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Light Figures and Surface Structures Revealed by Chemically Etched Germanium Single Crystals*

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Synopsis

Light figures projected on a plate screen from germanium single crystals, polished mechanically and etched with various chemical reagents, are examined in order to find out light figures or etching directions suitable for the orientation determination. Information regarding surface structures of germanium single crystals developed by mechanical polishing and by chemical etching has been obtained from the analysis of the observed light figures and from microscopic observations of crystal surfaces.

It has been found that distinct light figures suitable for the orientation work are obtained by a short time etching with concentrated nitric acid plus water (1:1 and 3:7; 70°C), with concentrated nitric acid plus water plus hydrofluoric acid plus silver nitrate (45 cc + 45 cc + 10 cc + 50 or 20 mg, and 20 cc + 40 cc + 40 cc + 2 g), with hydrofluoric acid plus hydroperoxide plus water (1:1:4), and with 30 percent hydroperoxide (100°C). Among these etchants, hydrofluoric acid plus hydroperoxide plus water (1:1:4) is most suited for accurate orientation determination. Generally, crystal faces developed by etching have been found to be those belonging to the principal crystal zones, but dilute nitric acid heated at 70°C develops some additional high-index crystal faces belonging to a high-index crystal zone. There is a tendency that low-index crystal faces appear by a short time etching and high-index ones by a prolonged etching. It is to be added that relatively clear light figures are obtained on germanium crystals as polished with silicon carbide powder.

I. Introduction

We have hitherto studied the light figure phenomena(1) revealed by various metal and semiconductor crystals etched chemically in order to find out light figures suitable for determining crystal orientations(2) and to examine crystal faces

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(1) M. Yamamoto, J. Watanabé, K. Masumoto, and T. Kawada, Nippon Kinzoku Gakkai-shi, **22** (1958), 75; Sci. Rep. RITU, **A12** (1960), 226 (Si), and references cited in those papers.

(2) M. Yamamoto, Nippon Kinzoku Gakkai-shi, **5** (1941), 214; Sci. Rep. Tôhoku Univ., **31** (1943), 121. M. Yamamoto and J. Watanabé, Nippon Kinzoku Gakkai-shi, **17** (1953), 5; Sci. Rep. RITU, **A7** (1955), 173 (cubic crystal rods). M. Yamamoto and J. Watanabé, Nippon Kinzoku Gakkai-shi, **13** (1949), No. 4; Sci. Rep. RITU, **A2** (1950), 270 (hexagonal crystal rods); Nippon Kinzoku Gakkai-shi, **B15** (1951), 572; Sci. Rep. RITU, **A5** (1953), 135 (trigonal crystal rods); Nippon Kinzoku Gakkai-shi, **17** (1953), 114; Sci. Rep. RITU, **A7** (1955), 161 (tetragonal crystal rods); Ôyô Butsuri, **24** (1955), 423; Sci. Rep. RITU, **A9** (1957), 395 (cubic crystal plates); Nippon Kinzoku Gakkai-shi, **20** (1956), 85; Sci. Rep. RITU, **A9** (1957), 410 (crystal grains); Kinzoku Butsuri, **6** (1960), 118 (review).

developed by etching.[1] It has been found that the determination of crystal orientations by light figures can be made rapidly and perfectly with a high accuracy comparable to X-ray methods.[3~5] Thus, the light figure method of orientation determination is now applied conviniently in various fields of fundamental researches. It has also been found that crystal faces developed by etching are generally the close-packed crystal planes belonging to the principal crystallographic zones, although high-index crystal faces appear sometimes in prolonged etching or in alloy crystals of high solute content.

Recently, the light figure method has been employed for orientating and cutting out single crystals of semiconductors with diamond structure such as germanium and silicon. Studies on the light figures and its application for orientation works with germanium crystals have been reported by several workers. Iida[6] observed light figures of germanium crystal (of 0.5 Ω-cm) etched with 30 percent hydroperoxide, with hydrofluoric acid plus nitric acid plus water (1:1:2), and with Westinghouse Ag solution (nitric acid+water+hydrofluoric acid+silver nitrate (20 cc+40 cc+40 cc+2 g). He found that light figures obtained by etching with 30 percent hydroperoxide for 30 hours consisted of distinct {114}, {112}, {110} and {111} light spots, although they were constructed only of {119} and {129} spots when re-etched with the same solution, and that the etching with hydrofluoric acid plus nitric acid plus water (1:1:2) for 50 hours produced light figures consisting of {110}, {113}, {334} and {111} spots, while the Westinghouse Ag solution revealed the {111} light figure of a three-arrow form. Kikuchi[7] recommended No. 2 solution (hydrofluoric acid plus hydroperoxide plus water (1:1:4)), while Hancock and Edelman[9] the etching with 30 percent hydroperoxide heated to 85°C for 5~7 minutes, for orientation works of germanium crystals. Wolff, Wilbur and Clark[5] tested No. 2 solution, Westinghouse Ag solution, hydrofluoric acid plus hydroperoxide (1:1) and 30 percent hydroperoxide (65°C and room temperature) and showed that the orientation determination can be made with an accuracy of 3.5~30′ by use of the {111} light figures obtained by etching with these etchants. Thus, only a fragmentary information is available. So, we have studied the light figure phenomena revealed and crystal faces developed by chemical etching in germanium single crystals as an extension of our previous study with silicon crystals.[9]

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(3) M. Yamamoto and J. Watanabé, Ôyô Butsuri, **24** (1955), 122; Sci. Rep. RITU, **A9** (1957), 24.
(4) G. A. Wolff, J. M. Wilbur and J. C. Clark, Z. Elektrochem., **61** (1957), 101.
(5) F. Haessner and W. in der Schmitten, Z. Metallkde, **49** (1958), 507.
(6) M. Iida, Kinzoku Butsuri, **1** (1955), 29.
(7) M. Kikuchi, Rep. Electrotechn. Lab. (Japan), **19** (1955), 938.
(8) R. D. Hancock and S. Edelman, Rev. Sci. Instr., **27** (1956), 1082.
(9) M. Yamamoto, J. Watanabé, K. Masumoto, and T. Kawada, Nippon Kinzoku Gakkaishi, **22** (1958), 75; Sci. Rep. RITU, **A12** (1960), 228.

