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ON THE MECHANISM OF HILLOCKS FORMATION IN VAPOUR DEPOSITED THIN FILMS

By

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Two types of growth hillocks (marked by Type I and Type II) have been identified in vapour deposited thin films. Type I develops inside the surface of large crystals, while Type II represents individual single crystals protruded over the average surface area of the film. Formation of Type I hillocks indicates the participation of foreign atoms in the film formation and their accumulation along the moving growth steps developing stable phases. Type II hillocks develop at higher growth rates in preferential crystallographic directions due either to the crystallography of crystals (e.g. Bi), or to the effect of selective uptake of foreign species on the crystallographic faces of different Miller indices developing covering layers on different surface areas controlling also the coalescence of the grains. The correlation between the partial pressure of oxygen and the formation of hillocks in Al films proved the effectivity of the last phenomenon.

1. Introduction

Most of as-prepared vapour deposited thin films exhibit so called "growth hillocks", i. e. crystallites protruding over the average surface plane of the film [1—10]. The tops of these hillocks are usually bounded by crystallographic faces and prove to be misoriented in epitaxial films (or in films exhibiting textures) [3, 4, 9].

Growth hillocks are very characteristic e. g. both of pure Al films [3, 4, 5, 9, 10] and of alloyed films [6, 7]. It is a common experience that additional hillocks can develop during the heat treatment of films [6—10].

The development of hillocks makes the films very disadvantageous in many cases of applications (e. g. in the fabrication of inter-level short-free crossovers [1] or in the preparation of front mirrors [2]).

One can conclude that the results published in literature dealing with growth hillocks are not quite sufficient to understand, control and/or prevent the formation of these hillocks. These publications do not offer any comprehensive and precise description of the morphology, crystal orientation, composition and the growth mechanism of these hillocks. The conditions of preparation of films are not well-defined either in most papers. These lead to contradictory data for the dependence of hillocks characteristics upon deposition parameters.

In this paper we are going to discuss the experimental results related to the formation of growth hillocks. Particular attention has been paid to the effect of the active components of residual gases (e. g. oxygen and water vapour) considering the results of experiments carried out on Al films. The details of these experiments have been published elsewhere [11].

2. Experimental results to be considered

2.1. *Effect of contaminations on the formation mechanism of growth hillocks (Al films)*

A very pronounced influence of residual gases on the morphology and structure of vapour deposited films can be found in the case of Al films. By increasing K_{oxygen} (the ratio of the impinging oxygen species to that of Al atoms) the surface of the films becomes rougher while the average grain size decreases. Additionally, as viewed by replica technique, the surface of the films generally exhibits typical configurations referred to as growth hillocks in the literature.

