X_{Si} in liquid alloys with In, Sn and Bi is smaller than 1 at%. For S = Ge, however, X_{Ge} in the liquidus at 650 °C is about 30 at% for alloys with In and Sn, and 7% for the Bi–Ge alloy. So the question remains whether the difference between In, Sn and Bi on the one hand, and Ag, Au, Cu, Ni and Pd on the other is also correlated with the difference in slope of the liquidi in the phase diagrams, or whether only differences in catalytic activity of the metals or liquid alloys towards the hydride decomposition play a role.

4.2. PHENOMENOLOGICAL TREATMENT OF THE GROWTH RATES

For the comparison of the results of the growth rate measurements we will use the expression from the kinetic theory of perfect gases in which the growth rate, g, due to the number of effective collisions of vapour molecules on a surface is given by

$$g = \alpha \frac{p}{\rho} \sqrt{\frac{M}{2\pi RT}}, \tag{5}$$

where for the case of decomposition of SH_4 molecules and formation of a solid phase S, with a vapour pressure much smaller than the pressure of the impinging SH_4 molecules:

p, T	pressure and temperature of SH_4,
M	M_S^2/M_{SH_4},
M_S, M_{SH_4}	molecular weight S, SH_4,
ρ	density of solid S,
R	gas constant.

In (5) the factor α represents the efficiency of the collision process or the fraction of the impinging molecules SH_4 yielding S. The factor α depends on the temperature T_s of the substrate surface and is generally written as

$$\alpha = \alpha_0 \exp(-E/RT_s), \tag{6}$$

where the activation energy, E, and the temperature-independent factor, α_0, are characteristic for the decomposition reaction. If g is expressed in μm/min and p in Torr, eq. (5) reads

$$\alpha = 0.13\times10^{-4}\,\frac{g}{p}\sqrt{T} \quad \text{for S = Si,} \tag{7a}$$

$$\alpha = 0.18\times10^{-4}\,\frac{g}{p}\sqrt{T} \quad \text{for S = Ge.} \tag{7b}$$

Thickness-growth rates of substrates are obtained from the rate constants k of the decomposition reaction; by using the differentiated form of eq. (3) one gets

$$g = -\frac{M_S}{RT_r}\,\frac{\mathrm{d}(pV)}{\mathrm{d}t}\,\frac{1}{\rho A} = \frac{M_S}{RT_r}\,\frac{kp}{\rho}, \tag{8}$$

with T_r = 300 °K.

In the calculation the density ρ is taken equal to that of crystalline S at room temperature, although the growth takes place at higher temperatures and the layers formed upon decomposition during the thickness growth are rather polycrystalline or amorphous. However, for temperatures up to 1000 °C the correction for thermal expansion is less than 1 %, and the density of even amorphous Si or Ge is at most 20 % lower than that of single crystals; both corrections are therefore negligible in view of the experimental errors.

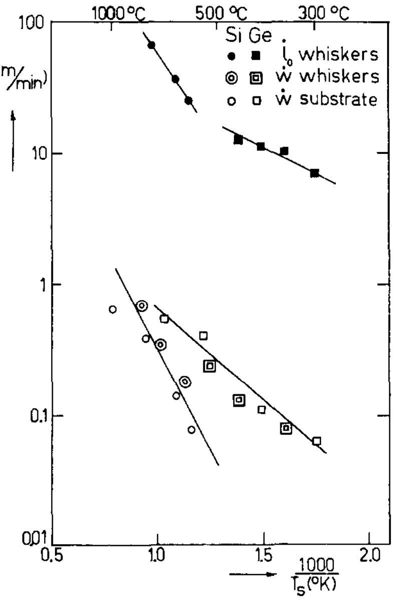


Fig. 9. Arrhenius plots of the growth rates, g, of silicon and germanium; for conditions with H_2, and SiH_4 or GeH_4 at a pressure of 10 Torr.

