

FUNDAMENTAL ASPECTS OF VLS GROWTH

E.I. GIVARGIZOV

Institute of Crystallography, Academy of Sciences of the U.S.S.R., Moscow 117333, U.S.S.R.

The kinetics and the mechanism of the vapor–liquid–solid (VLS) growth are discussed. Emphasis is placed on the dependence of the growth rate on the whisker diameter. It is found that the rate decreases abruptly for submicron diameters and vanishes at some critical diameter $d_c \lesssim 0,1 \mu\text{m}$ according to the Gibbs–Thomson effect. A new method for simultaneous determination of kinetic coefficients and of supersaturations has been developed. The method can be used to measure the coefficients of some materials as well as the temperature dependence of the coefficient for silicon and the activation energy of the process. From the dependence of supersaturation on the diameter we conclude that whiskers grow by a poly-nuclear mechanism. The periodic instability of the diameter is discussed and the rate-determining step is analysed. We conclude that phenomena on the liquid–solid interface are the decisive ones. In determining the role of liquid phase in vapor growth we measured the “liquid phase effectivity coefficient” as a function of crystallization condition; the coefficient typically was about 10^2 – 10^3 . It is stressed that the liquid phase reduces the activation energy both on vapor–liquid interfaces (for chemical reactions) and on liquid–solid interfaces (for nucleation). The liquid phase ensures growth rates as high as 1 cm/sec, provided there are no barriers between the interfaces. The growth mechanism of the side faces was studied, and it was observed that the faces grow mainly by a chain mechanism rather than by two-dimensional nucleation. In work on surface diffusion in the VLS whiskers growth by CVD, we found that the whiskers grow mainly by direct deposition rather than by diffusion on the side faces. It is concluded that the VLS mechanism is important also for the vapor growth of platelets, films, and bulk crystals.

1. Introduction

The vapor–liquid–solid (VLS) mechanism was given in 1964 by Wagner and Ellis [1–3] to explain unidirectional whisker growth involving impurities. Since then, few papers on vapor whisker growth omitted the mechanism, as VLS growth became more and more evident. Recently, the mechanism was found in Nature [4] and even on the Moon [5]. It is also important that the VLS process serves as a base for controlled growth of whiskers.

Recent vapor growth studies demonstrate that the VLS mechanism is also important for platelets, films, and bulk crystals. Nevertheless, we believe that the whiskers give the main information about the mechanism. Therefore, this paper is devoted principally to the kinetics of the VLS whisker growth and the role of the liquid phase in the process. Finally, some evidence regarding the VLS mechanism in crystal growth from the vapor phase is given.

2. Kinetics of whisker growth

2.1. Growth rate dependence on diameter and determination of kinetic coefficients

In kinetic studies the crystal growth rate is usually measured as a function of a driving force, e.g. of supersaturation. For whisker growth, the dependence of the axial growth rate on the whisker diameter [6,7] was most informative. A method was suggested for the determination of the supersaturation and of the kinetic coefficients of crystallization, provided the specific energy of the prismatic (or cylindric) whisker surfaces is known. This method is based on a combination of the Gibbs–Thomson equation and some kinetic law of growth.

Typical Si whiskers grown on a (111)Si substrate with the chloride ($\text{SiCl}_4 + \text{H}_2$) process and with Au as a liquid-forming impurity are shown in fig. 1. It can be seen that thin whiskers grow slower than thick

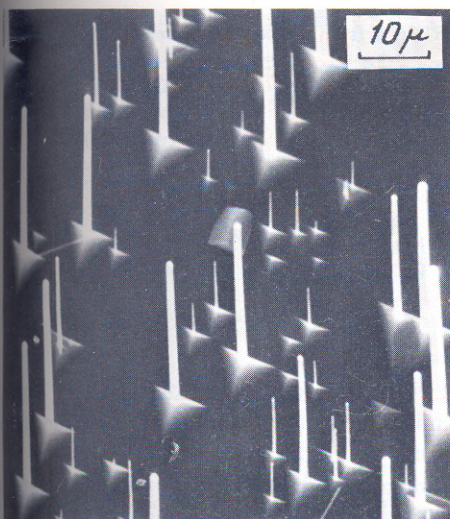


Fig. 1. Relative growth rates for thick and thin silicon whiskers.

The dependence is plotted in fig. 2a. Curves 1–4 correspond to various molar concentrations of SiCl_4 , hence to various supersaturations. These results show that there is a critical whisker diameter at which growth stops completely; i.e., the growth rate decreases because the supersaturation decreases. This is due to the increasing vapor pressure and solubility of Si as the diameter of the whiskers becomes smaller. According to the Gibbs–Thomson effect the decrease of supersaturation as a function of whisker diameter can be given as

$$\Delta\mu = \Delta\mu_0 - 4\Omega\alpha/d, \quad (1)$$

where $\Delta\mu$ is the effective difference between the chemical potentials of Si in the vapor phase and in the whisker, $\Delta\mu_0$ is the same difference at a plane boundary ($d \rightarrow \infty$), α is the specific free energy of the whisker surface, and Ω is the atomic volume of Si.