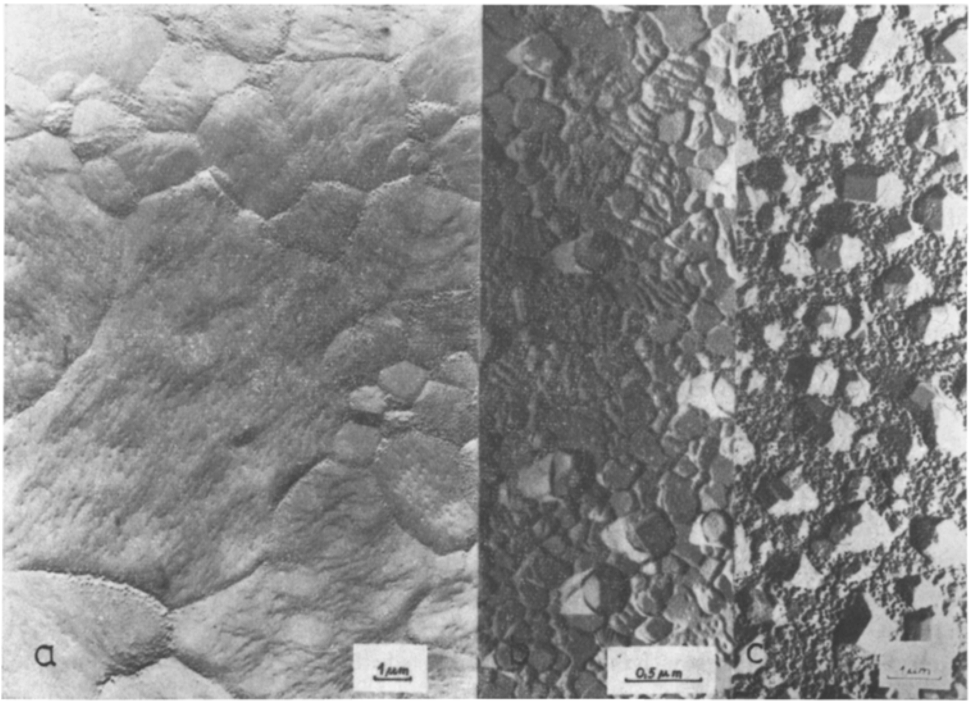

Fig. 1. **Characteristic surface structures of Al films deposited at different levels of oxygen contamination. Substrate temperature: 300 °C. a) thickness 1 μm, $K_{\text{oxygen}} \sim 10^{-2}$—$10^{-3}$; b) thickness 1 μm, $K_{\text{oxygen}} \sim 10^{-1}$; c) thickness 60 nm, $K_{\text{oxygen}} \sim 1$**

2.1.1. *Films deposited onto amorphous substrates* [11]

Characteristic structures in Fig. 1 follow each other continuously with increasing oxygen contamination level.

a) At low contamination level ($K_{\text{oxygen}} \sim 10^{-2}$—$10^{-3}$)

The films of 1 μm thickness exhibit a predominant (111) texture orientation. These films consist of crystallites of 1—10 μm lateral sizes displaying typical surface structures of layer grown single crystals (Fig. 2). From this Figure we may observe that at given sites the growth steps of the layers are stopped. These sites are presumably nuclei (precipitates) of oxide. Bunches of growth steps supposed to be covered by oxide layer are formed around these nuclei. On the surface of large single crystals protrusions (marked by A) of flat areas and dents (marked by B) can be observed. This type of protrusions can be termed "hillocks of Type I". These are limited by bunches of steps and many of these can develop within the surface area of a large single crystal. Consequently, they have the same orientation as the basic crystal. MINKOFF and NIXON have also observed the same kind of hillock for graphite grown in iron and nickel alloys [12].

The investigation of samples of the same film in HVEM indicates that crystals of higher degree of misorientation are present according to the Bragg

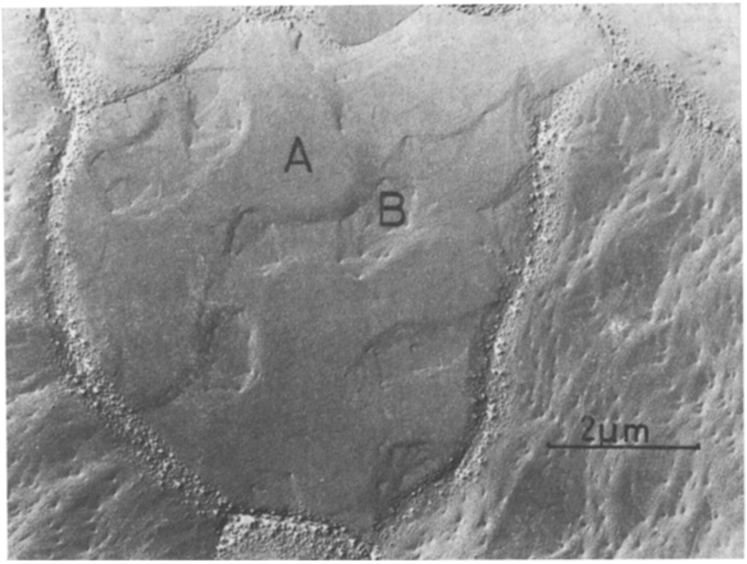

Fig. 2. Surface structure of large single crystals developed at low level of oxygen contamination (see Fig. 1a). Configurations of "Hillocks of Type I" are present.

