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MORPHOLOGY OF SILICON WHISKERS GROWN BY THE VLS-TECHNIQUE

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The morphology of silicon whiskers grown by the VLS-technique was investigated. The role of liquid-forming impurities (gold, gallium or indium) was noted. Habitus of silicon whiskers grown in the $\langle 1\bar{1}0 \rangle$ directions was determined. Influence of the chloride concentration in gas mixture on the whisker form was revealed. Morphology of the composite whiskers was studied.

1. Introduction

Wagner and Ellis[1,2]) have reported a new method for growing crystals, the vapor–liquid–solid (VLS) process. They showed that crystalline whiskers could be generated from liquid alloy droplets, with the droplets locally formed on a crystalline substrate and comprised of the substrate material plus a suitable impurity. Growth proceeded through addition of material to the droplet from a source-laden gas. Further work on the VLS process has been described by James and Lewis[3]), Filby et al.[4]), and Wagner et al.[5−9]).

In this paper we describe further experiments performed with the aim of correlating morphology with crystallization conditions for silicon and composite whiskers.

2. Experimental technique

Silicon (111)-orientation wafers, 0.8 mm thick, were mechanically polished and then etched in $HF/HNO_3/H_2O$ solution to remove 0.05 mm of silicon. A layer of gold, gallium or indium 500–1000 Å thick was then deposited at 10^{-5} torr over the entire surface of the wafers.

These wafers were placed in a vertical reduction cell of a silicon deposition apparatus described elsewhere[10]). For this work, the apparatus was modified so that the induction heating was essentially confined to the growing surface of the crystal. The wafers were then heated to bring about alloying of the metallic film with the substrate where upon the liquid alloy, under the influence of surface tension, broke up into separate globules. These globules then served as the "seeds" for whiskers growth. Whisker growth commenced when mixtures of silicon tetrachloride and purified hydrogen at 900–1050 °C were introduced into the system. In some experiments, the silicon whiskers were used as a base for growth of whiskers of other materials (such as lanthanum hexaboride or germanium). Lanthanum hexaboride was grown at 1050–1100 °C by vapor chemical transport from a LaB_6-source with hydrogen chloride. Germanium whiskers were grown at 750–850 °C from a mixture of germanium tetrachloride and hydrogen.

The resulting whiskers were initially examined by optical microscopy. All of the specimens were further examined with a scanning electron microscope using the surface topography mode of operation. Some of the specimens were also examined with a special light-figure goniometer.

3. Results and discussion

Scanning electron micrographs of the as-grown whiskers are shown in figs. 1 to 6.

1) A silicon whisker grown in the [111] direction at 1000 °C, with gold as the liquid-forming agent, is shown in fig. 1. Note that near the tip, the six principal lateral faces {211} are blunted by six {110} faces. As growth proceeds, however, the 12 sided region left behind by the growing tip evolves into a six sided structure of {211} faces only. This condition arises from lateral growth by direct vapor to solid (VS) de-

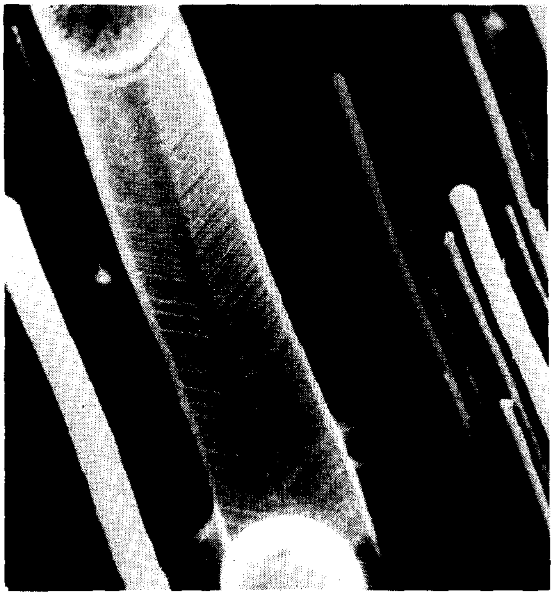

Fig. 1. Silicon whisker grown in the [111] direction by means of gold as liquid-forming agent.

