JOURNAL OF THE PHYSICAL SOCIETY OF JAPAN VOL. 17, SUPPLEMENT B-II, 1962
PROCEEDINGS OF INTERNATIONAL CONFERENCE ON MAGNETISM AND CRYSTALLOGRAPHY, 1961, VOL. II

The Anomalous Diffraction Contrast on (111)-Face of Lamellar Single Micro-Crystal of Colloidal Gold

EIJI SUITO AND NATSU UYEDA
Institute for Chemical Research, Kyoto University
Takatsuki, Osaka, Japan

The anomalous network pattern highly contrasted by diffraction effect has been observed on flaky (111) habit surfaces of single micro-crystals of colloidal gold by the transmission electron microscope. The characteristic point of the pattern is the direction of the striation making up the boudary line of hexagonal domains of the network pattern. The striations run in parallel to $[11\bar{2}]$, $[1\bar{2}1]$ or $[\bar{2}11]$ axes, which are quite different from those striations appearing on the surface of single-crystalline thin film of f.c.c. lattice assuming (111) orientation caused by lattice defects included in another three kinds of $(\bar{1}11)$ planes. The dark field images of the same pattern show that the squamous pattern is also caused by diffraction effect owing to the microstructure of the crystal including various lattice defects, the origin of which seems to have a close relation to the growth mechanism of the crystal itself in the solution.

The single micro-crystal of gold, prepared colloid-chemically under a definite condition usually takes a flaky crystal habit, the shape of which assumes many varieties containing regular hexagon, regular trigon, intermediate form of the two, and so on. Recently, the anomalous net patterns highly contrasted by the diffraction effect happened to be found on large habit surfaces of the similar crystals of colloidal gold by a transmission electron microscope. One of the most characteristic points of the pattern is the direction of the contrasted striations which compose the whole squamous network patterns. It is the purpose of this report to present the detailed aspect of the patterns together with a possible interpretation which leads to a conclusion that the origin of the patterns has a close relation to the growth mechanism of the crystal itself.

Specimen. The crystals used as the specimen in the present work have been prepared colloid-chemically by the reduction of dilute aqueous solution of acidic auric chloride with a small amount of saturated aqueous solution of salicylic acid at room temperature. Having the trigonal symmetry when observed by a transmission microscope, the large habit surface on which the crystal itself lies is (111) plane of the face-centred cubic lattice of gold. As for the lattice orientation in the crystal itself, the zone axes of $(11\bar{2})$ group run in the direction perpendicular to some of the edge lines of the crystal perimeter. This means, in turn, that the edge of the perimeter runs in parallel to either direction of $[1\bar{1}0]$, $[10\bar{1}]$ or $[01\bar{1}]$ axis. The thickness of the crystal is usually about 100 Å on an average as has been determined by the analysis of subsidiary maxima of electron diffraction spots, whereas the width of crystal often exceeds a few microns or much larger values. These crystallographic features have been determined by the use of selected area electron diffraction method and reported in the previous papers.[1)]

The Squamous Diffraction Contrast. One of the most characteristic squamous patterns observed on the large habit surface of above-mentioned gold crystal is shown in Fig. 1 for an example. As is apparent by the photograph, the squamous patterns are made up of the contrasted networks as a whole, which include hexagonal domains. The sharp change of contrast from dark to bright takes place on both sides of the boundary lines of those domains everywhere, which mainly makes the networks itself to be conspicuous. At several places, a white line in the dark background (A in Fig. 1) and a dark line in the bright background (B in Fig. 1) can be very clearly seen. This means the existence of dislocation in the crystal. The size as well as the shape of each domain seems to be quite irregular, and in the exceptional case, many lines come close to one another side by side giving a feature just like a slip band as is seen at C in Fig. 1. In spite of those varieties in the aspect of the domains, one of the most remarkable things in the present case is that those boundary lines of the domains or contrasted striations meet one another at an angle of 120°, running in the direction parallel to [1$\bar{2}$1] axis or to the one of the same group as pointed out by the arrows. Then, in this case, they become perpendicular and are not in parallel to each edge line of the crystal perimeter as is also indicated in the figure.

It is a well-known fact that many kinds of lattice imperfections, such as stacking faults, extended dislocations and even slip bands, often have a way taking place on the four kinds of {111} planes, so-called Thomson's tetrahedron in the case of the simple metals having the face-centred cubic lattice. If those imperfections are included in three kinds of (11$\bar{1}$)-type planes of thin films assuming (111) orientation, they give rise to striations lying in the direction parallel to some of the crystal axes of [1$\bar{1}$0] group respectively, as has been pointed out by Pashley[2] when observed by the transmission electron microscope. The white dotted lines in the figure schematically indicate this situation. The actual examples of such striations have been reported by many investigators so far. In the present case, however, the situation is quite different from those diffraction contrasts caused by the lattice defects lying on the three kinds of (1$\bar{1}$1)-type planes and it seems very reasonable to take into account the lattice imperfections included in the three kinds of (1$\bar{1}$0)-type planes as will be explained later.

