Section 2.

Crystal Growth in Electrodeposits.

The structure-sensitive character of crystal growth was first pointed out by Frank (1949) who introduced the concept of dislocations to explain the growth under conditions of low supersaturations. Earlier to this, crystal growth was attributed to fresh and continuous nucleation of layers on the growing faces. The kinetics of nucleation are comparatively complicated. The influence of factors such as temperature, supersaturation, evaporation and activation energies of atoms or molecules of the growing crystals and their diffusion coefficients and others, on crystal growth have been discussed in detail in Faraday Society symposium on crystal growth (vol.5, 19-9). However, it was found that these theories were inadequate to explain the growth rates under low supersaturation.
Frank's theory is based on the fact that crystals are not perfect, but contain dislocations. Dislocations that take part in crystal growth are screw type. Such dislocations emerging on a crystal face provide it with a step. It was argued that for the growth of such faces nucleation is not essential. The adsorbed atoms or molecules would diffuse to the steps and would be absorbed at those sites. It was further shown that, when angular velocity for all points of the step become constant, the growth assumes a spiral form. The spacing between the turns of such a steady state spiral would be proportional to the diameter of the critical nucleus for the growth on a perfect crystal, which is inversely proportional to supersaturation. Later the theory was further extended to include various other types of spirals which could arise due to cooperation among dislocations.

Spirals, in accordance with Frank's theory, were observed on many crystals such as beryl (Griffen, 1950), SiC (Verma, 1951), CH₂ (Forty, 1952) and long chain fatty acid crystals (Verma & Reynolds, 1953). Direct observations
of screw dislocations were also made on f.c.c. Au (Amelinckx, 1963), and Ag (Frank & Forty, 1959) and c.p.h. Mg and Ca crystals (Forty, 1959). Benschke (1958) reported the occurrence of crystal growth on cathodically sputtered Au films by pairs of double spirals following Frank-Read mechanism. Spirals have also been recorded in experiments of etching of crystals.

Vermilyea (1956) who extended Frank's theory to electrolytic crystal growth, showed that in this case nucleation does not occur till a critical overvoltage is reached. The overvoltage is found to vary with the surface energies of the growing crystals. Lower critical overvoltages are recorded on surfaces with steps. Applying similar arguments as those of Frank for kink density in the steps and mean free path of adsorbed atoms, he showed that spirals would appear on the crystal faces on which screw dislocations emerge.

However, not much work has been reported regarding the crystal growth in electrodeposits. Steinberg (1959) recorded some related spirals on titanium crystals grown
by electrolysis. The step heights for these spirals were of the order of a few hundred angstroms. This section is devoted to the studies of growth features of electrolytically produced silver crystals.

Experimental.

The silver crystals were grown electrolytically using AgI·O₃ solution as electrolyte between silver electrodes at room temperature conditions (30°C). The current density was controlled by a resistance in the circuit and a potential gradient of half volt was applied across the electrodes. Thin crystals in the form of flat dendrites were deposited at the cathode. It was noticed that the current density fell off in the later stages of the experiments from 7 mA to a negligible value and growth ceased.

The crystals were examined under high resolution microscopy and using multiple beam interferometry.
Fig. 6. ELECTROLYTICALLY GROWN SILVER DENDRITES, x 55
Usually fresh crystals revealed poor visibility for spirals and like features. Partly, it was due to uniform reflectivity of the crystals. It was found that if the crystals were exposed to air, after some time spirals became more distinct. Since crystals appeared in the form of thin dendrites of small dimensions, i.e., a few mm in length and about 0.5 mm in width, optical flats could not be used for interferometric examination. A thin layer of Canada balsam was therefore evaporated on the crystal face to be examined and later silvered to provide two faces for interferometry. To obtain good contrast fringes, the Canada balsam layer had to be kept fairly thin.

**Results & Discussions.**

**Growth Characteristics of Electrodeposited Silver.**

Fig. 6 (X5) is a typical micrograph of the crystals grown by electrodeposition at the cathode. On microscopic examination the dendrites were found to consist of regular
crystallites as seen in the figure. The branched dendrites are characteristic of nonequilibrium condition of electrolyte during growth. Such condition during growth by electrolysis is not uncommon as it is influenced by factors such as current density, overvoltage, ionic supersaturation, nature of ions and electrolytes and others. These factors could not be critically controlled in these experiments. It is known that common fibres in electrodeposits of silver contain (100)+(111), (111) and (110) orientations characteristic of f.c.c. silver lattice.†

The simple texture revealed in fig. 6 seems to be characteristic of such orientations.