The dependence of the growth rate V on supersaturation $\Delta\mu/kT$ (where k and T have the usual meanings) is unknown a priori and must be determined from experimental data. For the singular faces the dependence is not linear [8] and in many cases is of n th power:

$$V \sim (\Delta\mu/kT)^n. \quad (2)$$

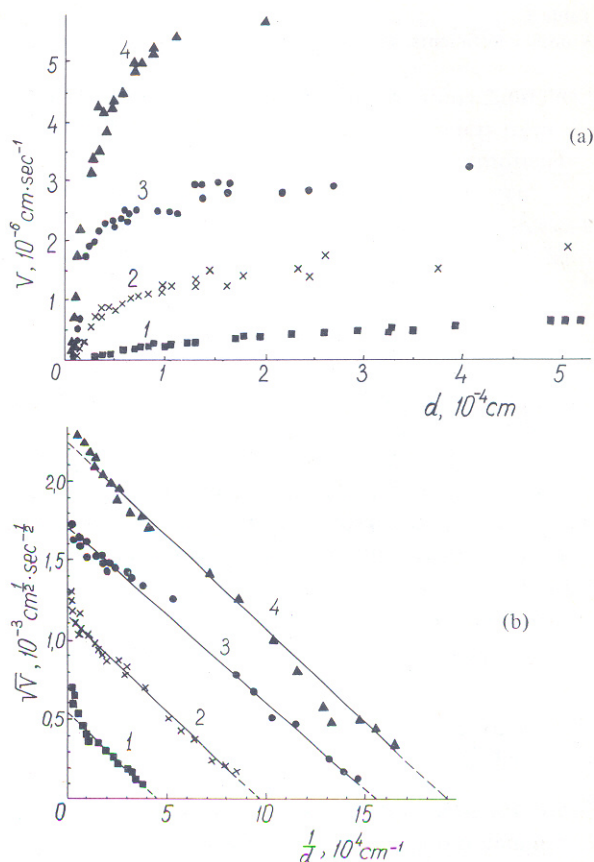


Fig. 2. (a) Measured growth rates of VLS silicon whiskers as a function of their diameter for various supersaturations; the supersaturation increases in the order 1 to 4. (b) Fitting of the data of (a) in coordinates $V^{1/2}$ versus $1/d$.

This proportionality can be written as an exact equation:

$$V = b(\Delta\mu/kT)^n, \quad (3)$$

where b is a coefficient independent of supersaturation. It is this independence that can be a criterion for the determination of n from experiments. Substituting $\Delta\mu$ from eq. (1) in eq. (3) we obtain

$$V^{1/n} = \frac{\Delta\mu_0}{kT} b^{1/n} - \frac{4\Omega\alpha}{kT} b^{1/n} \frac{1}{d}, \quad (4)$$

corresponding to a linear dependence of $V^{1/n}$ versus $1/d$. The experimental data of fig. 2a can be fitted to straight parallel lines only for $n = 2$ (fig. 2b). If we as-

Table 1

Kinetic coefficients, supersaturations and critical diameters for Si (Au) at 1000°C from whisker experiments

Expt. No.	SiCl ₄ /H ₂ (mole %)	Critical diam. d_c (cm) $\times 10^{-4}$	Effective supersaturation ($\Delta\mu/kT$) $\times 10^{-2}$	Kinetic coefficient (cm sec ⁻¹) $\times 10^{-4}$
1	0.3	0.20	3.3	4.6
2	0.75	0.11	6.9	4.5
3	1.5	0.07	11	3.8
4	3.0	0.05	14	4.2

sume that $n = 1$ or $n = 3$, the lines are not parallel but converge or diverge.

The intercepts cut off at the $1/d$ axis by extrapolation of the straight lines determine the critical diameters d_c . For these diameters and for the given overall supersaturations in the gas phase the real supersaturations in the droplet near the growth interface become zero and the VLS process stops. In other words, d_c can be considered as a diameter of the critical nucleus. Therefore

$$\frac{\Delta\mu_0}{kT} = \frac{4\Omega\alpha}{kT} \frac{1}{d_c} \quad (5)$$

Hence, the supersaturation of CVD reaction can be determined if α is known. The prismatic surface of Si whiskers at 1000°C usually contains equal numbers of {211} and {110} faces. The average value, $\alpha = 1610$ erg/cm², can be calculated from $\alpha = 1230$ erg/cm² measured [9] for Si {111} and the ratio of the density of broken bonds in {211} and {110} relative to {111} (1.41 and 1.22, respectively). The calculated values of $\Delta\mu/kT$ for various molar concentrations of SiCl₄/H₂ are given in table 1. From the slopes $4\Omega\alpha b^{1/2}/kT$, eq. (3), of the straight lines in fig. 2b the kinetic coefficients can be calculated. The coefficients given in

table 1 have an average value of 4.3×10^{-4} cm/sec, which is reasonable for the growth from concentrated solutions [8].

