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MICROSTRUCTURE AND SURFACE MORPHOLOGY
EVOLUTION IN THIN FILMS
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"Diagnostics and applications of thin films"
"Formation and characterisation of the structure of surface coatings"
"Fundamental structure forming phenomena of polycrystalline
films and the structure zone models"
"Growth mechanisms of polycrystalline thin films"

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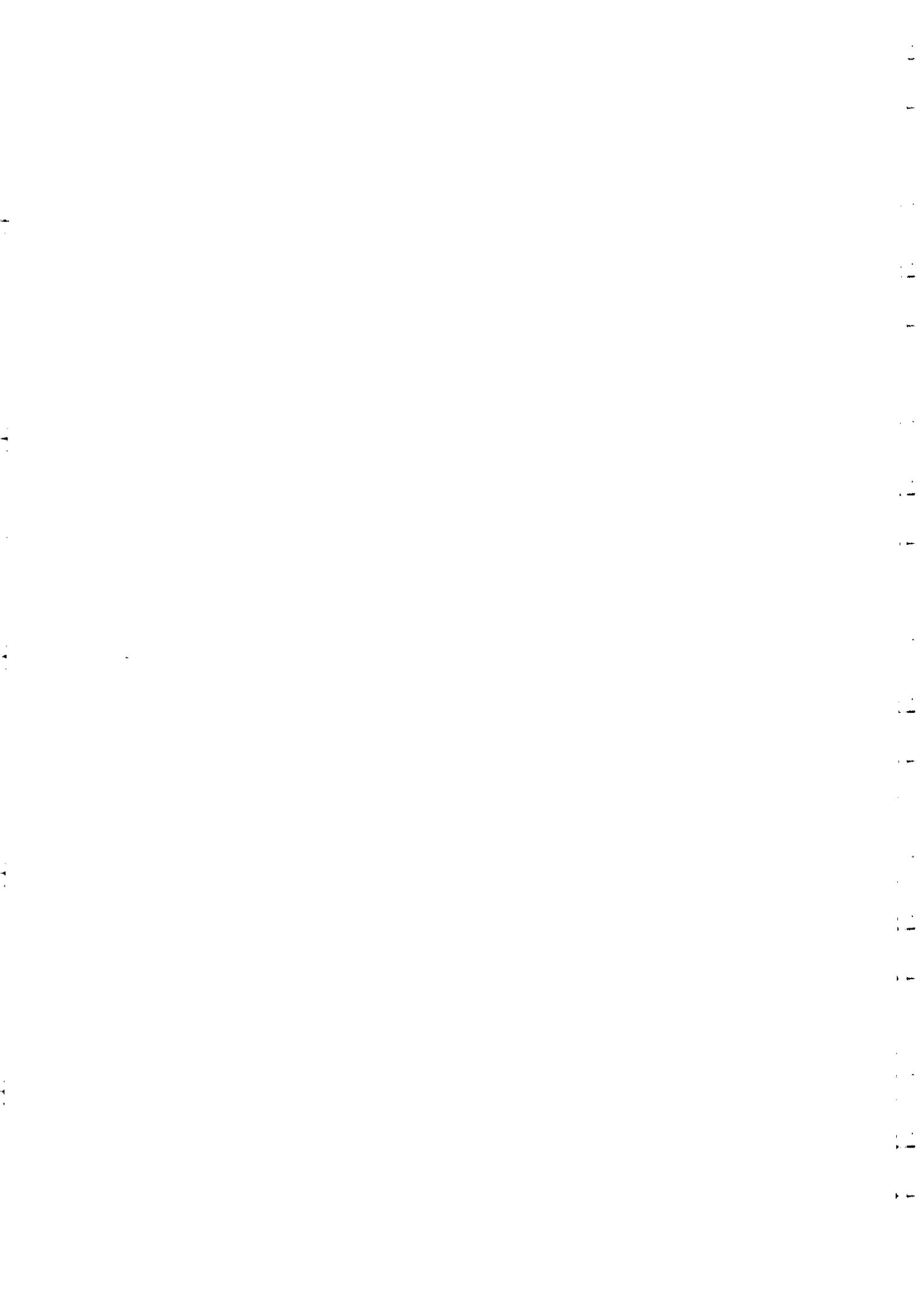
Diagnostics and Applications of Thin Films

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Crystal growth and recrystallization during structure evolution of thin films

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ABSTRACT: The growth and coalescence of crystals are used to describe the structure evolution of polycrystalline thin films. These processes are unique to each stage of structural evolution of the film. This is because the structural conditions controlling these processes are unique in each growth stage. The evolution of specific morphologies and textures in polycrystalline thin films are discussed by considering the process induced segregation of codepositing impurities and additives and by their accumulation on the surface of growing crystals.

1. INTRODUCTION

Polycrystalline thin films are applied in advanced technologies and in a wide range of devices and components including magnetic storage, optics, sensors, hard surface coatings, etc. Structure zone models have been derived to describe the vide variety of growth morphologies characterizing the polycrystalline thin films. (Thornton 1977, Messier 1984). These models clearly demonstrate the high sensitivity of the structure evolution against the preparation parameters.Beside certain parameters which can be determined (or monitored) with higher or lower accuracy (e.g. substrate temperature, impinging rate of adatoms, film thickness, etc) there are others which cannot be (or are not) identified and determined in many experiments. Among these latter ones the presence of various kinds of impurities (environmental, substantial or doping ones) are considered in the interpretation of the various peculiarities in the structural and physical properties found in numerous experiments (Stowel 1969; Francombe 1965; Pócza et.al 1974; Reicha and Barna 1980; Guenther 1982; Pulker 1982; Barna 1983; Van der Kolk and Verkerk 1986; Hashimoto et.al 1989).

The present paper is going to discuss the crystal growth phenomena which control the structural evolution of polycrystalline thin films. Special attention will be paid to the understanding of the effects of codepositing species of impurities and additives on these phenomena. The process induced segregation of these species and their accumulation on to the surface of growing crystals is considered as the most important phenomenon in these multicomponent systems.

The terms "adatom" will indicate the species of the main component, while "impurity species" the impurities and additives.

2. GROWTH STAGES AND PROCESSES OF THE STRUCTURE EVOLUTION OF POLYCRYSTALLINE THIN FILMS

From the results of early in situ transmission electronmicroscopic experiments (Pashley et al 1964; Stowell 1969; Barna et al 1969; Pocza et al 1974) the structure evolution of polycrystalline thin films can be grouped into characteristic growth stages (Figure 1). The atomic processes which create the polycrystalline thin films are identical to the processes of crystal growth. They are unique to each stage of the structure evolution of the film. This is because the structural conditions of each growth stage are unique, and the crystal growth processes in each stage are determined by the structural conditions developed during the previous stage.

Table summarized the processes of crystal growth in the stages of film evolution as well as the structural conditions unique to each stage.
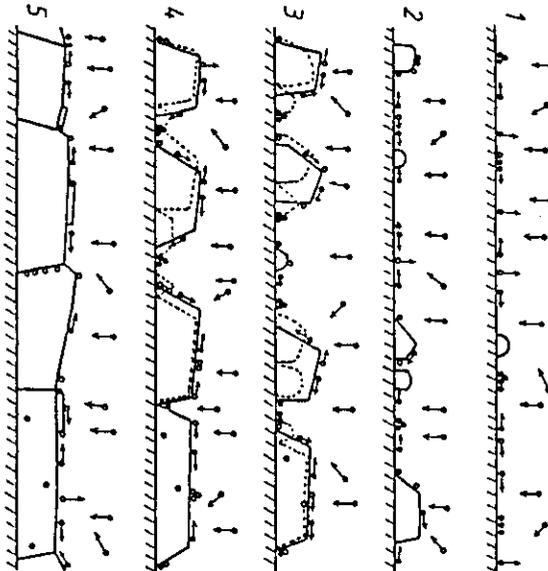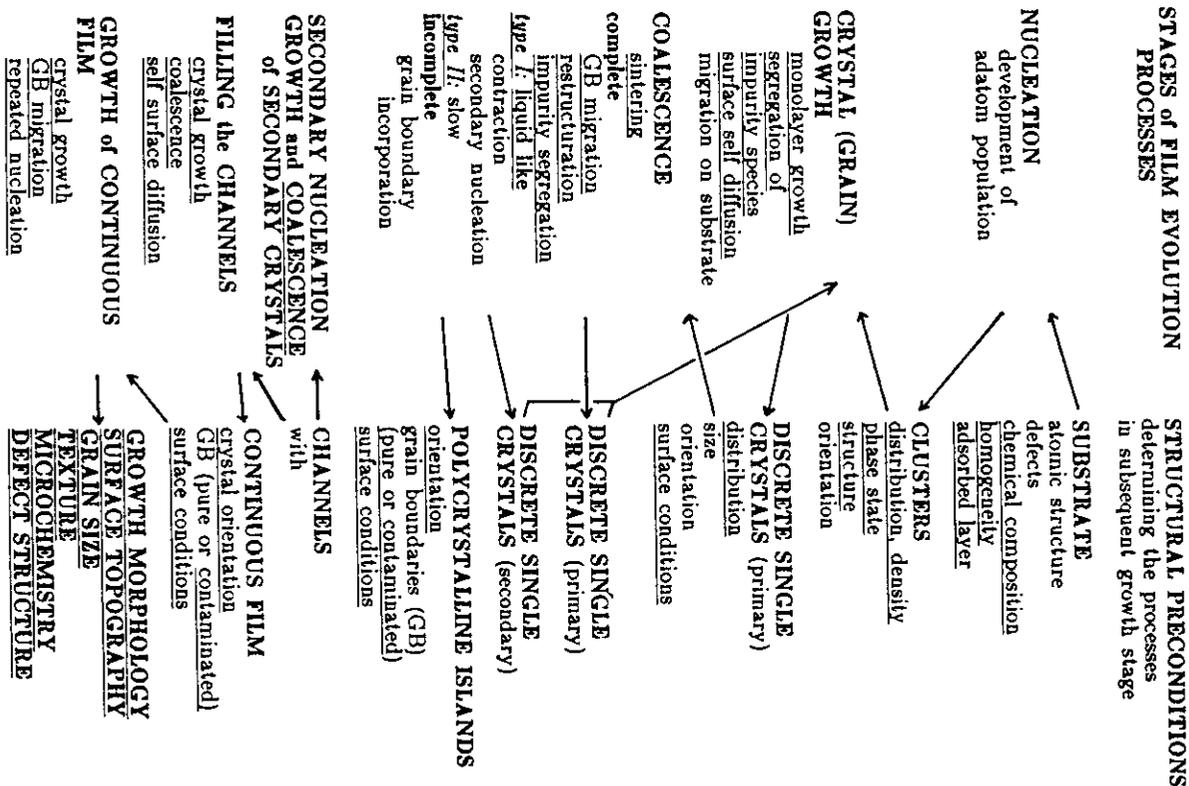
1

