KINETICS OF GROWTH AND STRUCTURE OF THIN FILMS OF TIN ON AN AMORPHOUS CARBON SUBSTRATE

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Abstract

The growth kinetics and the structure of evaporated thin films of tin on an amorphous film of carbon have been studied quantitatively with the electron microscope. The results show that after nucleation of the film three stages of development can be distinguished: (1) the archipelago stage showing a structure of islands, growing approximately linearly with time; (2) the labyrinth stage showing a structure of connected islands with canals separating them, the width of the canals decreasing exponentially with time; (3) the closing stage in which the canals are closed very rapidly. The electron micrographs show that the structure of the film cannot be explained in terms of interfacial energies alone. The analysis of growth kinetics of the first two stages reveals that in these stages the lateral growth is determined by transport of atoms along the substrate. In the closing stage the canals are of strikingly uniform width. To explain the rapid closing of the canals a sintering process is proposed. It has been found that remnants of the canals are present below the surface of the continuous film and that secondary nuclei are still existent in the closed canals.

1. Introduction

It is well known that the properties of thin films are in many respects strongly different from those of the bulk material. It is generally agreed that these differences are due to a characteristic structure of the film.

To understand the properties of thin films, a detailed knowledge of their structure is of great advantage. Therefore it is not surprising that many investigations have been done on the growth and structure of these films. Only relatively few of them, however, deal with the kinetics of growth between nucleation and the closing of the film.

In this growth process several stages can be distinguished:
(a) the archipelago stage in which the film appears as a collection of widely separated islands;
(b) the labyrinth stage in which a structure of connected islands is found with a labyrinth of canals separating them;
(c) the closing stage in which an extremely rapid closing of the canals occurs.

These stages have already been described in literature \(^1\) and their existence has been demonstrated very nicely by Pashley using a cinematographic technique. As far as the author is aware a quantitative experimental study of the growth process never has been made.
The purpose of this paper is to obtain information on the structure of the film from a quantitative study of the growth kinetics before the formation of a continuous film. For practical reasons tin is taken as the film material. To obtain a film that can be stripped and brought into the electron microscope an amorphous substrate (carbon) is used.

2. Description of the experimental results

2.1. Topography of the film

Tin films have been deposited on a carbon substrate, using exposures ranging from 2 to 30 s. The experimental details of preparation of the films and of the electron microscopy are given in appendix I. The interpretation of the electron micrographs is discussed in appendix II.

Films being deposited during 2 and 4 s did not show any visible structure in the electron microscope. After 5 s the first visible pattern appears, having an archipelago structure as shown in fig. 1. On this picture nuclei with sizes ranging from 15 Å to 100 Å diameter are observed. The lower limit is due to the lack of contrast of the smaller nuclei as will be explained in appendix II.

Characteristic pictures of the later stages are shown in figs 2, 3, 4 and 5. Figure 2 shows the film after 7 s. In this picture the differences in transmission of large and small nuclei are clearly visible.

The situation after 10 s is shown in fig. 3. The archipelago structure has

Fig. 1. Electron micrograph of tin film after 5 s exposure. The circle indicates the size of nucleus after 7 s exposure.
changed into a labyrinth structure. In this picture the following details can be observed.
(a) The canals are of strikingly uniform width.
(b) In the canals small nuclei are found.
(c) The original round nuclei have been combined into larger agglomerates

Fig. 2. Electron micrograph of tin film after 7 s exposure.

Fig. 3. Electron micrograph of tin film after 10 s exposure. The arrows indicate faded parts of the contours.
Fig. 4. Electron micrograph of tin film after 20 s exposure showing the grain boundaries and the uniform width of the canals just before closing. At the bottom of the canals small secondary nuclei are visible.

Fig. 5. Electron micrograph of tin film after 30 s exposure. The canals are just closed.

(the boundaries of the original grains are not visible on this picture, due to printing technique, but they are shown very nicely in fig. 4).

(d) Parts of large islands close to remnants of the original “ocean” appear to be slightly faded. This observation leads to a conclusion about the contact angle. If the shape of a nucleus were controlled by the equilibrium contact
angle this angle should be constant along the contour of a nucleus. The contact angle determines contrast. According to Fig. 3 contrast changes continuously along the contour. This shows that the contact angle is not constant. This will be discussed in detail in sec. 3.1.

