Growth of
Silicon and Germanium Whiskers
and their New Structures

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Contents

Acknowledgements

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Abstract

New form silicon and germanium whiskers have been grown by thermal decomposition of silane (SiH_4) or german (GeH_4) in argon atmosphere.

Silicon whiskers can be grown at around 550°C on the surface of silicon single crystal stained with small traces of finger grease or coated with metals of low melting point such as Pb, In, Bi, Zn and Te. The as-grown whiskers were amorphous as revealed by electron diffraction and three diffuse rings in pattern roughly correspond to Debye-Scherrer rings of diamond lattice.

At around 500°C fine whiskers of silicon have been grown on a gold plated surface of silicon crystal. It is demonstrated that most of them have a 6H structure (hexagonal, a=3.84Å and c=18.59Å) which accounts for their electron diffraction patterns. Besides, 27R, 51R and 141R structures have also been discovered. Each whisker has an outer crust of amorphous silicon at above 520°C. Raising the growth temperature converts these whiskers into amorphous whiskers.

New form germanium whiskers with a tetragonal structure (a=7.62Å, b=6.20Å) have been grown on gold alloyed germanium surface. The growth temperature ranged from 260° to Au-Ge eutectic point of 356°C.

The purpose of this thesis is to discuss about the growth and the structure of these entirely new materials. Polytypes and Amorphous state in Silicon are also of main interest.

§1 Introduction

A) Background

Study of growth and nature of whiskers is an important field of research not only for pure solid state physicists but for industrial engineers. Generally speaking, whiskers are metallic or non metallic filamentary single crystals with micron-sized widths or diameters and have ultrahigh strength (of the order of 10^6 psi) and high elastic moduli. Because of their remarkable characteristics whiskers have become the subject of intense study in recent years.

While in the field of solid state physics, growth mechanisms and physical properties of whiskers in a great number and variety of substances have been examined[1)]. A variety of methods have been developed to obtain large number of whiskers for subsequent studies of their physical properties, for examples "Evaporation-Condensation", "Chemical Reduction", "Vapor Phase Reduction","Growth from the Melt", "Growth from Solution", and so forth. Their characterization has also been done by using optical microscopes, electron microscopes, electron diffraction , X ray diffraction, X ray topograph and mechanical testing techniques like tensile test. For reviewing these and other previous works in whiskers an excellent textbook edited by Levitt should be consulted[2)]. Extensive references to many studies are given there.

B) Brief Historical Review

Whisker growth from the vapor had been usually explained by a mechanism proposed by Sears[3)]. The special growth form for a whisker crystal implies that the tip surface of the

crystal must be a preferred growth site. He proposed that, according to the Frank's theory[4], a whisker contains a screw dislocation emergent at the growing tip which provides a preferred growth site. Axial screw dislocations have been observed and reported for a few filamentary materials but reservations have arisen regarding its universal application. Nine different whisker materials were investigated by Webb[5] and a single axial dislocation was discovered only in the palladium whisker. Since that time these considerations have stimulated a careful study of the role of agents in filamentary crystals. The discovery by Wagner and Ellis of the vapor -liquid-solid (VLS) mechanism can be summarized as follows[6-8]. The presence of a liquid layer which is containing impurity and in contact with the growing crystal has an importance. The surface of liquid has a larger accommodation coefficient and is therefore a preferred site for vapor deposition. The liquid layer becomes supersaturated with material supplied from the vapor , and crystal growth proceeds at the liquid-solid interface by precipitation. In this case the screw dislocation theory is unnecessary to explain the experimental results.

As a matter of fact, silicon and germanium have an advantage of several independent techniques such as infrared absorption, electron paramagnetic resonance, electrical measurements and other methods mentioned already. It is practically convenient that these materials do not deform plastically at room temperature and therefore dislocations are not introduced into themselves during experimentation.

From now we are concerned with studies relating to the growth and the characters of whiskers in silicon and germanium.

C) Statement of the Problem

Recently, the present author has observed the growth of silicon whiskers with amorphous and 6H structure and germanium whiskers with tetragonal structure. Especially, growth of amorphous whiskers is rarely found in the field of crystal growth. Nobody has reported the structures of 6H and tetragonal in these materials too. It should also be emphasized here that growth of these three types of whiskers is not a kind of accidental one. It is a main purpose of this paper to present detailed experimental results and discuss the atomic arrangement of these entirely new whiskers. Role of agents on the filamentary growth is also discussed.

§2 Experimental Method

The apparatus used for the growth of whiskers is shown in Fig.1. It consists simply of a tube furnace containing a quartz tube (30 mm in diameter). The whole of the gas supply system was constructed of teflon pipes, cocks and their connectors. Argon and mixture gas consisting of 97% argon and 3% SiH_4 (or 1% GeH_4) at a measured flow rate were supplied through the tube. Thin (111) oriented silicon and germanium substrates(5 mm by 5 mm, 0.5 mm thick) were etched with CP4 solution, rinsed in an ultrasonic washer containing deionized water and boiled with acetone and dried in clean air at room temperature. After coating with an appropriate reagent with 99.99% purity in a thickness of about 2000 Å by evaporation in a vacuum of 10^{-6} Torr, these substrates in three quartz boats were pushed into the reaction tube by means of a clean silica rod.

In the beginning, the air in whole gas flow system was purged perfectly with semiconductor grade argon for 15 minutes and these substrates were heated up to the growth temperature in an argon stream (1 l/min). After the temperature was settled, the mixed gas was introduced into the reaction tube at the rate of 0.5 l/min. That made a total flow rate of 1.5 l/min. The furnace temperature was stabilized within $\pm$2°C. A chromel-alumel thermocouple was used to detect the temperature of the central position of the furnace. Figure 2 shows the temperature profiles of the reaction tube. After growth period (varied from 20 min. to 16 hours), the electric current of the furnace was cut off, the substrates were cooled down to 100°C in an argon stream and taken out.

A further precaution is necessary in growing good whiskers: It is desirable to cut off the incident ultraviolet rays from the fluorescent lights in the laboratory and the sunlight coming into the equipment, which stimulate the imperfect decomposition of silane that results in dirty depositon of half-decomposed molecules on all exposed parts of the growth system, especially in the flow meter.

Transmission electron micrographs (TEM), electron diffraction patterns taken at 100KV and scanning electron micrographs (SEM) were used for characterization, identification and crystallography of the whiskers.

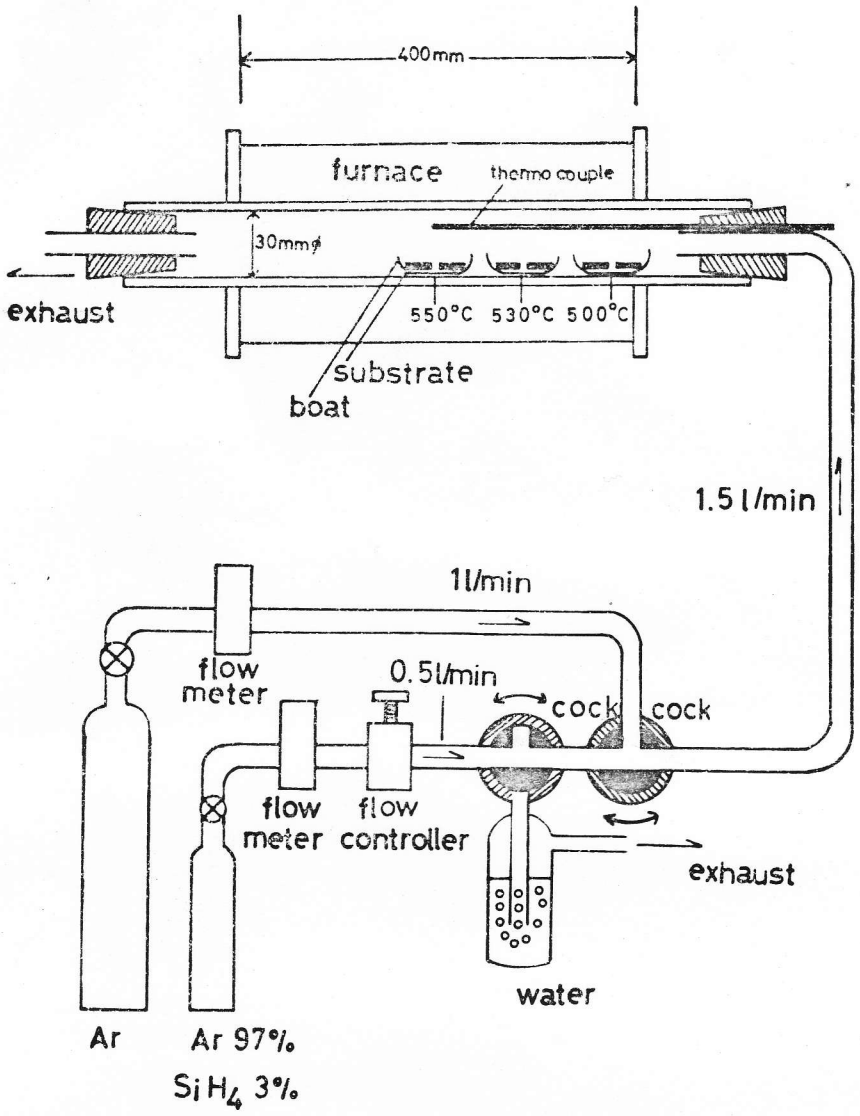


Fig.1 Diagram of apparatus used for growing whiskers.

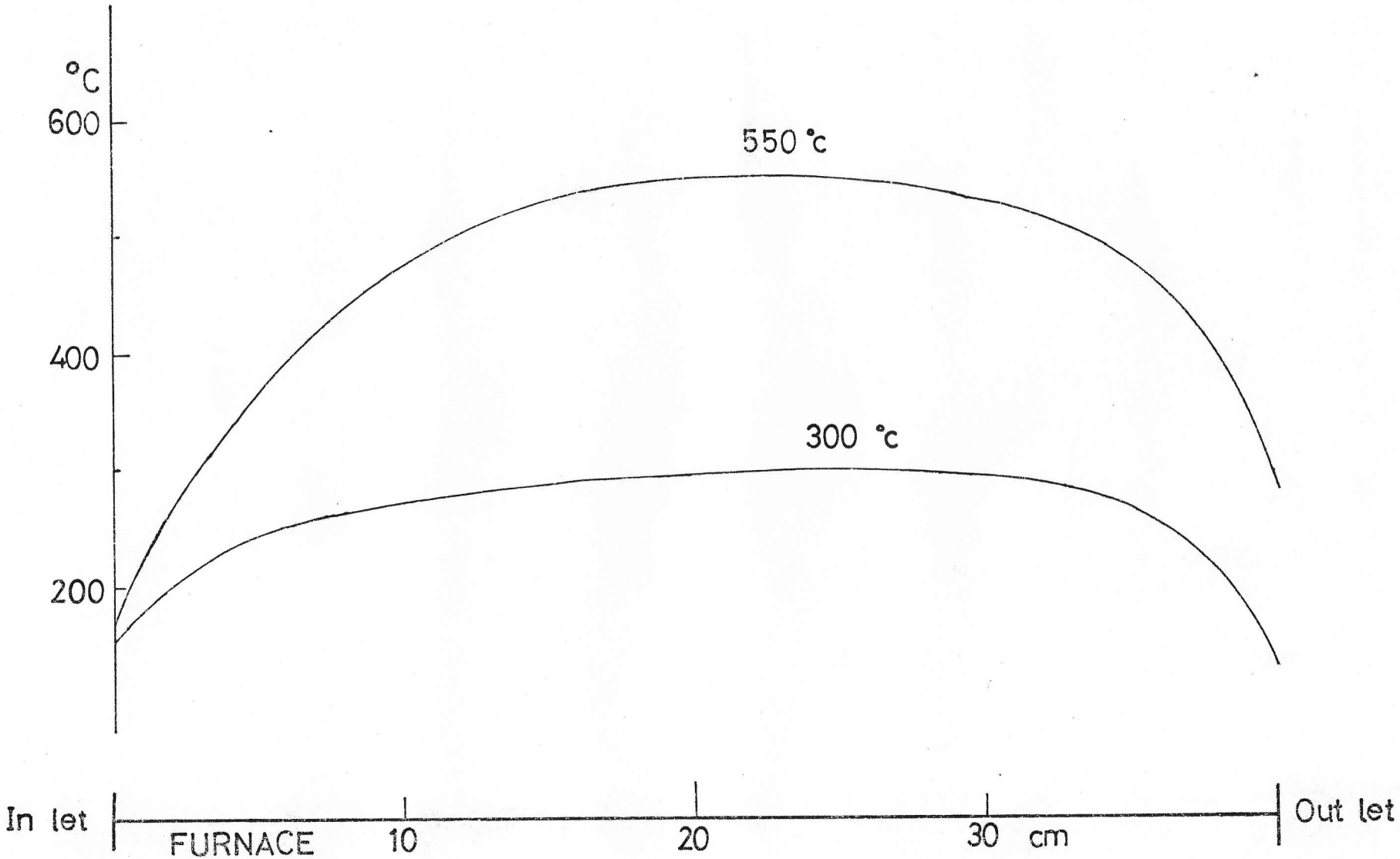


Fig.2 The temperature profiles of the reaction tube.

