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PERIODIC INSTABILITY IN WHISKER GROWTH

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The periodic instability of the diameter of whiskers grown by the vapor–liquid–solid (VLS) mechanism is studied. This phenomenon is especially distinct for silicon whiskers and, to a lesser degree, for germanium whiskers. The instability develops only in whiskers of submicron ($\lesssim$ 0.5 μm) diameters, the smaller the mean diameter, the more distinct is the periodicity, i.e. it occurs in the range of sizes where the Gibbs–Thomson effect manifests itself. The occurrence of the instability is related to experimental conditions such as crystallization temperature, supersaturation and impurities. Some morphological details of the whiskers are also studied. A working hypothesis to explain the instability is presented.

1. Introduction

The unusual morphology of some whiskers has attracted the attention of crystal growers in the past few years. Many different theories have been proposed to explain the whisker growth and the vapor–liquid–solid (VLS)[1,2]) concept seems to be the most convincing of them. This mechanism which involves the occurrence of a liquid alloy phase on the whisker apex has been found very effective for the explanation of some morphological phenomena such as kinking and branching[2,3]). These phenomena are due to instability that is inherent to the microscopic liquid phase.

Beside kinking and branching one can point to other whisker instabilities. Thus the formation of silicon whiskers with a rumpled surface has been observed[4]). The rumpling stems from an increased presence of small areas of highly mobile alloy particles on the side surfaces. There has been also described[5]) a certain periodic instability of germanium whiskers grown by the VLS technique.

It is the purpose of this paper to describe the periodic instability of silicon whiskers grown by the VLS technique. This instability has been observed for extremely small, submicron-diameter whiskers, the peculiarities of this phenomenon being related to the experimental conditions (crystallization temperature, vapor phase supersaturation, gaseous impurities, etc.). The periodic instability has been observed also for germanium whiskers. A mechanism based on the concept of self-oscillations can explain the periodic instability.

2. Experimental procedure

Crystallization was performed in an apparatus described elsewhere[5–7]). The main experiments were performed with silicon. The reaction of silicon tetrachloride with hydrogen was used as a source for silicon. Similarly, germanium tetrachloride and hydrogen were used for germanium whisker growth.

Silicon whiskers were grown in a wide range of temperature (900–1250 °C) and chloride concentration (0.4–4 molar percent ratios of $SiCl_4/H_2$). Germanium whiskers were grown at temperatures 650–850 °C and molar concentrations of $GeCl_4$ in H_2 from 1 to 3%.

As a rule, the liquid-forming impurity for the silicon whisker growth was gold. However, platinum, silver, nickel, gallium and gold–gallium alloy were also used. The germanium whiskers were grown by means of gold. These metals were evaporated at 10^{-5} torr as a layer of 50–500 Å over the entire surface of (111) silicon orientation wafers (for silicon crystallization) or (111) germanium wafers (for germanium crystallization). The wafers were heated to accomplish the alloying of the metallic film with the substrate whereupon the liquid alloy, under the influence of surface tension, broke up into separate globules of micron- and submicron sizes. These globules then served as the "seeds" for whisker growth.

Before crystallization the liquid-forming metal was mechanically removed from certain areas of the substrate so that only residual quantities of the metal were still retained. These traces of metal initiated the growth of rare whiskers offering the possibility for studing of the submicron whiskers from their root. The morphology of these whiskers was examined with a scanning electron microscope.

3. Results and discussion

A typical picture of the periodic instability of silicon whiskers grown with gold as an added impurity is shown on fig. 1. These whiskers consist of a row of knots and necks with approximately equal distances between them. It is known that the diameter of whiskers grown by the VLS technique is determined by the diameter of the liquid alloy droplet on its tip. We can conclude therefore that the variation of the crystal diameter is due to the instability of the droplet's diameter during growth. It is to be noted that although the variations are periodical, the individual knots have somewhat different diameters and lengths. In other words, the periodicity is not strict, the sequences of knot diameters being different for various whiskers. Hence, we can conclude that the cause of the variations is intrinsic to the growth process, otherwise the diameters of different whiskers would vary synchronously. In other words, each whisker follows his own law of oscillations. It can therefore be assumed that the periodicity is of a selfoscillatory mode.