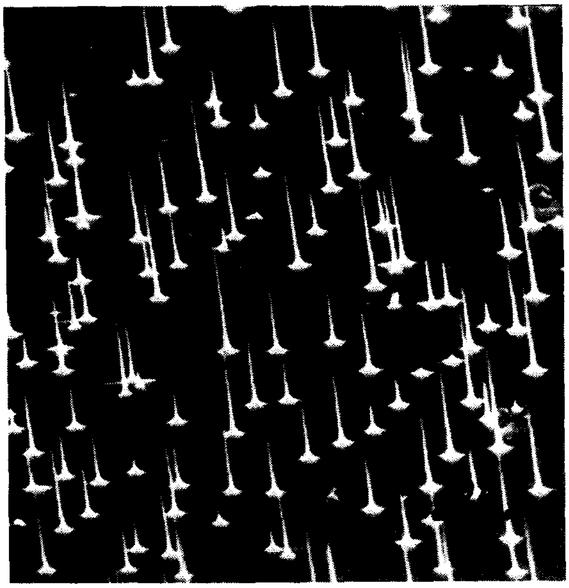

Fig. 3. Silicon whiskers grown by means of gallium as liquid-forming agent.

position. The change in morphology of the side faces of ⟨111⟩ whiskers has been reported and described by Wagner[8]). Evidently, at this growth temperature, the six-fold whisker is energetically more favorable than the twelve-sided whisker.

2) In fig. 2, in addition to the [111] direction whisker, there is also a whisker with a [1$\bar{1}$0] direction. Combined investigation of these crystals by means of the scanning electron microscope and the light-figure goniometer allowed determination of the crystal habit of the inclined whisker as an 8-fold prism, with 4 faces of this prism being {111} planes and the other 4 faces

Fig. 2. Habitus of silicon whiskers grown in [111] and [1$\bar{1}$0] directions.

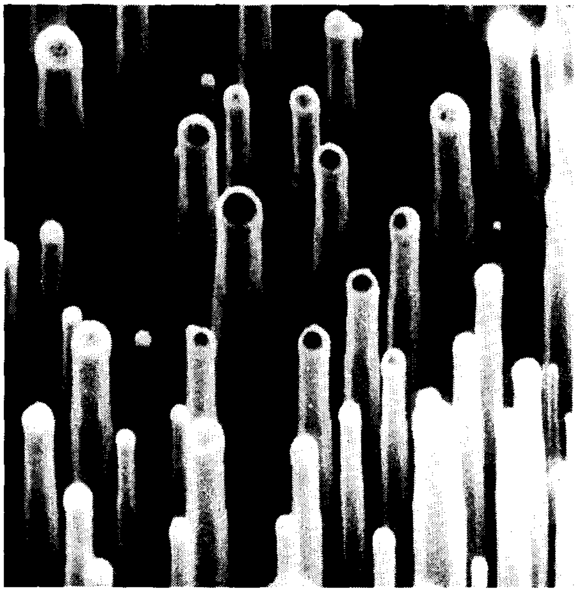

Fig. 4. Diameter contraction of silicon whiskers due to sharp increasing of chloride concentration in gas mixture.

being {311} planes. All of these planes are principal planes of the diamond lattice[11]).

3) Comparison of the morphologies of silicon whiskers grown with gold, gallium or indium as liquid-forming impurities was carried out. Gallium and indium provide practically similar results, these results being quite different from those with gold. Fig. 3, showing whiskers grown with gallium in isothermal conditions, illustrates the conic or pyramidal form typical of specimens grown with this agent. This contrasts with the results using gold which reveal a cylindrical or prismatic form. The conic form associated with gallium arises from the large distribution coefficient of gallium in silicon and from gallium removal from the liquid drop by gaseous reaction products.