§3 Experimental Results

A) Amorphous Silicon Whiskers

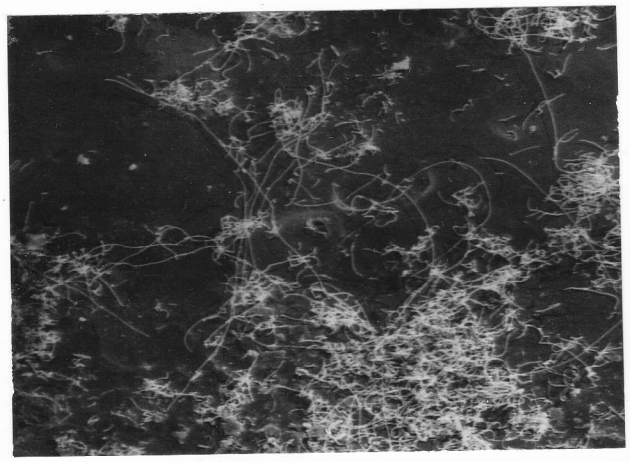
Most of growth experiments were carried out at the temperature region from 500°C to 600°C. In the early stage of this study, only the stain by small traces of finger grease on the substrate was known as playing an essential role in the growth of amorphous silicon whiskers. Later, whatever the explanation, it was also found that any of Au, In, Bi, Zn, Pb and Te could be an effective catalizer to grow amorphous whiskers. Especially, Au and In were found to be the best ones. Therefore, in the later stage of the experiment, mostly Au of 99.99% purity was evaporated in vacuum (10^{-6} torr) onto the surface of substrates to make good whiskers. Almost all whiskers were grown on (111) surface of silicon but growth was observed regardless of the Miller indices of the surface planes. A silica plate or an oxide layer on silicon surface can also be used as a substrate.

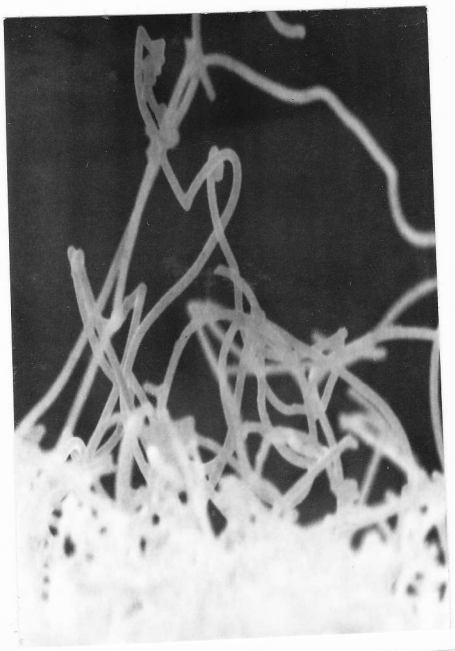
The obtained whiskers appeared as a spot of gray or light brown fuzz to the naked eyes. It has been found by scanning electron microscope at relatively lower magnification that whiskers are tangled and look like a spider's web. On the contrary to crystalline whiskers, long straight ones were seldom found among the gregarious whiskers as shown in Fig.3, where whiskers grown on the substrate stained with finger grease are given. No apparent difference in morphology and electron diffraction is observed between the whiskers grown on finger grease and metal films of low melting points. Figure 4 shows the whiskers grown on indium plated substrate. The diameter

of whiskers increases as the temperature of growth is raised from 500° to 600°C, ranging from a fraction of a micron up to 50 μm. Those grown on the areas of the same temperature have almost the same diameter. The maximum length obtained by 16 hours running was about 4 mm, while that grown for one hour was about 1 mm. Scanning electron microscope study has revealed characteristic features of the whiskers as follows. Each whisker has a uniform circular cross section with a hemispherical tip when its diameter is less than several microns. The tip becomes rather spherical as the diameter of the whisker increases. The surface of thin whisker looks very smooth at magnifications up to 10000 times (Fig.5), but it becomes rough with increasing the diameter (Fig.6). Finally, whiskers grown above 550°C are thick and rough and have a large rugged globule on each top. Hooks, branches and crossings were observed very often but there is no characteristic angle which reflects a crystal structure. Examples of SEM photographs of the crossing whiskers are given in Figs. 6 and 7. A sharp boundary line between two crossing is clearly seen in each picture.

The amorphous whiskers are firmly attached to the substrates, on the other hand they do not have enough mechanical strength in themselves compared with crystalline whiskers. By vibrating mechanically in an ultrasonic washer containing water, almost all whiskers were broken not at the root but in the middle part of the length. As shown in Figs. 8-A, B, broken sections look flat and no structure is recognized on them regardless of the outer shape or the roughness of the column surfaces.

By applying the Archimedean method, the density of amor-





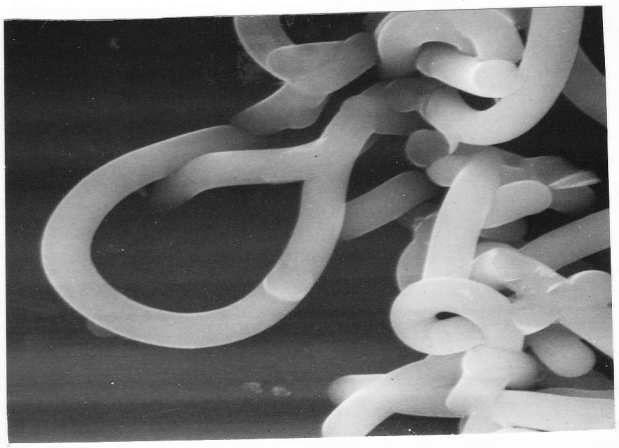
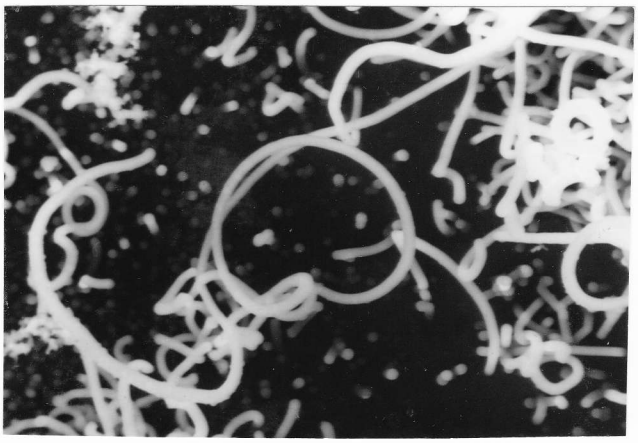
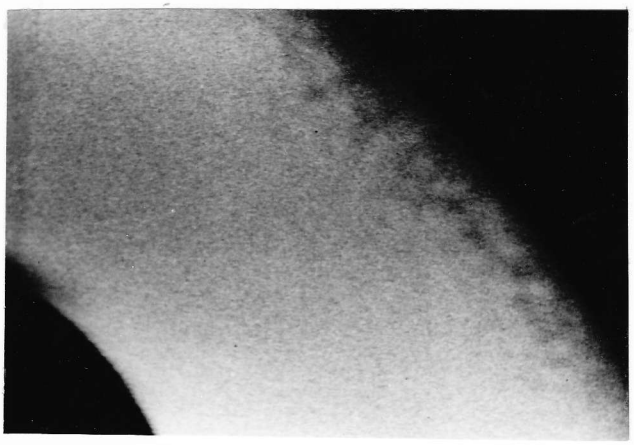


Fig.3 Scanning electron microscope (SEM) photographs of amorphous silicon whiskers grown on the substrates stained with finger grease.



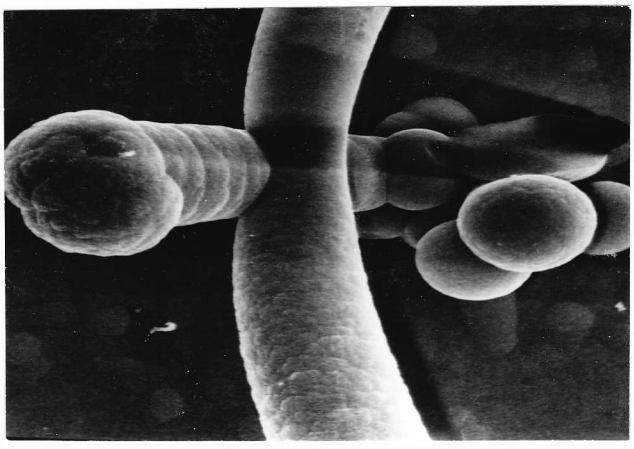
11.4μ

Fig.4 SEM photo. of amorphous silicon whiskers grown on In plated substrate.



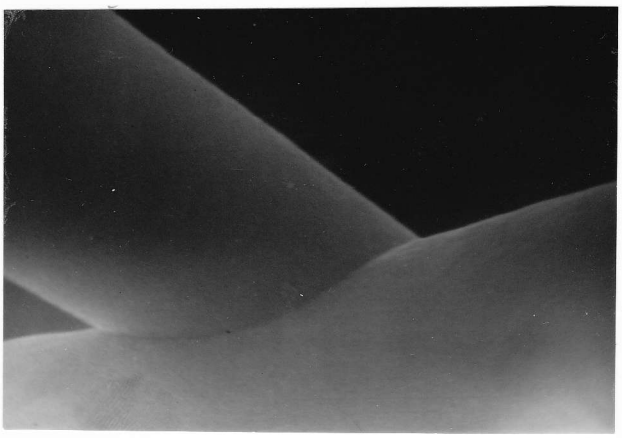
0.15μ

Fig.5 Surface of a thin whisker examined by SEM at the magnification of 10,000×.



14.6μ

Fig.6 SEM photo. of a pair of inter-crossed whiskers.



1.5μ

Fig.7 SEM photo. showing a sharp junction line at the crossing point of two whiskers.

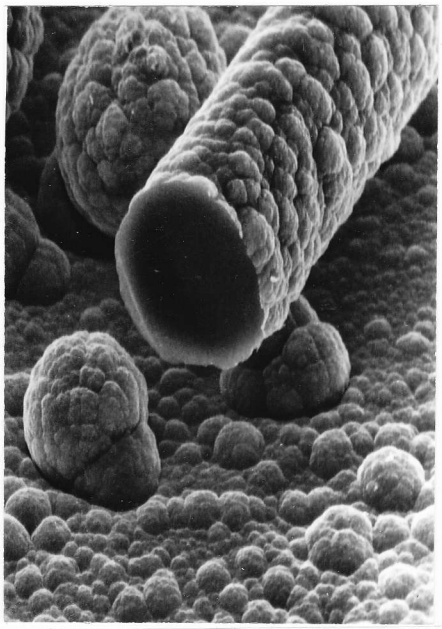


Fig.8-A SEM photo. showing a cross section of a broken large whisker grown at 600°C region in the furnace.

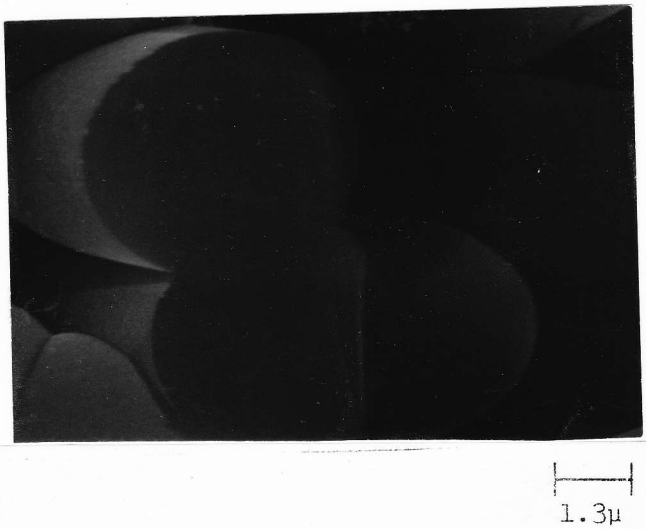


Fig.8-B Broken section of thin whiskers grown at 550°C region in the furnace.