We have studied the periodic instability of the silicon whiskers as a function of the following parameters: (1) mean whisker diameter, (2) crystallization temperature, (3) supersaturation in the vapor phase, (4) kind of liquid-forming impurity, and (5) presence of some gaseous impurities during crystallization. In addition, there were studied some morphological details of these whiskers.

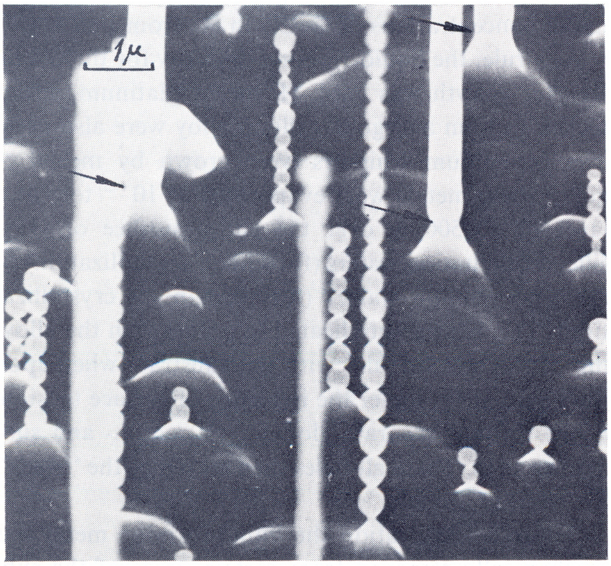


Fig. 1. Typical picture of the periodic instability for silicon whiskers grown at 1050 °C. Here and everywhere in following, unless otherwise noted, the scanning beam angle is $\vartheta = 45°$.

Fig. 2. Dependence of amplitude and frequency of oscillations on the mean whisker diameter.

The results of these studies, using gold as liquid-forming impurity (unless otherwise stated) are given below.

(a) *Dependence of the periodicity on the mean whisker diameter*. As can be seen in fig. 2, the larger the diameter, the weaker is the periodicity. In other words, the smaller the amplitude of the oscillations, i.e. the difference between maximum and minimum diameters, the lower is their frequency. For relatively large diameters there is no periodicity at all. It must be pointed out, that the disappearance of the periodicity relates with the abrupt change of the slope on the curve of growth rate versus whisker diameter[8,9]). It has been found that the smaller the diameter d, the lower is the whisker's growth rate v; the decrease is at first gradual but beginning from some diameter d_t it becomes rather steep. This transient diameter is approximately 0.5–1 μm. It has been found that such a kind of dependence of $v(d)$ is inherent for whisker growth by the VLS mechanism in general, because of its being observed for whiskers of silicon, germanium, gallium arsenide, gallium phosphide, cadmium selenide and silicon carbide. This phenomenon was ascribed to the Gibbs–Thomson effect, i.e. to the lowering of the supersaturation on the growth interface (liquid–solid) as the whisker diameter decreases. For a given vapor phase supersaturation there is a critical diameter for which the growth rate stops altogether.

(b) *The dependence of the periodicity on the crystallization temperature*. It was found that the occurrence of the periodic instability depends strongly on the crystallization temperature. Silicon whiskers were grown at fixed temperatures with 40 ° steps: 940, 980, 1020, 1060, 1100, 1140, 1180, 1220 °C *.

The periodic instability is never observed at 940 and 980 °C. The instability appears at 1020 °C, but only at high vapor supersaturations (see below). The most distinct picture is observed at 1060 and 1100 °C. At higher temperatures the phenomenon is apparently masked by vapor–solid (VS) growth mechanism: at the root of the whiskers, the necks between knots have been overgrown (fig. 3).