Similar dependences of $V(d)$ were obtained for Si at all investigated conditions (temperatures 900–1200°C, concentrations SiCl₄/H₂ from 0.3 to 6% and Au, Pd, Ni, Pt as liquid-forming agents) and for other materials. The kinetic coefficients for Ge, SiC and GaAs are given in table 2. Qualitatively, the same dependence was observed for GaP, CdSe, ZnS and ZnSe.

The results indicate that the dependence is a fundamental one for submicrometer whiskers. The exact nature of such a dependence is not yet completely understood because the quadratic law is believed to be typical of screw dislocation growth mechanism [10], while it has been shown that the thin whiskers, grown by the VLS mechanism even on high-dislocation substrates, contain no dislocations [3]. For the present it is possible only to speculate on a nucleation mechanism with a kinetic roughness in high-concentration solutions such as Si (Au) at high temperatures or, in other terms, with a decrease of the activation energy of the two-dimensional nucleation at this interface. The decrease can be rather strong, about 50 times [11], so that some section of the exponential can be approximated with a quadratic dependence. In any case, the dependence should be considered as an empirical one; this method of determining the kinetic coefficients and the supersaturations can be used for the kinetic studies.

2.2. Temperature dependence of the kinetic coefficients

The method was used to study the temperature dependence of the kinetic coefficients and to determine

Table 2

Kinetic coefficients for various materials

Material	Whisker orientation	Growth temperature (°C)	Kinetic coefficient (cm sec ⁻¹)
Ge	[111]	750	8×10^{-6}
SiC	[111]	1350	3×10^{-6}
GaAs	[111] A	670	1×10^{-2}
GaAs	[111] B	670	5×10^{-2}

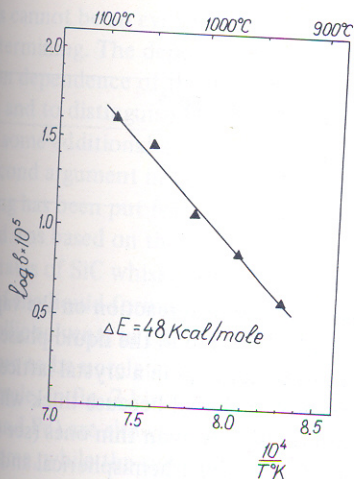


Fig. 3. Temperature dependence of the kinetic coefficients and determination of the activation energy for Si whisker growth.

the activation energy of the VLS process. The experiments were performed with Si (Au) at 930–1090°C. The kinetic coefficients were corrected for the temperature dependence of equilibrium solubility according to the Si–Au phase diagram. The results are plotted as $\log b$ versus $1/T$ in fig. 3. The activation energy is about 48 kcal/mole and relates evidently to the rate-determining step (see below).

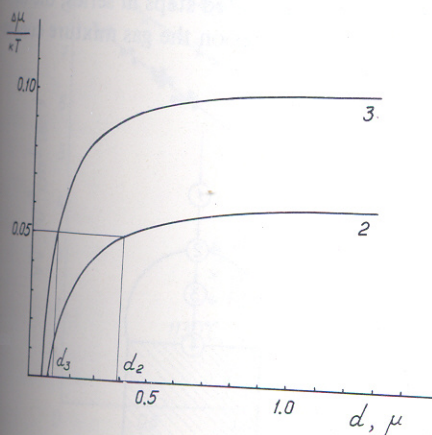


Fig. 4. Real supersaturations on the growth interface as a function of whisker diameters. Curves 2 and 3 correspond to curves 2 and 3 in fig. 2.

2.3. Dependence of supersaturations on whisker diameters

If d_c is known, the real supersaturations $\Delta\mu/kT$ can be determined as a function of diameters from eqs. (1) and (5). The supersaturations asymptotically approach $\Delta\mu_0/kT$ with increasing d . The greater $\Delta\mu_0/kT$, the steeper is the curve. This dependence can be used for an analysis of the whisker growth mechanism.

2.3.1. Poly-nuclear growth

For two experiments made at the same temperature but at different overall supersaturations, pairs of diameters can be chosen for which the real supersaturations on the growth interface are the same.

