

## FACES AND HABITS OF DIAMOND TYPE CRYSTALS

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### ABSTRACT

A study was undertaken of the natural faces and the habits of silicon, germanium, cubic arsenic trioxide and cubic antimony trioxide crystals. The sequence of the crystal forms in their order of appearance was found to be {111}, {001}, {113}, {011}, {013} for silicon, germanium, and {111}, {011}, {001} for cubic arsenic trioxide and cubic antimony trioxide.

### FACES OF THE EQUILIBRIUM FORMS OF DIAMOND TYPE CRYSTALS

#### *Silicon and Germanium*

The investigation of the crystal habits and the study of the natural faces of diamond type crystals reveal valuable facts regarding crystal orientation and surface properties. It is interesting to compare the theoretically expected growth and equilibrium forms with experimental results.

Equilibrium forms of crystals can be obtained by tempering crystals for a long time, at a constant temperature. Where crystals are of macroscopic size, equilibrium may not be reached even after extended tempering. However, by slight periodic alternation of the temperature of the crystal and its surrounding medium (or by very slow crystal growth) faces result which belong to the equilibrium form. These crystals are then said to have tempered, or growth-forms.

Silicon and germanium only, of all the elements with diamond structure, can be prepared in the form of single crystals with natural faces. When permitted to grow rapidly, silicon and germanium crystals display {111} faces only. In particular, silicon crystals grown from the melt and from solutions in gallium, indium<sup>1</sup> and tin, show {111} faces only. This does not confirm the results obtained by D. A. Petrov and A. A. Bukhanova<sup>2</sup> who observed {011} faces only in their study of silicon crystals from tin solution. In Fig. 1 a silicon single crystal, prepared by thermal decomposition of SiI<sub>4</sub> vapor on a hot silicon substrate, can be seen with {001} and {113} appearing in addition to {111}, and in Fig. 2 another crystal prepared by the same method is shown with {111}, {001}, {113}, {011} and {013}.

Germanium also crystallizes with {111} faces when grown rapidly

<sup>1</sup> Keck, P. H., and Broder, J., *Phys. Rev.*, **90**, 521 (1953).

<sup>2</sup> Petrov, D. A., and Bukhanova, A. A., *Izvest. Akad. Nauk USSR, Otdel. Khim. Nauk*, 396 (1949).

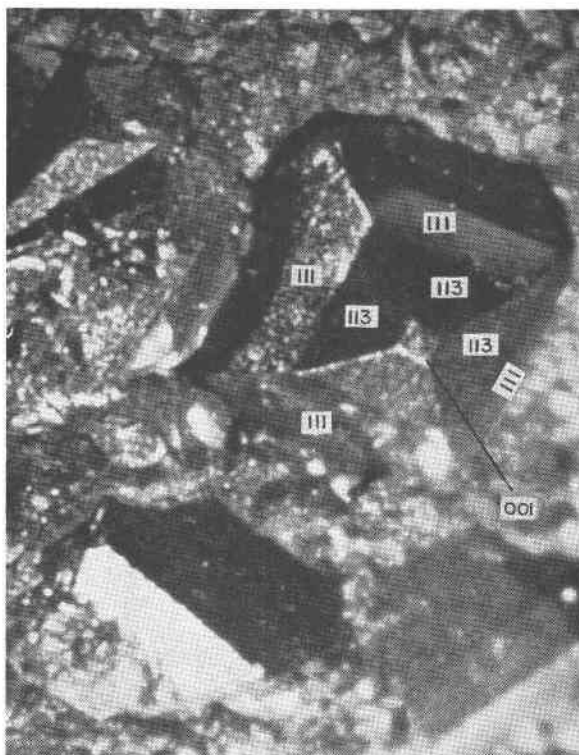


FIG. 1. Silicon crystal\* obtained by thermal decomposition of silicon tetraiodide on a hot silicon substrate showing  $\{111\}$ ,  $\{001\}$  and  $\{113\}$ -planes. All angles are convex ( $72\times$ ).

\* Crystals from Foote Mineral Company, Berwyn, Pa., by the courtesy of Mr. F. B. Litton.

from the vapor. It crystallizes in the same form from the melt,<sup>3</sup> from solutions in gallium and indium, and from the gaseous phase by reduction of germanium tetrachloride with zinc or cadmium vapor. On germanium octahedra grown from the vapor phase, truncated corners were observed which indicate that  $\{001\}$  appears next to the  $\{111\}$  plane. Among tempered germanium crystals, prepared by the hydrogen reduction of germanium tetrachloride,  $\{113\}$  planes were found frequently in addition to  $\{111\}$  and  $\{001\}$ . Finally, on several crystals  $\{011\}$  was also observed (Fig. 3). The results on silicon and germanium crystals are recorded in Table 1.