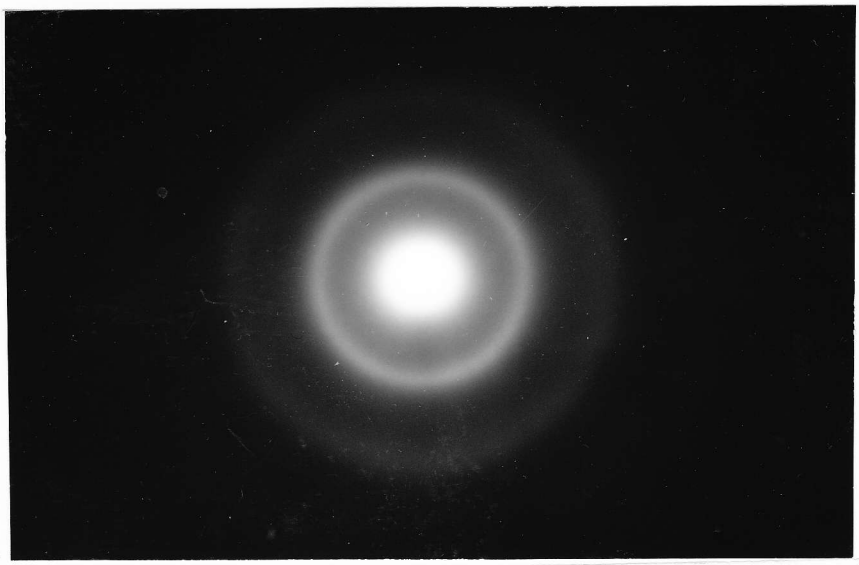
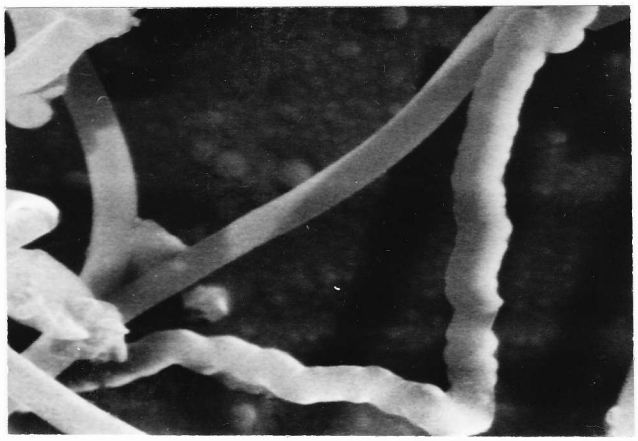


Fig.9 A Transmission electron diffraction (TED) pattern of an amorphous whisker.

phous whiskers has been measured. Prepared whiskers were immersed in aqueous solution of $ZnCl_2$ the density of which ranged from 1.0 to 2.4 $g \cdot cm^{-3}$. Floating or sinking fibers were observed by an optical microscope. The estimated density of amorphous whiskers is 2.07 ± 0.05 $g \cdot cm^{-3}$, which is 11.5% less than that of diamond type silicon.

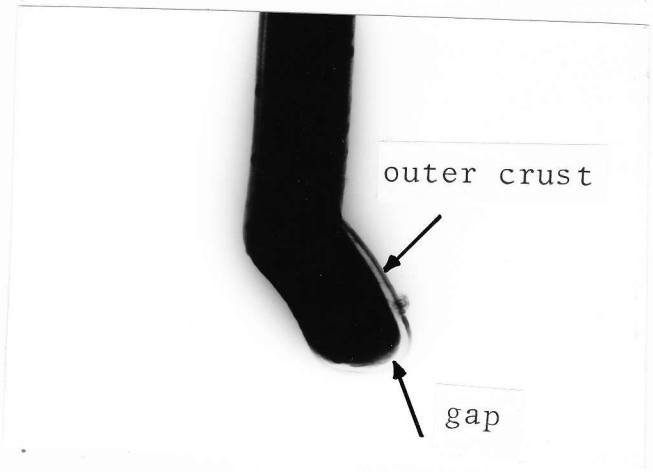
A transmission electron diffraction pattern of an amorphous whisker is given in Fig.9, which exhibits a typical halo ring pattern. After the heat treatment at 900°C for half an hour in argon atmosphere, these whiskers were examined by SEM. As shown in Fig.10 some whiskers shrinked but others did not. The whiskers which did not shrink were first examined. Although no annealing effect is found in appearance by TEM observation, the corresponding diffraction pattern in Fig.11 clearly exhibits the evidence of crystallization. The radius of each sharp ring corresponds exactly to {111}, {220} or {311} diffraction of ordinary diamond type lattice. Figure 12 also shows a TEM photograph of an unshrinked whisker with a kink. One finds a narrow gap between the material and an outer closed crust about 200 Å in thickness which is presumably the oxide film. This means that a small volume contraction took place during the heat treatment. Continuing electron beam bombardment caused further grain growth and volume contraction and resulted in a wrinkled and shrinked whisker. A well annealed whisker is a porous substance with an outer crust. The corresponding electron diffraction pattern is given in Fig.13. Most of the dotted rings in this diffraction pattern can be accounted for by the diamond structure but a few additional

spotty rings remained unidentified. These unknown rings are possibly from the silicon oxide crust, but its crystal structure could not be determined since silicon oxide has more than ten stable structures at around room temperature. Several electron diffraction photographs of the well annealed whiskers were taken immediately after etching by the aqueous solution of NH_4F and HF which dissolves silicon oxide only. The unknown spotty rings disappear by this chemical treatment, as Fig.14 shows. The final volume after full annealing and electron bombardment was roughly estimated to be less than 70% that of as grown one.



0.92μ

Fig.10 SEM photo. of amorphous whiskers annealed at 900°C for 30 min..



0.59μ

Fig.12 Transmission electron microscope (TEM) photo. of a kinked whisker after a heat treatment. Note a gap between the oxide crust and the body of whisker showing the diminution of volume.

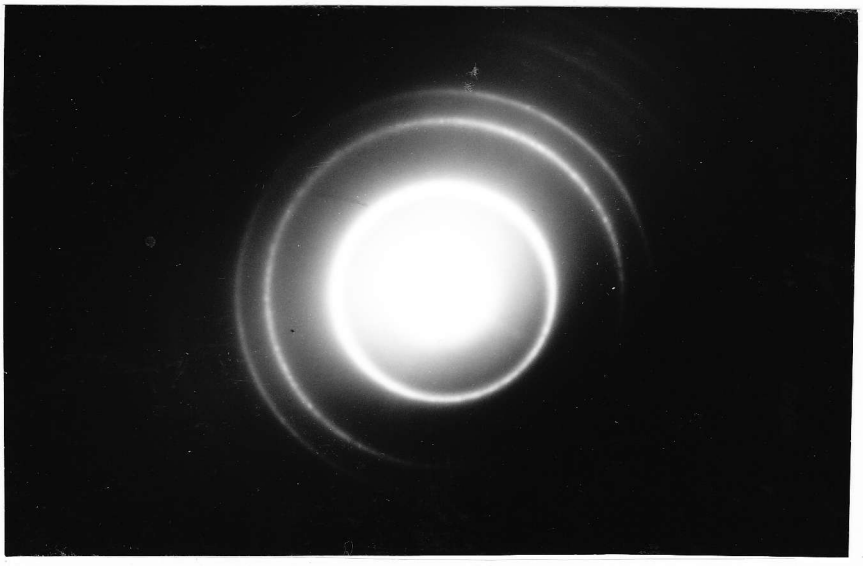


Fig.11 TED pattern of a half annealed whisker.

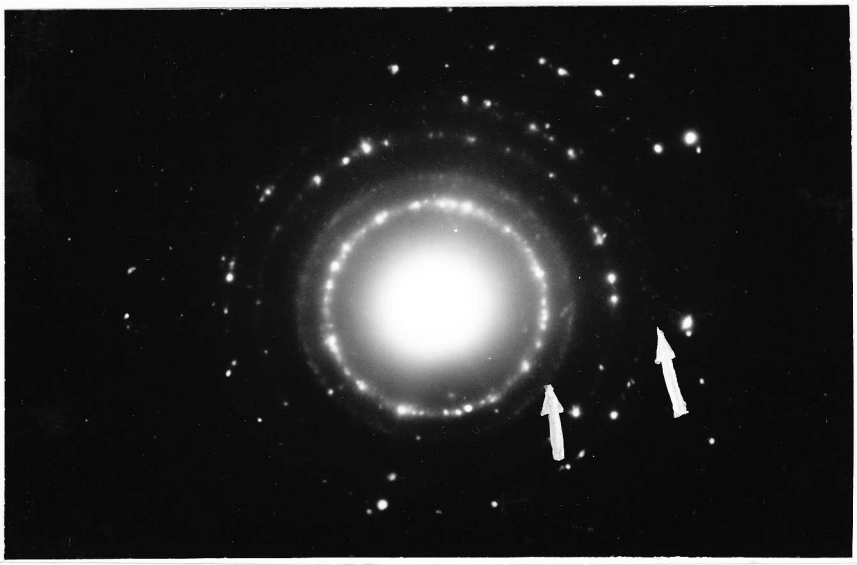


Fig.13 TED pattern of a fully annealed whisker. Most of the dotted rings are accounted for by the normal diamond type lattice. Additional unknown spotty rings are indicated by arrows.

Fig.14 TED pattern of an annealed whisker after the crust is etched off. Note that unidentified rings disappear.

B) Polytypes of Silicon Whiskers

Silicon whiskers grown on gold coated substrates exhibit a remarkable difference in electron diffraction and morphology from ones grown by using the other reagents mentioned before. That is, in contrast with the amorphous whiskers grown at the temperatures above 550°C, whiskers grown at the region at about 500°C in the reaction tube are not amorphous but monocrystalline as shown in Fig.15. Each whisker has a straight filamentary shape less than 1000Å in thickness and several hundred microns in length when grown by 40 minutes operation. No globule on the tip of each is found. The above features are different from those of silicon whiskers with the diamond structure reported by Wagner and Ellis[6-8].

The structure analysis of the new form whiskers grown at 500°C region was carried out by trial and error method using the data of d spacings and interplanar angles as follows. The whiskers placed on a copper mesh plate (#300) for TEM observation were so fine that a particular control of the angles between the whisker axes and the incident electron beam was not possible even if the tilting stage was employed. Therefore, the whiskers with such orientations as bearing so many diffraction spots were chosen in the sweep of electron microscope and many diffraction photographs were taken. These diffraction patterns were classified into nine groups each of which had the same symmetry. The largest group including twelve patterns has a six fold symmetry as shown in Fig. 16. It leads to the conclusion that the crystal structure of the whiskers has a hexagonal symmetry. From this pattern and

the other three types of diffraction patterns which are given in Figs. 17, 18 and 19, the structure was identified to be a hexagonal form with a=3.84Å and c=18.59Å. The reciprocal lattice planes of the four patterns are (001), (111), (201) and (331) respectively. These patterns cannot be accounted for by the ordinary diamond structure or its twin structure. The detailed results on electron diffraction of new form whiskers are summarized in Table I. On the assumption that a=3.84Å and c=18.59Å, d spacings of (hkl) planes d_c and interplanar angles between (hkl) and (h'k'l') planes θ_c are calculated. While the observed values, d_o and θ_o, are obtained directly from the spots of the diffraction patterns. Good agreements between the calculated and observed values are obtained in the table.

The present hexagonal unit cell can be interpreted as 6H structure. Let us consider the cubic diamond lattice (5.430Å) of silicon and convert the cubic unit cell into hexagonal one by the conversion of coordinate system. In this case hexagonal c axis is taken as the body diagonal line of the original cube. Then, the hexagonal unit cell of diamond lattice can be expressed as a=3.84Å and c=9.41Å in silicon, which includes three rugged layers stacking along the c axis or the original cubic <111> axis. This conversion is shown in Fig.20. The obtained value of c axis in our whiskers is twice as long as that of the diamond lattice. Thus, it is concluded that the structure is 6H in which six rugged layers are stacking along the c axis in the order (3,3) in Zhdanov's symbols[9] as shown in Fig.21.

In addition to 6H structure there still remain four types of diffraction patterns which cannot be interpreted as 6H

Fig.15 TEM photo. of a polytype silicon whisker grown at 500°C.

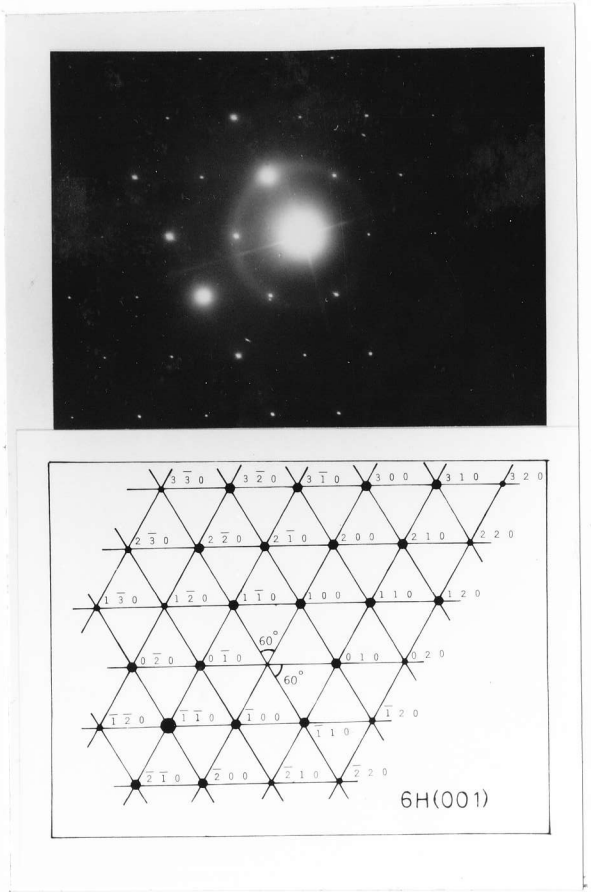


Fig.16 TED pattern of 6H type whisker showing a six fold symmetry.