A picture of the film after 20 s, that is, just before the closing of the canals, is shown in Fig. 4. The nuclei at the bottom of the canals and the boundaries of the original nuclei are clearly visible. The uniform width of the canals is even more pronounced than in Fig. 3.

The structure of the film after 30 s is shown in Fig. 5. The film is just closed. X-ray investigation of the film in this stage shows a texture with a preference for the tetragonal axis being parallel to the surface. Inspection of a large number of pictures of the structure just before closing shows that a canal always ends with only one type of grain boundary configuration shown in Fig. 12.

![Graph showing average diameter 2r of the nuclei as a function of exposure time t.](image)

Fig. 6. Average diameter $2r$ of the nuclei in a tin film as a function of exposure time $t$. The part after 10 s is not defined very exactly but serves to show that growth has become very slow.

A large number of pictures was prepared to study the growth kinetics. In Fig. 6 twice the average lateral radius $\bar{r}$ of the “large” nuclei is plotted as a function of time $t$. After an incubation time of $4.8$ s a rapid growth, approximately linear with time is observed. For the archipelago state $\bar{r}(t)$ can be represented by the empirical formula

$$\bar{r}(t) = 204 \left(t - 4.8\right) - 21.2 \left(t - 4.8\right)^2 \text{ Å.} \quad (1)$$

In the labyrinth stage the definition of the radius of a nucleus is less distinct. For the plot of Fig. 6 it has been measured from a fictitious centre of the nucleus; therefore the part of this plot beyond 10 s admits a qualitative interpretation only. Nevertheless it clearly shows the strong decrease of growth velocity in this stage.
The average width $b$ of the canals has also been determined as a function of time. The logarithm of the canal width has been plotted as a function of time in fig. 7. This function can be represented by

$$\log b (\text{Å}) = \log 3100 - 0.070 t. \quad (2)$$

Fig. 7. Average width $b$ of the canals in a tin film as a function of time (vertical scale is logarithmic).

2.2. Aggregation state and texture of the film

Electron and X-ray-diffraction patterns of the film after deposition have been made at several stages. It has been found that under the experimental conditions as described in appendix I the film is solid in all stages. The tetragonal axis of the nuclei shows a preference for being parallel to the substrate. The 5-s and 7-s nuclei are single crystals. This does not imply that the nuclei are solid during the deposition process. In fig. 4 the grain boundaries originating from the contacts of nuclei shown in fig. 2 are clearly visible. Apparently these nuclei are solid when they grow together. If they were liquid there could not be a boundary. Therefore nuclei of more than 700 Å diameter are certainly solid during their formation. For the smaller sizes such a strong evidence is not available. The fairly rare observation in fig. 1 that nuclei of 160 Å diameter may be found in contact with much larger ones is perhaps an indication in favour of the conclusion that even these small nuclei are solid.

3. Discussion of the results

3.1. General

At first sight interfacial energies and their consequences like contact angles must play an important role in all discussions on thin films. A beautiful example of the importance of interfacial energy in the formation of thin films of gold and silver is given by Pasbey et al. 2). In the case of tin, however, the situation appears to be quite different. If interfacial energies were the only factors determining the shape of the nuclei then it is to be expected that the shape as well as the contact angle will be constant during the growth process. The micrographs shown in figs 3, 8 and 9 demonstrate this not to be the case. The changing contrast along the contour of the nuclei shown
Fig. 8. Electron micrograph showing the contact angle in the archipelago stage.

Fig. 9. Electron micrograph showing the contact angle in the labyrinth stage.

in fig. 3 shows that the contact angle is not constant. Moreover, fig. 8 shows a contact angle quite unexpected for tin on carbon. Finally, fig. 9 (giving a lateral view to a nucleus in the labyrinth stage) directly shows a contact angle quite different from that of fig. 8.

The question arises what the origin of this discrepancy might be and what other mechanisms could be found to explain the growth behaviour.

The fact that the shapes due to surface equilibrium do not occur apparently is caused by a lack of mobility of the tin atoms. This lack of mobility is explained by the occurrence of oxide films. This idea is supported by the work of Caswell and Budo 3) on the behaviour of tin films prepared in an extremely high vacuum at low temperatures. The disagreement with the results of Pashley may be due to the large difference in affinity to oxygen of gold and silver on one side and of tin on the other.