Interferometric examination of the crystallites showed them to be plane within atomic thickness. Such surfaces would be formed if fresh nucleation does not occur, or condition of comparatively low supersaturation exist near the crystal face. With increased saturation under inhomogeneous conditions random nucleation would take place. In such cases, growth features such as 'growth pyramids' would appear.

† These orientations could not be verified as facilities for X-ray work were not available.
Fig. 7. x55

Fig. 8. x55

POLYGONAL GROWTH PYRAMIDS
Fig. 9. *X55*

**Fringe Contour of Growth Pyramids.**
Figs. 7 and 8 (V55) reveal some growth pyramids recorded on the silver dendrites. Mostly they exhibit triangular and polyhedral shapes and appear as overgrowth features on low index planes. Figs. 7 & 8 further show that the pyramids have a stepped character. The topography of such a growth pyramid has been beautifully brought out in the interferogram (Fig. 9 (V55)). The points of interest regarding the fringes are their smooth continuity, contours, and sharp shifts. Smooth fringes characterise the flatness of the faces within atomic thickness, and shifts record sharp changes on the surfaces. The fringes in fig. 9 as they cross the steps of the pyramids reveal breaks of varying magnitudes. The evaluated step height for these was found to vary from 300Å to 910Å. In some cases pyramids with flat tops were also observed as shown in fig. 10 (V55).

The appearance of growth pyramids is to be attributed to the vicinal faces formed during the growth and to the tendency of high index planes to convert themselves into low index planes, which gives rise to steps. This is in accordance with the minimum energy concept.
Polyhedral character of most crystals also requires that crystals should grow by successive layers. Kossel, Stranski, Volmer and others have shown that energy yield when an ion is added to an incomplete layer is greater than that for initiating a new layer. Hence a layer once started has a natural tendency to complete itself. This feature was amply revealed during the examination of crystallites during $\text{Ag}^+$ growth. Usually, layers were found spreading out from corners and edges of the crystals. Thin layers with irregular contours were found spreading from the centres of crystallites in some cases. Reversal of direction of growth, on reversing the current in the circuit, showed that initially the layers consisted of $\text{Ag}^+$ ions. The ions lost their charge before being absorbed at the cathode. In a large number of cases, it was observed that growth started simultaneously from a number of nuclei on the same face. The layers initially were too thin to be seen in reflected light. They became visible with increased thickness. Similar features have been recorded by Dunn and Emett (1949) in case of ionic crystals.
The conditions of growth for crystals produced by electroddeposition and for those grown from solution seem to be similar except for the fact that cathodic charge can, to some extent, influence the absorption of ions and growth of crystals. Initiation of layers from corners and edges can, however, be satisfactorily explained to the excess concentration of the solute at those sites. Berg (1939) attributed the growth from the centre of crystal faces to the arrival of more solute at the centre and the tendency of surfaces to stay flat. The cooperation among layers starting from different nuclei on the same face shows that this explanation is faulty. Frank (1949) attributed such growth to dislocations. With dislocation lines being effectively under tension surfaces exhibit a tendency to grow normally to the dislocation lines. Layers starting from nuclei with same line tensions for dislocations would exhibit strong cooperation.

Formation of thick layers is another interesting feature recorded in these experiments. A typical
Fig. 11. THICK LAYERS (INTERFEROGRAM), X110.
interferogram of these layers is shown in Fig. 11(VI10). The layers are recorded by shifts in the smooth continuity of the fringes. Typical figures for steps are 180, 270, 450, and 630Å. Even higher values were recorded in some cases. The formation of thick layers from thin ones is part of crystal morphology. Thin layers are characterised by high index faces and faster rate of movement. The bounding faces for crystals should be low index faces with minimum surface energy. Higher index faces characterised with faster rate of movement, therefore, eliminate themselves during growth. The elimination is accomplished by a process of breaking up of layers into steps. This also reduces the surface energy of the face.