2

3

4

5

Fig. 1. Stages of structure evolution in polycrystalline thin films. 1: nucleation; 2: crystal (grain) growth; 3: coalescence; 4: filling the channels; 5: growth of continuous film. Crystals before coalescence are marked by broken line; dark sircles mark adatoms, bright sircles impurity species.

2.1 The nucleation stage

The condensation starts by nucleation developing clusters of solid (crystalline, amorphous), or liquid phases. The sites of nuclei are connected in many cases to active centres present on the substrate surface (e.g. defects, impurity islands, etc). On defect free and homogeneous substrate surfaces the kinetics of statistical nucleation is determined by the development of the adatom population (Zinsmeister 1968). This in turn is controlled by the substrate temperature, the rate of impinging adatoms, and by the adsorption and diffusion energy between the substrate and adatoms. The phase states of nuclei are determined by the melting point of condensing material, by the substrate temperatu..., the adhesion energy, and by the presence of other

T A B L E   I

STAGES of FILM EVOLUTION PROCESSES	STRUCTURAL PRECONDITIONS determining the processes in subsequent growth stage
NUCLEATION development of adatom population	**SUBSTRATE** atomic structure defects chemical composition homogeneity adsorbed layer
	CLUSTERS distribution, density phase state structure orientation
CRYSTAL (GRAIN) GROWTH monolayer growth segregation of impurity species surface self diffusion migration on substrate	**DISCRETE SINGLE CRYSTALS (primary)** distribution size orientation surface conditions
COALESCENCE complete GB migration restructuration *type I:* liquid like impurity segregation *type II:* slow contraction secondary nucleation Incomplete grain boundary incorporation	**DISCRETE SINGLE CRYSTALS (primary)** **DISCRETE SINGLE CRYSTALS (secondary)** **POLYCRYSTALLINE ISLANDS** orientation grain boundaries (GB) (pure or contaminated) surface conditions
SECONDARY NUCLEATION GROWTH and COALESCENCE of SECONDARY CRYSTALS	**CHANNELS** with
FILLING the CHANNELS crystal growth coalescence self surface diffusion	**CONTINUOUS FILM** crystal orientation GB (pure or contaminated) surface conditions
GROWTH of CONTINUOUS FILM crystal growth GB migration repeated nucleation	**GROWTH MORPHOLOGY** **SURFACE TOPOGRAPHY** **GRAIN SIZE** **TEXTURE** **MICROCHEMISTRY** **DEFECT STRUCTURE**

material(s) (impurities). The nucleation of elementary semiconductor thin films (e.g. Ge, Si, Sb) takes place in the solid amorphous phase, while metals with low melting points nucleate in liquid phase at high temperatures. Semiconductors nucleate in the solid amorphous phase because this structure has lower free energy in small clusters than does the crystalline phase [Grigorovici and Manaila 1969]. The liquid phase of metal nuclei results from the decreased melting temperature of submicroscopic particles [Barna et.al 1969], which depends also on the interface energy between the substrate and the deposit and on the substrate structure.

Inhomogeneities in the structure and/or in the chemical composition of substrate surface produce changes in the local nucleation conditions and show up as decoration patterns both on single crystal surfaces and on amorphous substrates (Figure 2.).

The transformation of amorphous or liquid phases into crystalline ones can take place during post nucleation stages.
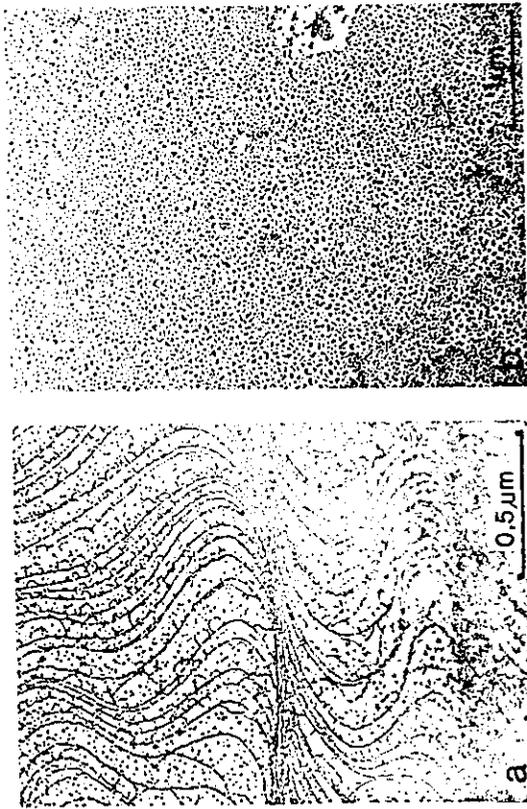
Fig. 2. Decoration patterns of nucleation reveal the active sites (a) and the surface inhomogenities (b) of the substrate surface. a) preferential nucleation of 1 nm thick Au (upper) and 2 nm thick SiO$_x$ (lower) deposit on air cleaved NaCl (001) surface; b) 1 nm thick Ag decoration pattern on a contaminated glass substrate.

2.2 The crystal (grain) growth stage

Nucleation is followed by the growth of discrete crystals dispersed on the substrate surface. Disregarding the fact that their adatom collection areas may overlap, such "primary crystals" grow independently of each other. The growth of these single crystals follow the well known phenomena of crystal growth. The orientation and defect structure of the crystals as well as how they are situated on the substrate will control the crystal growth processes.

The growth of the discrete single crystals takes place by joining the adatoms impinging directly from the vapour beam onto their surface and by the flux of adatoms adsorbed on the substrate surface which migrate to the crystals. In the very early stage of film formation, when the crystals are small, the latter process dominates.

A precondition for the growth of these crystals is that they be situated on a substrate. The arrival of adatoms is not isotropic but usually follow well defined vapour beam. The substrate affects the monolayer growth of single crystals if intersections between the substrate and the side faces of crystals are active in the nucleation of bidimensional monolayers. This will namely determine the moving direction of growth steps across the crystal faces. Since it is very important to understand the effects of codepositing impurities or additives in this stage, this point will be discussed in greater detail later.

The presence of a vapour beam affects the impinging rate of adatoms on the various crystal faces, and can control their rate of growth. Self surface diffusion of adatoms can be reduced by lowering temperature or by the presence of impurities on the crystal surface. In such circumstances the direction of the vapour beam will strongly influence the structural evolution of the film.

2.3 The coalescence stage

A very specific growth stage in the structural evolution of thin films is the coalescence of crystals (and/or liquid droplets). Coalescence takes place when the growing adjacent grains approach and touch each other. This is a process during which the previously isolated grains interact by interfusing their structures. At the moment of coalescence a new structural element is formed. The intergranular area developes, and the coalescing crystals will mutually influence the reorganization and growth of their structures.

The sintering phenomena are used to describe the coalescence (Pashley et.al 1964; Stowell 1969; Pashley 1975). Accordingly, the main processes of coalescence are: (i) the neck formation, (ii) filling the necks by surface self diffusion, (iii) formation of intergranular structure (grain boundary) upon joining of the lattices of crystals, (iv) moving out of the grain boundaries (GB) by diffusion controlled grain boundary migration (recrystallization). The coalescence can be considered "complete", when all the above mentioned coalescence can be considered "complete", when all the above mentioned processes have taken place, and "incomplete" when recrystallization has not taking place (Barna 1983).

During complete coalescence the structures (including also the orientation) of one or all of the participating crystals are reorganised. Complete coalescence results in the formation of new discrete single crystal (Figure 3a). Incomplete coalescence (Figure 3b) produces some kind of intergranular area containing defects, large or small angle grain boundaries, which are sometimes contaminated. The coalescence will be incomplete when the grain boundary cannot move out before the island engages in another coalescence, which develops unfavourable geometry for the grain boundary migration (Figure 4). The grain boundary migration can also be restricted by low temperature, by contamination (Figure 7) or larger grain sizes (Figure 4).

