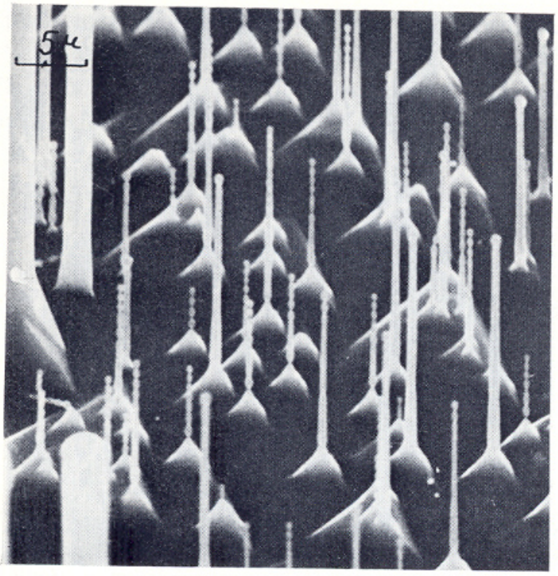

Fig. 9. Comparison of the "thin", "thick" and "intermediate" whiskers from the point of view of the first neck.

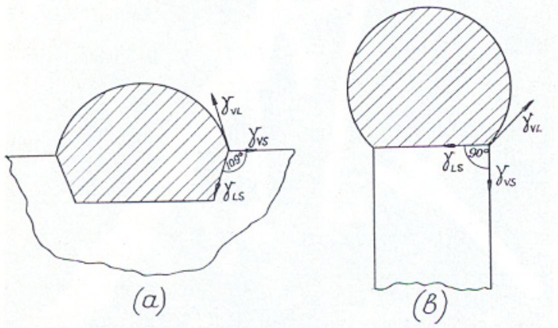

Fig. 10. Comparison of the equilibria for two positions of Si-Au alloy droplet: (a) the droplet is "alloyed-in"; (b) the droplet is upon the whisker tip. In the transition from (a) to (b) the value of γ_{VS} increases, but γ_{LS} and γ_{VL} are practically unchanged.

Let us consider the crystal growth from the molten solution in which the solubility of the material is rather high. In this case the droplet is not "sessile", but is "alloyed-in", and the higher the solubility, the larger is the alloying depth. The numerous experiments with gold alloying in silicon (111) wafers shows that the dissolution front is formed mainly with faces {111} (see, for example, ref. 12). Hence, at the stage (a) the angle between γ_{VS} and γ_{LS} is about 109°. On the other hand, the growing silicon whisker in typical conditions has side faces {211}, i.e. at the stage (b) the angle became 90°. In addition, the absolute values of γ_{VS} (and α_{VS}) change in the transition: $\alpha_{VS}(111) = 1060$ erg/cm^2, $\alpha_{VS}(211) = 1500$ erg/cm^2, see ref. 8.

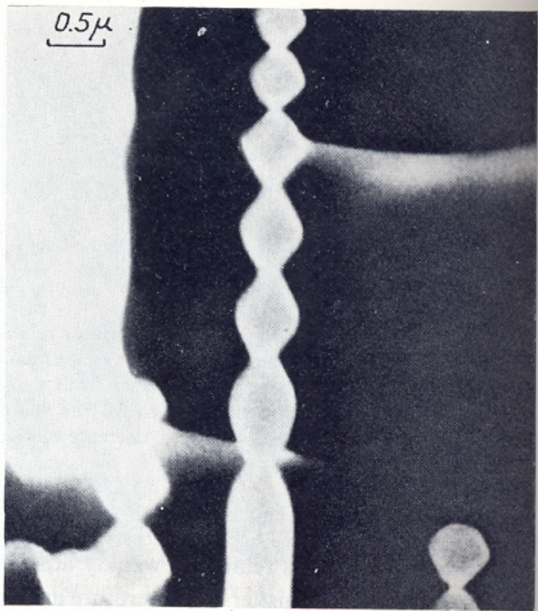

Fig. 11. "Swinging" of oscillations.

In other words, during the transition from (a) to (b) the polyhedral growth interface transforms to the monohedral one. This transformation occurs abruptly and so it can be the cause of an instability such as the formation of a neck. If there are some conditions favorable for the periodic instability, oscillations will develop. If there are no such conditions, prismatic (or cylindrical) whiskers will grow after the first neck.