II. Crystal specimens and experimental procedure

Germanium single crystals used as specimens are a semi-cylindrical shaped rod, about 25mm in diameter and about 12 mm in length, which were grown along the <111> direction from material of seven nine purity by the zone-melting method. Etching solutions tested are nitric acid, nitric acid plus silver nitrate, nitric acid plus hydrofluoric acid plus hydrochloric acid, sulphuric acid, hydrofluoric acid plus hydroperoxide, hydroperoxide, hydroperoxide plus acetic acid anhydride, and aqueous solutions of sodium and potassium hydroxide, of which concentrations and temperatures are given in Table 1. Concentrations of acids used are HCl 38.5%, HNO_3 63.3%, H_2SO_4 96.6%, and HF 46%. Nearly {100}, {110} and {111} surfaces, which several degrees inclined from the {100}, {110} and {111} planes, respectively, of the crystal specimens were polished carefully with emery papers 03~05 or lapped with #60 SiC powder and subsequently with Al_2O_3 powder on a glass plate in order to remove any trace of previous treatment, and then etched with a specified etching reagent. Angles among main spots composing the light figures observed were measured with an accuracy of ±0.1° by a two-circle goniometer and then the observed light figures were photographed on photographic films (Fuji, Neopan S, ASA 50). The color of light figures of germanium crystals is generally yellow for a light source of incandescent electric lamp (500 W). Microstructures of etched crystal surfaces were also observed under an optical microscope. It is to be noted that photographs or sketches of light figures and micrographs of the etched crystal surfaces which will be shown later are arranged in such orientations as shown in Fig. 1.

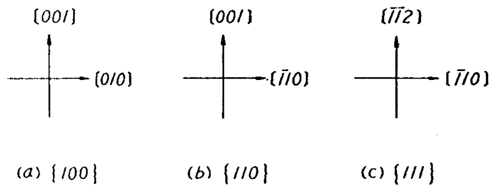


Fig. 1. To illustrate the orientational arrangement of the sketches and photographs of light figures and of the photographs of microstructures of the etched crystal surfaces.

III. Light figures and {111} surface structure revealed by roughly polished germanium crystals

Comparatively distinct light figures were observed in germanium crystals polished roughly with #60 SiC powder. The observed {100} light figure (Fig. 2 (a)) consists of four-arrows radiating from four apexes of a very indistinct square towards {111} poles. The {110} light figure (Fig. 2 (b)) is composed of four [100]-[111] arcs. The {111} light figure (Fig. 2 (c)) is a comparatively distinct three-arrow directing to {100} poles, and this light figure is suitable for the orientation determination.

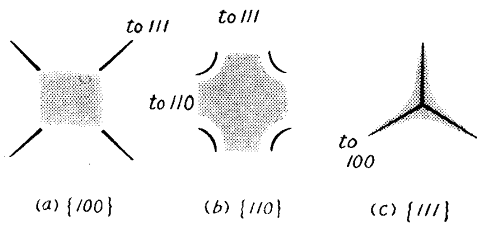


Fig. 2. Light figures of Ge crystal polished with #60 SiC powder.

The microstructure of a roughly

Table 1. Experimental results on the light figure phenomena revealed and crystal faces developed by mechanical polishing as well as by chemical etching in germanium crystals.
The mark ◎ denotes a distinct light figure, suitable to the determination of crystal orientations, ○ a distinct, but not so suitable, light figure and × an indistinct or no light figure.

No.	Etching reagent (Temperature)	Suitability of light figure on			Optimum etching time	Developed crystal faces
		{100}	{110}	{111}		
1	As polished with #60 SiC power	○	○	◎	——	——
2a and b	Conc. HNO_3 (room temp. and 70°C)	×	×	×	——	——
2c	Conc. HNO_3+H_2O(1:1)(70°C)	◎	○	◎	4 min	Short-time etching: {100}, {111}, {830}, {16, 9, 5}, and {533}-vicinal; Long-time etching: {100}, {111}, {10, 3, 0}, {19, 11, 5}, {522}, and {331}
2d	Conc. HNO_3+H_2O(1:1) (room temp.)	○	○	○	40 min	{111}, {520}, and {533}-vicinal
2e	Conc. HNO_3+H_2O(3:7)(70°C)	○	○	◎	3~6 min	Short-time etching; {111}, {520}, (or {730}), {772}, {11, 7, 6} (or {321} or {942}), {533}-{11, 7, 6} (or -{321}, or -{942}) vicinal, long-time etching: three more, {553}, {992} and {100}
2f	Conc. HNO_3+H_2O(3:7) (room temp.)	×	×	×	——	——
3a	$HNO_3+H_2O+AgNO_3$ (50cc+50cc+1g) (room temp.)	×	×	×	——	——
3b and c	HNO_3+H_2O+HF (4:4:2) and (9:9:2) (room temp.)	×	×	×	——	——
3d	$HNO_3+H_2O+HF+AgNO_3$ (45cc+45cc+10cc+50mg) (room temp.)	◎	◎	◎	30sec~1.5 min	Short-time etching: {111} and {110}; Long-time etching: {111}, {110}, {100} and {311} (or {411})
3e	$HNO_3+H_2O+HF+AgNO_3$ (45cc+45cc+10cc+20mg) (room temp.)	◎	○	◎	2 min	
3f	$HNO_3+H_2O+HF+AgNO_3$ (20cc+40cc+40cc+2g) (room temp.)	×	○	◎	2 min	{110} and {111}
4	$HF+H_2O_2+H_2O$(1:1:4) (room temp.)	◎	◎	◎	3 min	{111}, {100} (or {100}-vicinal), {110}-vicinal, {13, 4, 4}-vicinal, and {10, 7, 7}-vicinal
5a	30%H_2O_2 (100°C)	◎	◎	◎	1~1.5 min	{100}-vicinal, {110}-vicinal, {111}-vicinal, and {311}-vicinal
5b	30%$H_2O_2+(CH_3CO_2)_2O$(3:1)(room temp.)	○	○	○	2~2.5 hr	
6a and b	Aqua regia+H_2O(1:0) and (3:7) (room temp.)	×	×	×	——	——
7a and b	Conc. $H_2SO_4+H_2O$(1:0) and (3:7) (70°C)	×	×	×	——	——
8a~h	Sat. and 10% aq. sol. of NaOH and of KOH (room temp. and 70°C)	×	×	×	——	——