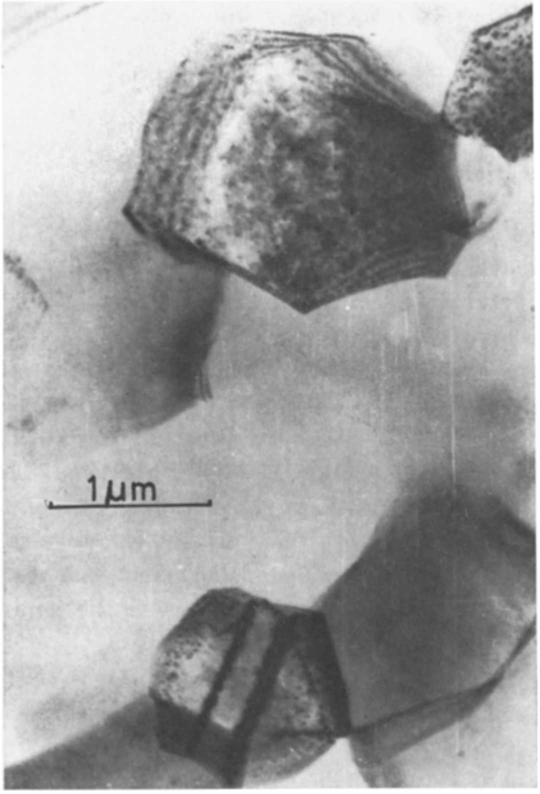

Fig. 3. HVEM image of the 1 μm thick Al film shown in Fig. 1a and Fig. 2

reflection and contrasts (Fig. 3). These crystallites are characterized by the higher concentration of defects and precipitates. The same structures are presented in HVEM micrographs of Al crystals formed in the presence of adsorbed impurities by Tochinsky [13].

b) At medium contamination level ($K_{\text{oxygen}} \sim 10^{-1}$—$10^{-2}$)

Films having a thickness of 1 μm exhibit grain sizes approximately equal to their thicknesses. The common characteristic of these films is a fairly rough surface and they exhibit a predominant random orientation in most cases. The electron microscopic examination of replicas shows an abnormal growth of some crystals referred to as growth hillocks in the literature. These hillocks represent single individual crystals grown over the average film surface plane (Fig. 4). The points of these protrusions are mainly composed of truncated octahedrons of well-developed faces of low Miller indices. Most of these faces are completely smooth. Their regularities are destroyed only at

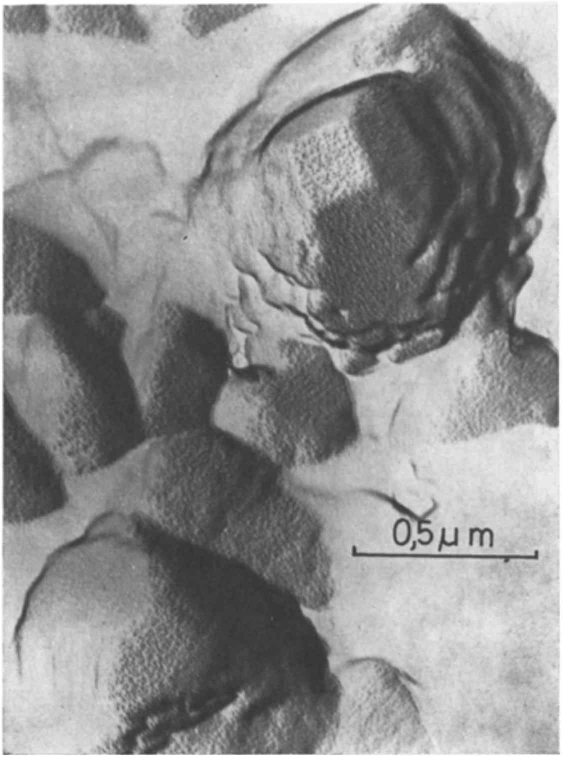

Fig. 4. Surface structure of a 1 μm thick Al film deposited at 300 °C substrate temperature and at $K_{\text{oxygen}} \sim 10^{-1}$. Protruded crystals, the so called "Hillocks of Type II" are developed.

the periphery (Fig. 4). Additionally, their lateral size nearly fits to the average grain size of the film. This type of protrusions represented by individual single crystals can be termed "hillocks of Type II".

c) At high contamination level $(K_{\text{oxygen}} \sim 1)$

Films prepared under these conditions show a very inhomogeneous structure. In films of a thickness of 60 nm it is clearly seen that most crystals are very small and overlapped while relatively large crystallites of well developed shapes protrude above the film surface (Fig. 5). Examination of these films by TED shows that they have random orientation.