The results of in situ electronmicroscopic experiments (Pashley et.al 1964; Barna et.al 1969; Honjo and Yagi 1980) have revealed two types of coalescence. Type I. is a very fast phenomenon, like the coalescence of liquid droplets and is called "liquid-like" coalescence (Figure 3a). Liquid like

coalescence, typical in the case of small crystals, is a priori complete coalescence and results in the development of three—dimensional, generally equiaxial single crystals. It is accompanied by a strong contraction of the coalescing crystals leaving bare area on the substrate. In these areas condensation results in secondary nucleation and the growth of new grains, or "secondary crystals".
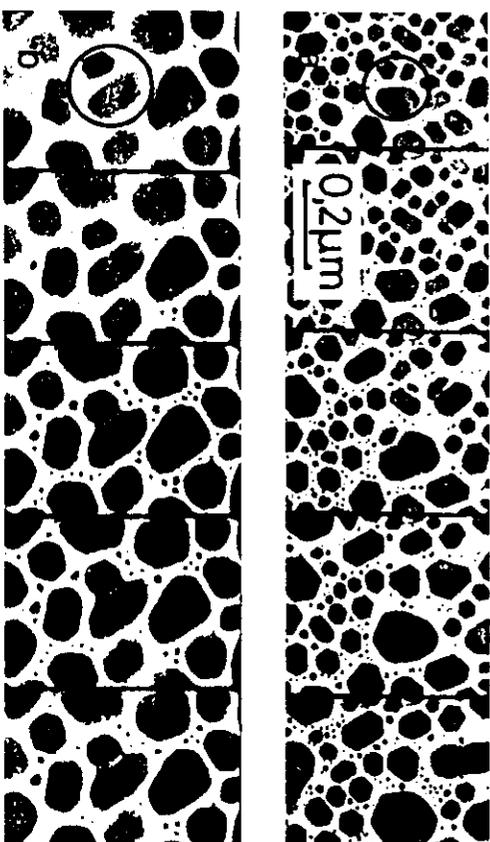
0.2μm

0.5μm

Fig. 3. Two types of coalescence of In crystals at 20°c (in situ TEM experiment a: Type I liquid like, complete coalescence and secondary nucleation; b: type II incomplete coalescence, incorporation of grain boundary.

¹ Type II, coalescence proceeds rather slowly (Figures 3b and 7). This coalescence can be complete (Figure 7) or incomplete (Figure 3b) but develops two—dimensional islands of generally irregular and sometimes scalloped shapes. Islands formed by coalescence are incomplete polycrystalline and their surface reflects the morphology and orientational relationships of crystals (Figure 4).

Fig. 4. Islands of Al crystals developed at 200°C on Si wafer covered by SiO₂, Pt+C replica.

The complete coalescences of both types result generally in the reorientation of crystals. Discrete primary crystals which develop on amorphous substrates are randomly oriented whether developed by nucleation or by crystallization of discrete amorphous grains or liquid droplets.

Any ordering of crystals (e.g. a texture) will develop during the series of complete coalescence processes of either, type. (Barna et.al 1969; Pócza et.al 1970; Pashley 1975). Under ideal conditions (i.e.high purity) the reorientation will follow in the directions of the interface energy between crystal and substrate which is determined partly by the reduced free energy state. At the growth stage when the coalescence of partly by the size of crystals.At the growth stage when the coalescence of primary grains (crystals) starts, grains with nearly the same sizes are coalescing and crystals with nearly equal sizes develop. These first coalescences and the consecutive coalescences of primary crystals are contributing to the ordering of crystal orientation, to the development of texture. However crystals growing by secondary nucleation in the vicinity of large primary crystals will have small sizes when they will approach and coalesce the primary ones. This coalescence can influence only slightly the orientation relationships of the primary crystals. The material of secondary crystals will increase the volume and slightly the size of the large primary ones. The coalescence of secondary crystals will leave bare area again on the substrate and the processes of secondary nucleation and grain growth repeat themselves. That is why channels between the islands of primary crystals can exist for rather long period of film growth and why the primary crystals can collect more material than that transported by the impinging vapour flux direct to their surface. When analysing the films of channel structure by selected area electron diffraction, the coexistence of texture and random orientation can be detected. The diffraction pattern due to the random orientation is produced by the secondary crystals present in the channels.

The above mentioned phenomena characterizing the complete coalescence, have strong influence on the structure evolution mainly when complete coalescences exist for a long periode of structure evolution. (E.g.the grain size, defect structure, orientational relationships of crystals and the texture will be determined by this way.) The nucleation stage has a less influence on structure evolution in that case.

2.4 Crystal growth in polycrystalline islands and in continuous polycrystalline films.

The structure of films in these growth stages are characterized by the presence of grain boundaries of various types and by the various orientations of crystals. (Radnóczi 1984) (Figures 1,4 and 5). Consequently one has to take into consideration, that the growth of different crystals proceds by the monolayer growth of different crystal faces. Grain boundaries are protruding to the film surface and can present preferential sites for monolayer nucleation (Barna et.al 1988). Growth competition can develop between the different crystals with different orientation and they can overcom each other. This idea was applied to explain the development of growth morphologies in thick films where numerous crystals are crushed down in the vicinity of substrate.

Grain boundaries can be displaced resulting in grain coarsening and recrystallisation during the deposition.

These considerations are related to ideal, one component systems. In that case the elementary processes and the structure evolution are determined by the

properties of substrate and film materials as well as by the substrate temperature. (The effects of high energetic particles are not considered here). What conclusions can be drawn? These films will have few bulk defects, the grain boundaries will be mobile and the structure could be modified by heat treatment. The surface topography will reflect the sizes and orientation relationships of the crystals. The surface of film will be set up from smooth crystal faces and be like the surface of polycrystalline NaCl films (Figure 5a.). (Krohn 1989).
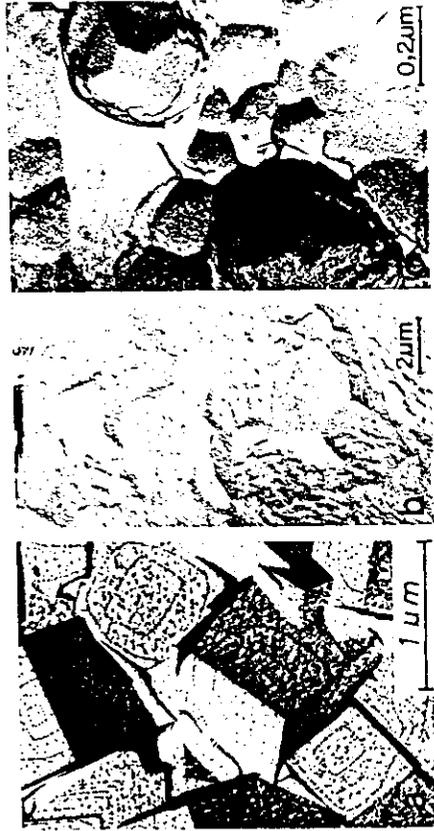
1 um   2µm   0,2µm

Fig. 5. Surface growth topography of polycrystalline films (Pt+C replica) a: 1 μm thick NaCl film deposited at 350°C on amorphous carbon layer and decorated by Au (Krohn 1990, with the permission of author); b and c: 1 μm thick Al films deposited at 300°C and at 5*10⁻⁵ Pa oxygen (b) and 5*10⁻⁴ Pa oxygen (c) partial pressures.

In the majority of real films the structure and structure evolution are however very different from this ideal one. This is mainly due to the effects of impurities present in the environment, in the evaporated material or are desorbed from the source and from its surroundings. (Barna 1983). Figures 5b and c show the surface topography of 1 μm thick Al films deposited at various oxygen partial pressures at 300°C on a Si wafer covered by SiO_2.

3. THE EFFECTS OF IMPURITIES, ADDITIVES ON THE STRUCTURE EVOLUTION

The analysis of experimental results on thin films and the processes of thin film formation indicated that the various structural characteristics, physical and chemical properties of real films can be understood better when considering the evolution of the film structures as the formation of multicomponent systems (Barna 1983). Here the codeposition of unevoidable impurities should be considered at the first place. The effects of impurities, doping elements, additives or other component materials are very important when their concentrations exceede their solubility limit in the main component
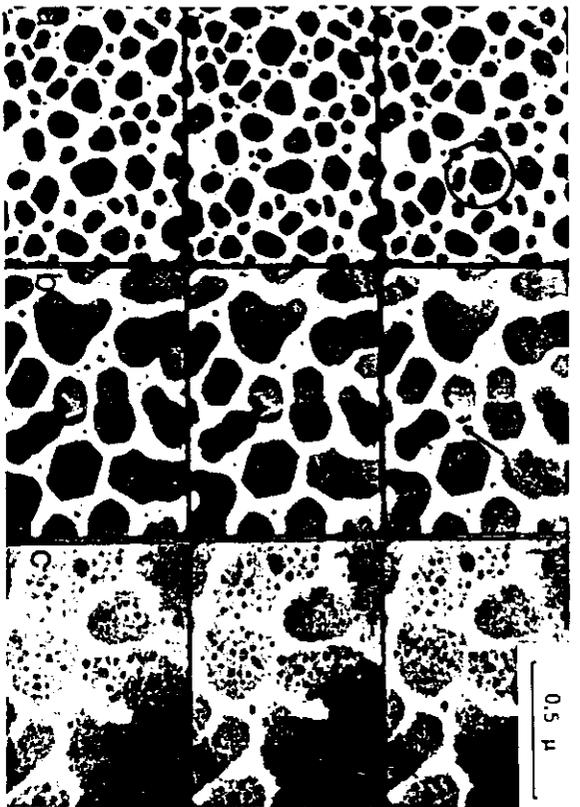
at the given temperature. At these conditions they are segregated during the atomic structure building processes. This is a process induced segregation taking place during the growth and complete coalescence of crystals. This makes the structure evolution very sensitive against the impurities or additives even when their concentration is extremely low (near or below the detectibility limit). It is mainly because the active sites of the growing crystal surfaces at which the structure building adatoms are sticked and incorporated into the lattice, are the most active ones also in binding the impurity species and/or catalysing surface chemical reactions. (Barna et.al 1980). Impurity species have also strong influence on the surface physical processes e.g. by blocking the sources of surface self-diffusion and changing the surface free energy.

The process induced segregation of impurity species accumulates them to some areas of the growing crystal surfaces and develop there a new solid phase. Depending on its surface self-diffusion coefficient, the accumulated component can form three dimensional segregates (Barna et.al 1979, Barna et.al 1991) (e.g. in case of metallic additives, Ni, Sn) (Figures 6 and 11) or two dimensional layers covering larger and larger surface areas of the growing crystals. (Figs 4 and 5b and c).