In fig. 4 dependences $(\Delta\mu/kT)(d)$ are shown for curves 2 and 3 from fig. 2. The intercepts of the curves with a horizontal line determine the diameters d_2 and d_3 (accordingly, areas $S_2 \sim d_2^2$ and $S_3 \sim d_3^2$) of whiskers with the same interface supersaturations. Returning to the original curves in fig. 2, we can determine the corresponding growth rates, V_2 and V_3 . The results are given in table 3. It can be seen that the areas are different more than 10 times while the growth rates are practically the same. If we assume that the nucleation mechanism is valid, it is possible to conclude that the whiskers grow by polycentric nucleation. It is the single-nuclear growth that can explain the high crystalline perfection of the whiskers.

2.3.2. Periodic instability

It was found that Si, Ge, GaAs and InAs whiskers show a periodic instability of diameter [12]. A typical picture of the instability for Si whiskers is shown in fig. 5. These whiskers consist of a row of knots and necks with approximately equal distances between them. The periodicity is not strict and differs for various whiskers. It can therefore be assumed that the periodicity is of a self-oscillatory model. The instability manifests itself at high temperatures, high supersaturations, and only for submicrometer ($\lesssim 0.5 \mu\text{m}$) whiskers. The suggested model of the self-oscillations is based on the idea that the contact angle of the droplet (i.e., the wetting of the growing face) depends on the roughness of the interface, which, in turn, depends on supersaturation ("kinetic roughness"), and, hence, on the curvature of the droplet. The greater the supersaturation, the steeper is the curve in fig. 4 and the

Table 3
Growth rates for pairs of whiskers from different experiments

Fig. 2	$d \text{ (cm)} \times 10^{-5}$	$d^2 \sim S \text{ (cm}^2\text{)} \times 10^{-10}$	$V \text{ (cm sec}^{-1}\text{)} \times 10^{-6}$
Curve 2	3.9	15.2	0.62
Curve 3	1.2	1.44	0.71

greater is the feed-back coefficient for self-oscillations. It is important that the instability diminishes if some impurities (AsCl_3 , PCl_3) are introduced in the gas phase that are known to change the contact angle [13].

3. Rate-determining step

Identification of the rate-determining step is of great importance in crystal growth [14]. The problem is a very complicated one in this process because it involves three phases and at least two interfaces (vapor–liquid and liquid–solid), and because the material is evolved by chemical reactions. Nevertheless, some conclusions can be drawn.

The process is schematically shown in fig. 6. We can distinguish four main steps: (1) mass-transport in

the gas phase; (2) chemical reaction on the vapor–liquid interface; (3) diffusion in the liquid phase; (4) incorporation of the material in a crystal lattice. Step (3) can be at once excluded because thick whiskers do not grow more slowly than thin ones (see fig. 1) while the droplet is almost hemispherical and, hence, the diffusion length is longer for thicker whiskers. Step (1) can be also excluded because of the very strong (i.e., exponential, $\Delta E \approx 48 \text{ kcal/mole}$) temperature dependence of the kinetic coefficient, while the mass transport in the gas phase usually follows a power law ($n \sim 1.5\text{--}2$). One must therefore choose between steps (2) and (4); both are activated so that the problem is complicated.

Bootsma and Gassen [15] studied the kinetics of whisker growth of Si and Ge by decomposition of SiH_4 and GeH_4 , respectively. Their conclusion, namely that step (2) is the rate-determining one, was based on the observation that the axial growth rates of Si and Ge whiskers were proportional to the partial pressures of the hydrides. These arguments, however, are not convincing.

If there are two activated steps in series, the dependence of growth rates on the gas mixture concen-



Fig. 5. Periodic instability in Si whisker growth.

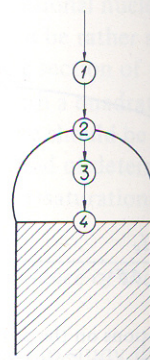


Fig. 6. Various stages of the VLS process.

ations cannot be an evidence that any of them is rate-determining. The dependence is nothing but the common dependence of the growth rate on supersaturation and to distinguish between the steps there are needed some additional criteria.

A second argument in favor of step (2) as rate-determining has been put forward by Tumanov et al. [16] and was based on the observation that the axial growth rates of SiC whiskers were dependent on the nature of the liquid-forming agent. However, as for the metallic solvents in the case of silicon, the differences seem to be unrelated to their catalytic activity. For example, in fig. 7 kinetic curves for three solvents (Pt, Ni, and Pd) are shown. The kinetic coefficients are the same, while the supersaturations are different. The differences are evidently due to the different solubilities of Si in these metals. Data on the solubilities are given in table 4. In the 4th column, the values are proportional to the supersaturations from eq. (1), and in the 5th column we list products of the solubilities and supersaturations, coinciding with our experimental results to within $\pm 10\%$.

On the other hand, there are some arguments in favor of step (4) as the rate-determining one:

The kinetic coefficients for the polar faces of GaAs are quite different (see section 2.1).