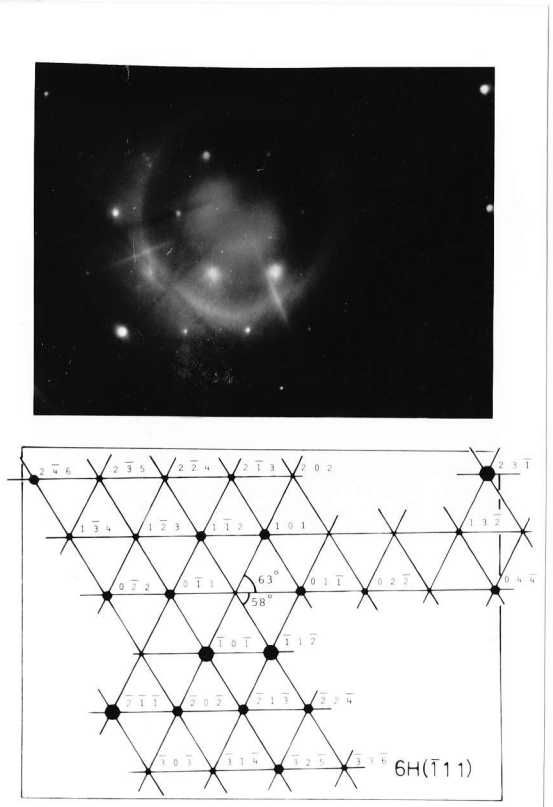


Fig.17

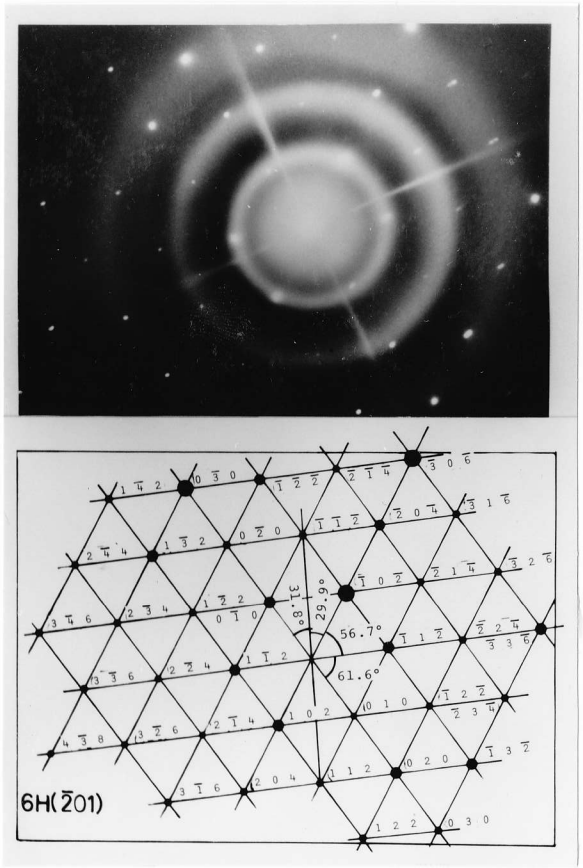


Fig.18

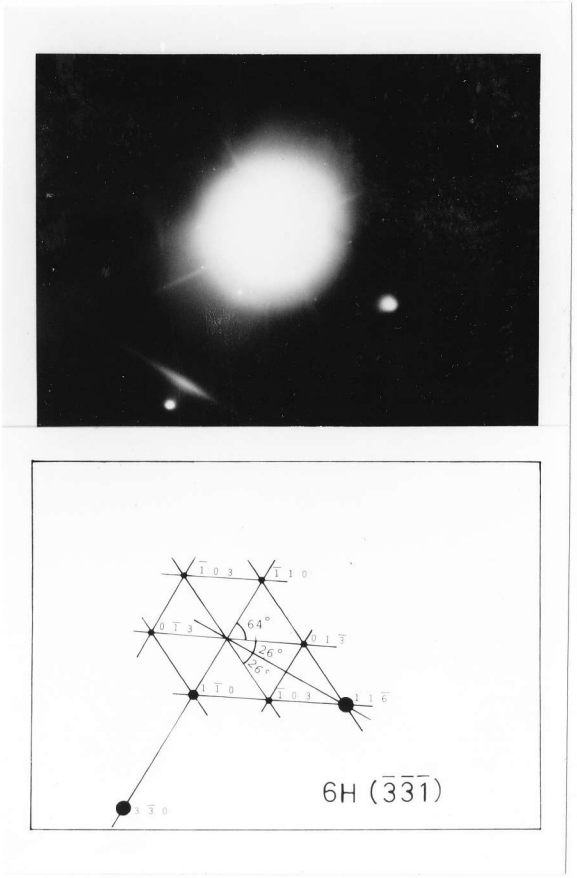


Fig.19

TED patterns of 6H type whiskers. The amorphous outer crust gives broad ring patterns.

Table I

Electron Diffraction Data for 6H Type Si

On the assumption that a=3.84Å and c=18.59Å of hexagonal form, d spacings of (h, k, l) planes d_c and interplanar angles between (h, k, l) and (h', k', l') planes θ_c were calculated. The observed values, d_o and θ_o, were obtained from the spots of the diffraction patterns.

hkl	d_c	d_o	h'k'l'	θ_c	θ_o
100	3.326 Å	3.340 Å	010	60.0°	60.0°
101	3.274	3.249	$01\bar{1}$	63.0	63.0
102	3.131	3.135	112	29.9	30.5
103	2.930	2.931	$1\bar{1}0$	63.9	64.0
110	1.920	1.910	010	30.0	30.0
$2\bar{1}3$	1.834	1.830	101	30.0	30.0
200	1.663	1.652	$\bar{1}20$	90.0	90.0
116	1.632	1.638	103	26.1	26.0
202	1.637	1.625	$1\bar{1}2$	58.5	58.5
$2\bar{2}4$	1.566	1.544	110	90.0	90.0

$a = A/\sqrt{2}$

$c = \sqrt{3}\,A$

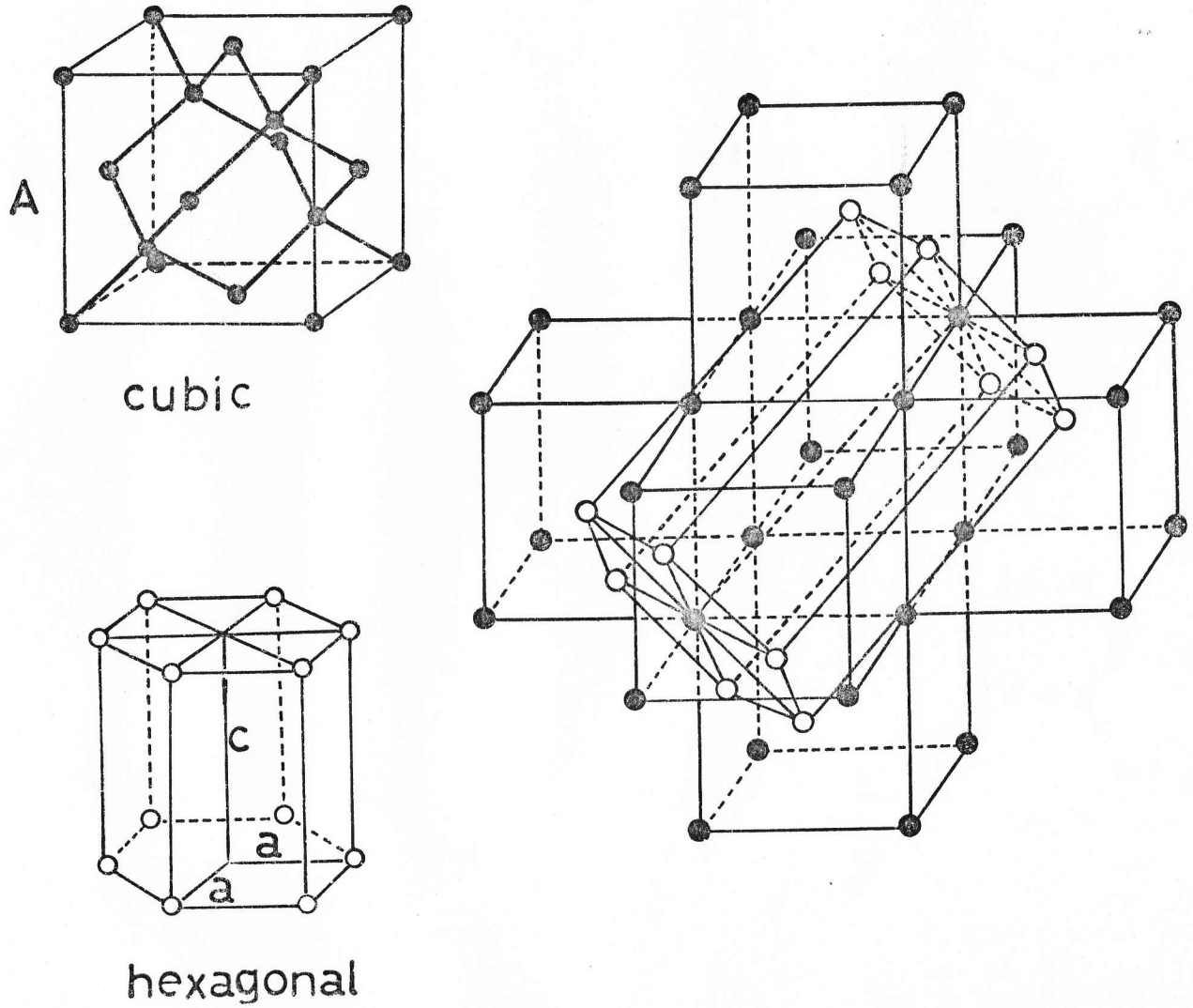


Fig.20 The conversion of coordinate system from the cubic symmetry into hexagonal one. The relation between hexagonal lattice parameters and cubic one is indicated.

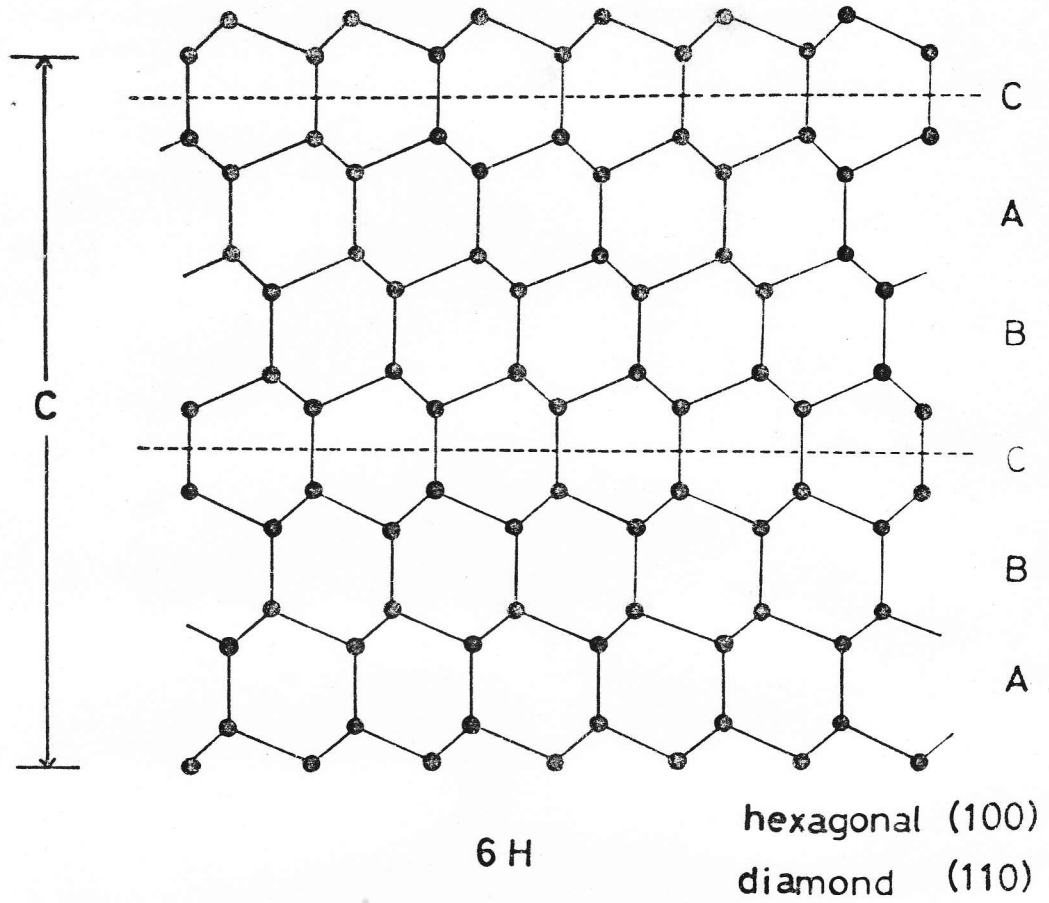


Fig.21 The $(100)_{hex}$ cross-section of the structure of 6H form silicon. Six rugged layers are stacking in the order of ABCBAC.

symmetry and also diamond lattice symmetry. They are shown in Figs. 22, 23, 24 and 25. They are not frequently observed in the present growth experiment. By the analysis it can be concluded that with the hexagonal indices they have a common "a" axis of 3.84Å and different "c" values of 84.61, 160.07 and 442.29Å respectively. Considering the interlayer distance, 3.135Å, along the c axis of the hexagonal unit cell of diamond lattice, one can suppose the lamination of 27, 51 and 141 layers from the c values of these cases. After the nomenclature for SiC polytypes[10], these structures are named as 27R, 51R and 141R rhombohedral silicon polytypes respectively. Their lattice parameters are listed in Table II. From the structure analysis and the relation between the TEM images and diffraction patterns of whiskers, it is concluded that the new form whiskers have the growth axis in a hexagonal <100> direction.