polished {111} surface is as shown in Photo. 1. Bright regions are shell-like fractured surfaces, in which parallel stairs running parallel to <110> directions are seen. This shows that three arrows in the {111} light figure (Fig. 2 (c)) are revealed

Photo. 1. Microstructure of a {111} surface of Ge crystal polished with ♯60 SiC powder. (×270)

by the scattering of the incident light from these three sets of stairs.

It is to be noted that no light figure was observed with crystal surfaces polished using emery papers of more fine-grained alumina powder, probably because the stair structure produced by previous rough polish is broken down finely.

IV. Light figures and surface structures revealed by chemically etched germanium crystals

(2a and b) Concentrated nitric acid (room temperature and 70°C).

The etching of Ge crystals with hot or cold concentrated nitric acid made blacken the crystal surface and thus no light figure was observed.

Then, variously diluted nitric acids were tested.

(2c) Concentrated nitric acid plus water (1:1) (70°C)

Ge crystals were readily etched with hot 1:1 nitric acid solution and, after etched for 4 minutes, revealed comparatively distinct light figures suitable to the orientation determination. In the {100} light figure (Fig. 3(a) : Photo. 2(a)), the {100} spot is surrounded by four {830} spots and four wide bands radiating towards {111} poles. The {110} light figure (Fig. 3(b) : Photo. 2(b)) has {830} spots at its both sides, arcs connecting {16, 9, 5} spots with each other at its upper and lower parts, and {111} spots

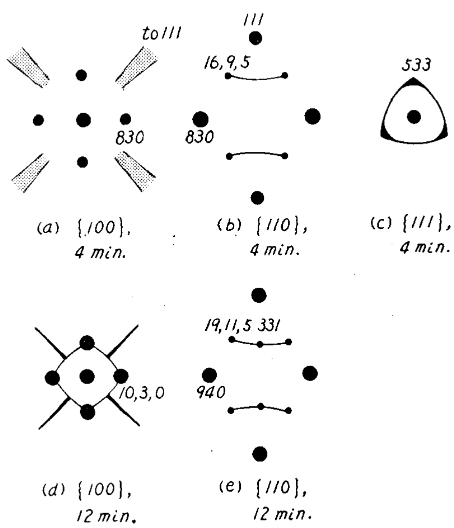
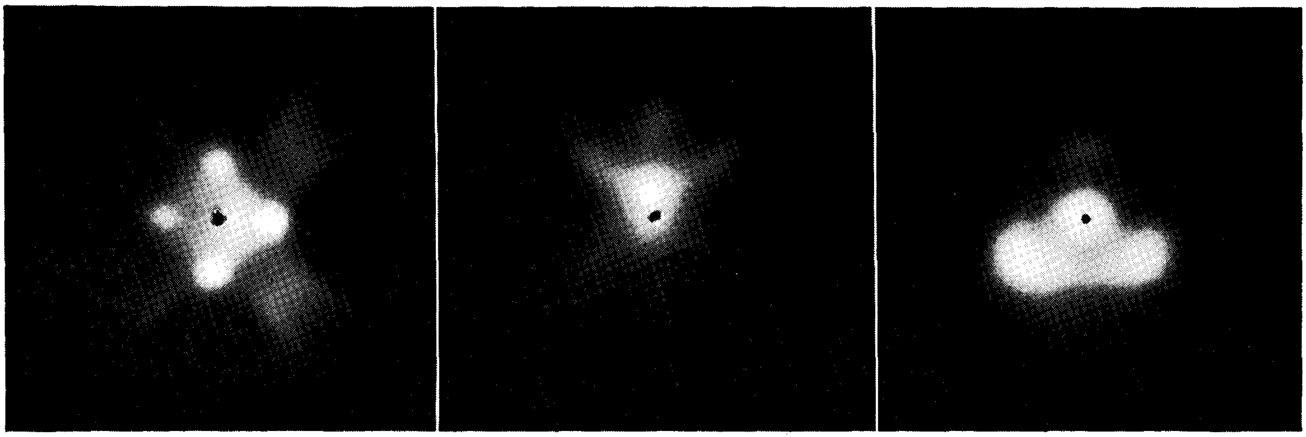


Fig. 3. Light figures of Ge crystal etched with conc. HNO_3+H_2O (1 : 1) (70°C).

outside the arcs. The {111} light figure (Fig. 3(c) : Photo. 2(c)) is a rounded triangle with the {111} spot at its center and {533} spots at its apexes. The spatial relationship among these light figures is as shown stereographically in Fig. 4.