Table 4

Metal	Ratio Si/metal at 1130°C	Solu- bility	Super- satura- tion (in $V^{1/2}$ units)	Product solubility \times su- persatura- tion
Pt	72/28	2.57	7.9	20.0
Ni	68/32	2.12	8.8	18.6
Pd	63/37	1.70	9.7	16.5

(b) The second argument complements (a) above.

In fig. 8 we show GaAs whiskers on a GaAs(111) substrate. Most of them are perpendicular but some (indicated by arrow) are inclined to the substrate. The thin inclined whiskers grow at a higher rate than do the thick perpendicular ones, and the inclined whiskers are oriented in a $\langle 211 \rangle$ direction [17] and, hence, have a stepped liquid-solid interface [18]. Due to a decrease of the activation energy of nucleation such interface is well known to enhance growth rate compared with the smooth $\{111\}$ interfaces. Therefore, it can be concluded that step (4) is the rate-determining one in this process.

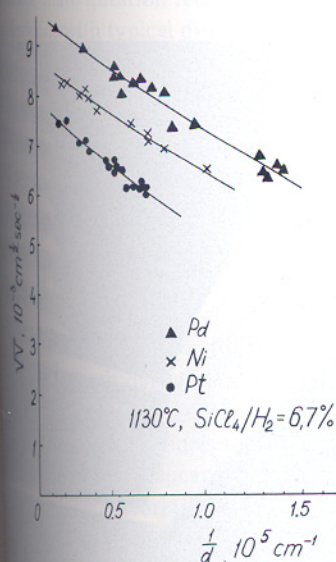


Fig. 7. Kinetic curves for different metallic solvents.



Fig. 8. Relative growth rates for GaAs whiskers of different orientations.

4. Role of the liquid phase

4.1. Liquid phase effectivity coefficient; "physical" and "chemical" catalysis

Wagner and Ellis [2] were the first to emphasize the role of a liquid surface as an "ideally rough" face for crystal growth. This qualitative argument was later supported by Bootsma and Gassen [15] who compared the axial (V_{\parallel}) and lateral (V_{\perp}) rates for Si and Ge whiskers in the hydride process. They found that the "condensation coefficient" for the compounds (i.e., the probability of decomposition with deposition) is $\sim 10^{-3}$ for the VLS process and $\sim 10^{-5}$ for the VS (vapor-solid) process, i.e., the liquid phase effectivity coefficient ($\text{LPEC} = V_{\parallel}/V_{\perp}$) is $\sim 10^2$. It is evident that the coefficient depends on the crystallization conditions — temperature, supersaturation, etc.

LPEC for Si whiskers grown in the chloride process with Pt is shown in fig. 9. It can be seen that LPEC depends both on growth temperature and on molar concentration SiCl_4/H_2 . The decrease of LPEC with temperature is mainly due to an increase of V_{\perp} and partly to a decrease of V_{\parallel} as a result of enhanced Si/Pt solubility and hence of a lowering of supersaturation. The increase of LPEC with concentration is due to an increase of the rates V_{\parallel} , which were measured by SEM for the same whiskers that are reasonably thick, so that the Gibbs-Thomson effect can be neglected. The results for some whiskers were averaged *. The metal (Pt in this case) is expected to be always present in atomic form on the side faces of the whiskers, so that the liquid phase as such rather than the nature of the metal is responsible for the accelerated axial growth of the whiskers. In other words, "physical catalysis" rather than "chemical catalysis" is operative.

4.2. Growth mechanism of side faces

The side faces of the whiskers are believed to grow by a two-dimensional mechanism [19], and it is this mechanism that is thought to be responsible for the

* It is to be noted that V_{\parallel} relates to the (111) face whereas V_{\perp} relates to the side faces {211} that are known to grow somewhat faster than {111} under otherwise equal conditions.

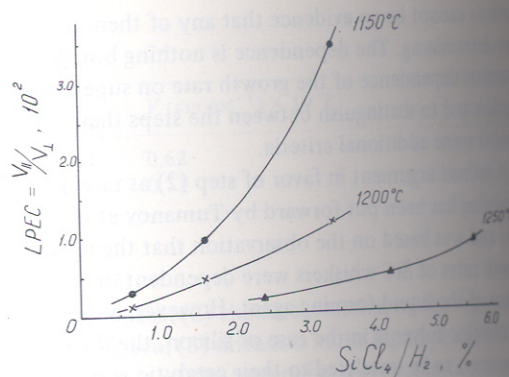


Fig. 9. Liquid-phase effectivity coefficient as a function of the crystallization conditions.

slow lateral growth of the whiskers. However, this may not be so. In many cases, the side faces are "stepped", and even then they grow far slower than the flat tip face. It is typical, for example, that for the fcc, diamond, sphalerite, and wurtzite crystal lattices the whiskers grow in the $\langle 111 \rangle$ or $\langle 0001 \rangle$ directions while the side faces are {211}, {110} or {1120}, {1010}. This fact is one of the objections against the dislocation model of Sears [20].