Screw dislocations \& circular spirals on electrolytic silver

Another important reason for the roughness of surfaces was given by Burton, Cabrera and Frank (1949). It was shown that close packed planes remain smooth within atomic thickness below a critical temperature which is as
high as the melting point in case of metals in contact with their vapours. For metals in contact with solutions the critical temperature is lowered, because the increased energy accompanying a transition from smooth to a rough surface is partly compensated by the hydration of the adsorbed atoms. The roughness may also be partly due to the presence of screw dislocation steps. Normally, these steps contain a large number of kinks where the atoms or ions are absorbed during growth.

The nature of growth resulting from the deposition of atoms or ions depends upon the $X_s$, mean free path of the adsorbed ions and $X_s$, the mean distance between the kinks of the steps. The mean free path of an ion is given by

$$X_s = \left( D_s \tau_s \right)^{1/2}.$$  \hspace{1cm} (2.1)

where $D_s$ is the surface diffusion coefficient, and $\tau_s$ is the mean lifetime for an adsorbed atom or ion. For metals in contact with their vapours activation energy is small as compared to the evaporation energy and
therefore $X_s$ is quite large. The value of $X_s$ is considerably altered in electrolytic crystal growth as the supersaturation for metals in contact with the solution is changed. $X_s$ however, remains constant.

Following Frank's concept Vermilyea (1956) showed that in electrolytic crystal growth spirals are formed with an overvoltage dependent spacing for $X_s > X_o$ provided $i \gg i_o$. In case $i << i_o$, steps of the screw dislocations remain straight. He also calculated the ratio of $X_s/X_o$ in case of silver from energy considerations which came out to be 1/70. According to the theory spiral growth would not be possible in such cases.

That $X_s/X_o$ is a widely varying factor in electrolysis is shown by the appearance of a large number of spirals on crystal faces in these investigations. Though exact physical conditions of the electrolyte could not be determined, supersaturation could easily be achieved by

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† $i_o$ is exchange current and is defined as the anodic or cathodic current when overvoltage is zero.
Fig. 12. RIGHT-HANDED CIRCULAR SPIRAL, X450.

Fig. 13. LEFT-HANDED CIRCULAR SPIRAL, X450.
controlling the current density. The arrival of Ag⁺ ions on the crystal faces could be lowered by decreasing the current density and conditions analogous to low supersaturation could be created. Of various types commonly observed circular spirals are the simplest. Figs. 12 and 13 (×450) are two typical micrographs of right and left handed spirals of three loops. Such spirals are usually seen in case crystal faces be free of over-growth features and be provided with dislocation steps. The steps of spirals are highly irregular due to unhomogeneous conditions of growth. Since both the spirals shown here developed in the close vicinity of the crystal boundary, it seems more loops could not be formed.

According to the theory, for circular spirals mean distance (Xₐ) between the kinks should be much smaller than the mean free path (Xₐ) of the adsorbed ions. The discharged ions in that case have a greater probability of being absorbed on the steps irrespective of orientations. The rate of advance for steps is also independent of crystallographic orientation and rounded spiral would
results. For a steady-state spiral, the spacing between successive arms of the spiral remains constant, and is given by the expression,

$$\delta r = 4\pi \cdot \rho_c$$  \hspace{1cm} (2.1)

where $\rho_c$ is the radius of critical nucleation. The values of $\rho_c$ for spirals shown in Figs. 12 & 13 were found to be $7 \times 10^{-6}$ cm and $4 \times 10^{-6}$ cm. Since spirals are formed only when $\rho_c$ equals the length of the dislocation step, these values would give an idea regarding the latter. Similar circular spirals have also been recorded by Shide and Nafie (1958) in case of silver.

**Polygonal spirals**

However, comparatively larger number of spirals recorded here on the basal planes exhibited polygonal geometry. The growth of such spirals is due to the dependence of the rate of advance of a growth front upon its orientation. The growth of steps parallel to the close packed direction is orientation sensitive. This is
Triangula spirals

Fig. 14  X 110

Fig. 15  X 110
TRIANGULAR SPIRALS
Hexagonal growth markings.