(a) {100} (b) {110} (c) {111}

Photo. 2. Light figures of Ge crystal etched with conc. HNO_3+H_2O (1 : 1)(70°C) for 4 min.

When the etching was continued further, the crystal surface became somewhat bright and the forms of the light figures changed slightly. After twelve minutes' etching, {10, 3, 0} spots appeared newly in place of the {830} spots in the {100} light figure (Fig. 3(d)), {940} spots and {331} spots at the middle point of the upper and lower arcs were newly revealed and {16, 9, 5} spots changed into {19, 11, 5} spots in the {110} light figure (Fig. 3 (e)), and the sides of the rounded triangle disappeared and the {533} spots changed into {522} spots in the {111} light figure. Further etching made the crystal surface brighter and spoiled the symmetry of the forms of the light figures.

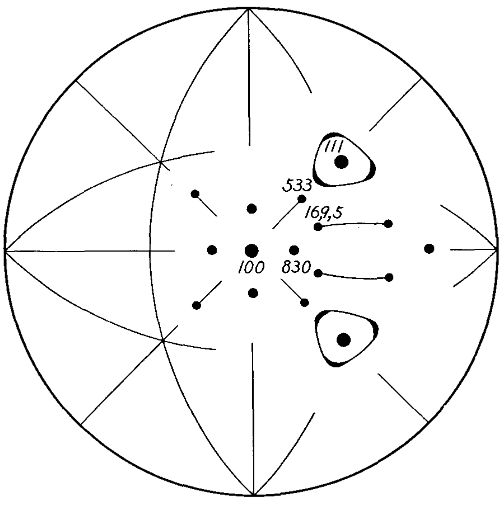


Fig. 4. Stereographic illustration of the spatial relationship among light figures of Ge crystal etched with conc. HNO_3 + H_2O (1 : 1) (70°C) for 4 min.

Surface structures of Ge crystals etched with this reagent for a short time are so fine as can not be dissolved by an optical microscope except the {111} surface structure, but they become coarse with continued etching. Microstructures of {100}, {110}, and {111} surfaces etched for twelve minutes are shown in Photos. 3(a)~(c). Etch pits of a rounded square form on the {100} surface (Photo. 3(a)) may consist of the {100} and {10, 3, 0} faces. The structure of the {110} surface (Photo. 3(b)) is fine and complicated. The {111} surface (Photo. 3(c)) shows a terrace structure, of which flat stages

(a) {100}

(b) {110}

(c) {111}

Photo. 3. Microstructures of the principal crystal surfaces of Ge etched with conc. HNO_3+H_2O (1 : 1) for 12 min. (×270)

may consist of {111} faces and curved steps may consist of a set of vicinal faces neighbouring to the {533} planes.

(*2d*) *Concentrated nitric acid plus water* (*1:1*) (*room temperature*)

The etching of Ge crystals with cold 1:1 nitric acid solution produced comparatively distinct light figures similar to those revealed by etching with the above-mentioned hot solution, although it required a much longer time (40 minutes) for etching. The {100} light figure (Fig. 5(a)) is composed of four {520} spots and four wide bands radiating towards {111} poles. The {110} light figure (Fig. 5(b)) consists of {520} spots at both sides, sharp arcs at the upper and lower portions, and {111} spots outside the arcs. The {111} light figure is the same as observed in the case of etching with the hot solution mentioned above (see Fig.

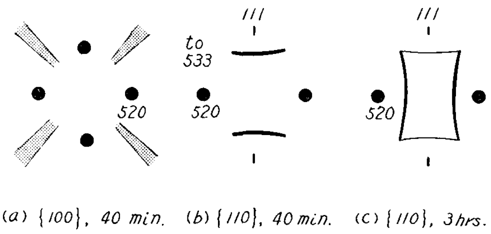


Fig. 5. Light figures of Ge crystal etched with conc. $HNO_3 + H_2O$ (1 : 1) (room temp.)

3(c)).

When the etching time was increased further, in the {100} light figure, the neighboring {520} spots were connected with lines and the radiating bands became indistinct, and, in the {110} light figure, sharp arcs appeared newly at both sides while the arcs at the upper and lower portions became indistinct, as shown in Fig. 5(c). Microstructures of etched crystal surfaces were not clear at a short-time etching, but, after a prolonged etching, they become similar to those observed in the above-mentioned case of etching with the hot solution (see Photo. 3).

It is to be noted that, when the temperature of the solution was raised up to 70°C in the way of etching, the group of light spots as illustrated in (2c) was observed to appear.

(2e and f) Concentrated nitric acid plus water (3:7) (70°C and room temperature)

Comparatively distinct light figures were obtained by etching for 3~6 minutes with concentrated nitric acid plus water (3:7) heated at 70°C. The observed {100} light figure is quite the same as that observed in the above-mentioned case of etching with cold 1:1 solution (see Fig. 5 (a)). The {110} light figure consists of {520}, {11, 7, 6}, {772}, and {111} spots (Fig. 6 (a)). And, the {111} light figure is composed of the central {111} spot and surrounding three arcs, which center at the {533} poles and end at {11, 7, 6} poles (Fig. 6 (b)). It is to be noted that, when thus etched crystals were polished and etched again with the same solution, crystallographic indices such as {11, 7, 6,} and {520} often varied to {321} or {942} and {730}, respectively.