At about 520°C a strange form of whiskers with a crystalline core and outer crust of amorphous silicon appeared. As shown in Fig.26, a dark field image formed by a part of the first broad ring of diffraction pattern exhibits the outer crust and that formed by one of the spots shows the sharp central core. This dual structure was also confirmed by etching test by CP4 solution. Figure 27 gives an electron image and diffraction pattern of a whisker after etching off the outer crust. The diffuse ring is no longer recognized in the latter. Thickness of the outer crust increased and the whole shape becomes wavy with raising the growth temperature as a series of pictures in Fig.28 shows. At around 550°C only perfect amorphous whiskers were grown, and no crystalline

center core was found even by careful TEM observation of broken end. The growth of steeples (Fig.29) and blades (Fig.30) were observed at above 800°C. The former have the diamond structure, hexagonal cross section, <111> growth axis and a small globule on the tip. The latter have a twin structure with (111) twin plane of diamond lattice. In Table III are summarized the structures and morphologies of the above three kinds of silicon whiskers, the amorphous, polytype and normal form, obtained in this study.

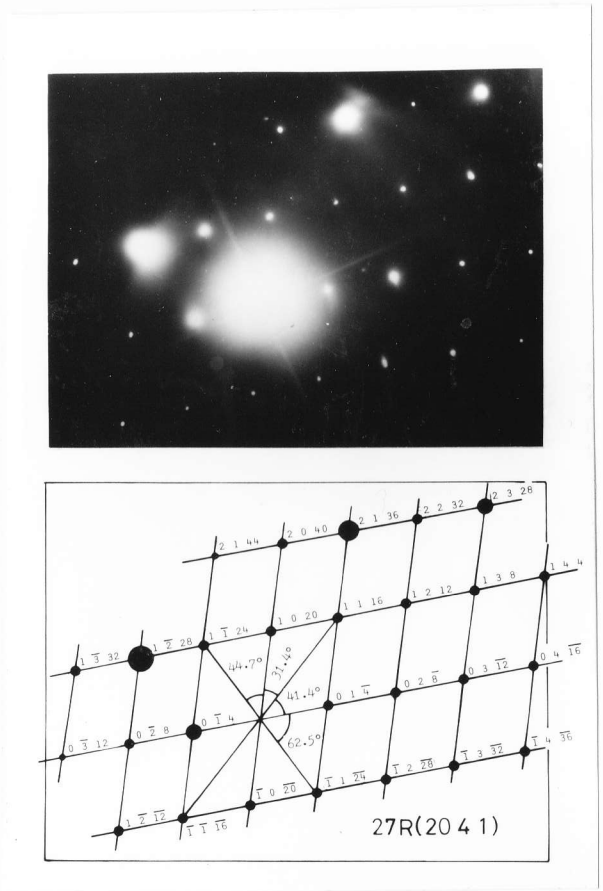


Fig.22 TED pattern of 27R type whisker.

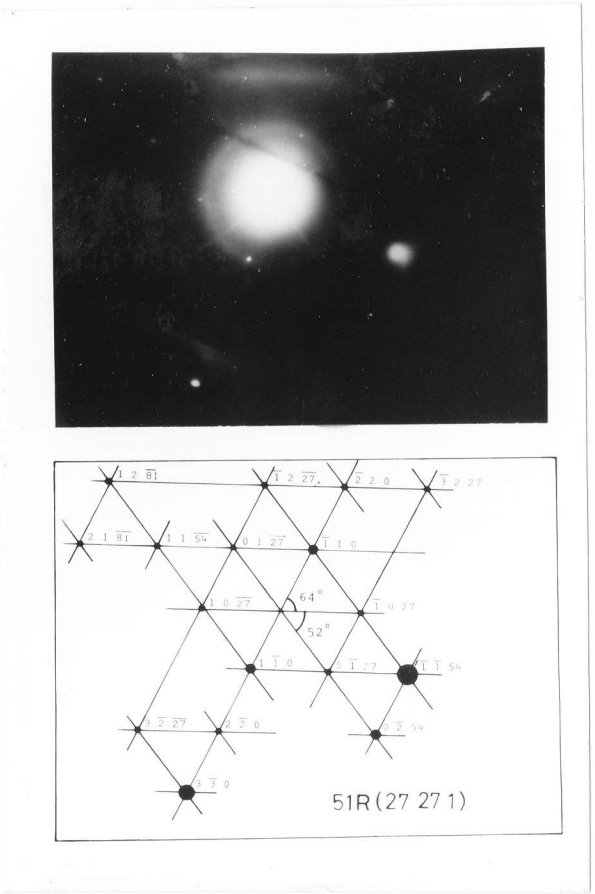


Fig.23 TED pattern of 51R type whisker.

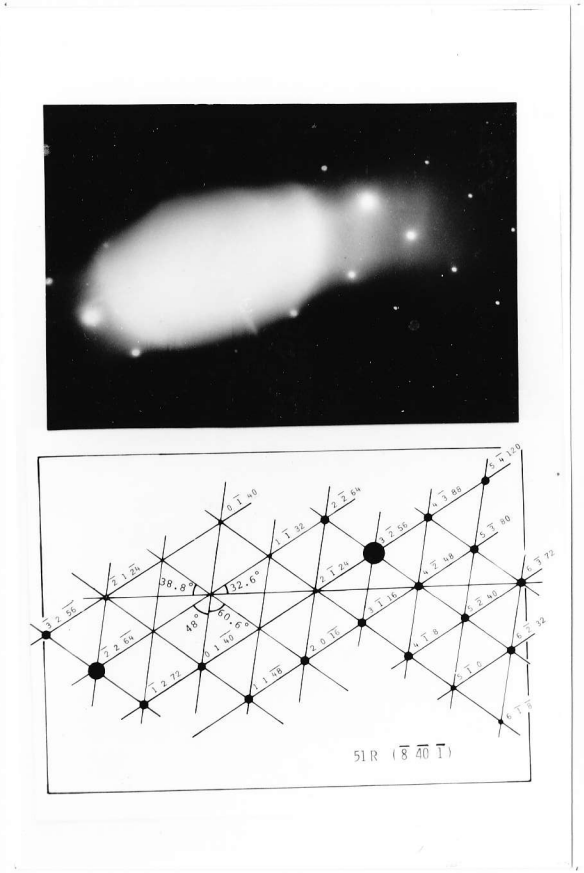


Fig.24 TED pattern of 51R type whisker.

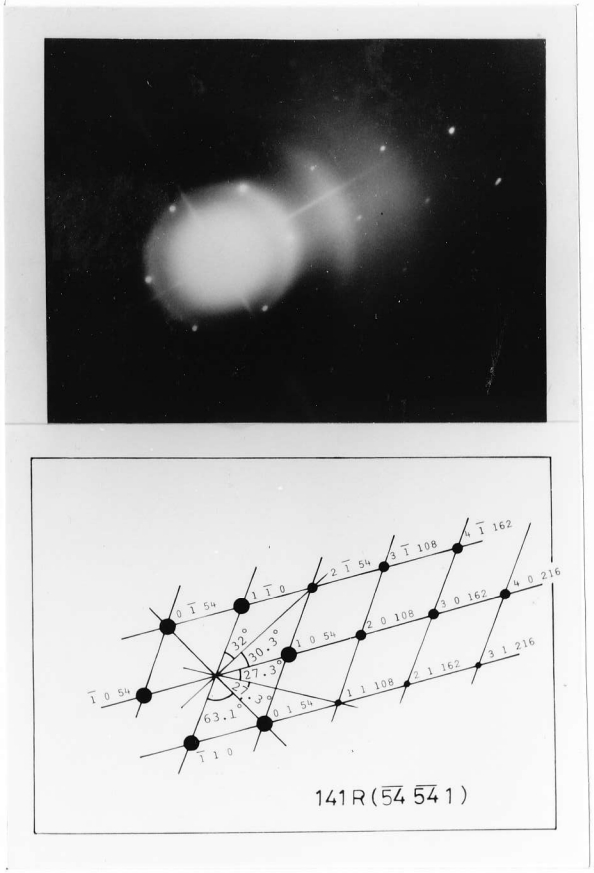


Fig.25 TED pattern of 141R type whisker.

Table II

Lattice Parameters for Polytype Si

Polytype Structures	a	c	$c_{cal.}$
6H		18.59Å	18.81Å
27R		84.61	84.65
51R	3.84Å	160.07	159.89
141R		442.27	442.05
3C		9.41	

H, R and C denote hexagonal, rhombohedral and cubic forms respectively. These forms are summarized with hexagonal lattice parameters. The values of "a" and "c" were analyzed from electron diffraction patterns, while the calculated "$c_{cal.}$" values were obtained from the ideal polytype lattices. Their lattice parameters are derived from the number of layer stacking periods multiplied by one period distance of 3.135Å (the average of the observed values is 3.13Å). The calculation is based on the hexagonal representation of diamond lattice (3C form).

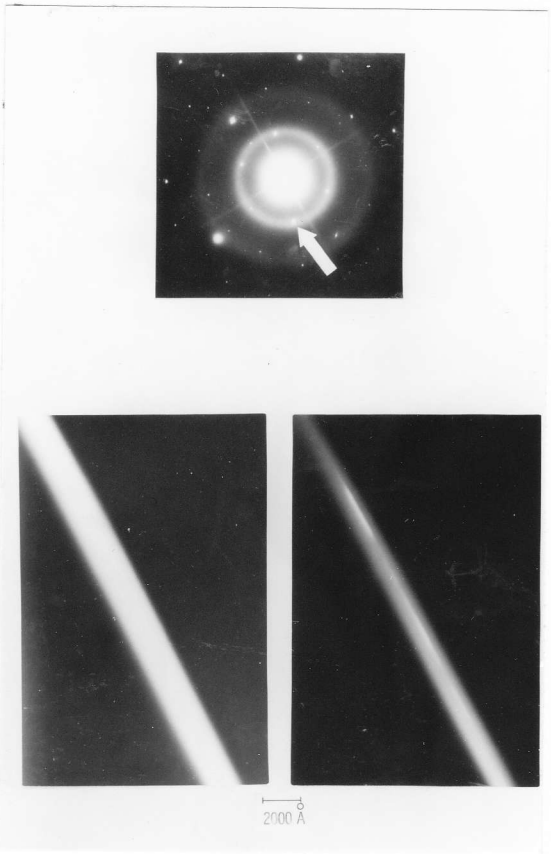


Fig.26 A dark field image from the first broad ring exhibiting a brightening crust of a whisker (lower left) and that from one of the spots indicated by an arrow exhibiting a thin crystalline central core (lower right).

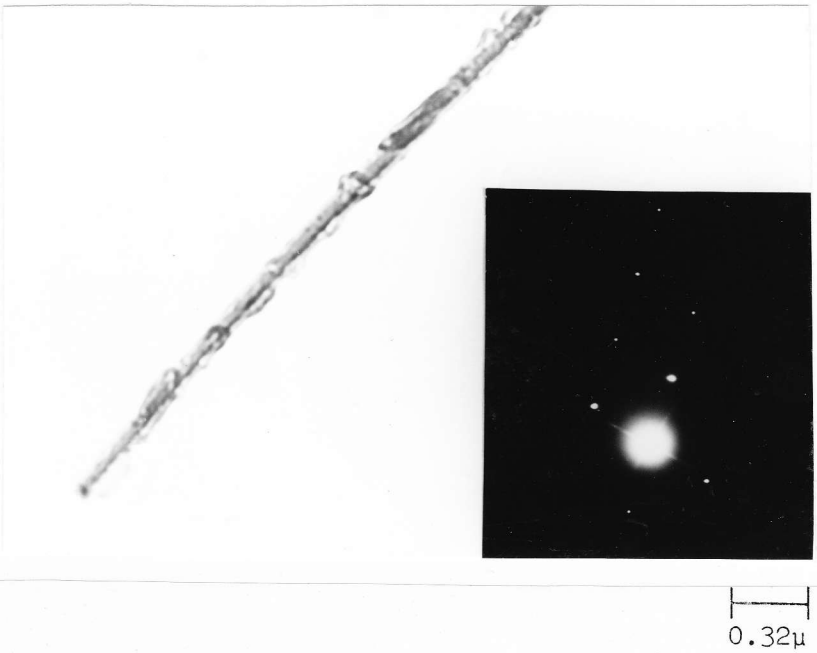


Fig.27 TEM photo. of a whisker whose outer crust is etched off and its TED pattern.