The complete absence of the expected equilibrium shapes and the change of the contact angle during the growth process excludes any explanation of the growth process in terms of interfacial energies alone and suggests that the kinet-
ics of the process is the predominant factor. An indication for the mechanism is found in the behaviour of the film in the labyrinth stage.

The exponential dependence of the canal width upon time, as shown in fig. 7, is very surprising. Apparently the lateral velocity of the edge of the canal is proportional to the canal width. This leads to the conclusion that the rate of material transport to the edge is proportional to the canal width. It looks as if the material for the lateral growth is supplied not straight from the vapour but by a subsequent transport along the substrate at the bottom of the canal.

This suggests that for a quantitative treatment of the growth kinetics of thin films the results of molecular-beam physics might give a very promising basis. The following summary of these results may serve to clarify our point of view.

(a) Metal atoms impinging on a substrate are scattered, even at substrate temperatures for which the saturated-vapour pressure of the metal is far below the pressure of the vapour above the substrate 4).

(b) The scattering by the substrate is not instantaneous. The atoms are adsorbed and will be re-evaporated after a short time 5,6). The average time during which an atom is adsorbed to the substrate is defined as time of adsorption 7).

(c) During their stay on the substrate the atoms move over considerable distances (lateral motion) 8).

(d) As soon as condensation occurs, scattering is reduced to a negligible level 4).

To describe the growth of thin films on the basis of these results the following assumptions have been introduced.

(1) The lateral growth of a nucleus is caused by atoms travelling along the substrate.

(2) All atoms impinging either on the surface or on the circumference of a nucleus are captured.

(3) The lateral motion of the atoms and the time of adsorption may be combined into the average distance \( \lambda \) travelled by the atom between impingement and re-evaporation.

3.2. Growth of the nuclei

3.2.1. Stability of nuclei

At first sight one would expect that the 5-s nuclei grow out to the 7-s nuclei. Comparison of figs 1 and 2 shows however that a "large" 7-s nucleus covers the area originally occupied by approximately 40 "large" 5-s nuclei as indicated by the circle in fig. 1. This might lead to the conclusion that a "large" 7-s nucleus is an agglomerate of about 40 crystallised 5-s nuclei.

It is however improbable that a collection of 40 randomly oriented single crystals grow together to one single crystal. Therefore one of the following explanations may be suggested.
(a) Only a small number, about 2%, of the "large" 5-s nuclei grows out to 7-s nuclei. The remainder disappears either by three- or by two-dimensional evaporation.

(b) Although electron diffraction shows the 5-s nuclei to be crystalline they might be in fact liquid during growth. This could be due to the bombardment of the nuclei by atoms having an energy distribution corresponding to the temperature of the source or simply by radiation from the source.

Both explanations imply that even nuclei as large as 80 Å lateral diameter are unstable in a sense. When undisturbed they are crystalline and stable, for otherwise they could not be observed at all. Under bombardment by the vapour beam or by radiation from the source they will either evaporate or melt.

If explanation (a) holds, the sizes of nuclei at different times may be compared. If (b) holds, a jump in the growth curve should be expected due to a change in the growth mechanism viz. from an atom-by-atom supply to an agglomeration of larger units. The fact that such a jump has not been observed favours possibly explanation (a).

3.2.2. Growth of nuclei in the archipelago stage

All atoms impinging on the area of the substrate with boundaries AB = λ; CD = λ and the circular arcs BC and AD and moving in a range of directions between φ and φ + dφ will reach the nucleus N (fig. 10) if they do not meet other nuclei on their way.

Fig. 10. Diagram showing the growth mechanism of a nucleus. All atoms arriving from the vapour on the area ABCD of the substrate and moving along the substrate in the direction of the arrow are captured by the nucleus. The average path travelled by an atom along the surface is indicated by λ.

For a nucleus of lateral radius \( r \) the number of these atoms (per s) equals

\[
\left( \frac{d\theta}{2\pi} \right) 2 \pi n \ s^{-1} \tag{3a}
\]

(\( n \) being the number of atoms hitting per second one cm\(^2\) of the substrate), giving on integration

\[
2 \pi n \ s^{-1}. \tag{3b}
\]

Only a fraction of these atoms is assumed to contribute to the lateral growth.
Fig. 11. Velocity of mean lateral growth $v_l$ of nuclei in a tin film as a function of time.

