R 635 Philips Res. Repts **22**, 375-387, 1967

EFFECT OF THE MOBILITY OF METAL ATOMS ON THE STRUCTURE OF THIN FILMS DEPOSITED AT OBLIQUE INCIDENCE

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Abstract

The structure of non-continuous thin films of Sn, Cu, Au, Pd and Pt in an early stage of growth, made at oblique incidence of the vapour beam, has been studied with the electron microscope. At oblique incidence Sn, Cu, Pd and Pt give elongated nuclei. With the possible exception of grazing incidence their long axes show a preference for being perpendicular to the plane of incidence. Gold gives circular nuclei even at grazing incidence. A mechanism based on inhibited mobility, either by chemisorbed oxygen or by a high melting point, and explaining the elongated shape of the nuclei of Sn, Cu, Pd and Pt as well as the exceptional behaviour of gold is suggested. This mechanism also gives a plausible explanation of: the three-dimensional shape of the nuclei, the porosity and the shape of the pores, the structure at the end of the labyrinth stage, the dependence of surface area on thickness and angle of incidence, and possibly of the compositional dependence of angle-of-incidence effects of alloys.

1. Introduction

It has been known for many years that thin films, made by evaporation at oblique incidence of the vapour beam, have anisotropic optical, magnetic, electrical and mechanical properties. An excellent review of the resulting *magnetic* anisotropies does already exist [1]). Hence only a short general review of the present situation will be given.

König and Helwig [2]) found with the electron microscope that Pt, WO_3 and Al, at oblique incidence, give a structure consisting of small towers. They suggested a self-shadowing mechanism as an explanation.

Magnetic anisotropy at oblique incidence was observed by Knorr and Hoffman [3]) and independently by Smith [4]). The latter gave an explanation [5]) based on König and Helwig's self-shadowing mechanism.

For Ni-Fe alloys Pugh [6]) observed that the anisotropy at a given angle of incidence strongly depends on the alloy composition. Cohen [7]) observed that "oblique" permalloy films in very early stages of growth consist of elongated

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nuclei. Near grazing incidence their long axis is in the plane of incidence. The nuclei are arranged in rows perpendicular to the plane of incidence. Elongated nuclei were observed in iron films by Schuele [8]) and in cobalt films by Speliotis [9]). Yelon [10]) postulated the existence of needle-shaped pores perpendicular to the plane of incidence to explain the observed magnetic anisotropies.

The surface area of thin films is much larger than the geometric area and often increases linearly with film thickness [11]). This surface area is larger at oblique incidence than at normal incidence [12]).

If the film contains oxygen, this oxygen content is observed to increase with the angle of incidence [9]). Apparently the films are porous. The literature on the corresponding decrease in density is confusing. A review is given in ref. 13. According to recent measurements [13]) it appears probable that the decrease, if any, is very slight.

Nieuwenhuizen found with the electron microscope that, in continuous aluminium [14]) and copper [15]) films, oblique incidence results in a structure of oblique columns slightly tilted away from the beam in the direction of the normal.

This review shows that a lot of work has been done on the macroscopic anisotropy. A systematic study of the *structure* of "oblique" films in the early stages of growth is lacking. A critical study of the literature shows that there is no satisfactory explanation of the origin of the elongated nuclei. Smith's theory cannot be accepted for the early stages (cf. sec. 4) and Kambersky's [16]) suggestion that the momentum component of the incident atoms in the plane of the film might be of importance did not receive much attention.

The object of this paper is to discuss the structure of oblique films and the formation mechanism of the elongated nuclei.

2. Experimental techniques

All films were deposited at a vacuum of 10^{-5} torr, on an amorphous carbon substrate of about 200 Å thickness on glass, and at a substrate temperature of about 25 °C.

Tin, copper, gold and palladium were evaporated from a molybdenum crucible and platinum from a tungsten wire coated with TiO_2 to prevent alloy formation. The source temperature was such as to give a suitable film in about 5s. The distance between source and substrate was 50 cm, giving a definition of the angle of incidence α (α is zero at normal incidence) of about 3°. Oblique incidence was achieved by tilting the substrate with respect to the beam.

The projected direction of the beam was marked by shadow casting. To this end dust particles were applied to the substrate and Al_2O_3 was used for shadowing because it has an extremely low mobility.