<sup>3</sup> See also Robinson, S. A., Ostapovich, P. L., Schlegel, E. S., and Gazzara, C. P., *Science*, 116, 362 (1952).

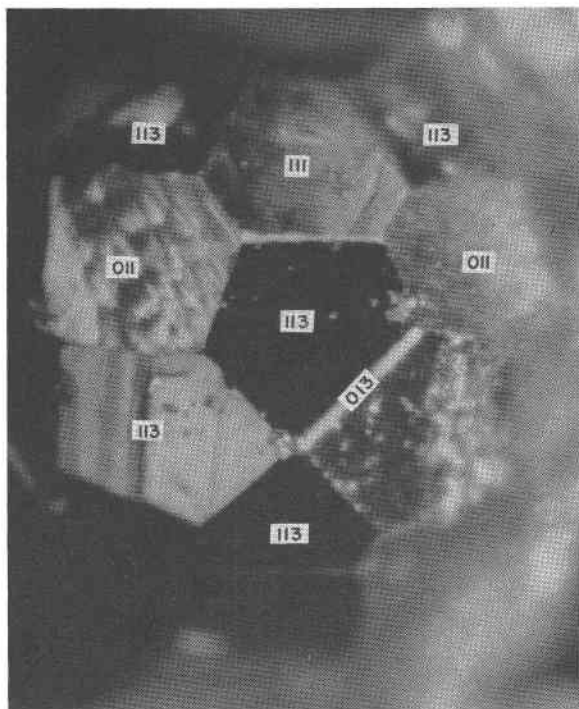


FIG. 2. Silicon crystal\* obtained by thermal decomposition of silicon tetraiodide vapor on a hot silicon substrate showing  $\{111\}$ ,  $\{113\}$ ,  $\{011\}$  and  $\{013\}$ . The  $\{001\}$  plane is poorly developed. One of the  $\{013\}$  planes represented by the truncated edges of adjacent  $\{113\}$  planes is brought out by light reflection. Notice the striation on  $\{113\}$  in  $[1\bar{1}0]$  direction (70 $\times$ ).

\* Crystals from Foote Mineral Company, Berwyn, Pa., by the courtesy of Mr. F. B. Litton.

From these observations, the sequence of the forms in the order of their appearance can be derived as follows:

Silicon:  $\{111\}$ ;  $\{001\}$ ;  $\{113\}$ ;  $\{011\}$ ;  $\{013\}$   
 Germanium:  $\{111\}$ ;  $\{001\}$ ;  $\{113\}$ ;  $\{011\}$

In the case of silicon, the sequence of the last two forms is not clear. Since  $\{013\}$  was not observed at all in germanium, it may be concluded that the final sequence for the diamond structure is, in general:  $\{111\}$ ;  $\{001\}$ ;  $\{113\}$ ;  $\{011\}$ ;  $\{013\}$ . Figure 4 shows a crystal model exhibiting these planes. This sequence, obtained experimentally, differs slightly from the calculated sequence  $\{111\}$ ,  $\{001\}$ ,  $\{011\}$ ,  $\{113\}$ ,  $\{013\}$ .<sup>4</sup> Details of this subject will be published at a later date.

<sup>4</sup> Stranski, I. N. Discuss. *Faraday Soc.*, 5, 13 (1949).

TABLE 1. CRYSTALLOGRAPHIC DATA ON SUBSTANCES WITH DIAMOND STRUCTURE

Substance	Planes appearing in growth forms or tempered forms	Preparation method and source of crystals	Twin plane	Slip plane	Cleavage plane
Diamond	{111} <sup>*</sup>	Geologic formation	{111}	{111} <sup>1</sup>	{111}, {011} <sup>2</sup>
Silicon	{111}	From melt, solutions (SiCl <sub>4</sub> +Zn) gas phase (SiBr <sub>4</sub> +H <sub>2</sub> ) gas phase	{111}	{111} <sup>3</sup>	{111}, {011}
	{111}, {001}	From (SiCl <sub>4</sub> +Zn) gas phase			
	{111}, {001}, {113}	From (SiCl <sub>4</sub> +Zn) gas phase from SiL vapor phase			
	{111}, {001}, {113}, {011}, {013}	From SiL vapor phase			
Germanium	{111}	From vapor, melt, solutions from (GeCl <sub>4</sub> +Zn, Cd) gas phase	{111}	{111} <sup>3</sup>	{111}
	{111}, {001}	From vapor			
	{111}, {001}, {113}	From (GeCl <sub>4</sub> +H <sub>2</sub> ) gas phase			
	{111}, {001}, {113}, {011}	From (GeCl <sub>4</sub> +H <sub>2</sub> ) gas phase			

\* While in diamond a variety of other planes than {111} have been observed, an unambiguous sequence of the appearance cannot be derived because of the complexity of the geological growth conditions.