(c) *The dependence on the vapor supersaturation*. The vapor supersaturation in this process is determined by the molar concentration of silicon tetrachloride in hydrogen. The direct measurement of the supersaturation is rather difficult in view of the complexity of the chemical vapor deposition. It has been shown [8]), however, that under some reasonable assumptions one can calculate the supersaturation on the basis of the dependence of $v(d)$. It was found, that in this process the supersaturation is a monotonic, approximately linear function of the molar concentration $SiCl_4/H_2$.

In this study, it was found that the periodic instability could vanish if the concentration (consequently, the vapor supersaturation) was decreased, under otherwise identical conditions, and, vice versa, the instability developed again if the concentration was increased. This effect is shown in fig. 4. The whiskers were grown in a three-stage process: at first they grew at relatively high concentrations ($\sim 0.8\%$); then, without interrupting the growth process, the concentration was decreased by a factor of two ($\sim 0.4\%$); finally, the concentration was restored up to 0.8%. Each stage continued 2 minutes. It must be pointed out that on the thinnest whiskers the instability was retained during all 3 stages, on the thickest ones the instability was absent at all and on the whiskers of intermediate diameters the instability practically vanished at the second stage and was restored at the third stage. This result proves that

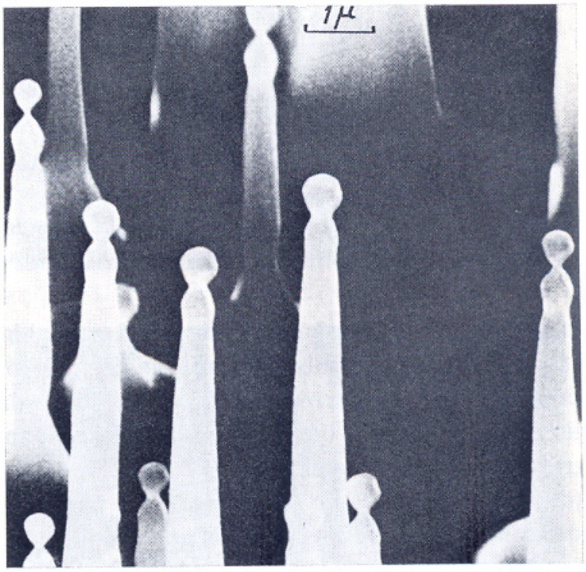


Fig. 3. Overgrowing of necks near the root of whiskers grown at high temperature.

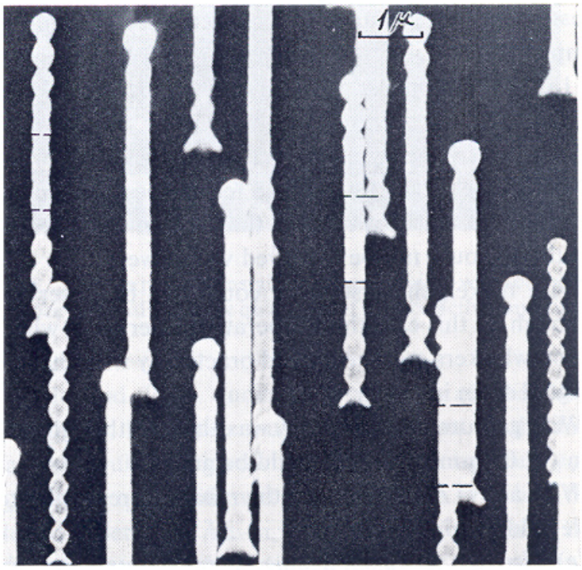


Fig. 4. Periodic instability at various supersaturations in the vapor phase. The dashed lines mark the boundary between the stages.

* The temperatures were measured by means of a pyrometer with disappearing filament. It is known that the absolute accuracy of such measurements is not high (not more than ± 10 °C in the temperature interval). The reproducibility of such measurements, however, is rather satisfactory (approximately ± 5 °C, according to our estimates).

the phenomenon has nothing to do with the formation of "gouttes solides" observed by Drechsler et al.[10]).