These segregates or layers will strongly alter or even block the crystal growth locally and can lead to the rounding of crystal shapes as shown in Figure 4. When larger areas of crystal surfaces are covered by these impurity layers by the condensation proceeds in repeated nucleation shown in Figure 5b. This process has been clearly revealed by in situ TEM experiments in the cases of In and Al films and hydrocarbon or oxygen impurities (Figure 7) (Pocza et.al 1974).

0,4µm

Fig. 6. Segregation of Ni during the growth of Al-Ni(5 at%) film at 300°C on silica substrate.

The process induced segregation of impurity species and the formation of new solid phases on the growing crystal surfaces will develop specific surface precoditions for the growth of crystals. They are indicated by underlining in the Table. The modified surface conditions can completely alter both the growth of discrete crystals and their coalescences as well as the growth of continuous films in contrast to the case of ideal film preparation. This is the reason why environmental impurities or codeposition of a second component having low surface self-diffusion coefficient (e.g. SiO_2 in case of metal deposits, cermet films) will result in the rounding of crystals (Figure 4) in the development of broad and deep groves of the surface areas of grain boundaries (Figure 5b) and in the decrease of the grain size. Globular (microcrystalline) or columnar structures are developing by this way, in which the crystals are separated by boundaries covered by an impurity (foreign) phase. Both the grain size and the development of textures are controlled by the impurities (additives). The process induced segregation of additives makes possible to prepare (tailor) specific structures of various phases and microchemistry.

Fig. 7. Segregation of cracking products of hydrocarbon residuals and their accumulation onto the surface of growing In crystals. In situ TEM experiment at 60°C substrate temperature. a: type II complete coalescence; b: type II incomplete coalescence; c: repeated nucleation. Various stages of structural development. The growth proceeds downwards.

The structure evolution itself and the growth morphology and crystal structure of films will be more complicated when the surface chemical interaction of codepositing impurity species with the growing crystal surface is different on the different crystallographyc faces. This has been demonstrated and analysed in detail for the Al and oxygen system. (Barna et.al 1979; Reicha and Barna 1980; Van der Kolk and Verkerk 1986; Barna et.al 1988). Both the development of bimodal grain size distribution in thinner films and the formation of various types of growth hillocks can be explained by this way.

The oxygen species can penetrate into the crystal lattice on the (001) and (110) faces while they are situated on the top of (111) faces. (Michel et.al 1980; Martinson et.al 1979). As a consequence of this the crystal growth on the (001) and (110) faces can incorporate the oxygen species while they are segregated on the (111) faces. These crystal faces have different surface growth topography in the presence of oxygen. (Barna and Reicha 1980) and the edges between (111) faces of Al crystals are rounded at first during the growth of crystals (Figure 8). The development of growth hillocks with points of truncated octahedrons (Figure 5c) can be explained also by this way. (Barna et.al 1980).

Before discussing the model of the segregation of impurity species during crystal growth, two effects of impurities will be referred, which influence the phenomena in the early stages of film formation. The small crystals with
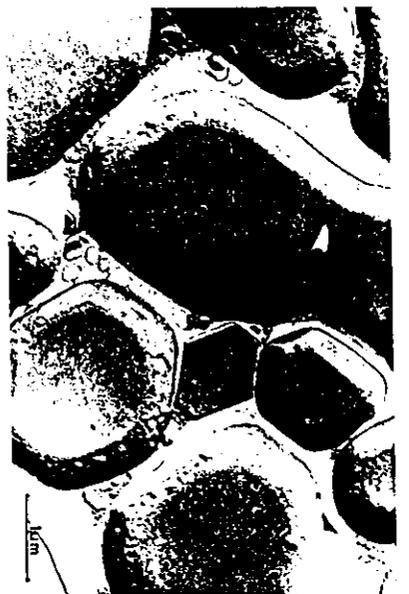
Fig. 8. Al crystals grown in <111> orientation on mica at 450°C. The rounding of crystal shape starts at the edges between (111) faces.

Fig. 9. The effect of contamination on the phase state and morphology of Sn grains deposited on a–C layer at various oxygen pressures. a: $5*10^{-5}$ Pa, b: $5*10^{-3}$ Pa.

contaminated surfaces (e.g. covered by an oxide phase) have higher melting temperature than the uncontaminated ones (Figure 9) (Pócza et.al 1974). Nuclei of predeposited metals can promote the crystallization of solid amorphous phase shown in the case of a–Sb. (Hashimoto et.al 1989).
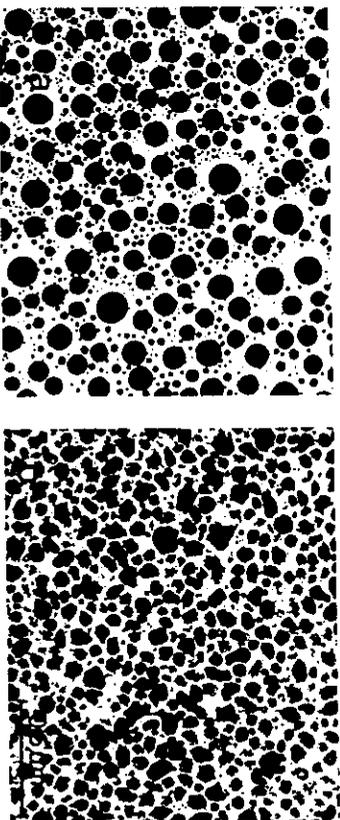
The process induced segregation of impurity species can be discussed by considering the atomic processes of monolayer crystal growth (Figure 10). (Barna 1983, Barna et.al 1988). The adatoms are incorporated at the kink sites of monolayer steps. Impurity species are sticked also at the same sites preferentially. They are generally in precursor state at first with low binding energy. The segregation of impurity species can take place at these sites when impurity species are replaced by an impinging adatom. However the impurity species can remain adsorbed and migrate along the step. This process can be repeated. The moving growth step will roll the adsorbed impurity species along the crystal face. Nuclei of a solid phase of impurity or its compound will develop at some sites of growth step later.

Three dimensional grains will form in the case of impurity with high self surface mobility at these nuclei (Figures 6 and 11). When the segregated

Fig. 10. Model for the segregation of impurity species (dark cubes) at the growth steps. White cubes mark the adatoms.

impurity forms a solid phase with low self surface mobility, the growth steps will becovered by the impurity phase growing along the steps. Bunches of growth steps decorated by pinning sites and deep, broad groves at the grain boundaries develop in that case (Figure 5b). The small crystals developed by repeated nucleation indicate that these groves are covered by an impurity layer (Barna et.al 1979)

Barna et al 1988 proposed a simple model for describing these phenomena and illustrated in the case of Al and oxygen system.

The growth of discrete single crystals situated on a substrate is affected by the segregation of impurity species. A layer of impurity can develop on specific areas of their surfaces when the impurity phase has low self surface diffusion coefficient. These surface areas are determined by the kinetics of the monolayer growth as mentioned before and are detectable by rounding or truncating the crystal shapes (Figures 4, 5 and 8) and by the appearance of bunches of steps decorated by pinning sites (Figure 5) (Barna et.al 1979; Barna et.al 1988).

The growth of crystals at the codeposition of Al and Sn made possible to study the monolayer growth kinetics and the role of the intersection between substrate and the side faces of Al crystals (Figure 11). The segregated Sn develops three dimensional grains which can be well detected (Barna et.al 1991). Sn has been accumulated at the intersection of crystal faces with the amorphous carbon layer substrate (Figure 11a), while Sn islands are formed on the top of Al crystals on NaCl substrate (Figure 11b). One can conclude that the monolayers nucleated on the top faces of Al crystals and the steps moved down to the intersection in case of a–C substrate. The intersection was however active in the monolayer nucleation on NaCl and the steps moved upwards.

The development of impurity layers on the surface of growing discrete crystals can strongly modify both their growth and coalescence. In case of impurities which have different interactions with the various crystal faces (e.g. in the case of Al and oxygen (Martinson et.al 1979; Michel et.al 1980)) these phenomena will strongly depend on the orientation of crystals. The development of bimodal structure in the first stages of film formation can be explained by these effects (Barna et.al 1979; Reicha and Barna 1980).

The oblique incidence of the vapour beam creates new situation in the presence of environmental impurities. Environmental impurity species imping isotropically while adatoms at a given angle in the incidence plane. The

relative impinging rates of adatoms and impurity species will be different on the crystal faces which are parallel or perpendicular to the incidence plane of the vapour beam. Side faces of crystals perpendicular to the incidence plane will be more contaminated than the parallel ones. By this way the coalescence will be more effective at the interfaces parallel to the incidence of crystals can be more effective at the interfaces parallel to the incidence plane than at those which are perpendicular. (The shadowing will increase this effect). This can lead to the development of grains elongated perpendicular to the incidence angle (Hashimoto et.al 1989).

Fig. 11. Segregation of Sn during the growth of codeposited Al–Sn (15 at%) thin films deposited at 210°C. Partial pressure of oxygen was 5*10^-4 Pa. Substrates a: amorphous carbon layer; b: air cleaved NaCl.

The difference in the surface chemical interaction of impurities on the various crystal faces will result in different surface conditions of crystals depending on their orientational relationships to the incidence plane. The author is on the opinion that the changing of <111> texture to <001> and the development of biaxial orientation present in obliquely deposited Al films in an oxygen atmosphere can due to these effects (Figure 12) (Hashimoto et.al 1989).