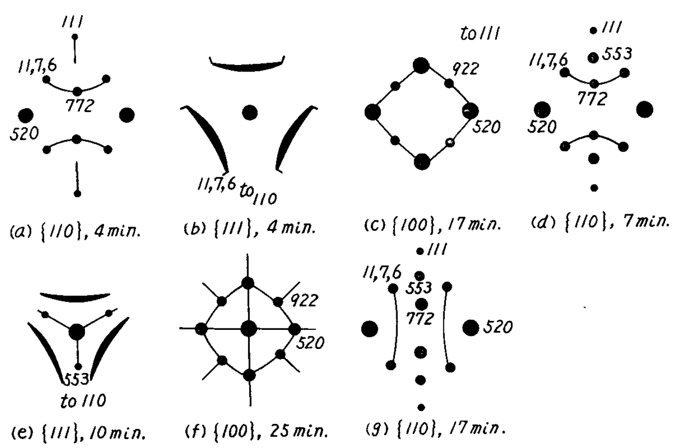


Fig 6. Light figures of Ge crystal etched with conc. HNO_3+H_2O (3 : 7) (70°C).

When the etching was continued, crystal surfaces, especially the {111} surface, became bright and light figures also changed their forms. Thus, in the {100} light figure, after etching for 17 minutes, comparatively indistinct {922} spots appeared between the {520} spots connected with a line (Fig. 6(c)), to which the {100} spot and a cross radiating from it through the {520} spots were added after 25 minutes (Fig. 6(f)). In the {110} light figure, {553} spots appeared between {111} and {772} spots after 7 minutes (Fig. 6(d)), and then the {772} spots and the arcs through them became indistinct and sharp arcs appeared newly at both sides after 17 minutes (Fig. 6(g)). In the {111} light figure, three arrows connecting the {111} spot with {553} spots were revealed after 10 minutes (Fig. 6 (e)), but it lost the symmetry of its form gradually with increasing etching time and became quite indistinct at 25 minutes.

Microstructures of crystal surfaces etched with this reagent were analogous to those observed in the case of etching with 1:1 solution mentioned before, corresponding to the similarity of the observed light figures.

On the other hand, the etching with concentrated nitric acid plus water (3:7) at room temperature produced no light figure even after 1 hour's etching because of its weak etching power.

As shown above, hot dilute nitric acid revealed distinct light figures after a comparatively short-time etching. Then, in order to obtain distinct light figures without heating the etching reagent, we tested concentrated nitric acid plus water (1:1) added with a small content of silver nitrate, hydrofluoric acid, or both.

(*3a*) *Concentrated nitric acid plus water plus silver nitrate* (*50 cc+50 cc+1g*), *and* (*3b and c*) *Concentrated nitric acid plus water plus hydrofluoric acid* (*4:4:2 and 9:9:2*)

Indistinct light figures were revealed only by the three principal crystal surfaces of Ge crystals etched with the (3b and c) solutions.

(*3d and e*) *Concentrated nitric acid plus water plus hydrofluoric acid plus silver nitrate* (*45cc+45cc+10cc+50 or 20mg*)

The etching solution containing 50 mg silver nitrate attacked Ge crystal comparatively vigorously and, at 30 seconds' etching, produced distinct {110} and {111} light figures, which are shown in Figs. 7(a) and 7(b). The straight line of the {110} light figure connects with three arrows of the {111} light figure. After 1.5 minutes, these light figures deformed into such forms as shown in Figs. 7(d) and 7(e) or 7(f) and the {100} light figure such as shown in Fig. 7(c) appeared newly. Somewhat diffused four spots located around the {100} spot in the {100} light figure correspond with the {311} planes. Over 4 minutes, the {311} spots changed to {411} spots and a diffused ring appeared around the {111} spot. The etching over ten minutes destroyed the symmetrical forms of the light figures.

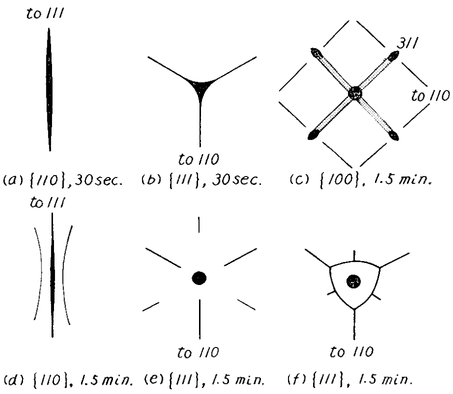
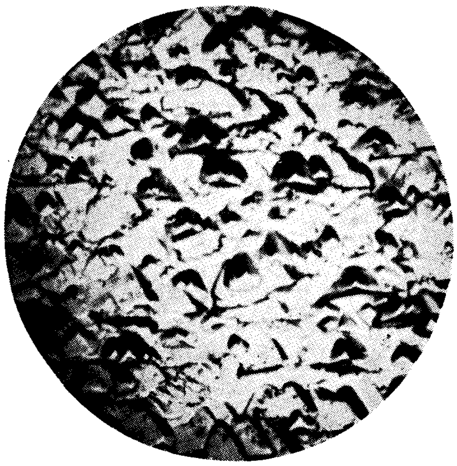


Fig. 7. Light figures of Ge crystal etched with $HNO_3+H_2O+HF+AgNO_3$ (45 cc + 45 cc + 10 cc + 50 mg).

Microstructures of the {100} surface etched for 4 minutes and {110} and {111} surfaces etched for 1.5 minutes with this etchant are shown in Photos. 4(a)～(c). The {100} surface (Photo. 4(a)) reveals etch pits of a square form, which are surrounded by the {100} and {411} faces. The {110} surface (Photo. 4(b)) shows a stepped structure which is composed of the {110} and {111} facets. On the {111} surface (Photo. 4(c)), we see etch pits of a triangular pyramid form or of a truncated triangular pyramid form which are constructed by the {110} and {111} or {311} facets.