The types of these protrusions are similar to that of hillocks of Type II. From Fig. 5 we can observe that the surface of these large crystals (hillocks) are not completely smooth as we have seen in the crystals at medium contamination level. These surfaces contain many dents and hillocks of Type I (marked by E). It can also be observed that some of the faces of hillocks of Type II are destroyed partly or completely as illustrated by D. Relatively

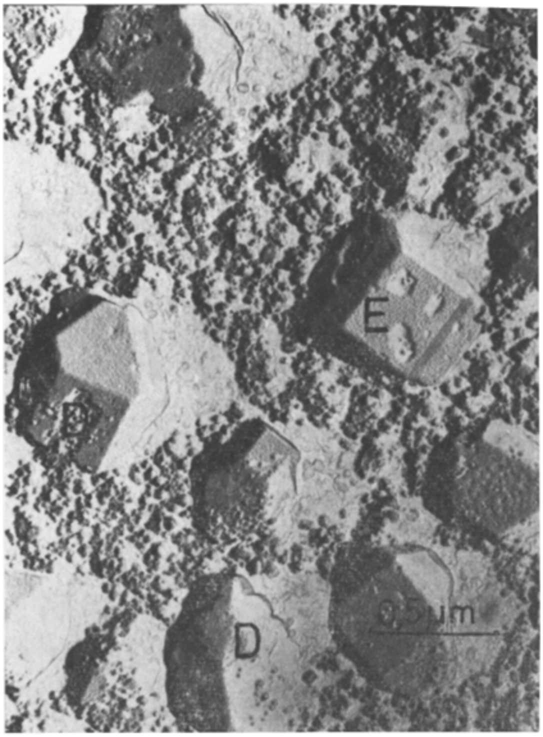

Fig. 5. Surface structure of a 60 nm thick Al film deposited at 300 °C substrate temperature and $K_{\mathrm{oxygen}} \sim 1$. Protruded large crystals of "Hillocks of Type II" and configuration of "Hillocks of Type I" marked by "E" developed on these are shown.

long and thin protrusions like whiskers have been detected in films of higher thicknesses (150 nm) (Fig. 6).

These films present large fluctuations both in thickness and local concentration of built in oxygen [11].

2.1.2. *Al films grown epitaxially on mica**

An unambiguous correlation proved to be existing between contamination level (oxygen and water vapour) and the morphology of these films, too.

At lower contamination level (pressure of residual gases 10^{-4} Pa) using a liquid nitrogen cooling trap and at deposition rate 12 nm/s most of the crystals are grown in the orientation (111) Al//(100) mica, (e. g. crystal marked by A in Fig. 7a.) [14]. These are large and very flat crystals and some of these

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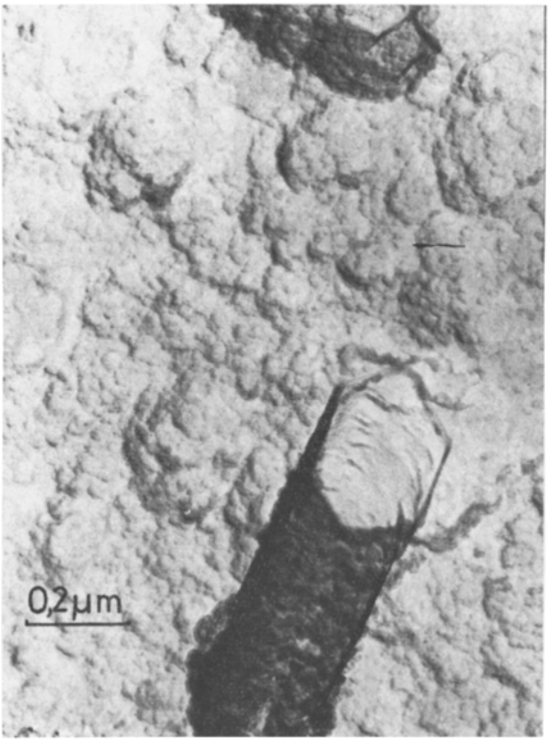

Fig. 6. Long protruded crystals, "Hillocks of Type II", developed in 150 nm thick Al film deposited at 300 °C and $K_{\mathrm{oxygen}} \sim 1$

have facets. Their shapes are the same as given by MATTHEWS for films grown epitaxially on NaCl [15]. There are, however, crystals protruded randomly which can be considered as Type II hillocks. They have a different orientation i. e. (312) Al//(100) mica determined by SAD in films detached from mica substrate and studied in TEM (marked by B in Fig. 7). The shapes of these seem to be partially destroyed by the probably crystalline oxide coverage developed.