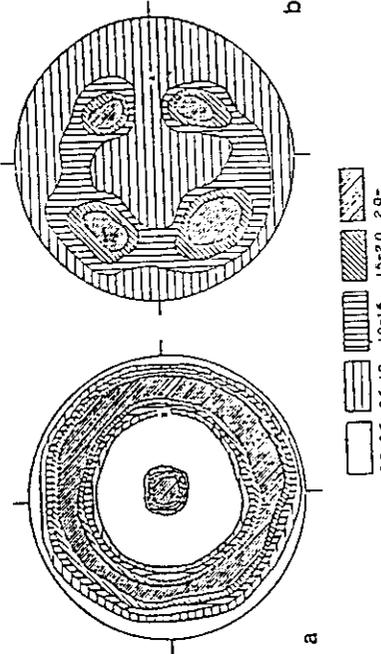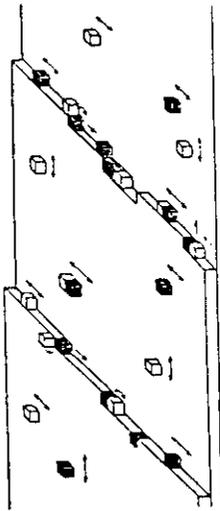0.0-0.5   0.5-1.0   1.0-1.5   1.5-2.0   2.0-

Fig. 12. The 111 pole figures of 1 mm thick Al films deposited at a: 100°C, b: -10°C and under oxygen introduction. The incidence angle of the vapour beam is marked by x. (Hashimoto et. al 1989: with the permission of the authors.)

The results and considerations mentioned above make the idea probable that in the presence of impurity species the coalescence and consequently the development of a texture are primarily controlled by the segregation conditions and by the nature of impurity or its developing solid phase.

The crystal growth in polycrystalline islands and continuous films is controlled mainly by the type and purity of grain boundaries. A model has been proposed for analysing the possible crystal growth phenomena related to grain boundaries with various conditions (Barna et al. 1988).

The intersections of pure grain boundaries and the free surface present active sides for the nucleation of two-dimensional monolayers. The growth steps starts in that case at the grain boundaries and propagate to the centres of adjacent crystal faces. The process induced segregation of impurities at the propagating monosteps will accumulate the impurities at the centres of crystal faces. The grain boundaries and the adjacent surface areas remain pure. This can be an explanation for the development of sharp grain boundary intersections on the surface and smooth crystal face(s) adjacent to these boundaries (Figure 5b). At low concentration of impurities the crystal surfaces far away from these boundaries are truncated and build up from bunches of growth steps decorated by pinning sites. Impurities are accumulated at these surface areas.

Contaminated grain boundaries are however not active in the nucleation. Consequently the monolayers nucleate somewhere within the crystal faces and the monolayer growth steps propagate to the grain boundaries. Impurity species will be rolled to these areas and will contribute to the growth of the impurity layer at the grain boundaries and on the areas of crystal faces adjacent to them. This process results in the development of contaminated grain boundaries and in the formation of deep and broad groves following the grain boundaries. Repeated nucleation will start on these surface areas (Figure 5b). Columnar structure develops in that case with grain boundaries stabilized by contamination. The concentration of impurities in the vapour beam will determine the diameter of columns.

At higher concentration of impurities the impurity layer can cover finally the whole surface of crystals. Their growth will be blocked and the condensation proceeds by repeated nucleation of crystals (Figure 7). These processes will be repeated many times during the deposition. Globular structure develops in that case and the interfaces between the crystals will be covered by an impurity phase. The size of crystals will depend on the concentration of impurities. Microcrystalline structure can be developed also by this way.

4. CONCLUSIONS

The elementary processes of crystal growth in thin films are unique in each growth stage. This is because the structural preconditions of crystal growth are unique. The process induced segregation of impurities and additives determine strongly the evolution of various structural preconditions. This is why various, sometimes peculiar morphologies and structures can develop in thin films deposited at various environmental conditions. The same effects of additives can be used also to govern the structure evolution, i.e. to tailor films with specific morphology, structure and microchemistry.

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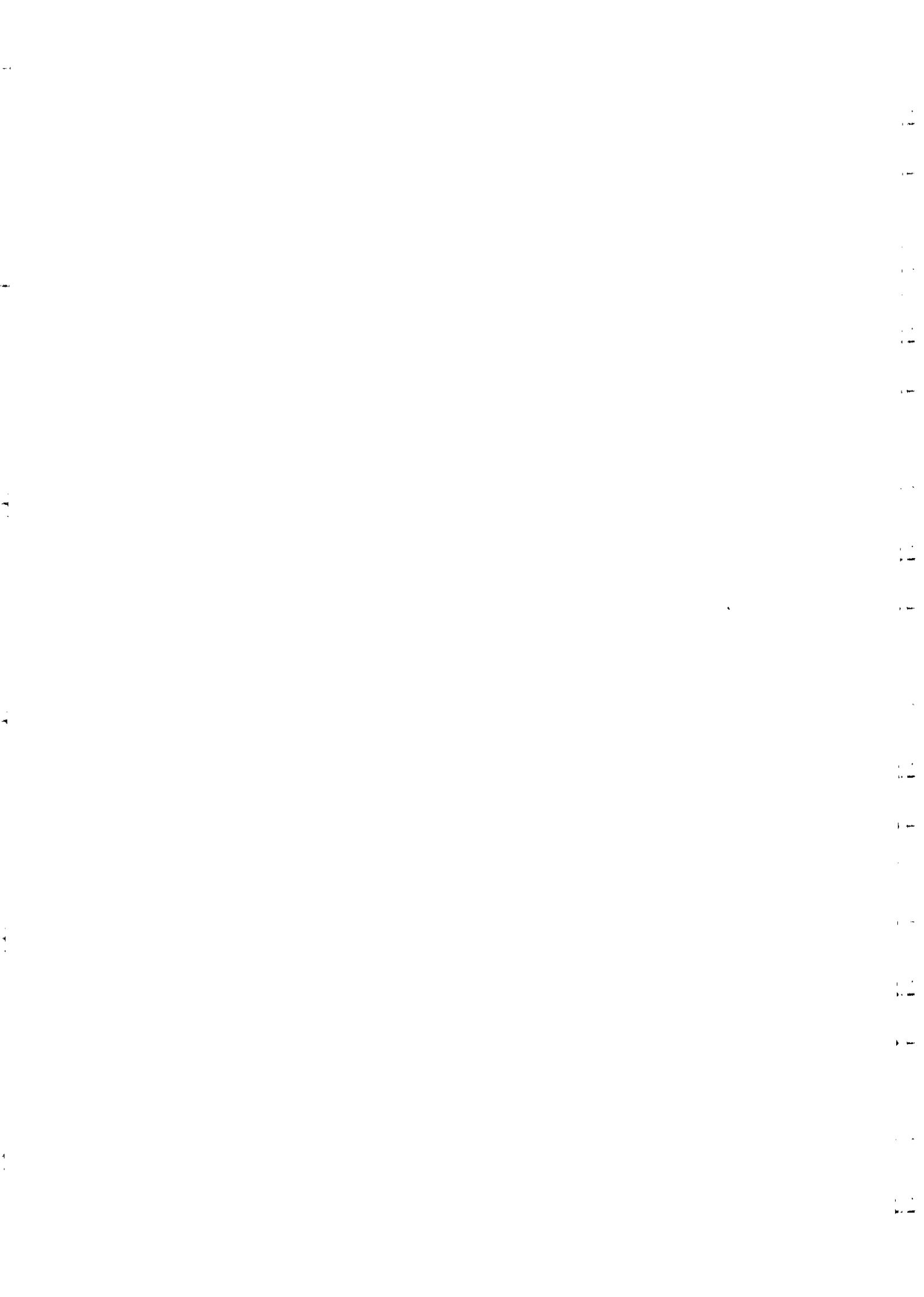
FORMATION AND CHARACTERISATION OF THE STRUCTURE OF SURFACE COATINGS