To obtain an Al_2O_3 shadow an Al source was used at 10^{-3} torr and a low evaporation rate. Further details of preparation of samples and of making electron micrographs have been described earlier [17]).

3. Experimental results

3.1. *Unidirectional transport of atoms along the substrate due to oblique incidence*

Oblique incidence is expected to result in a velocity distribution of the atoms on the substrate with some preference for the projected direction of the beam [16]. To prove this, dust particles, introduced to the substrate, were shadowed with Sn at a vacuum of 10^{-5} torr and subsequently with Al_2O_3 at a vacuum of 10^{-3} torr from the same source position. Since the mobility of Al_2O_3 is low, it marks off the geometric shadow. No Sn atoms can arrive at the substrate inside this shadow. Random migration of Sn atoms on the substrate may cause the Sn shadow to be somewhat vague, but is should coincide with the Al_2O_3 shadow if the average migration velocity is zero. The experiment shows that a region free from elongated Sn nuclei exists *outside* the geometric shadow given by the Al_2O_3 (fig. 1). This proves that the average migration velocity is different from zero and parallel to the projected direction of the beam. Hence, under extreme conditions, there is no supply of atoms along the substrate from the shadow region to the nucleus and consequently no two-dimensional growth of the nucleus towards the shadow region (fig. 1).

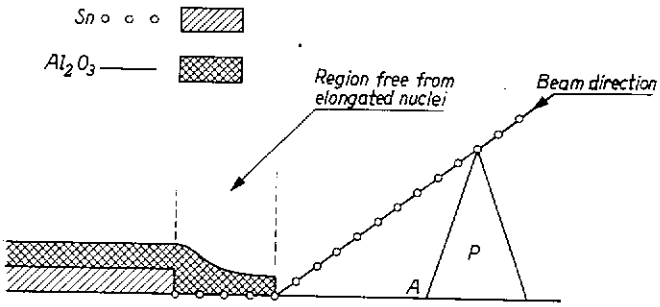

Fig. 1. The effect of a component of the beam velocity parallel to the substrate. A dust particle P has been shadowed with tin and subsequently with Al from the same source position. The tin-free region, observed with the electron microscope, shows that the atoms on the substrate have a preferred motion in the projected direction of the beam. Hence, under extreme conditions, no supply of tin atoms along the substrate occurs at A.

3.2. *Structure of discontinuous "oblique" films of tin*

Electron micrographs, one of a "normal" film and another of an "oblique" ($\alpha = 80°$) film, show the following characteristics (fig. 2).

(a) Nuclei of the "oblique" film generally have an elongated form and resemble rectangles; nuclei of the "normal" film are circular [17].

(b) In the shadow of dust particles, only small *circular* nuclei are found.

(c) The histogram of fig. 3 shows that the long axis of the elongated nuclei of the "oblique" film is preferably *perpendicular* to the plane of incidence. A χ^2 test was used to find out whether the distribution given in fig. 3 was a

