VAPOR-LIQUID-SOLID MECHANISM OF SINGLE CRYSTAL GROWTH

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Detailed studies of the morphology and growth of silicon whiskers[1] have led to a new concept of crystal growth from the vapor, which we call here the vapor-liquid-solid (VLS) mechanism. From these and subsequent studies, in which Si whiskers were grown by the disproportionation of SiI_2 or by the hydrogen reduction of $SiCl_4$, three important facts emerged: (a) silicon whiskers do not contain an axial screw dislocation;[2] (b) an impurity is essential for whisker growth;[3] (c) a small globule is present at the tip of the whisker during growth.

From fact (a) and related evidence, it became clear that growth from the vapor did not occur by the Frank[4] screw dislocation mechanism. From facts (b) and (c), and much additional evidence, the VLS mechanism emerged. In this mechanism, the role of the impurity is to form a liquid alloy droplet of relatively low freezing temperature. The liquid droplet is a preferred site for deposition from the vapor, which causes the liquid to become supersaturated with Si. The whisker grows by precipitation of Si from the droplet. Since the whisker grows from the liquid, a screw dislocation is unnecessary.

Growth of seeded whiskers of Si using gold as an impurity occurs as follows: A small particle of Au is placed on a {111} surface of a Si wafer and heated to 950°C, forming a small droplet of Au–Si alloy as shown in Fig. 1*a*. A mixture of hydrogen and $SiCl_4$ is introduced as described by H. C. Theuerer.[5] The liquid alloy acts as a preferred sink for arriving Si atoms or, perhaps more likely, as a catalyst for the chemical process involved. The Si enters the liquid and freezes out, with a very small concentration of Au in solid solution, at the interface between solid Si and the liquid alloy. By a continuation of this process the alloy droplet becomes displaced from the substrate crystal and "rides" atop the growing whisker, as shown in Fig. 1*b*. The growth direction is <111>, and the side faces of the whisker are usually {211} but sometimes {211} and {110}. The whisker grows in length by this mechanism until the Au is consumed or until the growth conditions are changed.

VLS growth of Si whiskers can occur over a wide range of cross-sectional dimensions, as shown by the 1000-Å whisker and the 0.2-mm needle in Fig. 2*a* and 2*b*. In these examples, VLS growth was interrupted before the Au was consumed. Similar results were obtained with Pt, Ag, Pd, Cu, or Ni either by placing a particle on the Si substrate or by co-deposition. VLS growth of twinned Si ribbons having a <211> or a <110> growth direction and {111} main faces[6] has been observed.

The selection of a proper impurity for VLS growth depends on a number of factors such as, formation of a liquid alloy at the deposition temperature, vapor-liquid-solid interfacial energies, distribution coefficient and inertness to the reaction products. The term impurity is used in a broad sense. For VLS growth of compound crystals, for example GaAs, an excess of one of the component materials can act as a liquid-forming impurity. In some cases a combination of two or more impurities can be used.

The VLS growth mechanism explains many observations of the effect of impurities in crystal growth from the vapor. Crystals of α-Al_2O_3 (ref 7) and

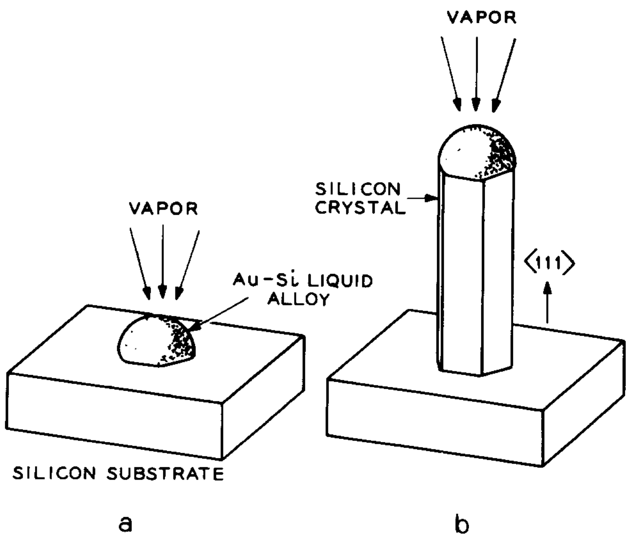

Fig. 1. Schematic illustration: Growth of a silicon crystal by VLS. *a*. Initial condition with liquid droplet on substrate. *b*. Growing crystal with liquid droplet at the tip.

SiC (ref 8), which have been shown to have rounded terminations, may have grown by the VLS mechanism. In the growth of BeO whiskers, which also show rounded terminations, Edwards and Happel[9] suggested that a droplet of molten Be was present at the tip of the growing whisker. However, they also postulated a solid shell of BeO enclosing the liquid Be, diffusion of oxygen through this shell and the need for a crystalline defect, presumably a screw dislocation. None of these features is a requirement of the VLS mechanism.

The proposed mechanism has widespread application to the growth of both filamentary and macroscopic crystals and of epitaxial layers. Controlled growth can be obtained through appropriate use of impurities in patterns or films on substrate surfaces and on single-crystal seeds of many substances. *P-N* junctions and heterojunctions can be made. Dislocation-free crystals can be grown.

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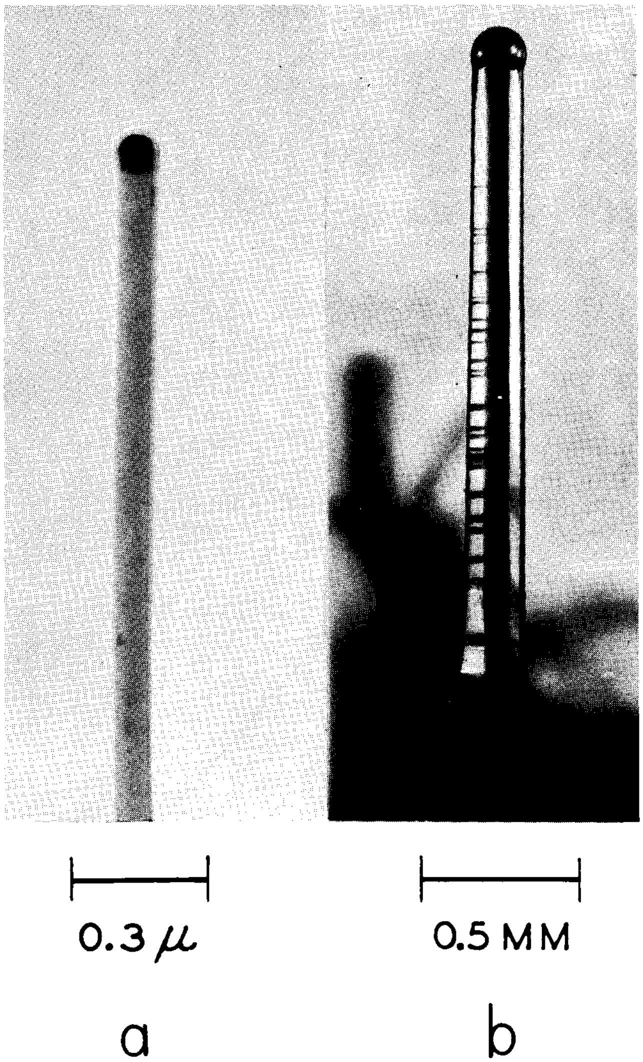

Fig. 2. **Silicon crystals showing solidified gold-silicon alloy at tip.** *a*. Transmission electron micrograph of a 1000-Å whisker. *b*. Photograph of a crystal seeded on a {111} substrate. This is a twelve-sided needle with alternating {211} and {110} faces.

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