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ABSTRACT. The formation of surface coatings as polycrystalline thin films is discussed by considering the fundamental structure forming phenomena: nucleation, crystal growth, grain growth by grain boundary migration and process induced segregation of impurity species forming new phases on the crystal surface or at grain boundaries. Universal structure zone models are constructed by using the fundamental structure forming phenomena for describing the various structures found in polycrystalline coatings. The correlation between the evolution of morphology and orientation of the crystals is analysed together with the formation mechanisms of various textures and with the decisive role of active impurities in these mechanisms.
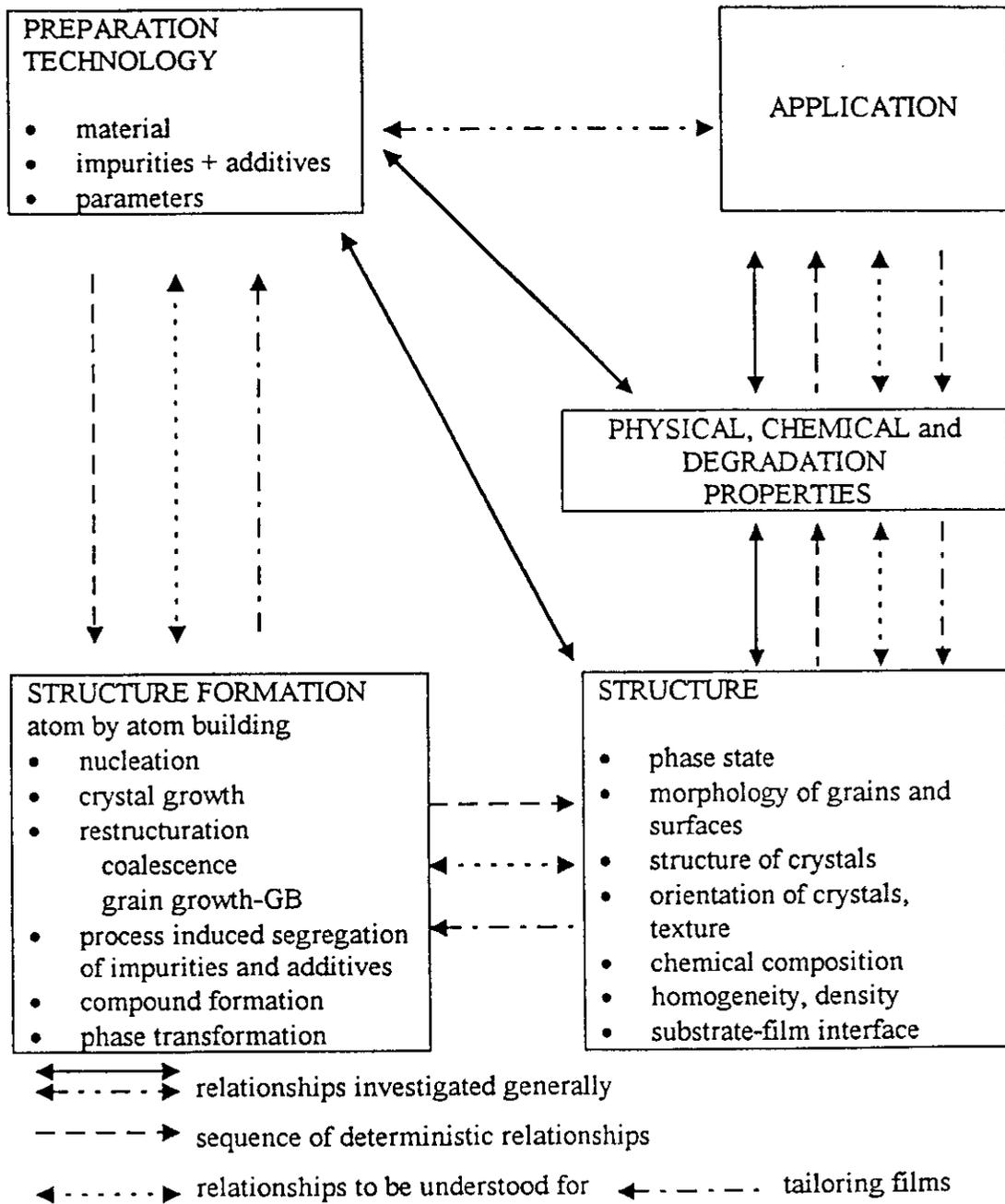
1. Introduction

Polycrystalline surface coatings used in various fields of applications exhibit a wide variety of the morphology and orientation relationships of crystals. The most general morphology of crystals of various dimensions are the columnar, V shaped, dendrite like and three equiaxial/globular, while the orientation relationships can be the random, the one order (I-O) and two order (II-O) textures [1]. In many cases the I-o textures or fiber textures contain coexisting components with different crystallographic axes. It has been generally found that both the grain morphology and the developing textures are sensitive to the environmental impurities being present during the film preparation characterising the applied technology as well as to the applied additives [2]. Surface coatings, first of all the protective coatings require high density structure i.e. compact grain boundaries.

Both the experimental results and the theoretical considerations on the structure-property relationships of surface coatings require not only the description of the as-received structures, but also the understanding of their formation mechanisms and the dependence of these on the technological parameters (Table 1.). Only a resource of these kind of knowledge can make possible the tailoring of given structures of coatings and technologies as well as the diagnostics of production technologies.

The present paper reviews the authors concepts [3-7] to give a rather comprehensive description of the basic elements of structure evolution in polycrystalline thin films by using the fundamental structure forming phenomena [7]

TABLE 1. Basic problems of thin film research and application

PREPARATION
TECHNOLOGY

- material
- impurities + additives
- parameters

APPLICATION

PHYSICAL, CHEMICAL and
DEGRADATION
PROPERTIES

STRUCTURE FORMATION
atom by atom building
- nucleation
- crystal growth
- restructuration
  coalescence
  grain growth-GB
- process induced segregation
  of impurities and additives
- compound formation
- phase transformation

STRUCTURE

- phase state
- morphology of grains and
  surfaces
- structure of crystals
- orientation of crystals,
  texture
- chemical composition
- homogeneity, density
- substrate-film interface

relationships investigated generally

sequence of deterministic relationships

relationships to be understood for   tailoring films

and their dependence on the main technological parameters. New universal structure zone models demonstrating the effects of active impurities and additives will be also described. (In the following the term "impurities" will be used for impurities and additives.)
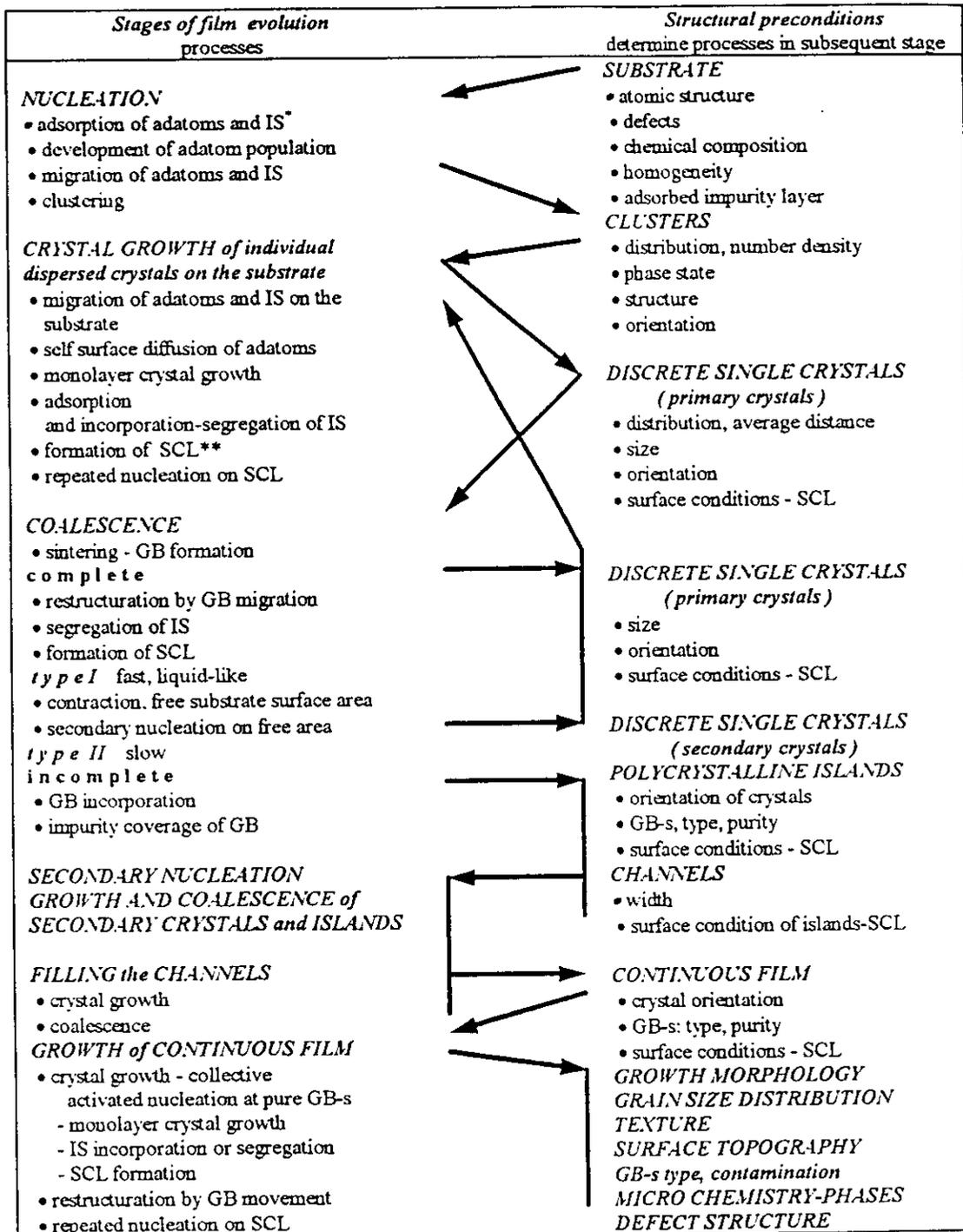
2. Course of Structure Evolution in Polycrystalline Coatings

The structure evolution of polycrystalline thin films takes place by the condensation of impinging species, their incorporation into the existing solid phase and growth as well as restructuration of the grains. The course of structure evolution has well defined consecutive stages characterised by specific structural conditions and structure forming phenomena [6-7]. The role of parameters in determining the structure of the coatings can be understood by considering the fundamental structure forming phenomena and their dependence on the parameters [7]. The structure forming phenomena can give account for the global effect of the atomic processes (surface and bulk diffusion, grain boundary migration) determined by the actual structural conditions beside the parameters and are responsible for the various features of the structure evolution.

The fundamental structure forming phenomena are

- the nucleation:
  - primary nucleation on the substrate at the very first stage of condensation [8-14];
  - secondary nucleation taking place on the bare substrate surface area developing during the liquid like coalescence of grains;
  - repeated nucleation taking place on the surfaces of crystals covered by the layer of segregated impurity phase [5]
- the crystal growth, which incorporates the deposited adatoms into the condensed phase:
  - growth of individual crystals situated separately on the substrates [6];
  - growth of individual crystals as parts of the polycrystalline structure [15, 29]
- the grain growth:
  - by coalescence of individual crystals on the substrate [16];
  - by grain boundary migration in the polycrystalline structure [17]
- the process induced segregation of impurity species and formation of impurity solid phase:
  - during the crystal growth on the growing crystal faces developing an impurity phase on the crystal surfaces (bi-dimensional surface covering layer in case of low self surface mobility, three dimensional segregates in case of high self surface mobility) [5,15];
  - during grain boundary migration increasing the impurity coverage of grain boundaries [18-19].