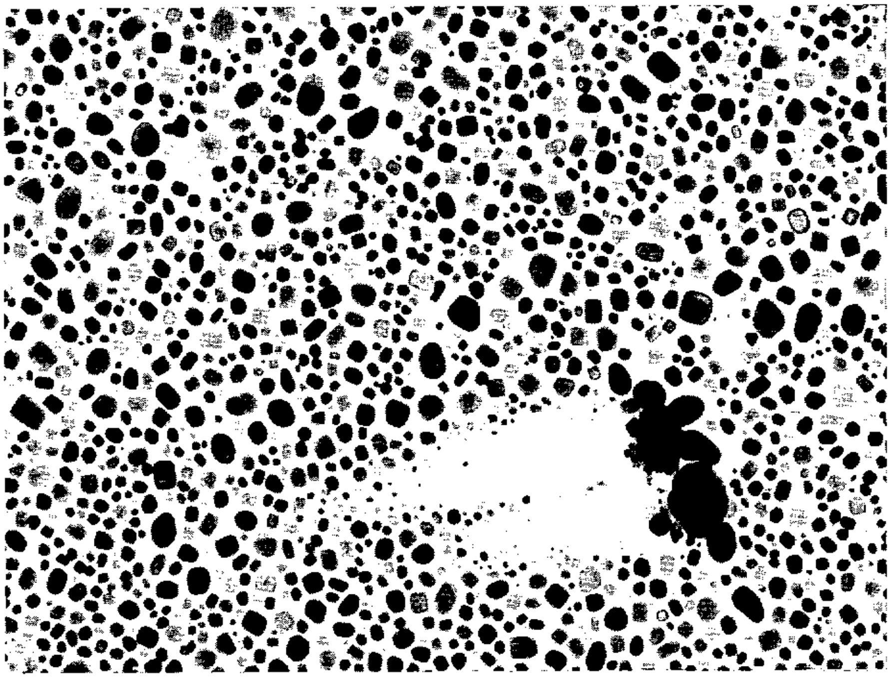

Fig. 2. Electron micrograph of a tin film on an amorphous carbon substrate ($\alpha = 80^\circ$). Small circular nuclei are visible in the shadow of the dust particle. The direction of the shadow represents the projected direction of the beam.

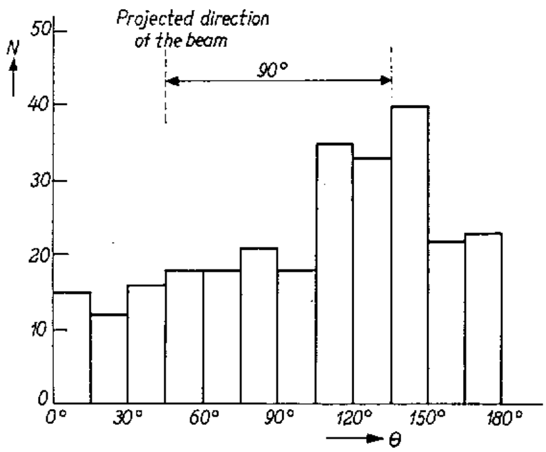

Fig. 3. Histogram of the number (N) of elongated nuclei with their long axes in classes of 15° width as a function of orientation. The orientation in the plane is given by the angle θ counted from an arbitrary direction in the plane.

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random one or not. The range of directions was divided into 12 equal classes which gives 11 degrees of freedom. The hypothesis of a random distribution may be rejected at a 95 per cent level of significance if χ^2 is larger than 19·7 [21]). Table I shows this to be the case for $\alpha > 40°$.

TABLE I

Percentage of elongated nuclei as a function of the angle of incidence. For the evaluation of χ^2 the same number of observations was used for each angle of incidence

angle of incidence (°)	percentage of nuclei with length/width ratio 1·1	χ^2 *)
0	0	—
20	20	16
40	45	20
70	70	30
80	90	35

*) The same number of observations was used in all calculations.

Electron micrographs of "oblique" films of tin ($\alpha = 80°, 70°, 40°, 20°$) show the following results:

(1) for all angles the nuclei are elongated; their long axes tend to be perpendicular to the plane of incidence;
(2) with decreasing α the corners of the rectangles become more rounded;
(3) the relative amount of nuclei having a length/width ratio 1·1 increases with α (table I).

3.3. *Three-dimensional shape of "oblique" tin nuclei*

Electron micrographs like the one shown in fig. 2, only give the projection of the nuclei upon the substrate. To obtain further information about the three-dimensional shape the following experiments were performed.

(a) An "oblique" discontinuous tin film was shadowed with Al_2O_3 from exactly the same direction as was used for deposition of the tin. Electron micrographs show the existence of an area free from Al_2O_3 in the shadow of the nucleus (fig. 4).
(b) An "oblique" tin film on a carbon substrate was folded along a line approximately parallel to the plane of incidence. Electron micrographs show that the angle-of-incidence effect, observed by Nieuwenhuizen and Haanstra, already exists for the nuclei themselves: the shadow side of the nucleus is tilted away from the beam towards the direction of the normal (fig. 4).

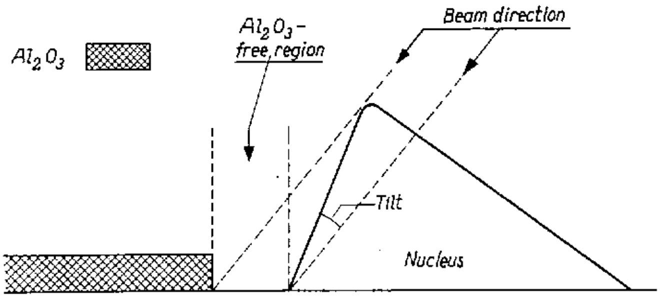

Fig. 4. Tilt of the shadow side of a nucleus, away from the beam and towards the normal. The tin nucleus has been shadowed with Al from the original source position. The Al_2O_3-free region has been observed with the electron microscope.