The dark field images have been obtained with another similar crystal. The strong

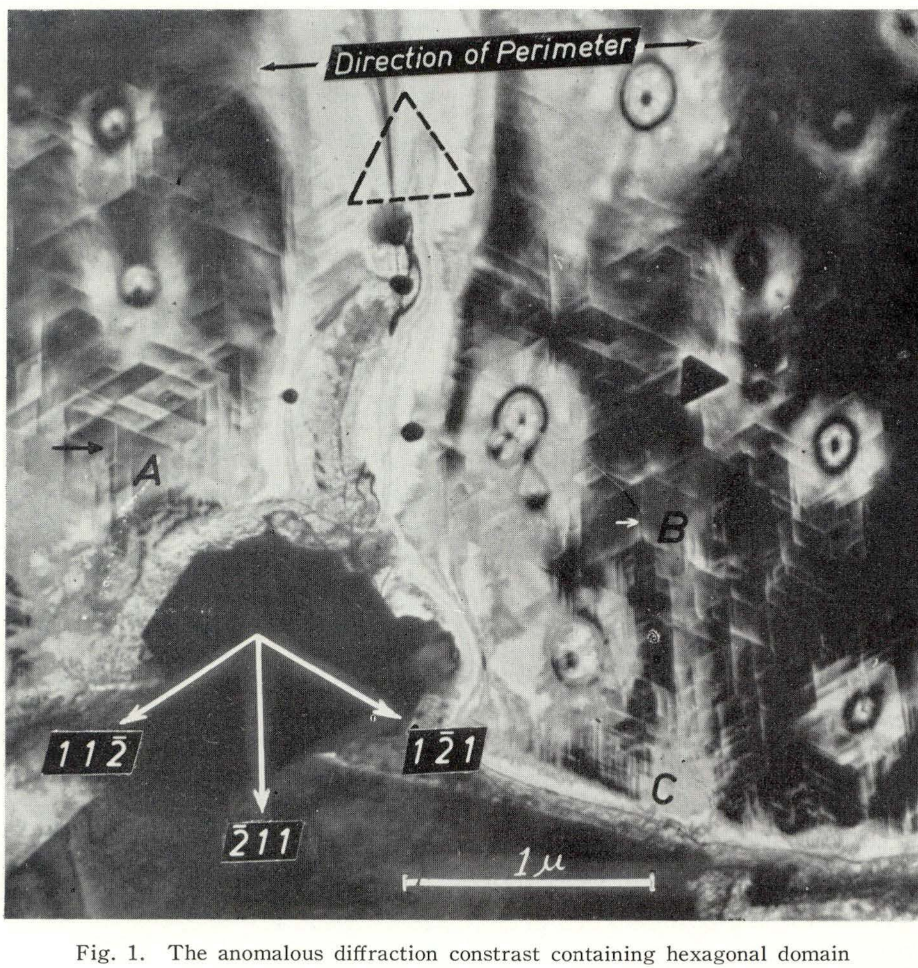

Fig. 1. The anomalous diffraction constrast containing hexagonal domain on (111)-face of single micro-crystal of colloidal gold.

diffraction spots used for the formation of dark field images mainly correspond to $(2\bar{2}0)$ reflections coming from the $(1\bar{1}0)$ planes which are perpendicular to the large habit surface of (111) plane. By the comparison of three dark field images formed by $(2\bar{2}0)$, $(\bar{2}02)$ and $(02\bar{2})$ reflections the lattice vectors of which meet one another at an angle of 120°, it has been revealed that some of the contrasted hexagonal domains simultaneously contribute to the three reflections while another domains give rise to only one reflection or two. This means that each domain contains much smaller micro-structure or considerable lattice strain and that those domains contain slightly tilt boundaries among themselves.

As for the contrasted boundaries of these domains, appears are very conspicuously in one dark field image as sharp bright lines which are parallel to the reflecting plane, while, in another dark field image, those boundaries which meet the lattice vector of the reflecting plane at the right angle are most conspicuous as the dark lines in the bright back ground. This means that these boundary lines are caused by the existence of some kind of dislocations lying on the $(1\bar{1}0)$ planes or the alike as has been pointed out by Hirsch, Howie and Whelan.[3] In any way, there will be no doubt that the squamous net patterns are caused by the diffraction effect owing to the micro-structure containing some kinds of lattice defects mainly lying on the boundary plane of each domain.

The Origin of the Domain Structure. The origin of the anomalous patterns having hexagonal network structure cannot be well explained without taking into account the growth mechanism of the crystal itself. It takes about one week or more for the crystal to be completely grown to the one which is enclosed by sharp perimeter in the solution at room temperature. At the intermediate stage of the growth process, however, the perimeter of each crystal takes no sharp straight line as that of the completed crystal but takes complicatedly indented ones which seem to be working as the actual growth front.[4] No matter how such indentation may be complicated, the perimeter is gradually inverted to a sharp straight line when the growth comes to an end. Usually, the size and the shape of the indentation are very irregular, but on very rare occasion, it takes the shape of hexagonal peninsulae as is shown in Fig. 2 (a) and schematically illustrated in (b). The side planes of each peninsula, which are considered to be perpendicular to (111) plane of the flaky habit surface, can be assigned with those indices, that is, $(1\bar{1}0)$, $(10\bar{1})$ and $(1\bar{1}0)$ as are indicated in the figure.