The crystallites of the orientation (111) Al//(100) mica seem to be coalesced without contraction while the protruding ones oriented (312) Al//(100) mica were developed mainly by liquid like coalescence (indicated by the large empty surface areas surrounding these crystals). It is remarkable that the surface of the large flat crystals oriented (111) Al//(100) mica and developed by coalescence are smooth without any detectable steps or bunches of steps on their surfaces. Because the individual crystals could have usually different heights before the coalescence as shown in Fig. 8, the smoothing of the surface of the developed large crystal has to be a very fast process.

At a higher contamination level (pressure of residual gases 5.10^{-4} Pa, without liquid nitrogen cooling trap, deposition rate 1,2 nm/s) most of the

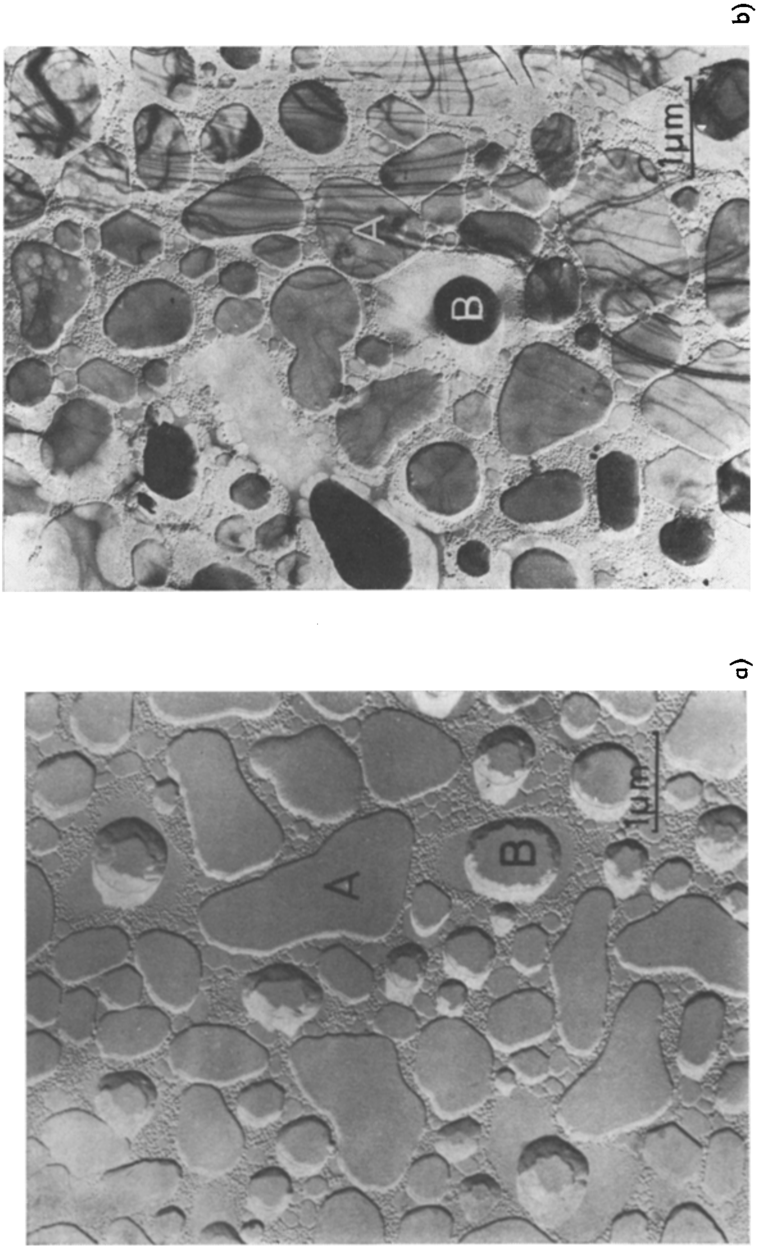

Fig. 7. **Al film deposited onto mica substrate at a temperature of 550 °C, deposition rate 12 nm/s and at 10^{-4} Pa using liquid nitrogen cooling trap. a) surface replica; b) TEM image (film is supported by at hin sheet of mica and shadowed by Pt at 30°.)**