<sup>1</sup> Tolansky, S., and Omar, M., *Mag.* **44**, 514 (1953).

<sup>2</sup> Kraus, E. H., and Slawson, C. B., *Am. Mineral.*, **24**, 661 (1939).

<sup>3</sup> Treuting, R. G., *J. Metals*, **4**, 1044 (1952).

### Diamond

While the observed sequence should hold true for crystals grown, or tempered, in their vapor phase (or any other highly diluted gaseous mother phase) it may not be valid for diamond crystals. The planes, which appear in addition to the predominant {111} plane in diamond, cannot be arranged distinctly into a sequence, because of the complex conditions during the geological growth.

### Arsenic Trioxide and Antimony Trioxide

A somewhat different sequence of planes is obtained from cubic arsenic trioxide (arsenolite) and cubic antimony trioxide (senarmontite), which are built up of As<sub>2</sub>O<sub>3</sub> and Sb<sub>2</sub>O<sub>3</sub> molecules in the diamond arrangement. These oxides display well developed octahedra, when grown rapidly.

After tempering in the vapor phase, cubic arsenic trioxide and cubic antimony trioxide crystals show {011}, in addition to {111}. In one case, {001} planes were found on arsenic trioxide. Since it is reported in the literature<sup>5</sup> that after tempering {111}, {011} and {001} planes appear on cubic antimony trioxide crystals also, the probable sequence for both cubic arsenic trioxide and cubic antimony trioxide can be given as {111},

<sup>5</sup> Weber, J., *Zeit. Krist.*, **44**, 235 (1908).

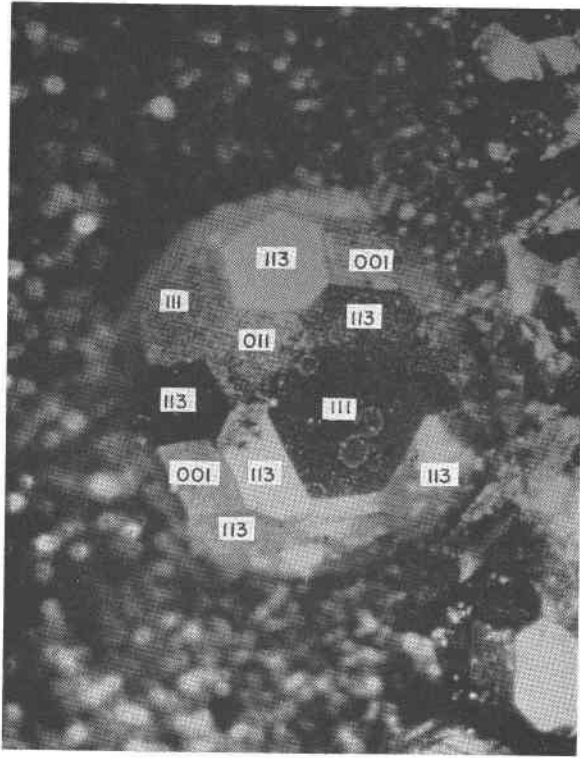


Fig. 3. Germanium crystal\* grown from the gaseous phase by reduction of germanium tetrachloride with hydrogen on a hot graphite block at 900° C. shows {111}, {001}, {113}, and {011} planes (72X).

\* Crystals from the Eagle-Picher Research Laboratories, Joplin, Mo., by the courtesy of Drs. W. E. Medcalf, R. K. Riel and C. E. Smith.

{011}, and {001}. This sequence differs from the sequence for silicon and germanium, and this difference can be explained by the non-spherical symmetry of the molecules ( $T_d$ ). Finally, it might be worthwhile mentioning that cubic basic beryllium acetate, in which the molecules  $\text{Be}_4\text{O}(\text{CH}_3\text{COO})_6$  occupy the positions of a diamond lattice also crystallizes in the form of octahedra. The results are summarized in Table 2.

#### TWINNING, CLEAVING, SLIPPING AND STRIATION OF DIAMOND TYPE CRYSTALS

Twinning, cleaving and slipping, which are functions mainly of crystal structure, do not depend as much upon growth or tempering conditions as do the crystal habits. Twin planes, cleavage planes and slip planes