(a) {100}, 4 min.

(b) {110}, 1.5 min.



(c) {111}, 1.5 min

Photo. 4. Microstructures of the principal crystal surfaces of Ge crystal etched with $HNO_3+H_2O+HF+AgNO_3$ (45 cc + 45 cc + 10 cc + 50 mg). (×270)

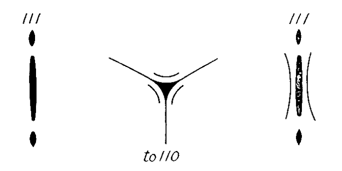
The etching with the solution containing 20 mg silver nitrate showed the same light figure phenomenon as in the case of the solution containing 50 mg silver nitrate, although a three or four times longer etching time was required to obtain distinct light figures owing to its weaker etching power.

(*3f*) *Concentrated nitric acid plus water plus hydrofluoric acid plus silver nitrate* (*20cc+40cc+40cc+2g*) (*Westinghouse Ag solution*)

When Ge crystal was immersed into this solution, the crystal surface was immediately covered with a white film, but the film disappeared soon and the crystal was etched, accompanying the production of gas bubbles. After etching for 2 minutes, we observed {110} and {111} light figures similar to, but more distinct than, those observed in the just-mentioned cases of etching with (3d and e) solutions (Figs. 7(a) and (b)). At 5 minutes, the {110} light figure isolated {111} spots at its both ends (Fig. 8(a)) and at the same time three faint arcs appeared around the central part of the {111} light figure (Fig. 8(b)). The {110} light figure changed further into such a form as shown in Fig. 8(c) at 7 minutes. Then, the light figures remained the same even after

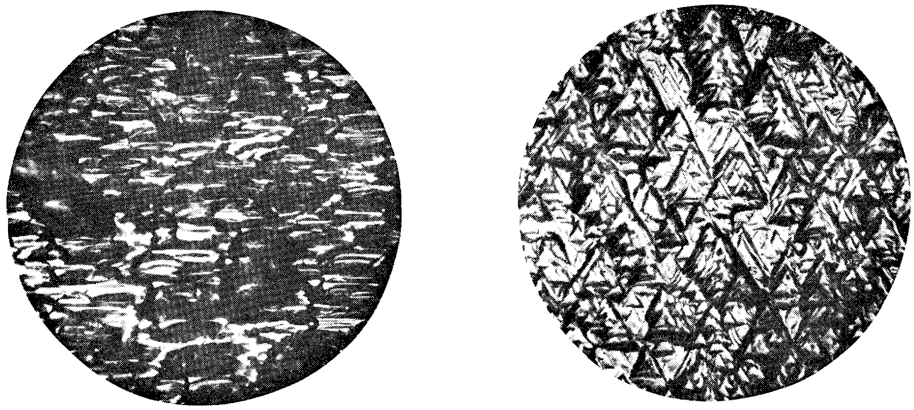
30 minutes. The {100} light figure did not appear at all.

Microstructures observed on the {110} and {111} surfaces etched with this solution for 5 minutes are shown in Photos. 5(a) and (b), respectively. The {111} surface structure (Photo. 5(b)) is composed of triangular etch pits quite the same as that observed by Wynne and Goldberg.(10)



(a) {110}, 5 min. (b) {111}, 5 min. (c) {110}, 7 min.

Fig. 8. Light figures of Ge crystal etched with $HNO_3 + H_2O + HF + AgNO_3$ (20cc + 40cc + 40cc + 2g).

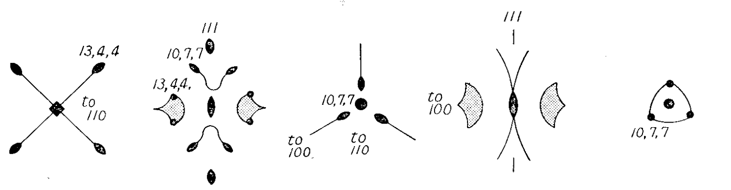


(a) {110} (b) {111}

Photo. 5. Microstructures of {110} and {111} crystal surfaces of Ge crystal etched with $HNO_3 + H_2O + HF + AgNO_3$ (20cc + 40cc + 40cc + 2g) for 5 min. (×270)

(4) Hydrofluoric acid plus hydroperoxide plus water (1:1:4) (No. 2 or superoxol solution)

Distinct light figures suitable to the determination of crystal orientations were produced by etching with this solution over 3 minutes. The {100} light figure is of a cross form in which the {100} light spot of a tiny square form is situated at the center and the {13, 4, 4} light spots locate at the ends of four arms (Fig. 9 (a)). The {110} light figure shows a complicated form which is composed of



(a) {100}, 3 min. (b) {110}, 3 min. (c) {111}, 3 min. (d) {110}, 17 min. (e) {111}, 17 min.

Fig. 9. Light figures of Ge crystal etched with $HF + H_2O_2 + H_2O$ (1 : 1 : 4)) (No. 2 solution).