In fig. 10 the side faces of a Si whisker are shown; the central face is {110} and the two others are {211}. According to Hartman and Perdok [21], both types of faces are S-, or stepped, ones. In fact, the {211} faces



Fig. 10. Growth mechanism for the side faces of the whiskers.

macrosteps intentionally made by periodic switching of the induction heating during the experiments.

Such "artificial rhythmicity" can generate time markers for kinetic studies (see below). It can be seen that the {110} face slowly overgrows from the root and from the sides, the growth being chain-type. As for the {211} face, one of them (left in fig. 10) overgrew also from the root, though the growth is slower than that of the {110} face; the other is rather stable despite of many steps*.

These indications, together with the above-mentioned comparisons of {211} and (111) liquid-solid interfaces (see fig. 8), suggests that in whisker growth (and presumably in vapor growth in general) not merely the surface structure itself but this structure in connection with the liquid phase plays a decisive role.

A few words concerning the peculiar role of the liquid phase may be in order here. First, the liquid phase seems to reduce barriers for chemical reaction at the VL interface [15]; second, it reduces the activation energy of nucleation at the LS interface [11] and, in a similar system for migration of Ge-Au atoms in the temperature gradient, were $\sim 0.07\%$.

Both advantages of the liquid phase can be realized only if there is no delay between steps 2 and 4. Gassner [23] seems to be correct in noting that in comparing the VLS whisker growth to common flux growth the main question relates possibly to dimensions. Indeed, with typical diffusion coefficients in liquids ($\sim 10^{-4} \text{ cm}^2 \text{ sec}^{-1}$) and typical whisker diameters ($\sim 10^{-4} \text{ cm}$) average diffusion rates in droplets are $\sim 10^{-4} \text{ cm}^2 \text{ sec}^{-1} / 10^{-4} \text{ cm} = 1 \text{ cm sec}^{-1}$. These are well above our rates ($\sim 10^{-4} \text{ cm sec}^{-1}$) but coincide with explosive growth rates (up to 1 cm sec^{-1}) reported by Gassner [3] and of Bootsma and Gassen [15].

Role of surface diffusion

It is usual to distinguish between two modes of crystal growth: physical condensation and chemical vapor deposition (CVD). On the other hand, there are two principal models for vapor whisker growth: the diffusion-dislocation model of Sears [20] and the model developed theoretically for physical conden-

sation conditions by Dittmar and Neumann [24], Blakely and Jackson [25] and Ruth and Hirth [26], and Wagner's model of VLS growth [1-3] with the experimental evidence mainly for CVD. In the following we want to demonstrate an application of the diffusion theory [24-26] to the VLS whisker growth by CVD.

The main result of the theory is a formula for the axial growth rate:

$$V = \frac{dl}{dt} = I + \frac{4I\lambda_s}{d} \operatorname{th} \frac{l}{\lambda_s}, \quad (6)$$

where I is the impingement current at the whisker tip, l is the whisker length, t is time, and λ_s is the root-mean-square diffusion distance on the whisker surface.

The formula consists of two terms. The first is the growth rate due to the direct impingement of atoms at the tip and the second is the rate due to the surface diffusion of adatoms on side faces. The formula was verified [24,27,28] for whisker growth by physical condensation. In these experiments, the vapor pressures were rather low ($\sim 10^{-4}$ – 10^{-5} torr) whereas the condensation coefficients were ~ 1 [29,30]. In this case, the first term could be neglected and the verification of eq. (8) reduced to determination of the elongation law: it was shown to be an exponential in the initial stage and a linear one in the next stage.

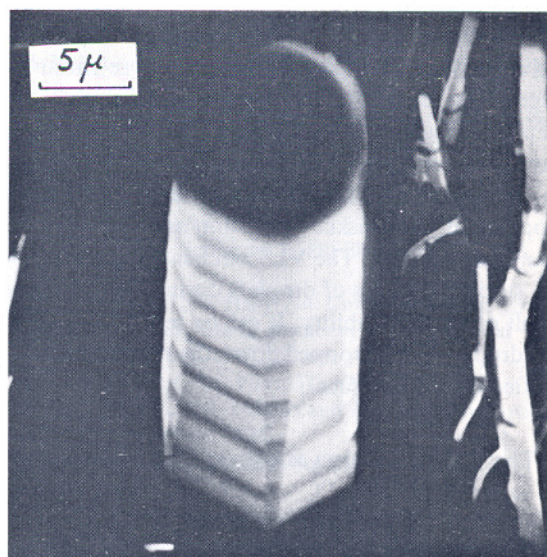


Fig. 11. On the elongation law for Si whiskers.