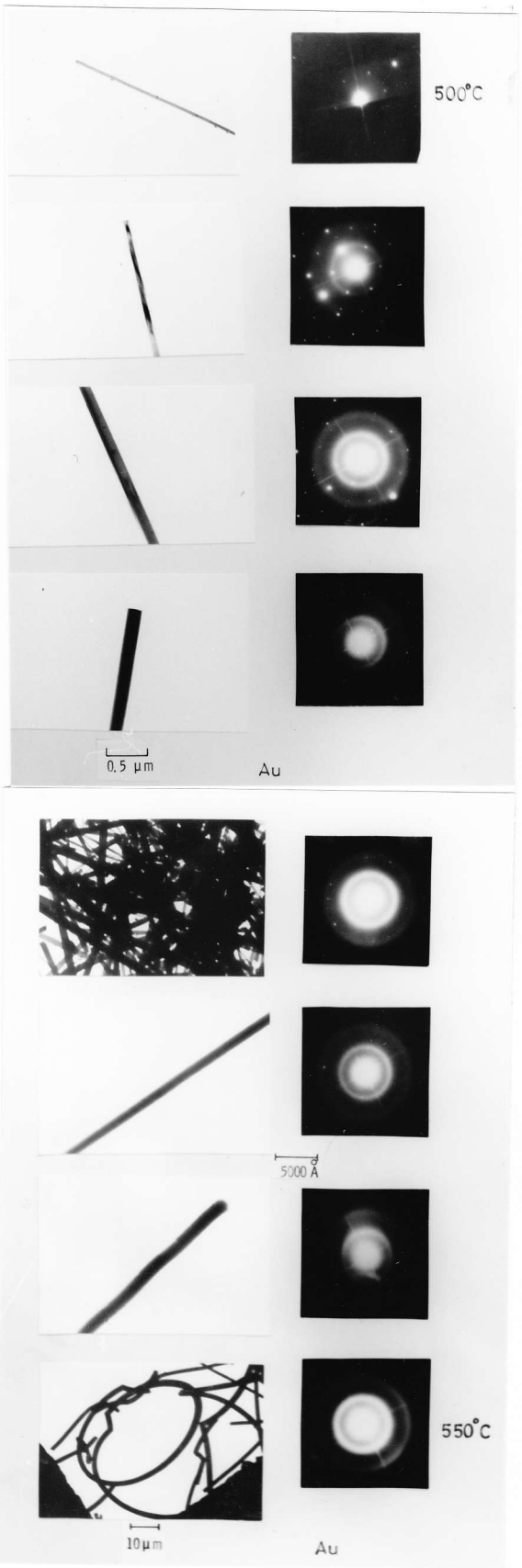


Fig.28 TEM photos and corresponding TED patterns of whiskers of various sizes grown at various temperatures. Thickness of the outer crust increases and outer shape becomes wavy with increasing growth temperature. Corresponding diffraction patterns change from spotty pattern to diffuse ring pattern.

Fig.29 TEM photo. of a normal form silicon whisker with steepled shape grown at 950°C.

Fig.30 TEM photo. of a blade shape crystal of normal form silicon grown at 950°C.

Table III

Polymorphism of Si Whiskers

	polytype form	amorphous form	normal form
growth temperature	500~520°C	520~600°C	>800°C
structure	hexagonal rhombohedral	amorphous	diamond cubic
lattice parameter	a= 3.84Å c= 18.59 (6H) 84.61 (27R) 160.07 (51R) 442.29 (141R)		a=5.43Å
morphology			
outer shape	filamentary	fibrous	steepled bladed
cross section	?*	circular	hexagonal
diameter	~1000Å	<50μ	<6μ
length	<600μ	<4mm	<200μ
growth direction	hex.<100>		cubic<111>

* The cross section of polytype Si whiskers are not confirmed by SEM observation.

C) New Form Germanium Whiskers

To grow the amorphous germanium whiskers has been intended sometime in the course of the present experiment. Considerable amount of efforts have been devoted but no success has been achieved by this time. Instead, on the way of the above study, the growth of germanium whiskers with a tetragonal unit cell has been discovered. They can be formed on the surface of gold-alloyed germanium crystal. The growth temperature ranged from 260°C to the Au-Ge eutectic point of 356°C. At first, the substrates covered by gold films of about 2000Å in thickness were pre-heated in a pure argon stream at 700°C for half an hour in order to make Au-Ge eutectic alloy. Then the furnace temperature was lowered down to the growth temperature and mixture gas containing GeH_4 was introduced. After the growth period ranging from 20 min to 2 hours, fine quadrilateral cross sectioned whiskers with uniform thickness from 400 to 6000Å and length up to 200 μm were obtained. As demonstrated in Fig.31, each of them has a globule with shirred rough surface which is exhibited in Figs.32 and a thin neck beneath the globule. In Fig.33 is shown a whisker with a rectangular cross section.

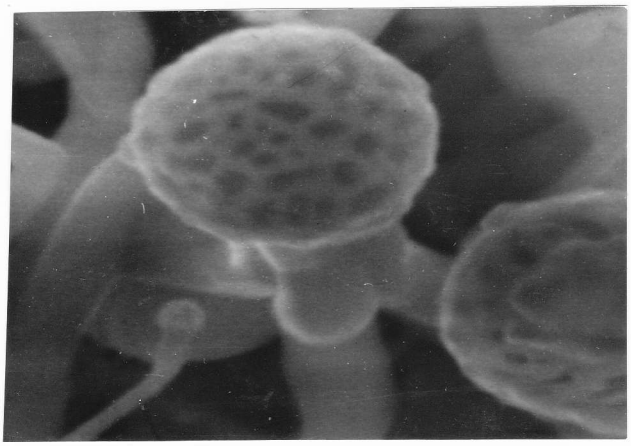
The electron diffraction spots can be interpreted by a tetragonal unit cell with a=7.62± 0.01 and c=6.20±0.01Å. Similar to the preceeding section, these parameters were determined by the trial and error method. For examples, diffraction patterns of (001) and $(1\bar{2}1)$ reciprocal planes are given in Figs.34-A and B. Fitting between the calculated parameters (a=7.62 and c=6.20Å) and the measured ones obtained

from the diffraction spots is shown in Table IV. The growth axis was identified to be <110> and lateral surfaces were $(1\bar{1}0)$ and (001) from the TEM images and diffraction patterns. Figure 35 gives a TEM photograph of branching of whiskers and the characteristic branching angle of 90° means that the growth directions of the two whiskers are <110> and $<1\bar{1}0>$ respectively. Bootsma and Gassen[11] have already reported the growth below the eutectic point of Au-Ge system but they did not mention about the crystal structure.

In the case of growth at 400°C, steeple whiskers with hexagonal cross sections have been obtained as shown in Fig.36. From electron diffraction study these structures were confirmed to be the cubic diamond lattice. Table V is to compare the morphologies of new and normal form germanium whiskers. The annealing at 850°C for one hour caused the phase transition from tetragonal lattice to a normal diamond lattice.

0.48μ

Fig.31 TEM photo. of new form germanium whiskers grown at 300°C.



0.42μ

Fig.32 SEM photo. of globules with shirred rough surface.

0.35μ

Fig.33 SEM photo. of new form germanium whiskers with quadrilateral cross ection.

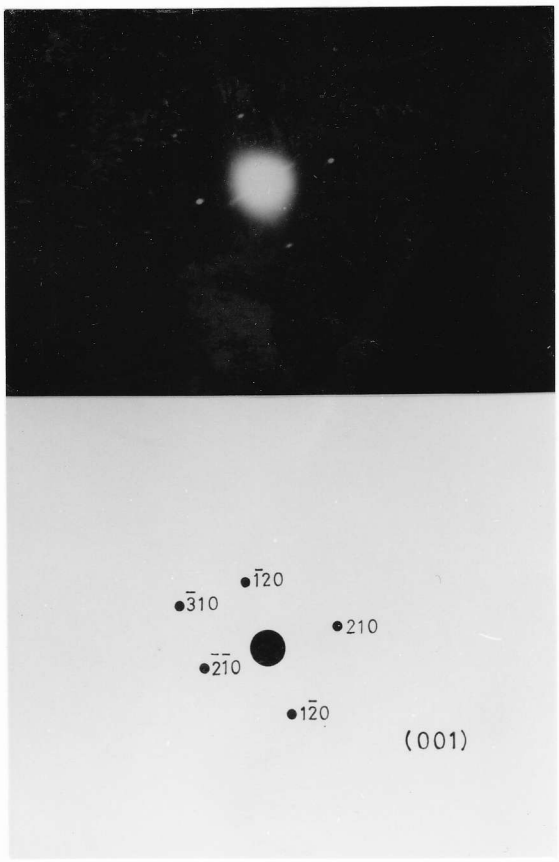


Fig.34-A

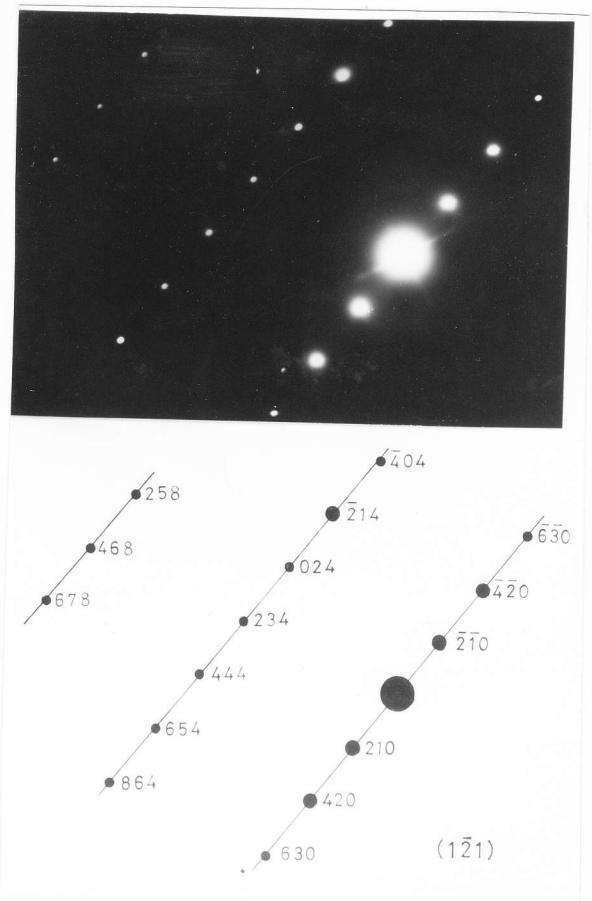
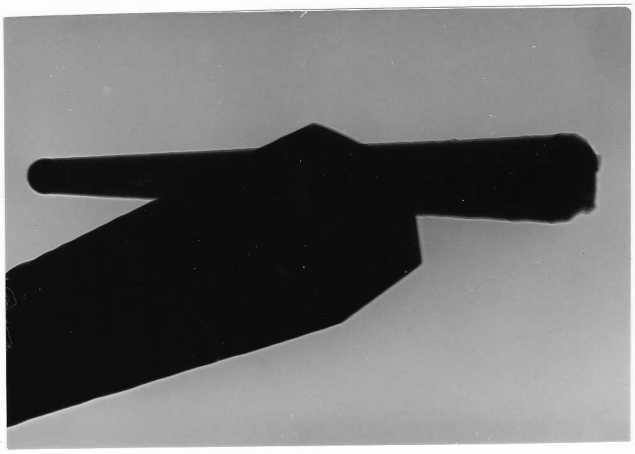


Fig.34-B

TED patterns of new form germanium whiskers.

0.43μ

Fig.35 TEM photo. of branching whiskers.



0.3μ

Fig.36 TEM photo. of normal form germanium whiskers grown at 400°C.

Table IV

Electron Diffraction Data for Tetragonal Ge

On the assumption that a=7.62 and c=6.20Å, d spacing of (h, k, l) planes d_c and interplanar angles between (h, k, l) and (h', k', l') planes θ_c are calculated. The observed values, d_o and θ_o, were obtained from the spots of the diffraction pattern.

hkl	d_c	d_o	h'k'l'	θ_c	θ_o
120	3.408 Å	3.465 Å	$\bar{1}30$	45°	45°
130	2.410	2.387	$\bar{1}44$	57.2	57.9
122	2.292	2.261	$02\bar{4}$	62.7	62.3
241	1.643	1.652	$3\bar{1}0$	82.2	82.8
412	1.587	1.603	$21\bar{2}$	79.4	79
511	1.453	1.432	$4\bar{2}1$	36.7	36.6
204	1.435	1.432	120	80.3	80
214	1.410	1.408	$\bar{1}30$	86.6	86.7
351	1.279	1.302	421	31.7	32.6
324	1.249	1.249	$\bar{1}30$	81.1	80.9
620	1.205	1.193	212	48.3	47.6
144	1.187	1.193	310	57.2	57.9

Table V

Polymorphism of Ge Whiskers

	new form	normal form
growth temperature	260~340°C	400~500°C
crystal structure	tetragonal	diamond cubic
lattice parameter	a=7.62±0.01Å c=6.20±0.01 c/a=0.813	a=5.66Å
morphology	filamentary	steepled
cross section	rectangle	hexagonal
diameter	400~6000Å	0.2~20μ-m
length	~200μ-m	~700μ-m
growth direction	<110>	<111>
lateral faces	$(1\bar{1}0)$ and (001)	(211) or (110)

A) Growth of Whiskers and Role of Impurities

It seems to be of great interest to discuss why the whiskers with amorphous state grow. Many sophisticated explanations on the formation of crystalline whiskers have been given by many researchers in the field of whisker growth. Among others Frank's dislocation mechanism[4] for proper whiskers, Sears' mechanism for vapor growth[3] and VLS mechanism proposed by Wagner and Ellis[6-8] are noticeable. It is quite difficult, however, to apply these mechanisms to the growth of amorphous whiskers except the last one because all other growth models require the existence of the crystal structure and also dislocations. In the present case the metals of low melting point or some ingredients in finger grease may act as a catalyst for the decomposition of SiH_4, form the nuclei of amorphous whisker or give preferred sites for adsorption of atoms. In the earlier period of this study, almost all organic or inorganic materials found in the laboratory were put on the substrates and the growth of amorphous whiskers were examined. For examples potassium bicromate, carbon black, activated carbon, polystyrene latex balls (7800Å diameter), glycerine, vaseline, olive oil, wax and their mixture were sprinkled or painted on the substrates. But, they were not effective for the growth except finger grease and the metals of low melting points which are in a liquid phase at the growth temperature. The growth was not observed on the clean or sandblasted substrate. The role of impurities in finger grease is still not clear at this time but the following can be stated: Impurities play an important role in the

nucleation and/or the growth of amorphous whiskers. To have a liquid phase of impurity metals may be a necessary condition for the amorphous growth and the liquid state may reflect the amorphous state of the growing whiskers.