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TABLE 2. Flow chart of structure evolution in polycrystalline films

Stages of film evolution processes	Structural preconditions determine processes in subsequent stage
NUCLEATION • adsorption of adatoms and IS* • development of adatom population • migration of adatoms and IS • clustering	**SUBSTRATE** • atomic structure • defects • chemical composition • homogeneity • adsorbed impurity layer **CLUSTERS**
CRYSTAL GROWTH of individual dispersed crystals on the substrate • migration of adatoms and IS on the substrate • self surface diffusion of adatoms • monolayer crystal growth • adsorption and incorporation-segregation of IS • formation of SCL** • repeated nucleation on SCL	• distribution, number density • phase state • structure • orientation **DISCRETE SINGLE CRYSTALS** **(primary crystals)** • distribution, average distance • size • orientation • surface conditions - SCL
COALESCENCE • sintering - GB formation **complete** • restructuration by GB migration • segregation of IS • formation of SCL **type I** fast, liquid-like • contraction. free substrate surface area • secondary nucleation on free area **type II** slow **incomplete** • GB incorporation • impurity coverage of GB	**DISCRETE SINGLE CRYSTALS** **(primary crystals)** • size • orientation • surface conditions - SCL **DISCRETE SINGLE CRYSTALS** **(secondary crystals)** **POLYCRYSTALLINE ISLANDS** • orientation of crystals • GB-s, type, purity • surface conditions - SCL
SECONDARY NUCLEATION GROWTH AND COALESCENCE of SECONDARY CRYSTALS and ISLANDS	**CHANNELS** • width • surface condition of islands-SCL

FILLING the CHANNELS
• crystal growth
• coalescence
GROWTH of CONTINUOUS FILM
• crystal growth - collective activated nucleation at pure GB-s
  - monolayer crystal growth
  - IS incorporation or segregation
  - SCL formation
• restructuration by GB movement
• repeated nucleation on SCL
	CONTINUOUS FILM
	• crystal orientation
	• GB-s: type, purity
	• surface conditions - SCL
	GROWTH MORPHOLOGY
	GRAIN SIZE DISTRIBUTION
	TEXTURE
	SURFACE TOPOGRAPHY
	GB-s type, contamination
	MICRO CHEMISTRY-PHASES
	DEFECT STRUCTURE

* IS : impurity species   ** SCL : surface covering layer

The course of structure evolution can be analysed by constructing the flow chart of growth processes including the fundamental structure forming phenomena and structural conditions existing in the various growth stages (Table 2.) [7]. The following discussion is related to the temperature range $T_s > 0.3\ T_m$ where both the surface diffusion and the grain boundary migration has a noticeable value and consequently the fundamental structure forming phenomena are effective in their entities. The participation of impurity species in the atomic processes of the structure forming phenomena as well as the influence of the segregated impurity phases on these phenomena are also discussed. The last one is considered as the effect of a new technology parameter [7], the concentration of impurity species in the impinging vapour beam on the film structure. The effect of substrate temperature will be discussed in connection with the structure zone models, while the effects of the deposition rate, the energy of impinging species and their incidence angle are not considered.

2.1. THE NUCLEATION STAGE

The condensation on the substrate surface starts by the nucleation. The atomic phenomena of nucleation are the adsorption and accommodation of impinging adatoms, development of an adatom population on the substrate and clustering of migrating adatoms. These atomic processes are controlled by the atomic structure, chemical composition, defect structure and homogeneity of the substrate surface. The effects of possible adsorbed impurity layer, which can influence the size of critical nuclei, should be also considered.

The nucleation results in the formation of stable clusters with the characteristics of their phase state, atomic structure, crystal orientation with respect to the substrate surface plain and their number density and distribution.

The orientation of the nuclei can be determined by the quality of the substrate and the surface energy conditions. The surface energy can influence the nucleation orientation at low supersaturations. At high supersaturations and on amorphous substrates the nucleation orientation is always random [4,20].

2.2 STAGE OF ISLAND GROWTH

In that case growth of individual clusters/islands dispersed on the substrate are analysed. Depending on the phase state of the clusters the growth of liquid droplets, amorphous grains or crystals should be considered in this respect. The growth of islands takes place by incorporating the adatoms impinging direct from the vapour phase and arriving at the islands by migration on the substrate. In the first stage of island growth the second component can represent the most important material transport.

In case of crystal growth the orientation of crystals will play a decisive role in the crystal growth phenomena as well as the condition that the crystals are situated on a substrate. The orientation of crystals is important mainly because of the possible different growth rate on the various crystal faces. The nature of the substrate might have an influence on the crystal growth processes because the intersection line between the substrate surface and the side faces of crystals might be active or passive in the

monolayer crystal growth on the various substrates [6]. Consequently the flow of monolayer steps is directed away or to this intersection line respectively. In both cases well faceted crystals develop.

The presence of active impurities in the impinging vapour beam has a strong influence on the growth of these individual crystals, therefore their segregation on the growing crystal faces by the atomic processes of crystal growth should be considered [15]. It is expected that the segregation of impurity species takes place at the monolayer growth steps by replacement mechanism and most of the replaced species remain as adsorbed at growth step. As a consequence of the consecutive segregation by replacement the condensed impurity species are rolled by the growth steps moving along the crystal face. The nucleation site of monolayer growth has a decisive role in determining the area of crystal surface where the impurity phase will develop. When the intersection line between the side face and the substrate surface is active in the monolayer nucleation, the impurity phase will develop on the top face or at the edges of the side and top faces. The crystal growth will be hindered in these areas resulting in the rounding of crystal shapes [21]. In the other case when the intersection line is passive in the monolayer nucleation, the impurity phase will start to develop at the substrate and will grow and cover the side faces. At high concentration of impurities the whole surface of crystals can be covered by the impurity phase blocking the growth of the crystal completely. In that case the condensation continues by repeated nucleation on the surface of primary crystals. The rounding of crystal shapes or the appearance of new grains on the surface of the primary crystals by repeated nucleation is a clear indication of the presence of active impurities [2,5-6].

The island growth results in the formation of discrete single crystals (primary crystals) dispersed on the substrate having the characteristics of sizes, orientation, density distribution and average distances between them, as well as surface conditions related first of all to the coverage by the layer of impurity phase. These are at the same time also the structural conditions which will control the structure forming phenomena being active in the next growth stage which is the coalescence stage.

2.3. COALESCENCE STAGE

The coalescence stage starts when the growing crystals will touch each other. This is the grain growth phenomenon by sintering [16]. The sintering takes place in two steps: one is the formation and filling up of the neck by surface diffusion and the second is the migration of the grain boundary. The coalescence can be complete, when it results in new single crystal or incomplete when it results in polycrystalline island containing grain boundary [6].

The complete coalescence is a real grain growth phenomenon related to grain boundary migration controlled by the grain boundary mobility, by grain boundary and surface energy as well as by the geometrical conditions. The type I. of complete coalescence is a very fast, liquid like phenomenon accompanied by remarkable contraction developing bare substrate surface area and rather three dimensional island. The complete coalescence type II. is a slower phenomenon considering both the filling up of the neck and moving the grain boundary out of the island. This coalescence results in more two dimensional singlecrystalline islands. The complete coalescence

might segregate the impurities incorporated into the bulk of the islands to the surface of the new island.

In case of incomplete coalescence the grain boundary developing at the touching of the crystals can not move out before the next coalescence of the island takes place. This can be related either to the low mobility of the grain boundary, to the large sizes of coalescing crystals or to the geometrical conditions when the filling up of the neck takes long time or is limited. Two dimensional islands are forming by this way and no valuable grain growth can be expected.

The coalescence is a short time process and very sensitive to the coverage of the crystal surfaces by the layer of impurity phase. Namely not only the self surface diffusion but also the filling up of channels and the migration of grain boundaries can be limited remarkably when the contacting surfaces and/or the neighbouring surface areas of the coalescing crystals are covered by an impurity layer. Consequently by increasing impurity concentration the incomplete coalescence will be more and more dominant and by this way the grain size strongly decreases. The nature of the substrate is also influencing the impurity effect mainly by determining the sites of impurity phase formation due to the mechanisms of monolayer crystal growth discussed in 2.2..

The coalescence stage exists for a long period until the film becomes continuous. Its last part is the formation and filling up of channels. During this stage the grain growth by coalescence, the secondary nucleation on the substrate and the growth of primary and secondary crystals coexist. At high purity conditions every crystal, both the primary and secondary ones, participate in a large number of consecutive coalescence until the continuous film develops. The impurity concentration has a strong influence on the number of consecutive complete coalescence processes in which the primary and secondary crystals can take part. The grain growth by consecutive coalescence is the most effective grain growth phenomenon during the film formation, because in that case the surface to volume ratio is very high and therefore the minimisation of the surface energy represents a high driving force for grain boundary migration. That is why near to the substrate surface the grain size distribution of the as deposited films is determined primarily by the effectivity of this growth stage. In high purity films where the grain boundaries have high mobility the abnormal grain growth and recrystallisation generally completes till the film becomes continuous resulting in monomodal grain size distribution. At increasing impurity concentration the number of impurity stabilised grain boundaries increases and bimodal grain size distribution develops.

The structural characteristics developed upon completing the coalescence stage which present at the same time the structural preconditions for the structure forming phenomena in the continuous film are the orientation of the crystals determining the types of crystal faces on the free surface of the film, the area and coverage of these crystal faces by impurity layer, the type and impurity content of the grain boundaries.