If each atom contributes an area of $S$ cm$^2$ one obtains for the growth velocity of the area of the nucleus

$$\frac{d(\pi r^2)}{dt} = 2fr\lambda n$$  \((4)\)

and for the lateral-growth velocity

$$\frac{dr}{dt} = f\lambda nS/n,$$  \((5)\)

which means that the growth velocity is constant.

The experimental results, represented in fig. 11, show however that the lateral-growth velocity decreases with time from the very start of the growth. Apparently there are many nuclei within a distance $\lambda$ from the nucleus under consideration.

This enables us to make an estimation of a lower limit for $\lambda$. The average distance between the edge of a nucleus and its nearest neighbours is approximately 500 Å, which means $\lambda > 500$ Å. If there were no other nuclei within a distance $\lambda$ the initial radial-growth velocity would have been larger than the observed one of 204 Å s$^{-1}$. This leads to a lower limit for

$$f\lambda nS/n.$$  

Using the experimental values for $n$ and $S$ we obtain $f\lambda > 49.5$ Å. As will be shown in appendix IV a reasonable value for $f$ is 0.012, which yields $\lambda > 4000$ Å.

In the actual situation many nuclei are present within a distance $\lambda$ from the nucleus under consideration. A quantitative treatment of this case is very complicated. It has been found possible to give a description in accordance to experiment with the aid of the model given in appendix III.
3.2.3. Growth in the labyrinth stage

The lateral-growth velocity decreases very rapidly in the labyrinth stage (fig. 11). The exponential dependence shown in (2) and fig. 7 leads to the conclusion that in this stage the velocity is proportional to the width of the canals:

\[ \frac{db}{dt} = -0.16 \bar{b}. \]  

This means that the lateral-growth velocity is proportional to the number of atoms supplied by the vapour to the bottom of the canal. This result suggests that the lateral growth might be due to transport of atoms along the substrate. This idea is quite familiar in molecular-beam physics. A quantitative treatment is given in appendix IV.

In the result two cases must be distinguished:

(a) canal width \( \lambda \) giving

\[ \frac{db}{dl} = -2fnS\lambda/\pi; \]  

(b) canal width \( \lambda \) giving

\[ \frac{db}{dt} = -2f(nS/\pi) \lambda [(b/\lambda) \arccos (b/\lambda) - \sqrt{1 - (b/\lambda)^2} + 1]. \]  

The first case leads to a velocity independent of the canal width, the latter to a very complicated dependence except when \( b \ll \lambda \). In this case (8) reduces to

\[ \frac{db}{dt} \approx -fnSb. \]  

Comparison of (6) and (9) gives

\[ fnS = 0.16 \text{ s}^{-1}. \]

Substituting the values of \( n \) and \( S \) given in appendix I we obtain

\[ f = 0.01. \]

This means that approximately 1% of the atoms reaching the wall is consumed for purely two-dimensional lateral growth.

3.3. Closing of the canals

It has been observed that just before closing the width of the canals decreases very slowly (fig. 7). On the other hand the number of canals decreases rapidly and canals having a width less than 80 Å have not been observed. This shows that the closing of the canals is an extremely rapid process and that below a canal width of 80 Å a new and rapid mechanism comes into action.

It is known that a sintering process, i.e. a process in which material is transported by diffusion to energetically favoured places, can be very rapid. However, it has been observed that all canals end with a grain boundary configuration that is known to move very slowly (fig. 12). Therefore a sintering process starting
Fig. 12. Detail of the situation after 20 s exposure. The arrows indicate characteristic grain boundary configurations at the end of a canal.

from the observed ends of the canals cannot explain the rapid closing of the canals.

For the occurrence of a rapid sintering process the creation of new energetically favoured places is necessary. Once this sort of places has been created the
Fig. 13. Formation of point contact between the upper edges of a canal by means of a geometrical effect. The arriving atoms are captured at the upper edges with the result that protrusions are built up.

Fig. 14. Schematic representation of the suggested closing mechanism.
(a) Formation of protrusions A at the upper edges of the canal. A secondary nucleus at the bottom of the canal is shown at C.
(b) Closing mechanism shown in perspective; A and B correspond to cross-sections shown in (a) and (c).
(c) Cross-section of the closed canal.

canal closes rapidly by diffusion. The following mechanisms for the creation of such places are suggested.
(a) Formation of a point contact between the walls of a canal due to fluctuations.
(b) Formation of contact under the influence of short-range forces.
(c) Formation of contact by means of a geometrical effect (fig. 13).