Eq. (6) could be verified in another way, i.e., by the dependence of the growth rate on the diameters. It can be seen, however, that for $d \gtrsim 1 \mu\text{m}$, where the Gibbs–Thomson effect no longer manifests itself, the rate does practically not depend on the diameter. Hence, the second term in eq. (8) can be neglected in this case, i.e., the material arrives at the growing tip mainly by direct impingement from the vapor phase. This is due to the high pressures of the decomposing species in the vapor phase (usually 1–10 torr) combined with very low “condensation coefficients” of the species on the side faces and/or with a small diffusion length λ_s .

This result was confirmed by morphological data. In fig. 11, a whisker with time markers is shown to illustrate that the axial growth rate is constant, beginning at $\sim 2 \mu\text{m}$ (the first section is somewhat shorter than the others because the initial droplet was submerged for $\sim d/3$ (see fig. 3.23 in [3])).

On the whole, however, the formalism of the diffusion theory [24–26] is applicable to the VLS whisker growth by CVD. Some differences are more of a quantitative than of principal nature, e.g. as an “active sink” on the whisker tip can be considered the droplet instead of a screw dislocation. Hence, a new conception of the “diffusion-droplet mechanism” can be considered for the whisker growth involving the physical condensation process. The model helps to solve some problems of the former diffusion-dislocation mechanism.

- (a) The dislocation model cannot account for the initial stage of whisker growth because any re-entrant edge at the root is at least as active as a dislocation step on the whisker tip. The liquid phase, on the other hand, is more active than any dislocation step.
- (b) The dislocation model does not explain the drastic stopping of the whisker elongation as observed in many experiments. The VLS mechanism accounts for the stopping by loss of droplets during the growth as a result of some instability. It can be seen in fig. 12 that the droplets have drooped down the tip and have solidified on the side faces.

5. The VLS mechanism as a general phenomenon in vapor crystal growth

The discovery and subsequent studies of the VLS mechanism stimulated an interest in liquid layers on

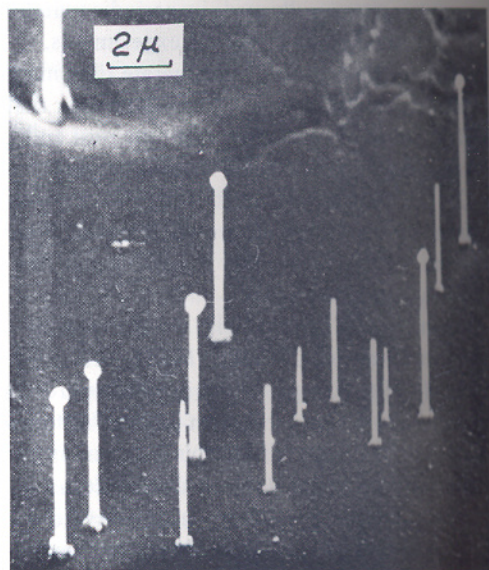


Fig. 12. “Loss” of droplets for Ge whiskers at the last growth stage.

vapor grown crystals [23]. The layers seem to confirm the general Ostwald’s “rule of stages”. They can be formed for a variety of reasons.

(a) *Noncontrolled impurities*. There are known Kowarski “protuberances” [31]. The phenomenon was initially considered as a result of melting [32] but it was shown later that, in fact, it is a two-dimensional VLS process [33,34].

(b) *Intentionally added impurities*. Two-dimensional liquid layers were also generated intentionally [35–37]. The layers substantially affect the growth kinetics and mechanism.

(c) *Nonstoichiometry*. In the vapor growth of compounds it is possible to have a deficit of one component when the compound grows from a solution with the other component. This is the case for growth of GdP at phosphorus deficit [38], for PbSe at selenium deficit [39], and for PbS at sulphur deficit [40]. It is important that the solution growth often gives more perfect crystals than the vapor growth, possibly because the above-mentioned lowering of the liquid–solid barrier.

(d) *Platelets by VLS*. Plate-like crystals grow often by the VLS mechanism. In this case, it is possible to obtain oriented growth of the platelets on a substrate [41]; see fig. 13.



Fig. 13. Oriented growth of CdSe platelets on the (0001)CdSe substrate.

Conclusions

Studies of whisker growth by the VLS mechanism are the most direct and the most reliable information about the mechanism.

A new method for the study of kinetics was developed. The method is based on the dimensional effect in the submicrometer region where the surface energy of the whiskers becomes essential. The method allows determination of some important growth parameters.

Acknowledgments

The author wishes to thank Dr. A.A. Chernov and G.A. Bootsma for helpful discussions and L.N. Bolenskaja and V.I. Muratova for experimental assistance.