crystals are grown also in the orientation of (111) Al//(100) mica but they have rather rough surfaces (Fig. 9). Bunches of steps can be identified inside the single crystals developing hillocks of Type I and dents as in the case for films grown on glass substrates. It is also shown in Fig. 9 that grain boundaries can protrude according to differences in the heights of the coalescing crystals.

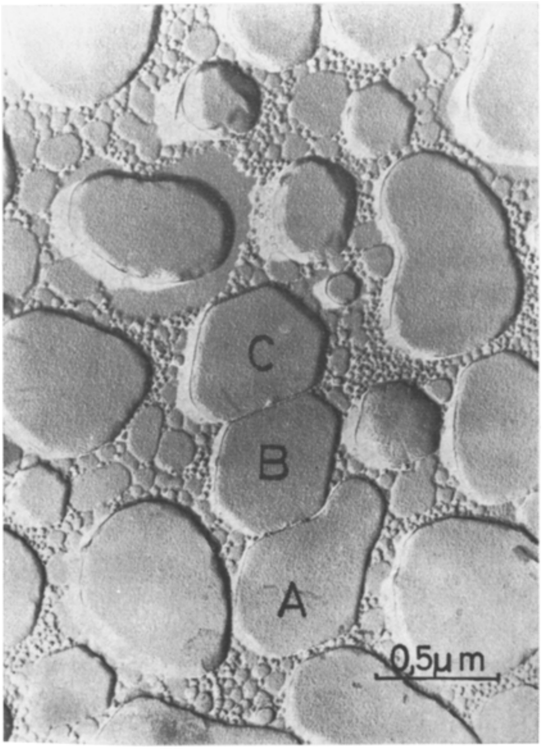

Fig. 8. Adjacent crystals of different heights developed in an Al film deposited onto mica substrate at a temperature of 550 °C, 12 nm/s and at 10^{-4} Pa (marked by A, B and C)

2.2. Growth hillocks in Bi films deposited onto glass and mica substrates [16]

Protruding crystals in continuous Bi films have been found to develop by increasing thickness both on glass and mica substrates. This type of protrusion is similer to hillocks Type II in Al films. The SAD in TEM of the shadowed samples detached from the substrate proved these crystals to be misoriented. They have C-axis perpendicular to the substrate while the C-axis of most crystals is parallel to the substrate.

3. Discussion

The analysis of the experimental results revealed both the types of hillocks and the role of impurities in the development of the various types. A pronounced effect of oxygen has been found in the case of Al films and an unambiguous correlation between the level of oxygen contamination and the types of hillocks could be determined.

3.1. Types of hillocks

Two characteristic types of hillocks have been identified:

Type I: protrusions developing inside large crystals; they have the same orientation as the basic crystals; they are bounded by surfaces covered by layers of impurities or their compounds; growth takes place on their top planes.
The growth of these hillocks is correlated to the building in and the local surface accumulation of the foreign impurity species.

Type II: Single crystals protruding over the average surface plane of the film; they are characterized by the development of low index faces bounding their points; their growth is correlated either to the difference in the growth rate at different crystallographic directions (e. g. in the case of Bi) or to impurity effects.

3.2. Formation mechanisms of growth hillocks

Impurities (residual gases or vapours) play a very important role in the development of growth hillocks. They participate in the atom-by-atom building up process. Their influence on these results also in the realization of conditions which can promote the special growth or coalescence of some crystals developing hillocks. By analysing the formation mechanisms of thin films from the point of view of impurity (gases) incorporation, we can get also direct information on both the nature of impurity uptake properties of the different crystallographic faces and the accumulation, as well as on the development of new phases or compounds important for the understanding of some phenomena of the real crystal growth. We are now also in the very propitious moment when the surface studies presented new and very important results both on the surface-vapour interactions and on the nature of the bonds developing between the surface layer and the adsorbed species [17, 18, 19, 20, 21] which support the ideas of hillocks formation presented in this paper.