The most probable place for each of these mechanisms is the region where new material is supplied, i.e. near the surface of the nuclei. Then closing takes place as sketched in fig. 14. If the closing of the film occurs as described here the canals are not filled but only closed. Below the surface tunnels must be found. At the bottom of these tunnels remnants of small nuclei, visible just before closing, must be present. Both phenomena have been observed. If a closed film is deposited on a thin "Formvar" rather than a carbon substrate, stretching of the film in the microscope by means of a tensile holder opens the tunnel and small nuclei at the bottom become visible (fig. 15). A replica of the back of the closed film makes the tunnels directly visible (fig. 16).

4. Conclusion

A quantitative description of the well-known growth phenomena in thin films has been given. The key to this description is the rapid decrease of the lateral-growth velocity to very low values in the labyrinth stage. In this stage the growth is described by an exponential law that can be obtained on the basis of a very simple model. One parameter is used to adapt the predicted to the observed result. The model implies the assumption that the radial growth in the labyrinth stage is determined by the atoms supplied to the canals directly from the vapour.
Fig. 16. Electron micrograph of a Pt-shadowed Pt-C replica of the back of a closed tin film, showing the tunnels below the surface.

phase. The parameter has a simple physical interpretation. It is that fraction of the atoms arriving at the edge of the canals that contributes to the purely two-dimensional growth. The growth velocity decreases linearly with the canal
width. This explains the remarkable phenomenon that at the end the canals have practically equal width. The observed fact that the exponential law holds even in a period strictly belonging to the archipelago stage, leads to the conclusion that the way travelled by an atom during its time of adsorption is very large compared to the canal width. The growth in the archipelago stage can be described as a linear function of time with a small quadratic correction. This correction can be understood from the same model where the atoms travelling along the substrate to the central nucleus are screened by the nuclei surrounding this nucleus.

The combination of a constant perpendicular- and a decreasing lateral-growth velocity together with the presence of oxide and water vapour leads to an increasing steepness of the edge of a nucleus. This leads to a situation favourable for closing of the canals at the upper side and therefore to the formation of tunnels below the surface. It has been made plausible that the extremely rapid closing is due to a sintering process.

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Appendix I

Experimental techniques

The films have been prepared by evaporation of tin (99.99%) from a molybdenum crucible kept at 1230 °C at a pressure of 10^{-5} torr with an evaporation rate of 40 Å film thickness per second.

The substrate is an amorphous carbon film of about 200 Å thickness on glass, at 25 °C. The glass has been cleaned by wiping with isopropanol and the carbon film has been deposited by the method used for carbon replicas. The distance between the crucible and the substrate is 25 cm. Two shutters are placed in the vapour beam, one close to the crucible as a cover, the other close to the substrate.
Fig. 17. Schematic representation of the geometry of the evaporation technique. The exposure is controlled by displacing shutter 1 successively to the positions 1, 2, ..., 10.

The film is removed from the glass, together with the carbon substrate, by scratching and floating on water. Then it is transferred to a copper grid in the usual way. The samples are observed in transmission with a Philips EM 200 electron microscope. In order to minimize heating of the sample by the electron beam only those parts of the sample very close to the wires of the grid are used for the photographs.

To study the structure of the back, the film is stripped from the carbon substrate by means of “Sellotape”. For observing this structure the use of a high-resolution replica technique is essential. For this purpose the method is used in which platinum and carbon are evaporated simultaneously onto the surface by using a hollow carbon electrode with a platinum wire inside. The simultaneous use of platinum and carbon is necessary to avoid the growth of platinum nuclei which would result in lower resolution.

To observe remnants of the canals after closing a special technique has been used. The film and the substrate were stretched as a whole during observation. To make this possible the use of a “Formvar” instead of a carbon substrate was necessary. The sample with the substrate is transferred to a copper grid of special form (fig. 18). This copper grid is placed in a sample holder, called

Fig. 18. Grid for the “tensile” sample holder. The grid is clamped in the holder along the lines A-A and B-B. The stress is applied in the direction of the arrow.
“tensile holder” *), enabling the sample to be stretched during observation with the electron microscope.