The results of (b) and (c) are summarized in the plot of fig. 5, where mark "plus" means the detection of the

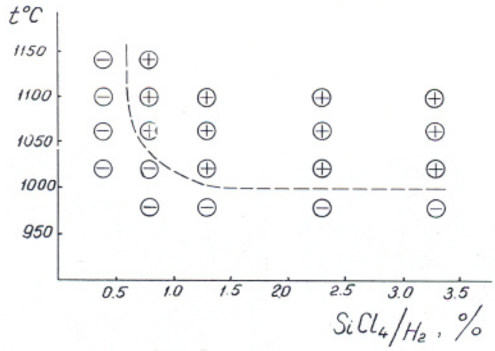


Fig. 5. Relation between instability and growth conditions (crystallization temperature and molar concentration of silicon tetrachloride in hydrogen).

instability, and mark "minus" its absence for the thinnest whiskers as far as resolved by our scanning electron microscope (resolving power ~ 250 Å). Thus, the region above and on the right of the dashed line corresponds to the instability.

(d) *The role of liquid-forming impurity*. It was noted above that the main results were obtained with gold as an added impurity. Experiments with other metals showed the following:

– With platinum, the instability was absent up to the most high temperatures and concentrations. Only at temperatures of 1250 °C and molar concentrations of $\gtrsim 15\%$, the thinnest whiskers revealed a weak instability.

– With silver, the temperatures at which silicon whiskers could be grown by the VLS technique were limited at $T \lesssim 1000$ °C, Possibly, for that reason the periodic instability could not be observed with silver.

– With nickel, the instability could not be observed, although in this case the temperature interval in which silicon whiskers grew coincided practically with the one for gold as an impurity.

– With gallium, the instability was absent although very thin ($\lesssim 0.5$ μm) whiskers could be grown.

– With alloys Au:Ga = 1:1 the results were similar to pure gold.

(e) *The role of vapor doping*. It was found that an addition of minute amounts of gaseous $AsCl_3$ to the reaction mixture (about 0.1 % in relation to $SiCl_4$) exerted a great influence on the morphology of silicon whiskers: the periodic instability disappeared even at the most proper crystallization conditions to develop the instability. Here it is appropriate to note that the similar $AsCl_3$ doping also greatly influenced the morphology of germanium whiskers[5]): instead of "fungaceous" whiskers (type I) there grew the whiskers (type II) with a morphology typical for silicon whiskers. It is very important to note that it is of the type I (fig. 6) which develop periodic instability similar to that of the silicon whiskers. In this case the droplet's diameter is much larger than the whisker diameter. It means that the specific free energy α_{LS} of the liquid–solid interface (or the corresponding surface tension γ_{LS}) is relatively large and the role of the gaseous doping ($AsCl_3$) consists in a decrease of α_{LS} (i.e. γ_{LS}), see fig. 7.

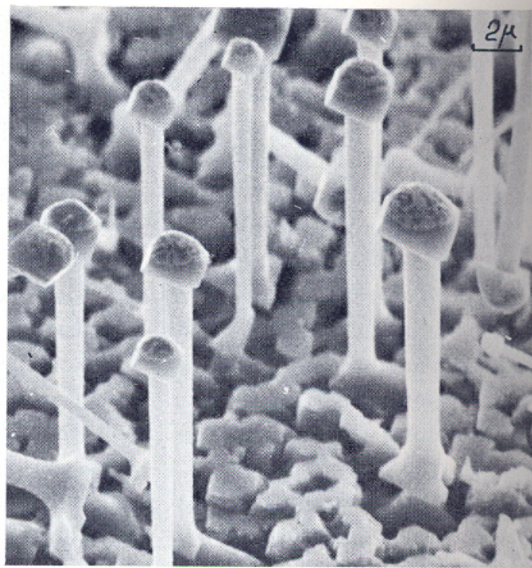


Fig. 6. Periodic instability of germanium whiskers grown without addition of gaseous impurity $AsCl_3$.