3.4. *Structure of discontinuous "oblique" films of gold, copper, palladium and platinum*

Films of Cu, Pd and Pt made at oblique incidence show the same angle-of-incidence characteristics as those of Sn. For Cu, at grazing incidence, the nuclei tend to have their long axes *parallel* to the plane of incidence. For Au, even at grazing incidence, all nuclei had circular shape. The other materials were not investigated at grazing incidence. The results, combined with some others taken from literature, are collected in table II.

TABLE II

Orientation of nuclei in thin films of several metals, made at oblique incidence (⊥ means long axis perpendicular to plane of incidence, ○ means circular nuclei)

metal	orientation of nuclei	
	$\alpha = 60°$	$\alpha = 90°$
Pt	⊥	?
Pd	⊥	?
Ni-Fe [7]	⊥	//
Cu	⊥	//
Au	○	○
Sn	⊥	?

4. Mechanism of the formation of elongated nuclei in "oblique" films

In order to explain the observed magnetic anisotropy Smith suggested a self-shadowing mechanism [5]. It is very plausible that such a mechanism is active in later stages of film growth. For the following reasons, however, it cannot be accepted as a mechanism for the formation of the elongated nuclei. It has been observed that an elongated shape occurs even in the case of the *smallest* nuclei. According to Smith this should be due to agglomeration of smaller isotropic nuclei. It is known, however, that at this size agglomeration, if it occurs, only gives rise to isotropic nuclei [17, 18]). Moreover, the nuclei of tin are known to be very flat [17]). Thus for this material Smith's assumption of nearly spherical nuclei apparently does not hold true. It is tempting to explain the observed anisotropy by relating it to a crystallographic orientation. Crystallographic orientation has been observed e.g. for thin films of tin. The *a*-axis is perpendicular to the substrate. No unambiguous indications have been found for a preferred direction of the *c*-axis in the plane of the substrate. Nevertheless, tin does give anisotropic films.

In the search for another explanation we start from the results of a previous investigation [17]) where it has been shown that *the rate of lateral growth of the nuclei is determined by the supply of material along the substrate*. With this in mind, three observations made in the present investigation seem to be of primary importance:

(1) the supply of atoms along the substrate is maximum in the direction of the projected beam (cf. sec. 3.1);

(2) with the possible exception of grazing incidence, Pt, Pd, Fe, Co, Cu, Sn give elongated nuclei with the long axis tending to be *perpendicular* to the plane of incidence;

(3) gold gives circular nuclei, even at grazing incidence.

Combination of (1) and (2) leads to the paradoxical conclusion that, except for grazing incidence, *growth is slowest at the point of maximum supply along the substrate* (fig. 5*b*). Hence a transport of atoms must occur along the boundary and possibly over the surface of the nuclei. A necessary condition for transport is sufficient mobility *).

Apparently even for Pt, which has the highest melting point in the series investigated, the mobility is sufficient, at least at the exposed side of the nucleus. In the case of Au this leads to circular nuclei, possibly of equilibrium shape. On the other hand tin, which certainly has a still greater mobility, gives elongated nuclei. The exceptional behaviour of gold compared with copper, which has the same structure and the same melting point, may be related to its low affinity for oxygen. It is known that oxygen has a strongly inhibiting effect upon the dewetting of Sn on a glass substrate [19]), that even at normal incidence Sn gives nuclei of a shape unexpected on the basis of surface-tension theory [17]), and that Au gives circular nuclei even at grazing incidence. A look at table III shows that gold has a very exceptional position among the metals investigated: the occurrence of circular nuclei coincides with an extremely low affinity for oxygen. We therefore propose as a mechanism for the formation of elongated nuclei a trans-

*) Throughout this paper the term "mobility" is used in the everyday sense.