To study the dependence of the contact angle of the nuclei upon time a special technique has been developed. By careful handling the floated carbon film can be folded up and subsequently transferred to a copper grid. This is drawn schematically in fig. 19. Inserting the grid together with the folded carbon film into the electron microscope we obtain an image of the flanks of the nuclei as indicated in fig. 20.

![Fig. 19. Schematic representation of the folded substrate on the copper grid.](image)

![Fig. 20. Schematic representation of the formation of an image of the folded film in the electron microscope.](image)

**Appendix II**

*Interpretation of the micrographs*

As has been said before, the radial growth of a nucleus is assumed to be due only to the transport of metal atoms along the substrate to the nucleus. This means that the nucleus has an edge of one atom thickness. During deposition the thickness of the nucleus increases, but the edge, although moving along the substrate, does not increase in thickness.

It is not certain that a nucleus of one atom thickness gives sufficient contrast

*) The “tensile holder” has been designed by Mr H. B. Haanstra of this laboratory.
to be observed. This might lead to an error if the observed radii are used for the calculation of lateral velocities.

A hypothetical cross-section of a nucleus at time $t$ is given in fig. 21. If $h$ is the thickness of a nucleus having just-observable contrast, only the part of the nucleus above the line $y = h$ is observed.

Fig. 21. Cross-section of a hypothetical nucleus in an early stage of growth. The thickness for just-observable contrast has been called $h$.

The shape of the cross-section is described by $x(y,t)$. The actual and the observed radial velocities are given by

$$v_{\text{act.}} = \frac{\partial x(0,t)}{\partial t}$$

and

$$v_{\text{obs.}} = \frac{\partial x(h,t)}{\partial t}.$$  \hspace{1cm} (5a)

We calculate $x(y,t)$ in order to find the error made if we use $v_{\text{obs.}}$ instead of $v_{\text{act.}}$. If we denote the perpendicular-growth velocity by $c$, we obtain

$$y(x,t) = h + c(t - t_0).$$  \hspace{1cm} (10)

Here $t_0$ is the moment at which the thickness at $x$ becomes greater than $h$. At this moment the nucleus becomes visible at $x$. Therefore $x(h,t)$ is the observed lateral-growth curve (as found in sec. 2.1):$$x = \mu t_0 - vt_0^2.$$  \hspace{1cm} (11)

Elimination of $t_0$ from (10) and (11) gives

$$x(y,t) = \mu [t - (y - h)/c] - v [t - (y - h)/c]^2,$$  \hspace{1cm} (12)

from which we have

$$v_{\text{act.}} - v_{\text{obs.}} = \frac{\partial x(0,t)}{\partial t} - \frac{\partial x(h,t)}{\partial t} = -2 \nu h/c.$$  \hspace{1cm} (13)

Substitution of the experimental values $\nu = 21.1 \text{ Å s}^{-2}$ (from (1)) and $c = 40 \text{ Å s}^{-1}$ gives for the difference of the velocities $h \text{ Å s}^{-1}$. On the assumption that a thickness of 10 Å certainly gives sufficient contrast we conclude that...
the error in the determination of the lateral velocity is less than 10 Å s\(^{-1}\). According to the results of this estimate it is allowed to calculate the radial-growth velocity from the observed radii.

### Appendix III

#### Geometrical screening in the archipelago stage

If the geometrical screening has an influence upon the growth behaviour of the nuclei in the archipelago stage the situation can be represented by fig. 22.

The first ring of neighbours at an average distance \(a_1\) prevents part of the atoms, coming from larger distances, to reach the central nucleus. Of the atoms, coming from the region between the first neighbours at distance \(a_1\) and the second neighbours at distance \(a_2\), only a fraction will reach the central nucleus. Calling the number of first neighbours \(q\), this fraction is found to be

\[
\frac{2\pi a_1 - q2r}{2\pi a_1} = 1 - qr/\pi a_1.
\]

(14)

Inspection of fig. 2 shows that ignoring contributions from outside the ring of second neighbours will not introduce large errors. For the lateral-growth velocity of the area covered by the central nucleus we obtain

\[
\frac{d(nr^2)}{dt} = fnS2\pi \left\{ a_1 - r + (a_3 - a_1)(1 - qr/\pi a_1) \right\}
\]

or

\[
\frac{dr}{dt} = f(nS/\pi) a_2 \left( 1 - ar/a_2 \right),
\]