Fig. 16. X 110

Fig. 17. X 110
Fig. 18. POLYGONAL MARKINGS. X 110
because the kink energy for such directions is high, and steps have lower kink density, i.e. $x_s \ll x_0$.

Vermilyea (1956) showed from current voltage relationship that straight steps would be formed in electrolytic growth if $x_s > x_0$ and $\lambda \ll \lambda_i$. But as geometrical pattern can not be bounded on all sides by same directions, the steps would not be straight on all sides.

A number of spirals of triangular and hexagonal geometry were recorded on silver dendrites in this case. Figs. 14 to 18 are some typical examples. Figs. 14 & 15 (X110) are triangular growth patterns with multiple loops. Another spiral [Fig. 16 (X110)] with straight steps and originating as a triangular pattern is later found to grow in a hexagonal pattern. Fig. 17 (X110) shows a complicated growth probably due to cooperation among some independent sources. A concentration of some polygonal spiral markings is revealed in Fig. 18 (X110).

A circular spiral resulting from a single dislocation creates fast moving circular layers. Similarly, polygonal spirals advance radially. The advance of growth fronts has
Fig. 19. Spiral Obstructed by a Faulted Zone, x 110

Fig. 20. Nonintersecting Spirals, x 55
been considered similar to the production of waves from a source. Waves bend round the corners of an obstruction. Similarly, layers initiated from a dislocation would bend round corners. This is shown in fig. 19 (X110), layers being obstructed by a faulted zone.

**Nonintersecting & close loop spirals**

The case of nonintersecting double spirals rarely observed in crystals is comparatively more interesting. These have been recorded only in case of SiC (Verma, 1951) and a few organic crystals. Some beautiful spirals of this type which were rendered visible by decoration technique were photographed during these studies. Fig. 20 (X56) reveals such a growth pattern. The spiral marked A is a double spiral, whereas that at B exhibits more than two independent ledges.

Theoretically, such spirals originate due to cooperation among two or more dislocations of same sign. In case dislocation distance is less than \( 2 \pi \rho_c \).
Fig. 21. CLOSE-LOOP SPIRAL. X110
nonintersecting spirals with exactly parallel ledges are produced. That the spirals are independent of each other is clearly shown in the micrograph 20. In case the dislocation separation is greater than $2\lambda$, the ledges would intersect.

The cooperation among the growth fronts emanating from screw dislocations of opposite signs gave rise to close loop spirals. Dislocations of opposite signs emerging on the same crystal face are joined by a ledge between them. In case the diameter of the critical nucleus $2\rho$ under proper saturation is less than the length of the ledge, growth would be initiated. As long as saturation remains constant at this value, growth of the spirals continues uninterrupted. In these cases, spirals from two sources join up to form close loops. The growth of such layers is similar to the operation of Frank-Read source shown earlier in fig. 4 in section 1. Fig. 21 (Y10) represents a typical micrograph of large number of close loops recorded in these studies. The growth appears in the form of a flat pyramid with layers topping one over the other.
Fig. 22. SAME AS Fig. 21. (INTERFEROGRAM)
X 110
Large step heights & Dislocation strength