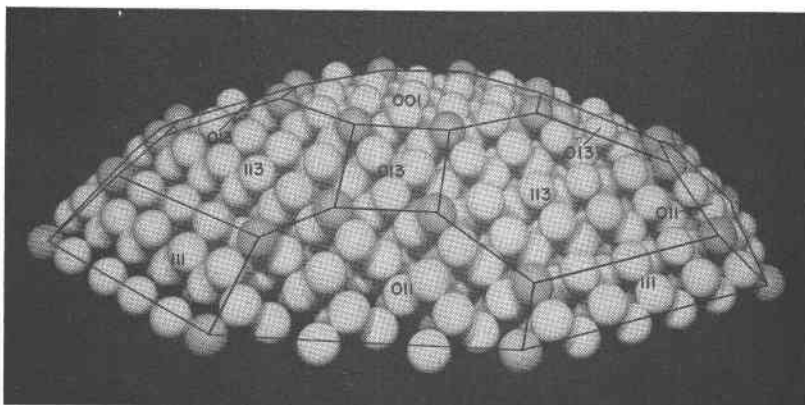


FIG. 4. Model of the supposed equilibrium form of crystals with diamond structure with  $\{111\}$ ,  $\{001\}$ ,  $\{113\}$ ,  $\{011\}$  and  $\{013\}$  planes. The marked balls represent the apexes atoms.

are  $\{111\}$  for silicon and germanium, in all cases. This is also true for diamond crystals. The cleavage planes for cubic arsenic trioxide and cubic antimony trioxide are  $\{111\}$ , however twinning along  $\{111\}$  is not observed. This is in agreement with the theoretical expectation.

In all diamond type crystals striation was found on  $\{111\}$  in the direc-

TABLE 2. CRYSTALLOGRAPHIC DATA ON SUBSTANCES WITH A MOLECULAR LATTICE IN THE DIAMOND ARRANGEMENT

Substance	Planes appearing in growth forms or tempered forms	Preparation method and source of crystals	Twin plane	Cleavage plane
Arsenic trioxide (arsenolite) $\text{As}_2\text{O}_3$	$\{111\}$	From vapor, hydrochloric solution	Not found*	$\{111\}$
	$\{111\}$ , $\{011\}$	From vapor		
	$\{111\}$ , $\{011\}$ , $\{001\}$	From vapor		
Antimony trioxide (senarmontite) $\text{Sb}_2\text{O}_3$	$\{111\}$	From vapor	Not found*	$\{111\}$
	$\{111\}$ , $\{011\}$	From vapor		
	$\{111\}$ , $\{011\}$ , $\{001\}$	From vapor		
Basic beryllium acetate $\text{Be}_4\text{O}(\text{CH}_3\text{COO})_6$	$\{111\}$	From solutions in organic solvents		

\* As it will be pointed out later  $\{111\}$  twinning in arsenolite and senarmontite is not expected.

tions  $[1\bar{1}0]$ ,  $[10\bar{1}]$ ,  $[01\bar{1}]$ , on  $\{001\}$  in the directions  $[110]$ ,  $[1\bar{1}0]$ , on  $\{011\}$  and  $\{113\}$ , in the  $[1\bar{1}0]$  direction (Fig. 2). It may be mentioned here that in some cases all major planes in the  $[1\bar{1}0]$  zone between  $\{111\}$  and  $\{001\}$  were found to be developed in silicon crystals grown by the zinc reduction process.

#### ZINCBLENDE STRUCTURE

On zincblende structures the general sequence of forms is  $\{111\}$ ,  $\{1\bar{1}1\}$ ,  $\{001\}$ . The zincblende structure may be regarded as a diamond structure with alternating atoms  $A$  and  $B$ , having a partial ionic character in addition to the valence bondings. Details will be published at a later date.

#### CRYSTAL HABITS

Various types of habits of silicon and germanium crystals from gallium, indium and tin solutions, are formed by cooling. The following habit types were observed: needles with  $[001]$  as needle axis, having the appearance of a string of octahedra along the  $[001]$  axis; twinned and untwinned needles with  $[011]$  as needle axis; plates and rhombus-like plates or rhombohedra. The octahedra appear if there is almost no temperature gradient present during slow cooling; the needles result where there is an appreciable temperature gradient during fast cooling; the plates appear where there is a temperature gradient, near the surface of the solution, resulting from heat losses by radiation. Occasionally, all the types show hollow pits. Dendritic growth was found in silicon plates grown from solution, the growth direction being  $[112]$ . Silicon needles from zinc reduction of silicon tetrachloride in the gaseous phase were found to show almost exclusively the  $[111]$  orientation. They sometimes show interpenetrating twinning. Silicon single crystal fibers (average diameter  $1\ \mu$ , length up to 1 cm.) of the same orientation were found by E. R. Johnson and J. A. Amick<sup>6</sup> to occur as cotton wool-like cocoons in the reaction chamber. One batch of silicon crystals prepared by the same process gave a preferred  $[001]$  orientation. These crystals are very similar to the needles obtained from metal solution. Germanium needles prepared by zinc reduction of germanium tetrachloride in the gas phase showed  $[111]$  orientation only.

#### ACKNOWLEDGMENT

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<sup>6</sup> Johnson, E. R., and Amick, J. A., *J. Appl. Phys.*, **25**, 1204 (1954).