The growth of amorphous silicon whiskers arises from decomposition of SiH_4 and not from the supply of silicon stoms from the substrate because no whisker was grown without introducing SiH_4 gas into the reaction tube. If one assumes the ideal gas approximation the mass rate of impingement of SiH_4 molecules or Si atoms on the top end of whisker is given by

$$\frac{d\bar{W}}{dt} = 2\pi r^2 P \left(\frac{m}{2\pi kT}\right)^{\frac{1}{2}} \tag{1}$$

where r is the whisker radius, P the pressure of SiH_4 or Si around the whisker, m the mass of the molecule or the atoms, k the Boltzman's constant and T the growth temperature. In this estimation the top end is assumed to be hemisphere. If all atoms which strike the whisker end are taken into the whisker and the whisker radius is assumed as constant, we have the following equation:

$$\pi r^2 \frac{dl}{dt} = \frac{dw}{dt} \tag{2}$$

where $\frac{dl}{dt}$ is the rate of length increase and ρ the density of whisker. By combining Eqs.(1) and (2), $\frac{dl}{dt}$ is obtained as

$$\frac{dl}{dt} = \frac{2P}{\rho} \left(\frac{m}{2\pi kT}\right)^{\frac{1}{2}} . \tag{3}$$

The vapor pressure of SiH_4 in the reaction tube was approximately 7.6mm Hg, the growth temperature was about 820°K and the ρ has been estimated to be 2.0 grams/cc. Then the growth

rate calculated from Eq.(3) is given by

$$\frac{dl}{dt} \simeq 9.0 \times 10^{-2} \text{ cm/sec} \qquad (4)$$

On the other hand the maximum length of the whiskers prepared after one hour operation has been measured to be about one millimeter. The calculated rate is 3000 times larger than the actual growth rate which is assumed to be constant during the growth period. The discrepancy in growth rates arises from either a very small sticking probability of gas molecules arriving at the top end of whisker or a very slow catalytic reaction to dissociate the molecules and take silicon atoms into the body of whisker from the surface of the tip. Looking at Fig. 37, one finds some small hemispheres on the substrate whose diameters differ from one to another, all being smaller than those of grown up whiskers. These hemispheres were not observed before the substrate was inserted into the reaction tube. The whisker grown at above 550°C has a globule on the tip, which is considered as a growth point and possessing characteristics different from those of other parts of the whisker. Regarding the growth of amorphous whiskers we have the following conceptions: Im the begining of the growth, the nuclei of small hemispheres form on the substrates. Some impurity metal of low melting point acts as a catalyst for the nucleation. The radius of each hemisphere increases until it becomes a characteristic size which is a function of the growth temperature and possibly of the surface energy of the hemisphere material. After this stage, whiskers grow along the direction of their growth axes by VLS mechanism.

Because of the lack of the detailed informations as to the growth kinetics of the polytype silicon whiskers, it is still

hazardous to propose a definit growth model at the present stage of our study. Since these whiskers have no globules on their tips, it seems difficult to understand that they have been grown by the ordinary VLS mechanism. As in the case of the polytypes in SiC, the screw dislocation growth mechanism should be applicable, but no dislocation has been discovered as yet unfortunately in these whiskers by TEM observation.

With regard to the growth of new form germanium whiskers mentioned already, it should be noticed that they can grow even at 260°C. According to the phase diagram of Au-Ge system, the material must be in a solid phase at such low temperature region. Therefore, their growth cannot be accounted for by VLS mechanism. But the globules on their tips may play the same role as those of liquid droplets in VLS growth. Observing carefully by SEM (Fig.32) one can recognize bright dotty contrast on the globules which may mean the existence of two phases, germanium rich and gold rich respectively. As well known, gold is an effective emitter of secondary electrons so the bright regions on the globules must be rich in gold. Nevertheless, the main portion of the whisker may not be contaminated so much with gold. If the gold atoms which had been distributed in the globule at the early stage of growth were transferred to other parts, the size of the globule and also the diameter of the whisker must have been reduced as the growth proceeds. If this is the case, the final shape of the whisker should be steepled and the final length must be limited by the exhaustion of gold rich globule.

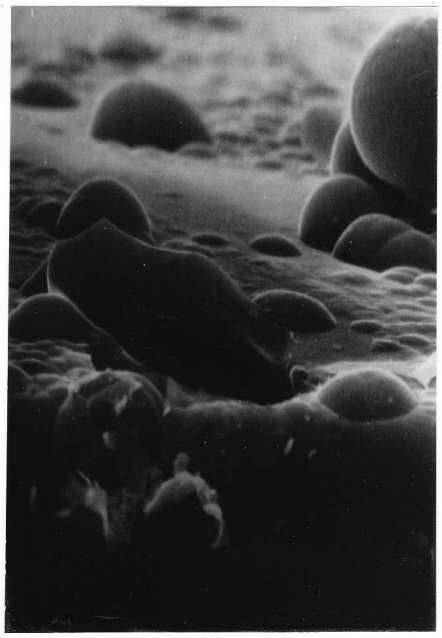


Fig.37 Small hemispheres appearing on the substrate at an earlier stage of the whisker growth.

B) Crystal Structures of Whiskers

First, let us consider the structure of amorphous silicon whiskers. The electron diffraction intensity distributions along the radial direction and the radii of diffuse rings were drawn by using an optical microphotometer as in Fig.38. Though there are two diffuse rings in Fig.9, an extremely weak third outer ring can sometimes be found. With regard to the innermost ring the position of the maximum intensity approximately corresponds to that of {111} diffraction of crystalline silicon (Fig. 38). Similarly that of the second ring spreads around the positions of {311} and {220} diffraction rings of a diamond type crystal. The third weak ring seems to distribute at around {331} diffraction. This indicates that the structure of amorphous whiskers is distorted but may not be too different from the perfect diamond lattice. Whereas, it has been already mentioned that together with the growth of amorphous whiskers, the polytype whiskers could grow at about 500°C region of the furnace. One can also recognize in Fig.38 that main diffraction spots of 6H polytype Si just correspond to the positions of diffuse rings. No other diffraction lines of the 6H form appear between the diffuse rings. It is unnecessary to take account of other polytypes than 6H form because of their small abundance compared with that of the common 6H structure. Silicon polycrystal particles were also deposited on the substrates, the surface of quartz boats and the inside of reaction tube whose temperatures are above 520°C. Therefore we can imagine loosely packed small cells and each of them is assumed to have a polytype-like or a diamond-like lattices. A similar concept has been proposed for the structure of amorphous carbon film

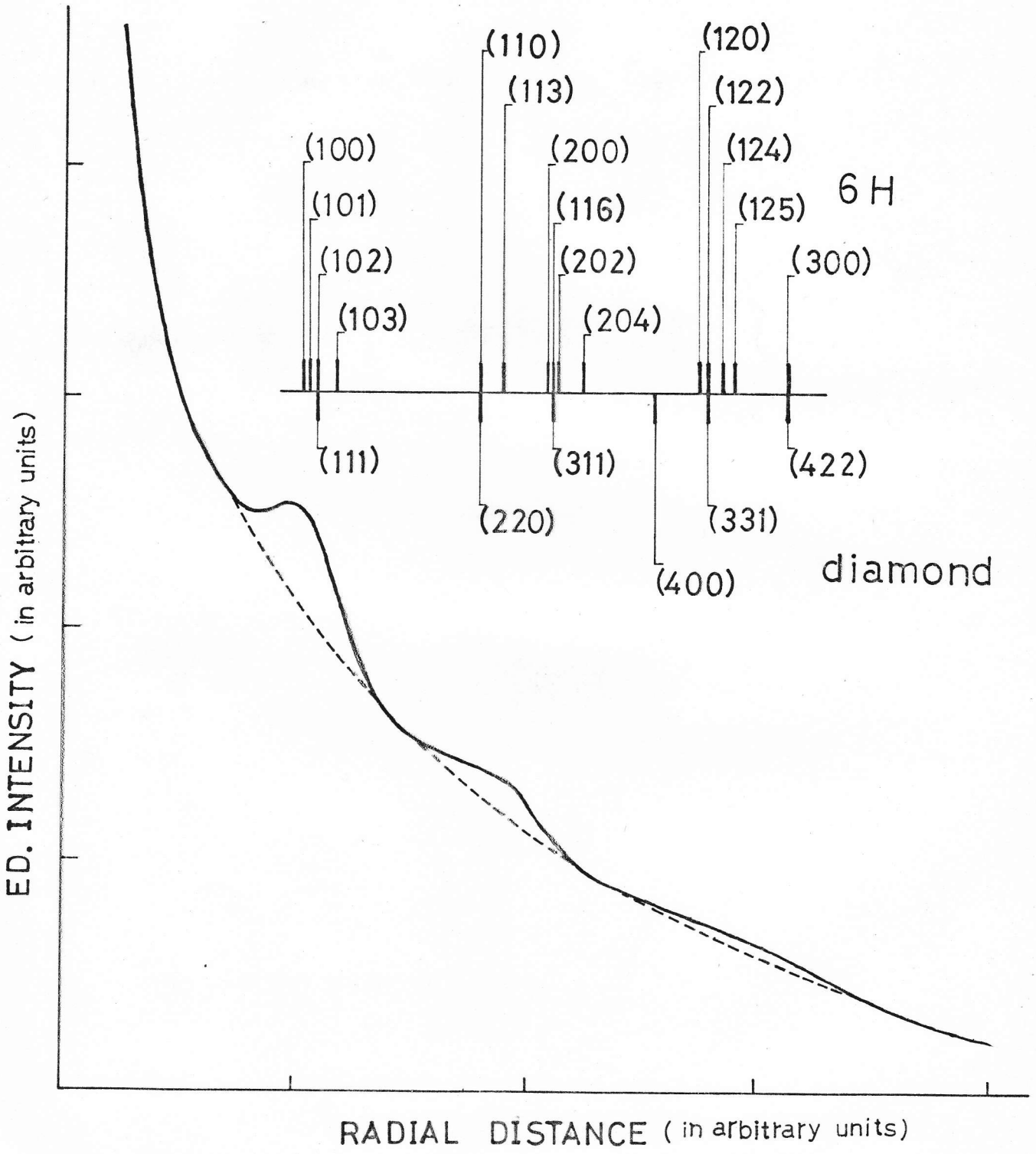


Fig.38 Electron diffraction intensities vs. radial distance in halo pattern.

by Kakinoki, Katada, Hanawa and Ino.[12] In or among these cells there may exist many cavities or hollows as was supposed by the volume reduction after the annealing. Assuming this model, we can discuss about the size of the cells. If it is assumed for convenience that each cell has approximately same size and structure as those of a unit cell of the diamond structure shown in Fig.39, it can cause {111} diffraction. In this figure a pair of (111) planes are illustrated. On each plane there are three or six atoms. But, a cell of this size will not cause {331} diffraction because a parallel pair of (331) planes are not fiqured out by using the atoms in the unit cell. An assembly of two or three unit cells connected in a single file is needed if one tries to draw a nearest parallel pair of (331) planes containing more than three atoms respectively. Similar considerations about the 6H structure would be effected. Adopting the present model, we ultimately estimate the mean size of the cells to be larger than that of the assembly mentioned above. Irrespective of the crystalline size and structure, in order to explain the density of whiskers 11.5% lower than that of bulk crystal, one might assume that the whiskers contain vacancies uniformly up to a concentration of 11.5%. However, this type of structure may not be stable at the growth temperature. If vacancies were introduced into a crystal by the above amount at 500°C, by the condensation of vacancies to form a large number of voids. As is well known, the formation energy of a single vacancy has been estimated to be about 3.6eV[13] and the binding energy of a divacancy is larger than 1.6eV[14,15]. A single vacancy is mobile even at -200°C[16] and divacancy, trivacancy and tetravacancy centers anneal out below 350°C[17].