Let us now consider the "swinging" of the oscillations. This phenomenon is illustrated by fig. 11: as the whisker grows, the oscillations develop progressively, their frequency becoming successively higher. Similar behavior can be seen in fig. 9 as well. One of the possible explanations of the "swinging" is the following. As the whisker grows, a droplet liberates itself from uncontrolled impurities that have been captured when the droplet was formed on the substrate. It is known, that in silicon the distribution coefficients K are in general larger for donors as compared with acceptors (for example, K is 0.35 and 0.30 for phosphorus and arsenic, and 0.01 and 0.0005 for gallium and indium, respectively). Hence, the droplet will lose primarily the donor impurities, and so they will develop oscillations.

(g) *Some morphological details.* In some cases, kinking of the periodic whiskers was observed (fig. 12). Initially, the whisker grew perpendicular to the (111) plane; then, possibly under the influence of an occasion-

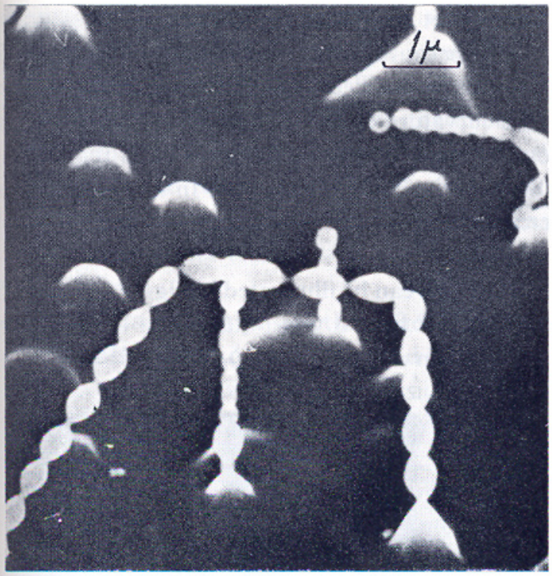

Fig. 12. Kinking of periodic whiskers.

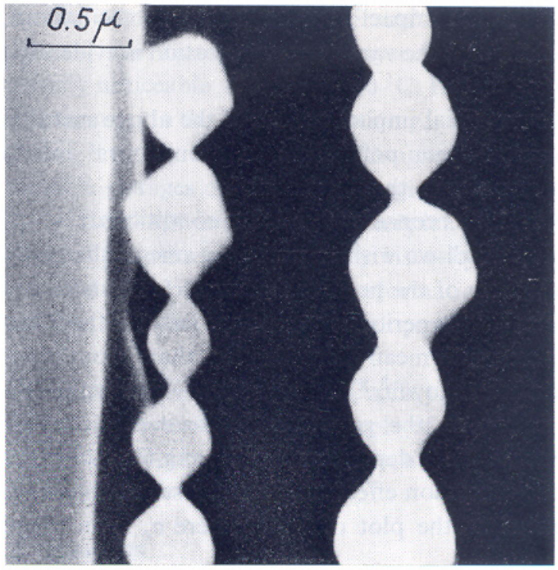

Fig. 14. Faceting of knots at relatively high crystallization temperature.

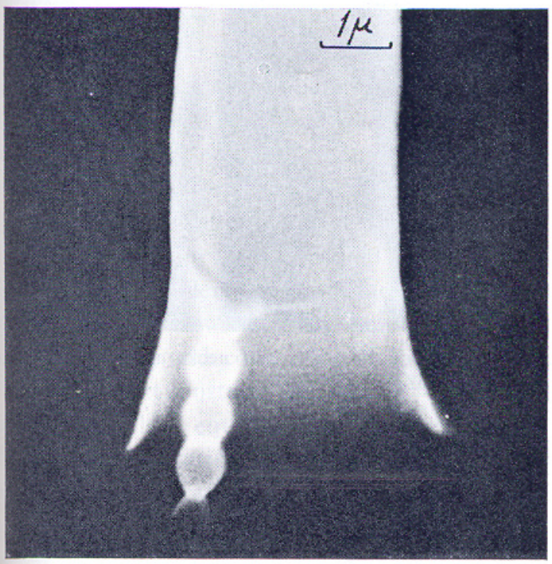

Fig. 13. Branching with formation of periodic whisker at the initial stage of whisker growth.

al reason, e.g. fluctuations of temperature and/or gas flow, kinking for a certain angle occurred. It must be noted that, first, the periodicity is retained after the kinking and, second, between and after the kinking the whisker grows in well-defined, apparently crystallographical, directions.