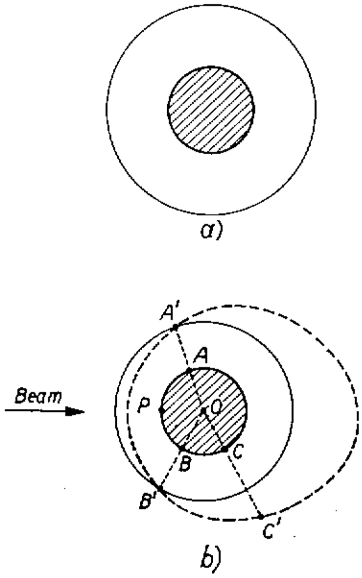

Fig. 5. Schematic polar diagram of the oxygen/metal ratio for a circular nucleus during deposition at normal (*a*) and oblique (*b*) incidence. The point of maximum supply is at P. The length of OC′ represents the oxygen/metal ratio for atoms arriving at C; OA′ and OB′ represent the critical ratio. Large mobility along the contour exists only on APB.

TABLE III

Standard potentials as a measure for the affinity to oxygen for several metals arranged in the order of their melting points

metal	melting point (°C)	standard potential (mV)	shape of nuclei
Pt	1773	1200	elong.
Pd	1554	987	elong.
Fe	1539	— 440	elong.
Co	1495	— 280	elong.
Ni	1455	— 250	elong.
Cu	1083	340	elong.
Au	1063	1700	circular
Al	660	—1600	elong.
Sn	231	— 140	elong.

port for which *the driving force is given by the gradient of the mobility* along the contour.

For the non-noble metals this gradient is a consequence of the increase of the oxygen/metal ratio, when passing along the contour from the point of maximum supply to the opposite side. The increase results from the anisotropic supply of metal along the substrate combined with the isotropic supply of oxygen from the background gas. This leads to a trapping of metal atoms beyond a point on the contour where this ratio exceeds a certain critical value (fig. 5*a*, *b*). With increasing angle of incidence this point will move in the direction of the point of maximum supply of metal atoms, thus explaining by one single mechanism the two orientations of the elongated nuclei.

For the high-melting noble metals Pt and Pd this method of trapping by oxygen cannot work. Another gradient of the mobility does exist since the atoms, arriving at the contour, are not in thermal equilibrium with the nucleus [20]). On the plausible assumption that atoms of high-melting metals like Pd and Pt have only sufficient mobility in this non-equilibrium state, the transport is due to the loss of energy by atoms on their way along the contour. This explains the occurrence of elongated nuclei for Pt and Pd.

For gold as a low-melting noble metal, neither of these mechanisms works, which leads to spherical nuclei.

5. Discussion

The suggested mechanism and the observed facts give support to some already existing ideas and explain a number of hitherto unexplained observations described in literature.

5.1. *Elongated nuclei*

The formation of elongated nuclei has been explained in terms of anisotropic supply, transport along the contour, and trapping of the atoms in a region where the mobility becomes too low, either due to oxide formation or to loss of thermal energy. This region will be shifted towards the point of maximum supply by: increasing α, decreasing substrate temperature, increasing affinity for oxygen, increasing melting point, increasing pressure of the background gas (oxygen!) and decreasing source temperature. Hence it is to be expected that all the factors mentioned lead to situations formally corresponding to larger angles of incidence. Thus this mechanism makes it possible to understand the hitherto unexplained compositional dependence of angle-of-incidence effects for alloy films [6]), in terms of affinity for oxygen.

5.2. *Formation of rows*

The unidirectional transport described in sec. 3.1 provides a natural explanation of the formation of rows, consisting of nuclei elongated perpendicular to the row, as observed by Cohen [7]) for high angles of incidence and elevated substrate temperatures. Although it appears to be a shadowing effect it is not in the strict sense. The regions between the rows, containing only very small nuclei, are an extreme example of the regions, free from nuclei, outside the geometric shadow shown in fig. 1.

5.3. *Three-dimensional shape of the nuclei, columnar growth, porosity*

Regions exposed to the beam have a low oxygen/metal ratio and atoms in these regions have a high mobility. At the shadow side AC of a nucleus (fig. 6) no atoms can arrive directly from the beam. At this side the oxygen/metal ratio is high and the mobility is low. Hence atoms crossing the edge C will be trapped at the shadow side. This leads to a transport over a short distance across the edge, thus explaining the observed tilt (cf. sec. 3.3) of the shadow side towards the normal (fig. 6). Due to the unidirectional transport along the substrate, away from the source (cf. sec. 3.1), lateral growth can stop at A under extreme conditions. In the absence of other nuclei it will grow indefinitely at the opposite side B (fig. 6). If, however, this lateral growth causes a nucleus to reach the geomet-