As usual, the growth of polycrystalline thin films can be divided into the following stages [22, 23, 24]

a) Nucleation

b) Growth of nuclei developing isolated islands (single crystals or liquid/solid amorphous grains)

c) Growth of isolated islands

d) Coalescence of adjacent islands producing either liquid droplets or larger single crystals. (Liquid-like coalescence leaving bare area of substrate. Secondary nucleation in the clear area.)

e) Coalescence of adjacent single crystals developing larger islands composed of numerous crystals (growth coalescence). Development of channels and holes.

f) Filling the channels and formation of continuous film.

g) Growth of crystals in composite islands and in the continuous film: lateral growth increasing the grain size; perpendicular growth increasing the film thickness.

In addition to nucleation three basic processes can be considered as governing the film growth:

A) Development of the structure by the atom-by-atom process (growth of single crystals — layer growth; growth of liquid droplets or solid amorphous networks). These are the basic processes in growth stages b, c and g and exist also in the stages e and f.

B) Coalescence by melting or surface diffusion characterizing the growth stages d and e.

C) Recrystallization in the growth stages e and g.

The influence of residual gases on the structure and properties of films is studied in numerous experiments but the mechanisms by which their influence is realized are not well known yet. These problems are discussed by BARNA et al in a paper dealing with the surface chemical interactions where the possible mechanisms which can result in the codeposition of impurity species during film formation are reviewed [17].

The environment—film interaction takes place on the developing film surface, therefore process A is influenced directly by this. Its direct influence in process B can be neglected first of all in the case of liquid-like coalescence. Process C, the recrystallization is mainly a "bulk" process, determined by the structure developed during processes A and B.

In what follows we are summarizing the phenomena related to impurities which can contribute to the development of hillocks.

i. Accumulation of impurity species can take place on the growing crystal faces by the atom-by-atom and layer growth processes, by the replacement of the impurity atoms bonded in precursor state by the impinging film adatoms and by the formation of stable phases or compounds developing

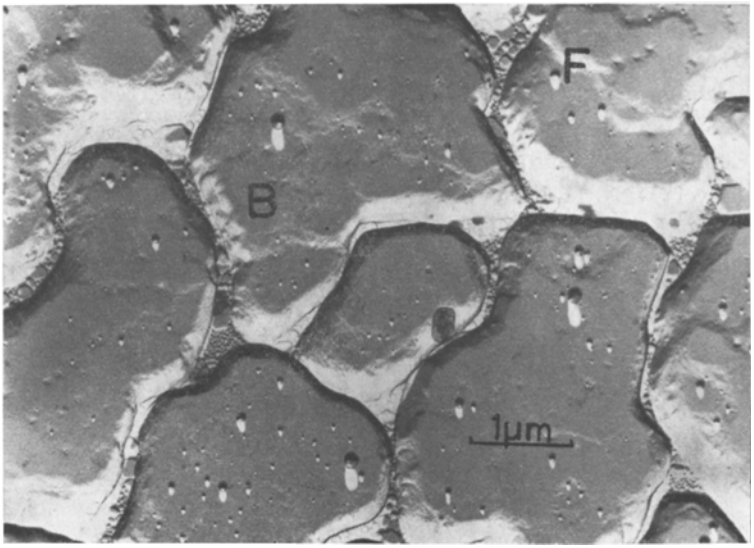

Fig. 9. Surface structure and morphology of crystals grown in Al films deposited onto mica substrate at 550 °C, deposition rate 1,2 nm/s, $5 \cdot 10^{-5}$ Pa without cooling trap. "Hillocks of Type I" (marked by B) developed inside the single crystals and protruding grain boundaries covered by oxide (marked by F) are shown.

two or three dimensional layers covering the surfaces of the growing islands partially or completely [11].

ii. The binding and arrangement or rearrangement of impurity species on the various crystallographic faces can be very different during the precursor state. The very recent results of MARTINSON et al [18], JOHANSSON et al [19], HOFMANN et al [20] and MICHEL et al [21] on Al proved that oxygen species are situated outside the surface atomic layer of the (111) face while they are arranged on the surface both in the "bridge" and "well" positions of (100) faces. For the (100) face they have found that oxygen is penetrating into the bulk and oxide phase is developing at lower coverage.