References

[1] R.S. Wagner and W.C. Ellis, *Appl. Phys. Letters* 4 (1964) 89.
 [2] R.S. Wagner and W.C. Ellis, *Trans. Met. Soc. AIME* 233 (1965) 1053.
 [3] R.S. Wagner, in: *Whisker Technology*, Ed. A.P. Levitt (Wiley, New York, 1970) pp. 47–119.
 [4] R.B. Finkelman, R.R. Larson and E.J. Dwornik, *J. Crystal Growth* 22 (1974) 159.

[5] J.L. Carter, *Science* 181 (1973) 841.
 [6] E.I. Givargizov and Yu.G. Kostjuk, in: *Rost Kristallov (Crystal Growth)*, Vol. 9 (Nauka, Moscow, 1972) p. 242 (in Russian).
 [7] E.I. Givargizov and A.A. Chernov, *Soviet Phys.-Cryst.* 18 (1973) 89.
 [8] A.A. Chernov, *Soviet Phys.-Cryst.* 16 (1971) 734.
 [9] R.J. Jaccodine, *J. Electrochem. Soc.* 110 (1963) 524.
 [10] W.K. Burton, N. Cabrera and F.C. Frank, *Phil. Trans. Roy. Soc. London A243* (1951) 299.
 [11] B. Mutaftschiev, R. Kern and G. Georges, *Phys. Letters* 16 (1965) 32.
 [12] E.I. Givargizov, *J. Crystal Growth* 20 (1973) 217.
 [13] E.I. Givargizov and N.N. Sheftal, *Kristall und Technik* 7 (1972) 37.
 [14] E. Kaldis, *J. Crystal Growth* 17 (1972) 3.
 [15] G.A. Bootsma and H.J. Gassen, *J. Crystal Growth* 10 (1971) 223.
 [16] A.T. Tumanov, K.I. Portnoi, V.N. Gribkov, A.A. Mukaseev and A.S. Isaikin, *Dokl. Akad. Nauk SSSR* 218 (1974) 1089 (in Russian).
 [17] E.I. Givargizov, *Kristall und Technik* 10 (1975) 473.
 [18] R.S. Sangster, in: *Compound Semiconductors*, Vol. 1, Eds. R.K. Willardson and H.L. Goering (Reinhold, New York, 1962).
 [19] W. Dittmar and A. Köhler, *J. Crystal Growth* 2 (1968) 271.
 [20] G.W. Sears, *Acta Met.* 3 (1955) 361, 367.
 [21] P. Hartman and W.G. Perdok, *Acta Cryst.* 8 (1955) 49, 521, 525.
 [22] S.A. Greenberg and E.I. Givargizov, *Soviet Phys.-Cryst.* 18 (1973) 236.
 [23] E. Kaldis, in: *Lectures at Intern. Spring School on Crystal Growth, Japan, 1974* (North-Holland, Amsterdam, to be published).
 [24] W. Dittmar and K. Neumann, *Z. Elektrochem.* 64 (1960) 297.
 [25] J. Blakely and K.A. Jackson, *J. Chem. Phys.* 37 (1962) 428.
 [26] V. Ruth and J.P. Hirth, *J. Chem. Phys.* 41 (1964) 3139.
 [27] S. Budurov, N. Stojcev and I. Avramov, *Kristall und Technik* 7 (1972) 387.
 [28] R.L. Parker, R.L. Anderson and S.C. Hardy, *Appl. Phys. Letters* 3 (1963) 93.
 [29] F. Hock and K. Neumann, *Z. Physik. Chem.* 2 (1954) 241.
 [30] R.L. Parker and S.C. Hardy, in: *Condensation and Evaporation of Solids*, Eds. E. Rutner et al. (Gordon and Breach, New York, 1964) p. 659.
 [31] L. Kowarski, *J. Chim. Phys.* 32 (1935) 303.
 [32] G.G. Lemmlein, E.D. Dukova and A.A. Chernov, *Soviet Phys.-Cryst.* 2 (1957) 426.
 [33] E.D. Dukova and D. Nenov, *Soviet Phys.-Cryst.* 17 (1972) 1059.
 [34] D. Nenow and E.D. Dukova, *Kristall und Technik* (1972) 779.
 [35] F.A. Kuznetsov, *Thin Solid Films* 13 (1972) 363.

- [36] G.E. Rhead, *Surface Sci.* 15 (1969) 353.
- [37] T. Kobayashi, *J. Crystal Growth* 26 (1974) 6.
- [38] E. Kaldis, *J. Crystal Growth* 24/25 (1974) 53.
- [39] V.P. Zlomanov, E.V. Masyakin and A.V. Novoselova, *J. Crystal Growth* 26 (1974) 261.
- [40] A. Lopes, D. Duh and J. Zemel, *Mater. Sci. Eng.* 17 (1975) 63.
- [41] E.I. Givargizov, *Dokl. Akad. Nauk SSSR* 211 (1973) 332.