The points of interest with regard to dislocations that gave rise to spirals are their strength and densities. The strength of screw dislocation is easily determined from the step height, which according to theory for a simple spiral would equal the Burgers vector of the dislocation. In case of double spirals, the step height usually is the sum of the Burgers vectors of cooperating dislocations. The step heights for the spirals observed in these investigations were found to vary and were of the order of a few hundred angstroms. Fig. 22 (X110) shows an interferogram taken on the close loop spiral shown in fig. 21. The interference being obtained by thin layer technique, fringe resolution is poor. The step height was found to be equal to 70 ± 135 A. Spirals with such large step heights are known to occur in crystals grown from solution. Steinberg (1950) recorded a step height of 240 ± 100 A for spirals in case of titanium crystals grown by electrolysis.
Fig. 23. Spiral Growth Following Lang's Concept.
The origin of large step spirals is still not fully explained. The earlier workers assumed that such spirals are due to dislocations of multiple strength. Cabrera (1953) also showed on stacking fault considerations that large steps are possible. However, Long (1967) has recently suggested that such spirals did not necessarily imply the existence of large dislocations. They may be formed by the 'bunching' of monolayers during growth. Melinckx et al (1957) also showed that spirals with large steps appear during the etching of the crystals containing helical dislocations. These result from bunching of layers. According to Long, spiral growth could occur even in absence of dislocations provided growing face had slight curvature. The growth proceeds along concentric circles. The presence of 'mistakes' in the early stages of the growth would --- lead to asymmetric growth and bunching of steps. The process is supposed to give rise to spirals with large steps as shown in fig. 23. A critical study, however, shows that nonintersecting double spirals and close loop spirals as shown in figs. 20 and 21, would not possibly follow this mechanism.
Fig. 24. An asymmetric growth pattern, X 110
In case of random and asymmetric growth, the ledges of the spirals would intersect each other. That it is possible is shown in fig.24 (Y110). Layers starting from two independent sources interfere with each other in a very irregular way, which shows that Lang's concept cannot be applied faithfully to explain nonintersecting spirals. However, it is probable that this mechanism may give rise to some simple spirals as seen in earlier figs.12,13.

**Spiral density on silver crystals (electrodeposits)**

Other interesting aspects of spirals are their distribution and dislocation densities. The density for dislocations usually quoted for metal crystals is of the order of $10^8$ /cm$^2$ as shown by x-ray studies. However, the dislocation density revealed by spirals is always found to be much less than this value. Forty and Frank (1953) have observed only one or two dislocations emerging on 0.1 mm square on the cubic face of Ag crystals grown from vapour. This difference between the two values was
attributed to the perfection of the crystal faces. Screw dislocation densities as high as $10^5$ /cm$^2$ have been reported in case of SiC (Verma, 1953). The spirals discussed in this section did not reveal any definite correlation with dislocation. The concentration of spirals on the crystals was found to vary from one dislocation to five dislocations per mm square.

Such low values for the number of spirals can only be attributed to unhomogeneous conditions of electrolyte during growth. In case low supersaturation conditions did not exist throughout, many of the probable spirals would either not grow or would be suppressed. Another important point in this connection is the suggestion given by Vermilyea regarding electrolytic current. He showed that in case exchange current exceeds the electrolytic current, spirals would not grow even if supersaturation ratio remains in order. In this case, steps remain straight. Since in the final stages of experiments, the current fell to negligible values, possibility for such a behaviour is fairly strong.
SUMMARY

The growth features of silver crystals grown by electrolysis have been investigated. Silver crystals were grown by electrodeposition using aqueous AgNO₃ solution as electrolyte between silver electrodes at room temperature conditions (about 30°C). The current density of about 0.1 amp. was controlled by a resistance in series of the circuit, and a potential gradient of half volt was applied across the electrodes. Thin silver crystals were deposited at the cathode in the form of branched dendrites which exhibited rectangular, and triangular facets, characteristic of (100), (111), (111), and (110) orientations common in the electrodeposits of silver. The crystal faces revealed various growth features such as stepped growth pyramids, and large step circular and polygonal spirals. Nonintersecting double spirals and close loops following Frank-Read mechanism were also found. The quantitative measurements for the growth features were made using multiple beam interferometry.
The step heights of spirals were found to be of the order of a few hundred angstroms.

The stepped character of growth features is attributed to the vicinal faces formed during growth, and due to the tendency of high index faces to convert themselves into low index faces. It is in accordance with crystal morphology and minimum energy concept. The spirals are supposed to arise from dislocations of multiple strengths.

Recently Long (1967) suggested that large step heights for spirals did not necessarily imply the existence of large Burgers' vectors. Such spirals may also be formed by the 'bunching' of monolayers during growth. According to this concept, spiral growth would occur even in the absence of screw dislocations, provided the growing faces had slight curvature. The growth proceeds along concentric circles. The presence of 'mistakes' in the early stages of the growth leads to an asymmetric growth and bunching of steps. The process is supposed to give rise to spirals.

A critical study, however, showed that nonintersecting double
spirals and close loops would not possibly follow this mechanism. In case of random and asymmetric growth, the ledges were found to interfere with each other in a very irregular way, showing that Long's concept could not be applied faithfully to explain such spirals.
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