(15a) (15b)

where

\[
a = 1 + [(a_2 - a_1)/a_1] q/n \approx 1 + q/n.
\]

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Fig. 22. Geometric screening, during growth of a nucleus A, due to the presence of other nuclei. The average distances of first and second neighbours have been indicated by \(a_1\) and \(a_2\).
From (15b) we obtain by integration

\[ \ln (1 - \alpha \frac{r}{a_2}) = -\alpha f(nS/\pi) (t - t_0) \]  

(16a)

or

\[ 1 - \alpha \frac{r}{a_2} = \exp \{ -\alpha f(nS/\pi) (t - t_0) \}, \]

(16b)

where \( t_0 \) is the time at which the growth of the nuclei has started.

An estimate for \( q \) based on fig. 2 gives the value 6 or \( \alpha \approx 3 \). We shall see in appendix IV that \( f_nS = 0.16 \), giving

\[ \alpha f(nS/\pi) \approx 0.16; \]

Expanding the exponential in (16b) into a power series the terms after the quadratic one can be neglected without serious error if \( t - t_0 \ll 6 \). Thus we obtain

\[ r(t) = \left( \frac{a_2}{\alpha} \right)^2 \alpha (f_nS/\pi) (t - t_0) - \frac{1}{2} \left( \frac{a_2}{\alpha} \right)^2 \alpha (f_nS/\pi) (t - t_0)^2. \]  

(17)

Using the experimental values in expression (1), being 204 Å s\(^{-1}\) for the value of the coefficient of \( (t - t_0) \) and 21.2 Å s\(^{-2}\) for the coefficient of \( (t - t_0)^2 \) we obtain

\[ \frac{1}{2} \alpha f(nS/\pi) = 21.2/204 = 0.104 \text{ s}^{-1}, \]

or \( \alpha = 4.4 \) and \( a_2 = 4000 \) Å.

Appendix IV

**Mathematical treatment of the growth in the labyrinth stage**

Plotting the logarithm of the canal width as a function of time shows that this exponential relation holds very accurately even for part of the archipelago stage. The experimental results are represented by fig. 7. From this figure we deduce

\[ \frac{d\bar{b}}{dt} = -0.16 \bar{b}. \]  

(18)

To explain this on the basis of the assumptions of sec. 3.1 we have to distinguish two cases (fig. 23):

(a) The canal width is greater than \( \lambda \).

Of the atoms impinging on \( dxdz \) only the fraction

\[ \frac{1}{\lambda \pi} \arccos \left( \frac{z}{\lambda} \right) \]

reaches the wall of the canal. A fraction \( f \) of the atoms reaching the wall contributes to the two-dimensional growth. Hence

\[ \frac{d\bar{b}}{dt} = -2 (f nS/\pi) \int_0^\lambda \arccos \left( \frac{z}{\lambda} \right) dz. \]  

(19)
The right-hand side of (19) is not dependent on $b$ and consequently cannot lead to an exponential expression.

(b) The canal width is smaller than $\lambda$.

In this case practically the same expression as (19) is obtained with the difference that $b$ instead of $\lambda$ is taken as the upper limit of the integral. Integration yields

$$\frac{db}{dt} = -2 \left( fnS/\pi \right) \lambda \left[ (b/\lambda) \arccos (b/\lambda) - \sqrt{1 - (b/\lambda)^2} + 1 \right].$$ \hspace{1cm} (20)

This implies a very complicated dependence of $b$ upon time except when $b \ll \lambda$.

In the latter case $\arccos (b/\lambda) \approx \pi/2$ and $\sqrt{1 - (b/\lambda)^2} \approx 1$ and

$$\frac{db}{dt} \approx -fnSb.$$ \hspace{1cm} (21)

Comparison of (18) and (21) gives

$$fnS = 0.161 \text{ s}^{-1}.$$

From the values found in appendix I ($n = 1.45 \times 10^{16} \text{ cm}^{-2} \text{s}^{-1}$ and $S = 9.10^{-16} \text{ cm}^{2}$) we obtain $f = 0.012$.

REFERENCES

1) T. A. McLaughlan, R. S. Sennett and G. D. Scott, Canadian J. Res. 28, 530, 1950.