4) During the growth of the whiskers shown in fig. 4, the concentration of the chloride in the gas mixture had been abruptly increased (to approximately three times the preceeding value). The clearly observable result was a contraction in the whisker diameter due most probably to the change in surface tension of the drop in the enriched chloride ambient. This phenomenon thereby permits some control over the form of the whisker during growth in isothermal conditions.

5) A composite whisker is shown in fig. 5. A silicon whisker grown on a (111) silicon substrate, with gold as the liquid-forming impurity, is the base of the composite whisker and its apex is a lanthanum hexaboride whisker. It should be noted that both lanthanium hexaboride and silicon crystallize in the cubic lattice. At the heterojunction, the number of lateral faces increases from 6 to 12, due probably to the fact that the surface tension of the lanthanum hexaboride–gold alloy is higher than that of the silicon–gold alloy. From the figure it is clear that the lanthanum hexaboride whisker grows epitaxially on the silicon whisker.

When a germanium whisker was grown on a silicon whisker base (fig. 6), the transition from the faceted silicon whisker to the rounded germanium whisker was observed. We believe this phenomenon is attributable to the high surface tension of germanium–gold alloy at the crystallization temperatures of germanium (750–850 °C).

4. Conclusion

The morphology of silicon whiskers grown by the VLS-technique was investigated. The role of liquid-forming impurities (gold, gallium or indium) was noted. Habitus of silicon whiskers grown in the $\langle 1\bar{1}0 \rangle$ directions was determined. Influence of the chloride concentration in gas mixture on the whisker form was revealed. Morphology of the composite whiskers was studied.

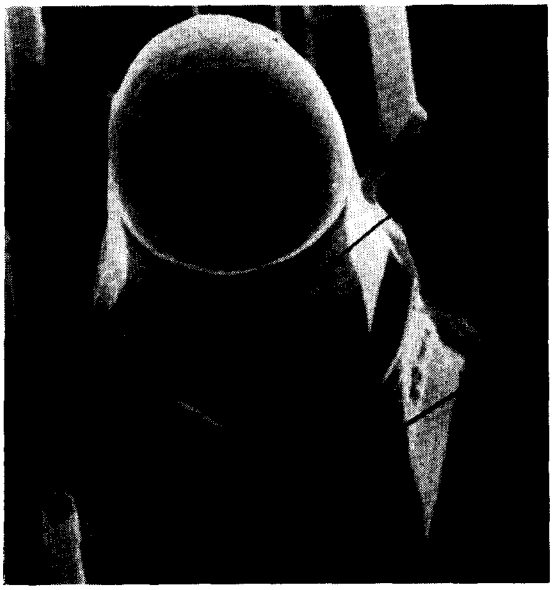

Fig. 5. Composite whisker "silicon+lanthanum hexaboride" on (111) silicon substrate.

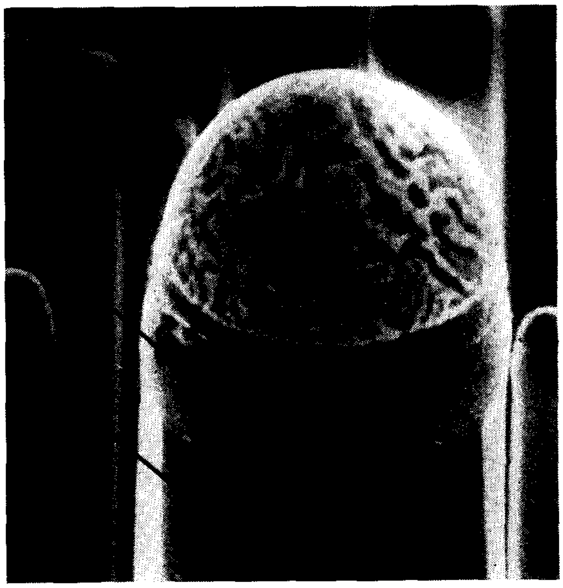

Fig. 6. Composite whiskers "silicon+germanium" on (111) silicon substrate.

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