{110}, {13, 4, 4}, {10, 7, 7}, and {111} light spots (Fig. 9(b)). In the {111} light

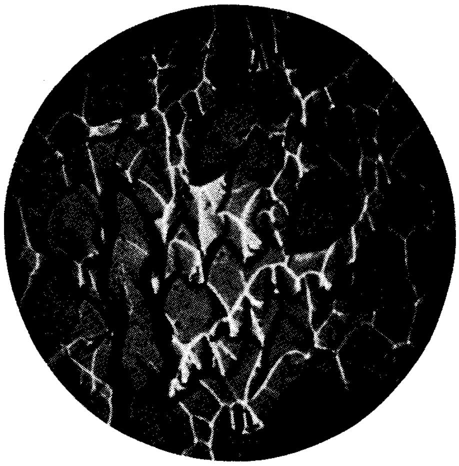
(10) R. H. Wynne and C. Goldberg, J. Metals, **5** (1953), 436.

figure, faint three arrows radiate from the {10, 7, 7} light spots which are situated around the {111} spot. (Fig. 9(c)). When the etching time was increased further, the {110} and {111} light figures changed into such forms as shown in Figs. 9(d) and (e), respectively, while the {100} light figure became somewhat indistinct.

Microstructures of the {100}, {110} and {111} surfaces etched with this reagent for a short time are very fine, but they became coarser as the etching time was increased. Surface structures observed after 25 minutes' etching are as shown in Photos. 6(a)～(c). The {100} surface (Photo. 6(a)) consists of etch pits of an

(a) {100}

(b) {110}



(c) {111}

Photo. 6. Microstructures of the principal crystal surfaces of Ge crystal etched with No. 2 reagent ($HF+H_2O_2+H_2O$ (1 : 1 : 4)) for 25min. (×270)

approximately square form, surrounded by curved facets, and the {111} surface (Photo. 6(c)) is covered by etch pits of a rounded and truncated triangular pyramid form, of which the flat bottom faces coincide with the {111} planes, while the structure of {110} surface (Photo. 6(b)) is rather complicated, and reveals more than three crystal faces.

(5a) 30 percent hydroperoxide (100°C) and (5b) 30 percent hydroperoxide plus acetic acid anhydride (3:1)

Distinct light figures suitable to the determination of crystal orientations were observed with the three principal crystal surfaces of Ge crystals etched for 1~1.5 minutes with 30 percent hydroperoxide heated to 100°C. The {100} figure (Fig. 10(a)) is of a cross form, in which the {100} spot is situated at the center and the {311} spots locate at the ends of four arms. These light spots are diffused over about 3°. The {110} light figure (Fig. 10(b)) is composed of the {110} spot, which is elongated linearly over about 3° in the direction pointing to the {111} poles, two {111} spots and four {311} spots. The {111} light figure (Fig. 10(c)) has the {111} spot, which is diffused over about 3°, and six arrows, of which three arrows radiating from the {111} spot towards the {311} poles are sharp and the alternative three arrows directing to the {110} poles are diffuse. When the etching was con-

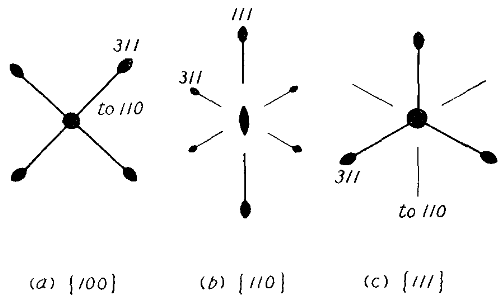
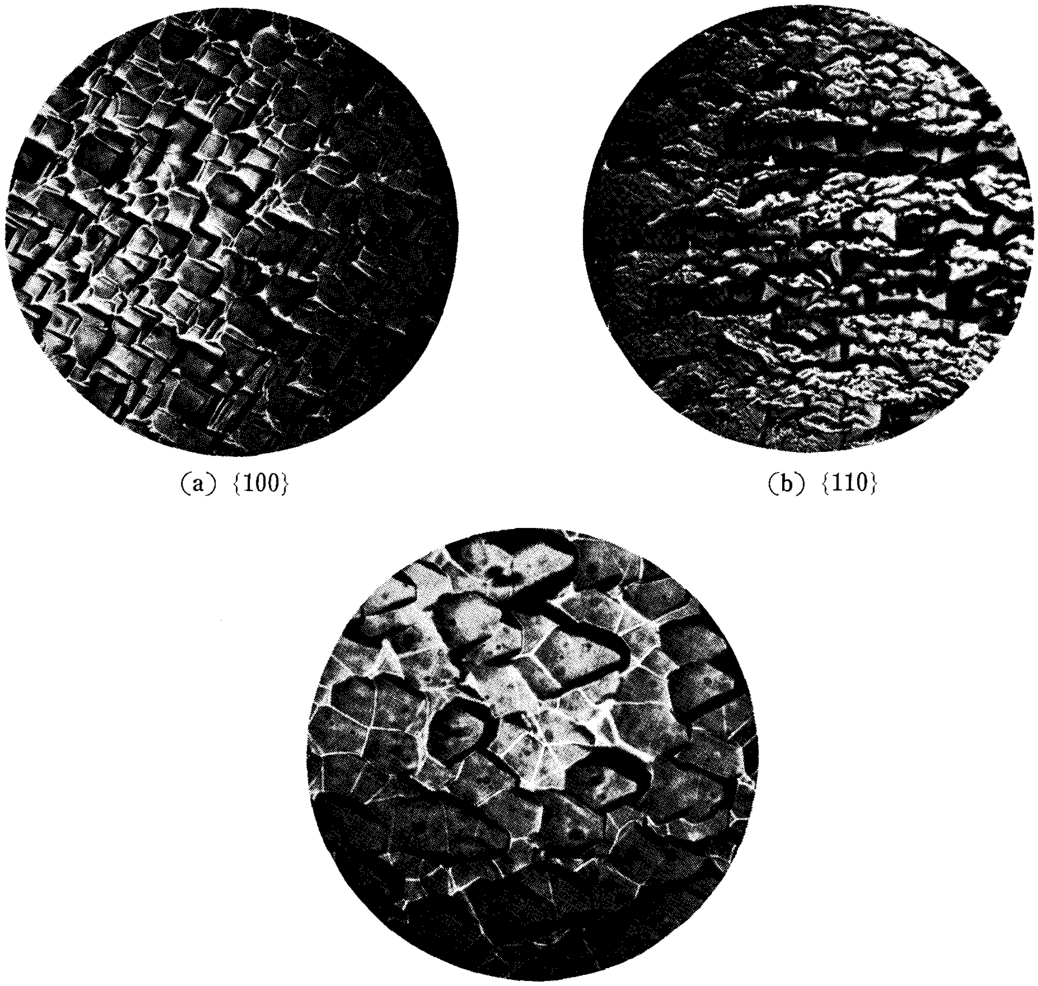