Too high $AsCl_3$ dopings, however, produce some new instabilities in germanium whiskers of type II: the growth direction instability (fig. 8a) and rhythmic bending of ribbon-like crystals (fig. 8b). Both these instabilities indicate the relative (and absolute) decrease of the specific free energy α_{VL} of the vapor–liquid interface. The explanation of the doping action is consistent with the general concept of the VLS mechanism: the liquid surface as an ideally rough one adsorbs all gaseous components far stronger than any crystal-

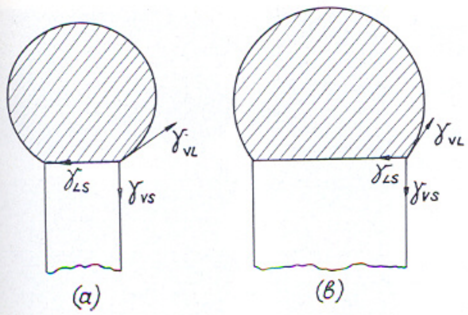


Fig. 7. Shape of whisker tip with droplet for various relations of interface tensions. (a) Corresponds to growth of germanium whiskers without intended doping, (b) to growth with gaseous impurity $AsCl_3$. In the transition from (a) to (b) the value of γ_{VS} is practically unchanged, but γ_{VL} and γ_{LS} decrease markedly due to the adsorption of the impurity.

line surface. In other words, the impurity ($AsCl_3$ or its decomposition products) is relatively weakly adsorbed by the side faces of the whisker and therefore has only little influence on α_{VS}.

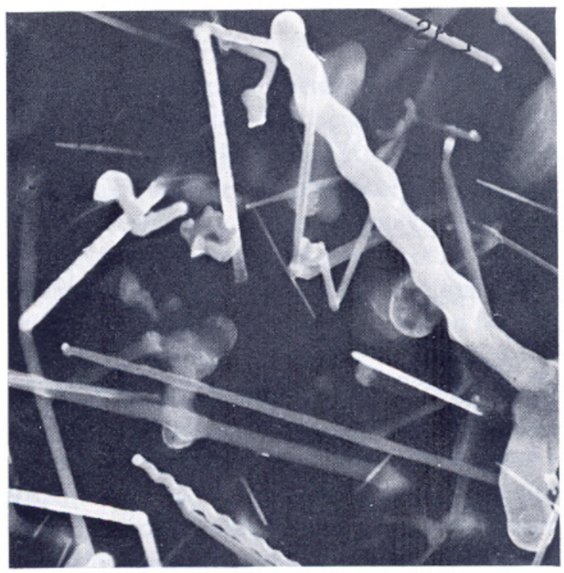
Thus the periodic instability of silicon whiskers, as well as of germanium whiskers of type I (figs. 7a and 7b), seems to be related to the high values of α_{LS}.

(f) *Onset and development of the periodicity.* Here we have to pay attention to two facts: the occurrence of necks at the root of the whiskers, and the "swinging" of oscillations.

We will divide all investigated whiskers to three groups in accordance with their diameters: "thin" whiskers (the periodicity is developed practically along the whole length); "thick" ones (the periodicity is absent at all); "intermediate" ones (the periodicity is developed only along some section). The latter are of special interest because they are the most sensitive to crystallization conditions and therefore we can observe on them some details. For example, the intermediate whiskers have rather distinct necks at their root (indicated by arrows in fig. 1), and the smaller the diameter, the more profound is the neck. The thick whiskers do not show any necks at all (fig. 9), and on thin whiskers the first neck can not be distinguished from the next ones.

The formation of the first neck can be explained if we pay attention to the critical importance of the initial growth stages, involving the rise of the liquid droplet from the substrate. Wagner[11]) pointed out that the alloying process of the impurity agent with the substrate and the initial stages of growth are the most

(8a)



(8b)

Fig. 8. Various types of instability of germanium whiskers in the presence of relatively large quantities of surface-active impurities.

difficult and least understood aspects of the VLS mechanism. Here one must pay attention to the fact that the equilibria involving the surface tensions γ_{VL}, γ_{LS}, γ_{VS} are quite different for two cases: (a) when the alloy droplet, say Au–Si, is in equilibrium with the substrate, e.g. silicon (fig. 10a); (b) when the droplet is on the whisker tip, i.e. it has been rised over the substrate (fig. 10b).