In fig. 9 the results of the growth rate measurements for silicon and germanium are plotted as a function of the reciprocal temperature, for conditions with 10 Torr SH_4 added to 10 Torr H_2. The systematic differences between the thickness-growth rates of the substrate as determined from pressure readings with eq. (8) and of the whiskers as determined by direct microscopic measurement, are insignificant in view of the errors in the experiments. For both silicon and germanium the rates of growth of the whiskers in the length direction, $\dot{l}$, are of the order of 100 times higher than the rates of growth in width, $\dot{w}$.

Values of α_0 and E calculated from the lines in fig. 9 with eqs. (6) and (7) are given in table 2. In the calculation we have assumed that the SH_4 molecules taking part in the reaction at the surface are at substrate temperature T_s and at a pressure derived from the pressure reading outside the reaction vessel by means of eq. (2). The holographic data reported in section 3.3 show that this assumption is not far from correct, a possible correction will moreover be equal for the different growth processes in the same conditions of T_s and p. For both silicon and germanium the order of magnitude of the α values is 10^{-5} for the thickness growth and 10^{-3} for the growth in the length direction.

TABLE 2

Values of E and α_0 calculated from the rates of growth of the whiskers in the length direction, $\dot{l}$, and of the thickness growth of substrate and whiskers, $\dot{w}$

S	g	E (kcal/mole)	α_0
Si	$\dot{l}$	11.9	1.0
	$\dot{w}$	15.5	0.031
Ge	$\dot{l}$	4.1	0.012
	$\dot{w}$	6.9	0.0011

In the derivation of α from the growth rates in the length direction of the whiskers by means of eq. (5) it is assumed that the area of the vapour capturing surface is equal to the cross-sectional area of the whiskers.

For whiskers grown by the VLS mechanism a correction factor has to be introduced which takes into account the difference between A_{VL} and A_{LS}, the surface area of the V–L and L–S interface respectively:

$$\alpha' = \alpha \frac{A_{\mathrm{LS}}}{A_{\mathrm{VL}}}. \tag{9}$$

For whiskers with a circular cross-section (diameter d_{S}) and with a droplet on the tip which has the shape of part of a sphere (diameter d_{L})

$$\frac{A_{\mathrm{VL}}}{A_{\mathrm{LS}}} = 2\left(\frac{d_{\mathrm{L}}}{d_{\mathrm{S}}}\right)^2 \left\{1 \pm \sqrt{\left[1 - \left(\frac{d_{\mathrm{S}}}{d_{\mathrm{L}}}\right)^2\right]}\right\}. \tag{10}$$

The ratio $d_{\mathrm{L}}/d_{\mathrm{S}}$ and the choice of the plus or minus sign in (10) are dependent on the surface energies of the V–L, L–S and S–V interfaces. In the known cases of VLS growth the droplets on the tips of the whiskers had the shape of about a half sphere or more than a half sphere, suggesting that in (10) the plus sign is valid and $d_{\mathrm{L}} \geq d_{\mathrm{S}}$. In the rare cases where we could observe a droplet in this study, values of $d_{\mathrm{L}}/d_{\mathrm{S}}$ were found between 1.0 and 1.5, which gives with eqs. (9) and (10): $0.13\,\alpha < \alpha' < 0.5\,\alpha$. The introduction of this correction would decrease the difference in pre-exponential factor between thickness and length growth correspondingly.

For both substances the activation energies E associated with $\dot{l}$ are lower than those for $\dot{w}$, and the pre-exponential factors, α_0 or α'_0, higher.

4.3. CONCLUSION

The enhancement of growth in the length direction of the silicon and germanium whiskers is an effect of impurities, most probably in the form of a VLS mechanism. The pressure dependence of the growth rates suggests that, in terms of this mechanism, it is not the crystallization at the L–S interface but the decomposition reaction at the V–L interface that is rate-controlling. The changes in E and α_0 with respect to normal growth suggest that the enhancement is due to local catalysis of the decomposition at the V–L interface.

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