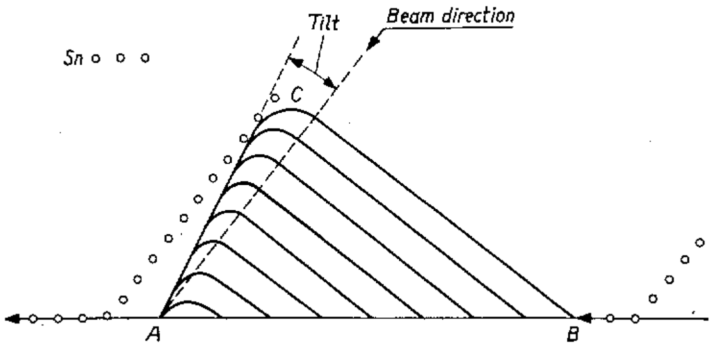

Fig. 6. Origin of the tilt of the shadow side. Atoms supplied to CB migrate in all directions. Those crossing the edge C are trapped on AC by oxygen atoms. Supply along the substrate, controlling the two-dimensional growth, is indicated by arrows.

ric shadow of a second one, lateral growth of the first will stop through lack of supply along the substrate (fig. 7). The growth of the first nucleus then proceeds roughly parallel to the shadow side of the second.

This gives rise to the columnar growth observed by Nieuwenhuizen and Haanstra [14, 15]). At the same time a flat pore, elongated in a direction perpendicular to the plane of incidence, will be formed. These pores presumably correspond to the acicular pores postulated by Yelon [10]).

5.4. *The closing mechanism of films made at normal incidence*

It has been shown in ref. 17 that nuclei of thin films of tin have a very peculiar shape, especially near the end of the labyrinth stage. The walls of the canals

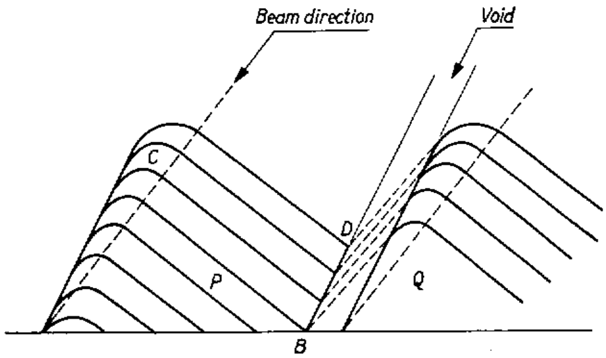

Fig. 7. Origin of columnar growth. The two-dimensional growth of nucleus P at B stops when it reaches the shadow of nucleus Q. From then on, the front CB moves parallel to itself in the direction of the source and BD will be roughly parallel to the shadow side of Q. Hence the direction of the columns is tilted away from the beam towards the normal.

between the nuclei are nearly perpendicular to the substrate. At a width of about 80 Å, the canals close very rapidly. The shape of the nuclei was quite unexpected from surface-tension theory. A relation with inhibited mobility, due to absorbed oxygen [19]), was suggested [17]). The present results stress the importance of oxygen once more. Moreover, the mechanism leading to the tilt, described in sec. 5.3, also explains how the walls of a canal grow nearly perpendicular to the substrate (fig. 8). When the walls have become perpendicular, no metal atoms can

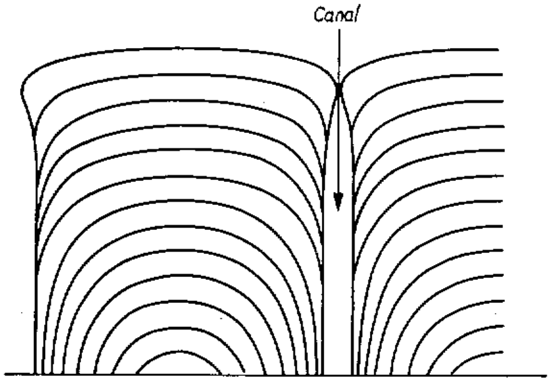

Fig. 8. Closing of the canals in films made at normal incidence. The directions of beam and normal coincide. If the canal wall has become vertical, a tilt occurs here too. The curves indicate subsequent stages of growth.

reach them directly from the vapour. But atoms of the background gas can. Hence a difference in mobility between the metal atoms in the exposed and unexposed regions results. A transport over a short distance across the edge of the canals will occur and the upper side of one wall may come into contact with the opposite wall. This is the mechanism underlying the geometrical effect mentioned in ref. 17.