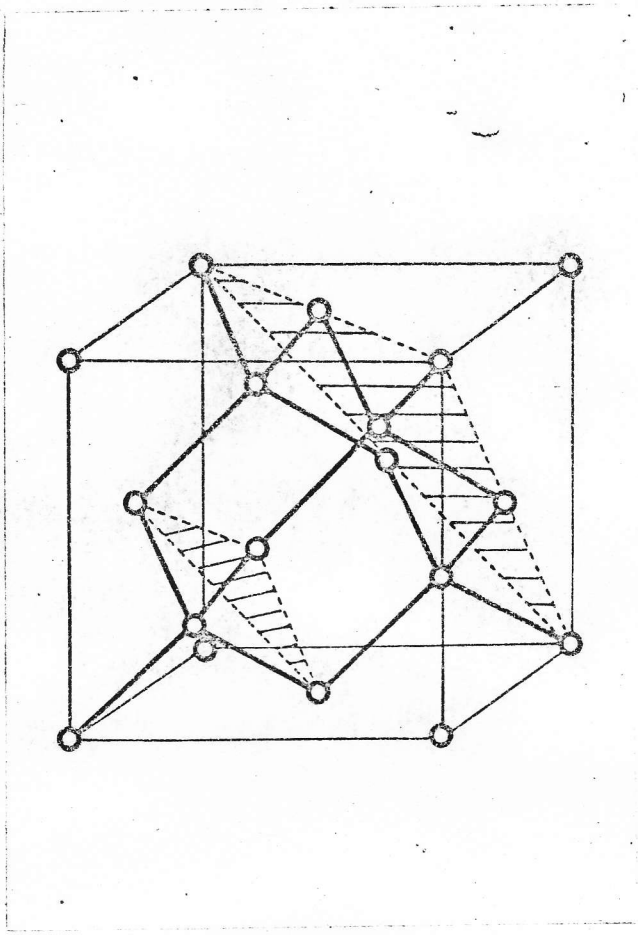


Fig.39 A pair of (111) planes in a unit cell of diamond type lattice.

Taking these situations into account, we conclude that the low density of amorphous whiskers is caused by such a structure as having many small voids, cavities, or hollows.

The annealing behavior of amorphous whiskers at 900°C is well understood in accordance with the following model. At an early stage of annealing, only short range atomic rearrangements to change the structure from distorted polytype-like or diamond-like lattice to perfect diamond lattice will occur, and it scarcely gives volume diminution and gives rise to sharp diffraction rings of poly crystals of diamond lattice. While at the advanced stage of annealing, the grain growth associated with long range diffusion will occur and the cavities will disappear. It must give a large apparent volume diminution and spotty ring patterns as are actually observed.

Usually, amorphous silicon or germanium can be obtained by vacuum evaporation, by cathodic sputtering, electrolytic process, and r.f. decomposition of gaseous compounds in the form of thin films[18]. Two structural models for the amorphous films have been proposed; One is the microcrystallite model which is demonstrated as the structure composed of hexagonal, wurtzite-like microcrystals[19] or its mixture with diamond-like ones[20], and the other is the model of random network structure consisting of their bond configurations[21]. To determine which model is better, further investigations such as the precise analysis to obtain radial distribution in electron diffraction or TEM dark field image observation with precision are needed.

The wurtzite type Si has been discovered after the heat treatment of high pressure phase Si by R. H. Wentorf, Jr. and J. S. Kasper[22]. This structure was also noted in amorphous

Si and Ge films[21]. However, these polytype crystals are very small comparing with the 6H and 27R, 51R, 141R form whiskers obtained in this study. In our case, many diffraction patterns exhibit Kikuchi lines indicating the good crystalline character. As already mentioned, various polytype forms are predicted and calculated from the parameters of diamond lattice, and their calculated lattice parameters are listed in Table II, where the distance between adjacent two stacking layers is taken as 3.135Å. Very good agreements are obtained between the lattice parameters of actual samples and calculated ideal forms. This means real existence of Si polytypes and suggests that the structures do not include many foreign atoms such as of gold or oxygen in the lattice. Hexagonal lattice of 6H form Si is shown in Fig.21. This structure is abbreviated as (33) by Zhdanov symbol[9] related to the layer sequences of hexagonal basal planes. It has a eclipsed bond configuration layer (wurtzite type) between two of two fold staggered ones (diamond type). These two kinds of bond configurations are illustrated in Fig.40. Since they are so similar in geometry and produce no difference in the first neighbor interactions, the energy differences between them must be small. In the same way, the layer sequences of 27R, 51R, 141R forms are expressed as $(2223)_3$, $[(33)_2 32]_3$, $[(33)_7 32]_3$, respectively. The choice of 12 atoms per 6H unit cell gives a calculated density of 2.36 $g \cdot cm^{-3}$. This value is similar to the density of diamond type silicon or the ideal 6H form (2.33 $g \cdot cm^{-3}$). The number of obtained diffraction patterns of 6H Si was a overwhelming majority and some patterns of rhombohedral Si have been obtained from a part of 6H form whisker. Therefore it is considered that 6H form Si is a common structure and the other

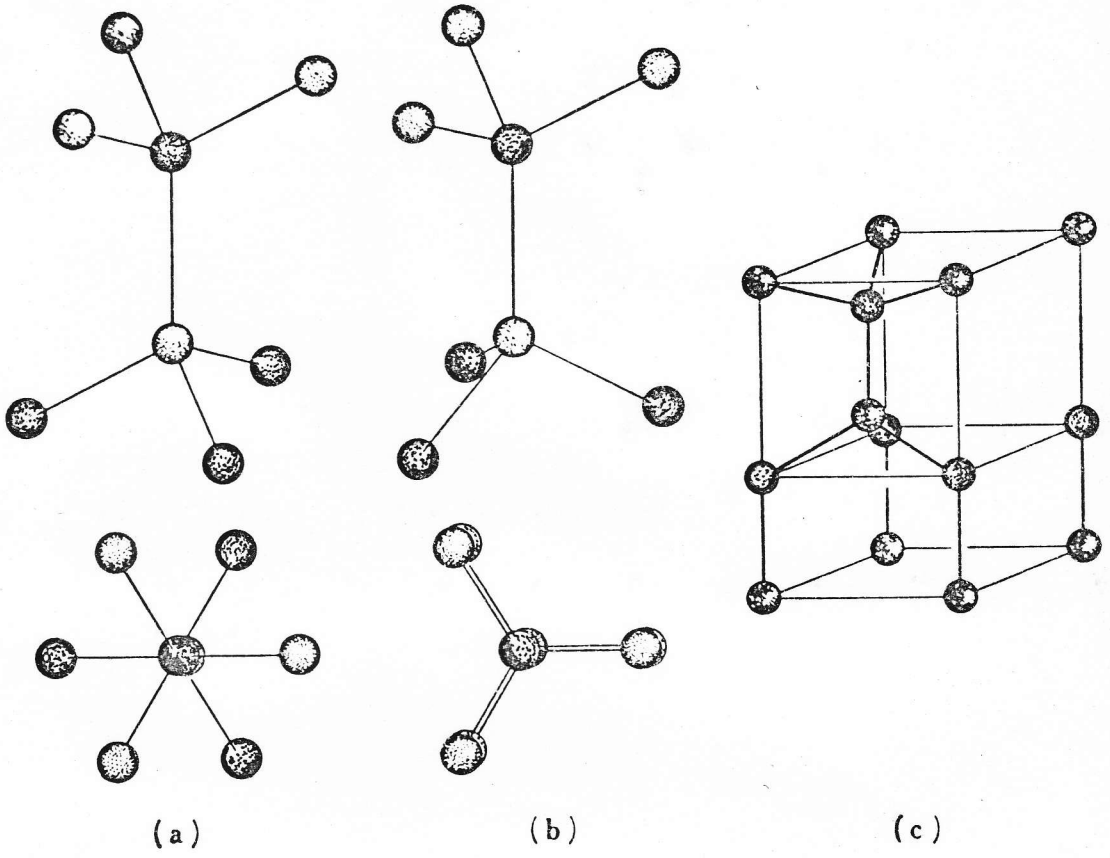


Fig.40 Two types of configuration in a tetrahedral bonding
a) Staggered configuration (diamond type).
b) Eclipsed configuration (wurtzite type).
c) Unit cell of wurtzite lattice.

rhombohedral form Si are intergrowth ones in 6H crystal. The diffraction pattern of wurtzite 2H form were not totally observed. The above crystallographic characters are nearly the same as polytype SiC which is well known as a typical example of polytypes[10].

As for the tetragonal crystal structure of new form germanium whisker, the lattice parameters are considerably larger than those of diamond lattice (5.658Å). Although we have not enough information to determine the atomic arrangement in the new structure from experiment, the following two structures seem to be helpful to reproduce it. A high pressure phase Ge with a=5.93, c=6.98Å, z=12[23] which appears above 130Kb and white tin are typical tetragonal forms in IVb group elements. After these structures we assume that the atomic configuration in the new structure is not so much different from the tetrahedral bond configuration of diamond lattice and has the same interatomic distance (2.45Å). Then, a plausible structure can be conjectured as follows. First, based upon the daimond structure, consider a tetragonal unit cell as shown in Fig.40. When this unit cell exactly follow the original diamond form, it has parameters of a=8.00 and c=5.658Å and the volume is twice as larger as that of the original lattice. If "a" axis is reduced from 8.00 to 7.62Å and a characteristic bond angle is minimized from 109.5° to 102° as given in the figure , one obtains a new tetragonal unit cell with the parameters a=7.62 and c=6.17Å. These parameters are close to those obtained in the present experiments. If this is correct, the new unit cell contains 16 atoms, and the calculated density is 5.36g·cm^{-3} which is 0.7% higher than the normal Ge density of 5.32g·cm^{-3}.

Further investigations are needed to verify the proposed structure.

It is worthy of note that polytypism of silicon found in the present study is much the same as those of silicon carbide and diamond and polymorphism of germanium discovered is similar to those found in the high pressure experiments[23]. And, therefore, a unified prospect on the crystal structures and their modifications among the IVb elements seems to be established by the present study. Further detailed investigations of physical properties of whiskers with newly found structures would be fruitful.

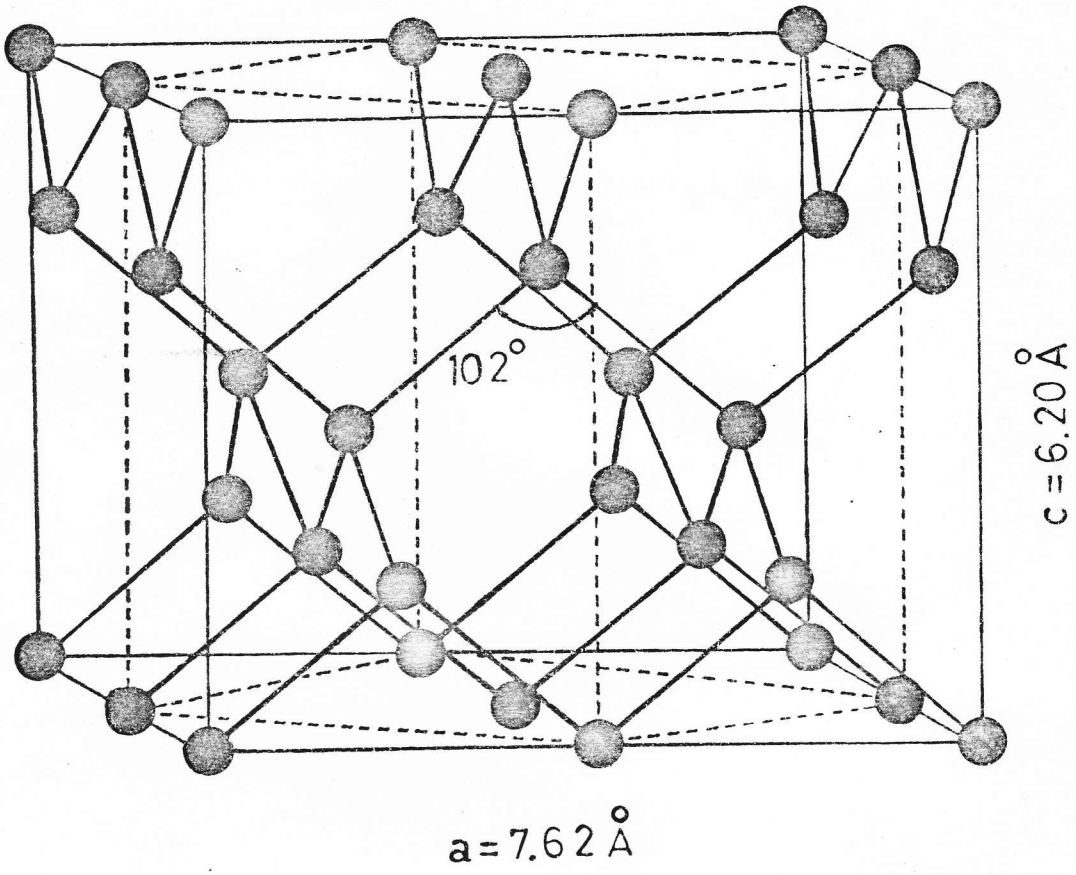


Fig.41 The proposed unit cell for the new form germanium whisker. Dotted lines correspond to the original diamond lattice.

§5 Summary and Conclusions

The experimental results in the present study are summarized as follows.

(1) Amorphous silicon whiskers are grown at around 550°C by thermal decomposition of SiH_4. Metal impurities of low melting point and some ingredients in finger grease act as catalysis or nuclei in the whisker growth. An idea similar to VLS model can be applied to interpret the growth mechanism. The amorphous structure is accounted for by the mixture of diamond-like and polytype-like lattice.

(2) 6H and 27R, 51R, 141R polytype silicon whiskers are grown around 500°C by using gold impurity. The crystallographic characters are very similar to α-SiC.

(3) Tetragonal form germanium whiskers grow below the Au-Ge eutectic point of 356°C using gold impurity. VLS mechanism is not always applicable in this case, but the globules on their tips may play the same role as those of liquid droplets in VLS growth.

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