Branching was observed, leading to the formation of a periodic whisker (fig. 13). In this case the thin whisker grew as a periodic one, whereas the thick whisker is retained as a straight one. One can see from fig. 13 that the branching has taken place at the stage where the conical (base) section of the whisker converts to the cylindrical section, i.e. where the polyhedral interface transform to the monohedral one. In other words, the phenomenon is related to the above mentioned effect of the "first neck", connected with transition from polyhedral to monohedral interface.

At relatively high crystallization temperature (1150–1200 °C) the knots are faceted (fig. 14). This phenomenon is evidently due to the growth by the vapor–solid mechanism. One can see that various knots are faceted identically; it confirms the monocrystalline, oriented structure of the whiskers.

(h) *The model of formation of the periodic whiskers.* It has been noted above that each whisker had his own law of oscillations; it seems, therefore, that the process has a self-oscillating nature. Here we wish to propose one of the possible mechanism of the self-oscillations. It is known in general that self-oscillations develop only if several conditions are fulfilled. In particularly, there must be:

– a certain mechanism of positive feedback;
– a certain mechanism of limitation of the avalanche process;
– a certain driving force of the process;

– an "initial impact" for beginning of oscillations.

In our case the vapor supersaturation is evidently the driving force.

As an initial impact can serve the above mentioned transition from polyhedral to monohedral interface that give rise to the "first neck".

Now let us consider two other conditions.

First of all we wish to point out one of the possible mechanism of the positive feedback. It has been noted above that the periodicity develops only for the thinnest whiskers with mean diameters less than about 0.5 μm. It has been shown[8,9]) that for such whiskers the supersaturation on the growth interface depends on their diameter. This dependence is a manifestation of the Gibbs–Thomson effect and can be schematically represented as the plot of fig. 15; here σ_0 is an effective

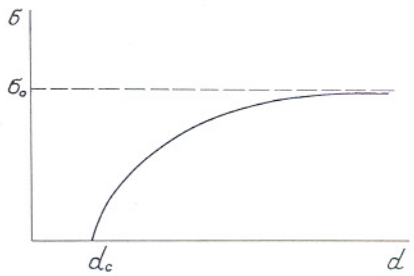

Fig. 15. Dependence of growth interface supersaturation on diameter of whisker (and/or of droplet). σ_0 is determined by molar concentration of reaction mixture.

total supersaturation in the vapor phase corresponding to a plane surface and d_c is the critical diameter corresponding to ceasing of growth.

Consider now the structure of the liquid–solid interface (in our case the liquid is the solution of silicon in gold). Voronkov and Chernov[13]) studied the atomic roughness of a crystal–solution interface in the case of a similar binary solution. They predict a critical temperature for the smooth–rough transition of the interface, the temperature depending on the solution concentration. In addition, one can consider the "kinetic roughness" that depends on the supersaturation of the solution. Further, it has been shown[14]), that the contact angle of a droplet on the solid surface depends on the roughness of the surface: the higher the roughness, the smaller is the angle. Hence, for a given droplet its curvature depends on the substrate roughness.

We assume the following mechanism of the positive feedback: if, as a result of a fluctuation, the curvature of the droplet increases, the solution supersaturation decreases (because it depends on the curvature, see fig. 15), the roughness decreases, the contact angle increases, the curvature of the droplet increases further, and so on. Such a sequence of events is valid for the stage of the constriction of the droplet. In the opposite case, where the droplet is extending, the sequence will be reversed.

These stages can be illustrated by figs. 16 and 17. The micrograph of fig. 16 was obtained at a rather large scanning beam angle ($\vartheta = 80°$), so that the beam was

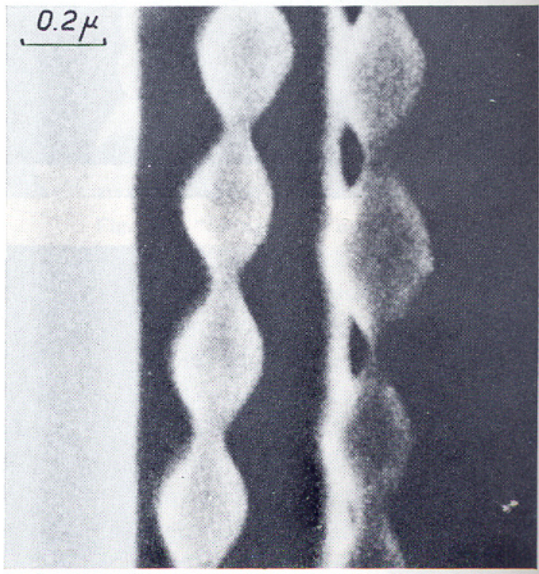

Fig. 16. Shape of the knots and necks as observed at large scanning beam angle ($\vartheta = 80°$).