Fig 10. Light figures of Ge crystal etched with 30% H_2O_2 (100°C) for 1.5 min.



(a) {100} (b) {110}

(c) {111}

Photo. 7. Microstructures of the principal crystal surfaces of Ge crystal etched with 30%H_2O_2 (100°C) for 5 min. (×270) tinued further, the forms of the light figures as well as the crystallographic indices of the light spots remained the same, although the crystal surfaces became bright.

Microstructures of the three principal crystal surfaces etched with this solution for 5 minutes are as shown in Photos. 7(a)~(c). The {100} surface reveals etch pits of a square form, surrounded by curved facets, indicating that vicinal faces inclined slightly to the {100} plane are developed by etching (Photo. 7 (a)). The {110} surface contains etch pits of a hollow-trough form and of a stepped-hill form (Photo. 7 (b)). The bottom face of the hollow trough is bordered with curved lines, showing that vicinal faces inclined slightly to the {110} plane are developed by etching. While, the stepped-hill constitutes a peak with an angle of 120°, of which the stepped surfaces coincide with vicinal faces inclined slightly to the {311} plane. The {111} surface shows etch pits of pentagon and hexagon forms with curved boundaries (Photo. 7(c)),

The light figures and microstructures of the etched crystal surfaces observed in the case of etching with 30 percent hydroperoxide plus acetic acid anhydride (3:1) are the same as in the above-mentioned case of etching with 30 percent hydroperoxide heated to the 100°C, although it takes 2~2.5 hours for obtaining distinct light figures.

(6a) Aqua regia and (6b) aqua regia plus water (3:7)

In these cases, the crystal surface colored grey and an indistinct light figure or no light figure was observed.

(7a) Concentrated sulphuric acid, (7b) concentrated sulphuric acid plus water (3:7) (70°C), and (8a~h) saturated and 10% aqueous solutions of sodium hydroxide and potassium hydroxide (room temperature and 70°C)

In these cases, the crystal surface remained nearly the same as the initially polished state even after a prolonged etching.

Experimental results obtained are summarized in Table 1, in which the mark ◎ denotes a distinct light figure, suitable to the determination of crystal orientations, ○ a distinct but not so suitable light figure, and × an indistinct or no light figure. Distinct light figures suitable to the orientation determination are revealed by Ge crystal etched for a short time (less than several minutes) with (2c and e) concentrated nitric acid acid plus water (1:1 and 3:7)(70°C). With (3d, e, and f) concentrated nitric acid plus water plus hydrofluoric acid plus silver nitrate (45 cc+45 cc+10 cc+50 or 20 mg and 20 cc+40 cc+40 cc+2g) (Westinghouse Ag), with (4) hydrofluoric acid plus hydroperoxide plus water (1:1:4) (No. 2), or with (5a) 30 percent hydroperoxide (100°C). Among these etchants, the (2c) solution produces not so distinct light figures as other reagents do and has a disadvantage of the necessity of heating, while the (3d and e) and (4) solutions reveal the {100} and {111} light figures suitable to the orientation determination and the {110} light figures less suitable in view of their forms. In the case of the (5a) solution, distinct light figures suitable to the orientation determination are revealed by the three principal crystal planes, but the accuracy of orientation determination by these light figures is somewhat worse since the light spots located at the symmetric centres of these light figures are elongated over about 3°. Distinct light figures are also observed by etching with (2d) concentrated nitric acid plus (1:1) or with (5b) 30 percent hydroperoxide plus acetic acid anhydride (3:1), although a long etching time is required.

V. Crystal faces developed by etching

Crystal faces developed by etching in Ge crystal, as analysed from the forms of the light figures and the microstructures of etched crystal surfaces, are given in the last column of Table 1. In the cases of etching with hot dilute nitric acid and with concentrated nitric acid plus water plus hydrofluoric acid plus silver nitrate (45 cc + 45 cc + 10 cc + 50 or 20 mg), the developed crystal faces vary with an increase of the etching time and crystal faces of higher indices are likely to be developed by a prolonged etching time, while, in the cases of etching with other reagents, the indices of developed crystal faces remains always the same. It has been found that the developed crystal faces belong to the principal crystal zones except for {16, 9, 5}, {19, 11, 5} and {11, 7, 6} faces developed by etching with hot dilute nitric acid. The development of such high-index crystal faces not belonging to the principal crystal zones has not ever been observed.(1) It seems, however, that such crystal faces are not so stable, since their indices vary when the etching time is increased or the crystal specimen is re-etched with a fresh solution. Similarly to metal and Si crystals,(1) Ge crystal has a tendency that crystal faces of low indices are developed by a short-time etching and, when an etching is prolonged, high indexed crystal faces are developed newly or the low-index crystal faces change to high-index ones. It is to be noted that the temperature of nitric acid changes the numbers of developed crystal faces and its concentration influences upon the indices of the developed crystal faces.