Fig. 3 schematically shows the series of growing process of these penisulae in the solution. When the growth front of each elementary peninsula independently expands at a definite rate as is shown in (b), confronting side planes of the two neighbouring penisulae will soon come close together and finally contact to each other as is shown in (c). In most cases the lattice may

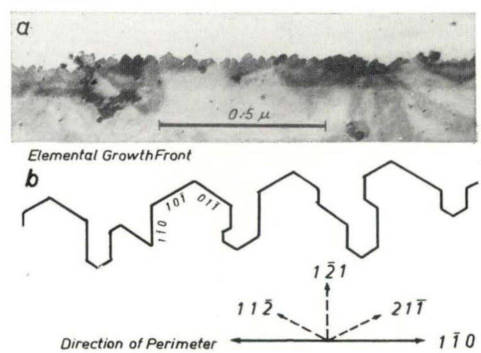

Fig. 2. The indented perimeter of growing crystal of colloidal gold, which shows the hexagonal micro-growth front.

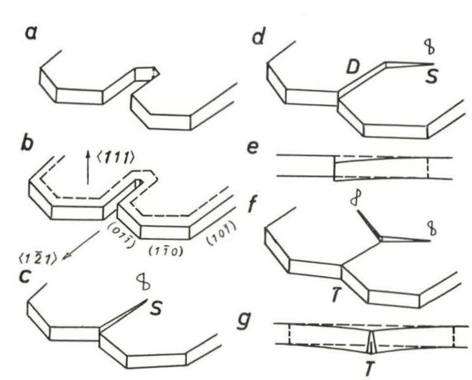

Fig. 3. The schematic illustration of the origin of hexagonal micro-structure in the single crystal lamella of colloidal gold.

be well fitted to each other without any discrepancies. But some unexpected origins, such as the adsorption of some impurities, diffusion of reaction products and so on, give rise to the misorientation of each lattice at the contacting planes as has been pointed out by Fisher, Fullman and Sears.[5] Fig. 3 (c) is an example of such misfit resulting in the appearance of a screw dislocation, the Burgers vector of which is normal to (111) plane. The combination of various kinds of contacting manners of the growth gives rise to various kinds of lattice misfits respectively, some of which are shown in (d) and (f) for the example. In the case of (d), the screw dislocation is included at S, and a discrepancy takes place at D just in a manner of a slip plane, the lateral view of which is shown in (e). When two screw dislocations of opposite signs are included at the side edges of a peninsula just as is shown in (f), the contacting plane becomes a tilt boundary including some extra planes which are perpendicular to the (111) plane as is shown in the lateral view (g). In this case, the edge dislocations the Burgers vector of which is contained in (111) plane, run in parallel to $[11\bar{2}]$ axis which is normal to the final direction of a completed perimeter. It is very clear from the figure that these dislocations and discrepancies are always parallel to $[11\bar{2}]$, $[1\bar{2}1]$ or $[\bar{2}11]$ direction, which is just the same as that of the boundary line of the contrasted domain mentioned above, and it seems to be very reasonable to consider that the origin of the squamous network pattern is caused by the diffraction effect at the various kinds of lattice defects coming from the micro-structures which have been included in the crystal at the intermediate stage of the growing process in the solution.

When the crystal having squamous diffraction contrast is suffered from heavy electron bombardment, the diffraction contrast once disappears, and new striations take the places of the former ones. The direction of the new striations is parallel to $[1\bar{1}0]$, $[10\bar{1}]$ or $[01\bar{1}]$, quite in the ordinary manner as the case of the lattice defects included in the three kinds of $(1\bar{1}1)$-type planes of Thomson's tetrahedron. Much heavier electron bombardment destroys the crystal, and local spontaneous evaporation of the material takes place in the crystal finally leaving the zig-zag edge line the direction of which is parallel to the new striations. Owing to the above-mentioned growth mechanism, many vacancies can be included in the crystal, which are accumulated on $(11\bar{1})$, $(1\bar{1}1)$ and $(\bar{1}11)$ planes and give rise to the latter striation as well as the spontaneous evaporation when exposed to heavy electron bombardment.

References

1 E. Suito and N. Uyeda: Proc. Japan Acad. **29** (1953) 324, 331. *Proc. Internat. Conf. E. M. London* (1954) 224.
2 D. W. Pashley: Phil. Mag. **4** (1959) 316.
3 P. B. Hirsch, A. Howie and M. J. Whelan: Phil. Trans. Roy. Soc. London **A252** (1960) 499.
4 E. Suito and N. Uyeda: Proc. Japan Acad. **37** (1961) 388.
5 J. C. Fisher, R. L. Fullman and G. W. Sears: Acta Metal. **2** (1954) 344.