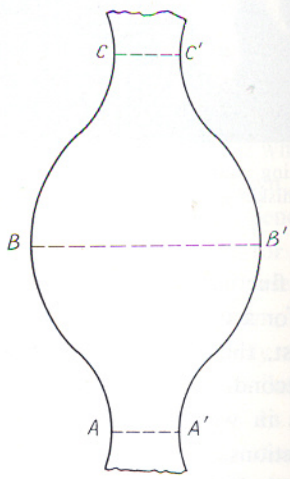

Fig. 17. Schematic illustration of the fluctuations of the diameter.

nearly perpendicular to the growth axis. One can see that the maximum whisker diameters exceed the minimum ones by a factor of 3–5. Typical shapes of a periodic whisker, in accordance with the micrograph, are shown in fig. 17. Two regions can be distinguished: from A to B the roughness gradually increases and from B to C it decreases. Accordingly in positions AA′ and CC′ the interface tension is maximum, and in BB′ it is minimum*.

A more detailed analysis of the stages involving the shape of the droplet and the liquid–solid interface in the extreme positions, as well as a discussion of the consideration of the interface energy is beyond the scope of this paper and will be published later.

Finally, let us consider a possible mechanism for stopping the avalanche. There are two interfaces in the VLS growth: the vapor–liquid and the liquid–solid interface. On the first interface the processes which take place are a catalytic chemical reaction by which the crystallization material (in our case silicon) does evolve; this interface we will call the "supplying" one. On the second interface the material is deposited – the interface we will refer to as the "consuming" one. The material is transported from the supplying to the consuming interface by diffusion. It has been shown[7–9], however, that the diffusion stage is not the limiting factor, otherwise thin whiskers would grow more quickly than thick ones. Hence, the interface supersaturation depends, under otherwise equal conditions, on the ratio of the supplying and consuming surfaces, S_{supl}/S_{cons}. When the droplet constricts (the stage B → C), the ratio increases, which is equivalent to the decrease of the solution supersaturation; then a moment will come at which the two opposing processes are equalized and a further constriction droplet will stop. When the droplet extends (the stage A → B), the events are reversed.

Now, according to this model, let us consider some of the above mentioned experimental facts.

– The higher the vapor phase supersaturation, the steeper is the slope of the initial region of the plot $\sqrt{v}$ versus $1/d$ (see fig. 5a in ref. 8), and the larger is the feedback coefficient of self-oscillation system, the higher are the frequency and amplitude of the oscillations.

* It must be noted that the growth rate of such a crystal will change with time, therefore the properties of the whisker will also be non-uniform along its length.

– As the temperature rises, the surface tension γ_{VL} decreases, the decrease for the system Au–Si being especially noticeable above ~ 1000 °C. Hence, the role of the term γ_{LS} in the Young equation $\gamma_{VL}\cos\theta+\gamma_{LS}=\gamma_{VS}$ rises, i.e. any changes of the roughness will cause noticeable changes of the contact angle θ and, respectively, of the shape and size of the droplet. In addition, as the temperature rises, the alloy viscosity decreases, i.e. the kinetics of the shape transformations is facilitated. Both factors favor the development of oscillations.

– When gaseous impurities (say, $AsCl_3$) are added, the value of γ_{LS} decreases, hence the role of the roughness in changing of γ_{LS} becomes negligible, and the periodicity disappeares.

4. Conclusions

The phenomenon of the periodic instability of a whisker described here is characteristic for the VLS mechanism. This phenomenon is observed only for certain experimental conditions and is related to the surface energy effects. Further experimental as well as theoretical studies are necessary to determine a relationship between the frequency and amplitude of oscillations, on the one hand, and the growth conditions (temperature, supersaturation, etc.) and crystal/liquid characteristics (interface energies, contact angle, etc.) on the other hand.

Studies of this phenomenon would help to understand the mechanism of formation of many unusual crystalline forms such as helical[15]) and coiled[16]) whiskers.

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