5.5. *Surface area, oxide content and density of thin films*

Consider a film in the labyrinth stage, made at normal incidence. Let it have a thickness d and contain n nuclei per unit of geometric area. The surface area of the canal walls per unit of geometric area of this film is proportional to $n^{1/2}\, d$. Hence in this stage the surface area will increase linearly with thickness. After this initial stage a non-linear dependence will occur due to the observed increase of the size of the nuclei with thickness as shown in ref. 14. When this size has become nearly stationary, the dependence will become linear again. This has actually been observed by Frennet [22]). At oblique incidence, the surface of the walls is proportional to the "oblique" height of the flat pores described in sec. 5.3, and hence increases with the angle of incidence. This has been found experimentally [11]).

As the nucleation density decreases, at least initially, with increasing angle of incidence the increase of the area will be slower than expected.

On the assumption that the oxygen is concentrated at the shadow sides of the nuclei it is to be expected that the oxygen content will increase with the angle of incidence in the same way as the surface area. Although the oxygen content is known to increase with the angle of incidence [9]) quantitative data on the relation between oxygen content and surface area are lacking.

The literature on the density of thin films is very confusing. Some report densities about 30% below the bulk densities. Recent investigations [13]) make it probable that even in the case of very thin films the density is only slightly different from the bulk density.

If the above explanation holds true a film with a large area can have a normal density. Deviations can be expected if the volume of the canals contributes appreciably to the volume of the film, i.e. if the nuclei are very small. This might occur with films deposited at very low substrate temperatures.

Acknowledgement

The authors are greatly indebted to Mrs J. R. M. Gijsbers-Dekkers and Miss M. A. Haarmeijer for their stimulating enthusiasm and for making the electron micrographs, to Mr D. M. N. Bemelmans for making the prints, to Mr H. B. Haanstra and Mr J. M. Nieuwenhuizen for their valuable technical advice, to Mr J. Hornstra for stimulating discussions and to all who by their help at the right moment made the writing of this paper possible.

Eindhoven, January 1967

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REFERENCES

1) M. Prutton, Thin ferromagnetic films, Butterworths, London, 1964.
2) H. König and G. Helwig, Optik **6**, 111, 1950.
3) T. G. Knorr and R. W. Hoffman, Phys. Rev. **113**, 1039, 1959.
4) D. O. Smith, J. appl. Phys. **30**, 264S, 1959.
5) D. O. Smith, M. S. Cohen and G. P. Weiss, J. appl. Phys. **31**, 1755, 1960.
6) E. W. Pugh, E. L. Boyd and J. F. Freedman, I.B.M. J. Res. Dev. **4**, 163, 1960.
7) M. S. Cohen, J. appl. Phys. **32**, 87S, 1961.
8) W. J. Schuele, J. appl. Phys. **35**, 2558, 1964.
9) D. E. Speliotis, G. Bate, J. Kalstad and J. R. Morrison, J. appl. Phys. **36**, 972, 1965.
10) A. Yelon, J. R. Asik and R. W. Hoffman, J. appl. Phys. **33**, 1949, 1962.
11) J. A. Allen, C. C. Evans and J. W. Mitchel, Structure and properties of thin films, John Wiley & Sons, Inc., New York, 1959, p. 46.
12) J. W. Swaine and R. C. Plumb, J. appl. Phys. **33**, 2378, 1962.
13) A. R. Wolter, J. appl. Phys. **36**, 2377, 1965.
14) J. M. Nieuwenhuizen and H. B. Haanstra, Philips tech. Rev. **27**, 87, 1966.
15) J. M. Nieuwenhuizen, unpublished.
16) V. Kambersky, Z. Málek, Z. Frait and M. Ondris, Czechoslovak J. Phys. **B11**, 171, 1961.
17) J. G. W. van de Waterbeemd, Philips Res. Repts **21**, 27, 1966.
18) D. W. Pashley et al., Phil. Mag. **10**, 127, 1964.
19) H. L. Caswell and Y. Budo, J. appl. Phys. **35**, 644, 1964.
20) G. W. Sears and J. W. Cahn, J. chem. Phys. **33**, 494, 1960.
21) W. J. Dixon and F. J. Massey, Introduction to statistical analysis, MacGraw Hill, New York and London, 1951.
22) A. Frennet, personal communication. To appear in J. Chimie phys.