iii. According to these results the participation of oxygen species in the growth mechanism can be varied on different faces. On the (111) face they can be collected and accumulated by the layer growth mechanism mentioned in point i. [11]. On the (100) face the oxygen species can be "absorbed". It follows that oxygen species will be accumulated at edges between (111) faces by the layer growth while those drawn by the growth steps to the edges between (111) and (100) faces will be "absorbed" by the (100) face near to this edge. As a result of the selective surface accumulation of oxygen species a surface oxide layer starts to develop mainly at the corners and along the edges between (111) faces and destroy the edges themselves (Fig. 10 and Fig. 4 in [17]).

iv. This mechanism can promote the growth of hillocks of Type II (or whiskers) shown in Fig. 4 which have points of truncated octahedrons. These

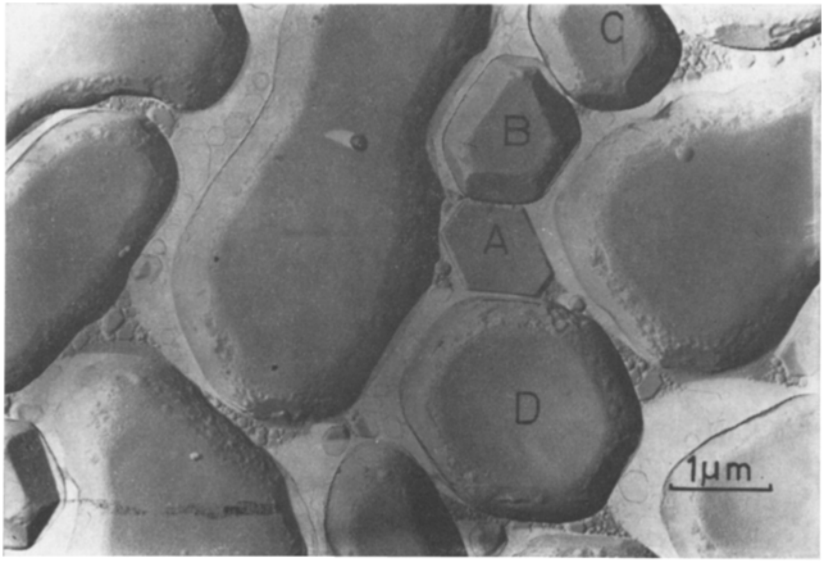

Fig. 10. Surface structure and morphology of crystals grown in Al film deposited onto mica substrate at a temperature of 550 °C, 12 nm/s and at 10^{-4} Pa. The presence of covering oxide layers is to be seen on the surfaces of crystals marked by A, B, C and D resulting in the development of new crystallographic faces. Crystal B is rotated by 60° from the position of crystals A, C and D.

hillocks are bounded namely by (100) and (111) faces as well as by edges between (111) and (100) faces.

v. A significant local concentration of foreign species (impurities or doping elements e. g. Ni, Cu) is required for the nucleation of their stable phases or compounds [25]. Layers or three dimensional segregates of the foreign species or their compounds can be formed on surface areas of growing crystals determined by the mechanisms mentioned above. New crystal faces can start to develop as illustrated in Fig. 10, namely the covering impurity layers can hinder or stop the crystal growth locally.

vi. The coalescence by adjacent crystals is controlled both by their sizes and orientation as well as by the surface covering impurity layer developed before.

4. Summary

The basic features of the formation of different types of hillocks can be summarized as follows:

a) Differences in the growth rate at the various crystallographic directions (formation of Type II hillocks, e. g.: Bi films [16]).

b) Condensation of foreign species accumulated on the surface of the growing crystals

— Development of covering layers on the surfaces of individual single crystals before coalescence. They can control the type of coalescence: liquid-like in case of pure contacting surfaces (formation of Type II hillocks) growth coalescence in the case of covered surfaces.

— Development of the coverage of growth steps resulting in the formation of bunches of steps inside large single crystals (formation of Type I hillocks).

— Selection of crystals of favoured orientation when there is a difference in the uptake properties and in the binding conditions of foreign species on the various crystallographic faces (formation of Type II hillocks).

c) Selection between liquid-like and growth coalescence by the relative orientation interface energy of contacting crystals (formation of Type II hillocks).

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