2.4. THICKNESS GROWTH OF CONTINUOUS FILM

In that stage of film formation the crystal growth phenomenon is controlled by the intersection lines of grain boundaries and film surface [15]. The intersection lines of pure grain boundaries present active nucleation sites for the monolayer growth on the

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neighbouring crystal faces, while the intersection lines of impurity covered grain boundaries are passive in this process. The monolayer growth proceeds away from grain boundaries in the first case. In the second case the nucleation of monolayers takes place within the crystal faces and the monolayer growth proceeds to the grain boundaries.

At pure conditions the growing surfaces of the individual crystals are faceted and composed of well developed crystal faces of Miller indices according to the orientation of the crystals. If active impurities are codeposited, they will be segregated at the monolayer growth steps described in 2.4. The monolayer growth steps will roll the segregated and adsorbed impurities species along the crystal faces. The concentration of impurity species increases at the steps by this way and the nucleation of the solid impurity phase can set in during the course of step movement. Starting from these nuclei the impurity phase will grow along the growth step and hinder the incorporation of adatoms at the step. The next growth step will be blocked nearly at the same site, and bunches of growth steps develop by this way which are decorated by pinning sites due to the first nuclei of the impurity phase. This phenomenon results in the truncation of crystal shapes in case of pure grain boundaries and tilted crystal faces. In case of contaminated grain boundaries the monolayer growth segregates the impurities to the surface area near to the grain boundaries developing deep and broad grooves following the grain boundary. At high impurity concentration this impurity layer can cover larger surface area which will be decorated by overgrown crystals developed by repeated nucleation. In case of large growing crystal faces when the monolayer crystal growth proceeds by the formation of numerous bi-dimensional nuclei within the crystal face the segregation of impurities will result in the formation of secondary hillocks on the crystal surface [22-23]. The side faces of these hillocks are composed of curved bunches of growth steps decorated by pinning sites. The phenomena mentioned above will preserve, during the film growth, the purity conditions of grain boundaries developed at the end of the coalescence stage.

Grain growth by grain boundary migration is the other structure forming phenomenon responsible for the structure evolution in that growth stage. By increasing film thickness beside the surface and interface energy minimisation, the grain boundary energy will be the decisive driving force of the abnormal grain growth [17]. In high purity films the grain boundaries have high mobility and the abnormal grain growth can proceed fast and , at elevated temperatures, monomodal grain distribution can develop already during the film formation. In this columnar structure nearly all of grain boundaries are perpendicular to the film plain (Fig.1.).
In the presence of impurities the abnormal grain growth slows down because of the limited mobility of the contaminated grain boundaries. The grain boundary migration is limited also by the deep grain boundary grooves, which are the very general structural characteristics of contaminated films. The grain size distribution becomes more bimodal by increasing impurity concentration, the grain boundaries will have higher density and crystals with random orientation will develop. The columnar morphology is changing to globular one.
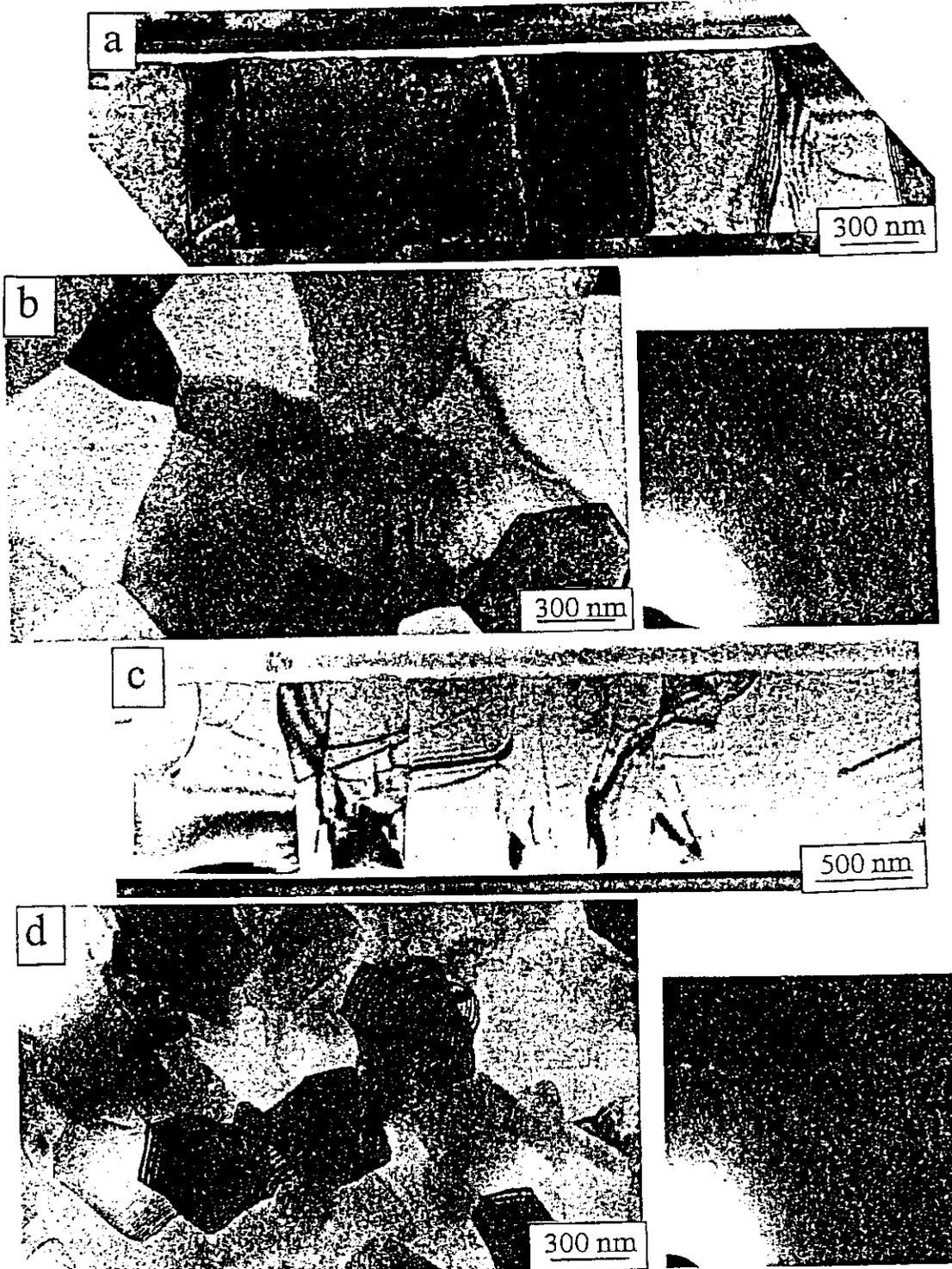
Figure 1. Al films deposited in high vacuum (a-b) and with low oxygen contamination (c-d) at 50 °C substrate temperature on Si substrates. (a) and (c) are cross sectional (b) and (d) are in plane TEM images. Inserts are transmission electron diffraction patterns illustrating the existence of the main <111> texture.

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3. Structure Zone Models

The wish to give a systematic description of the structure of polycrystalline films depending on the deposition conditions has been realised in the well known structure zone models [24-27]. These models clearly demonstrate that the structure is changing according to the deposition conditions and behaves systematically in a certain temperature range. The extension of these models have been also carried out according to differences in various deposition techniques. The effect of sputtering gas pressure have been considered in the model of Thornton [25] and that of the bias voltage in the model of Messier et.al. [26]. The backbone of these models is that they are constructed simply by the compilation of the results of the authors and only two elementary atomic processes, the surface diffusion and volume diffusion as well as their temperature dependencies were considered at the interpretation of the various structure zones. The zone boundaries are related to the set on of surface diffusion at about $0.1-0.2T_m$, which is the boundary between zone I and T, and to the set on of volume diffusion at about $0.3-0.4T_m$, which is the boundary between zone T and II. Although the general behaviour of the films can be described by these models, deviations in case of different materials and deposition conditions can be observed.

3.1. IDEAL AND REAL STRUCTURE ZONE MODELS

Experiments of the past and more recently the development and application of two component polycrystalline and nanocrystalline advanced materials made it clear that the incorporated impurities and intentionally introduced additives play a crucial role in the structure evolution of polycrystalline films and coatings, and can have drastic influence on the structure zones. In order to understand these phenomena one has to clarify by which mechanism do the impurities influence the structure evolution, and which are the characteristic structural features that appear as a result of impurity incorporation. For this reason one has to build the structure zone model by analysing the role of the fundamental structure forming phenomena in the different structure zones. This analysis leads to two types of structure zone models describing the structure evolution characteristics of pure films with respect only to the substrate temperature (ideal structure zone model) and describing the effect of impurities and substrate temperature simultaneously (real structure zone model) (Fig.2.) [7]. In the following sections the various structure zones are described keeping in sight the above stated principles.

3.2. ZONE I.

At low substrate temperatures, below $0.1T_m$ due to the high overcooling the nucleation density is extremely high. Because the impinging adatoms have no or extremely low surface mobility on the substrate surface they stick in the near vicinity where they fall. Neither coalescence nor grain boundary migration can occur, therefore the development of large grains is inhibited and the structure preserves the morphology inherited from the nucleation stage. The lateral grain size due to the nucleation density, and the texture if exists, is related to substrate effects. In the ideal case of pure

ZONE I - ZONE III

d)

HIGH

0   0.1   0.2   0.3   0.4   0.5   0.6   0.7

ZONE I   ZONE T   ZONE III
                     competitive texture

c)

MEDIUM

0   0.1   0.2   0.3   0.4   0.5   0.6   0.7

ZONE I   ZONE T   ZONE II   ZONE III
         competitive texture   restructuration texture

b)

LOW

0   0.1   0.2   0.3   0.4   0.5   0.6   0.7

ZONE I   ZONE T   ZONE II
        competitive texture   restructuration texture

a)

PURE

0   0.1   0.2   0.3   0.4   0.5   0.6   0.7

impurity content

T_s/T_m
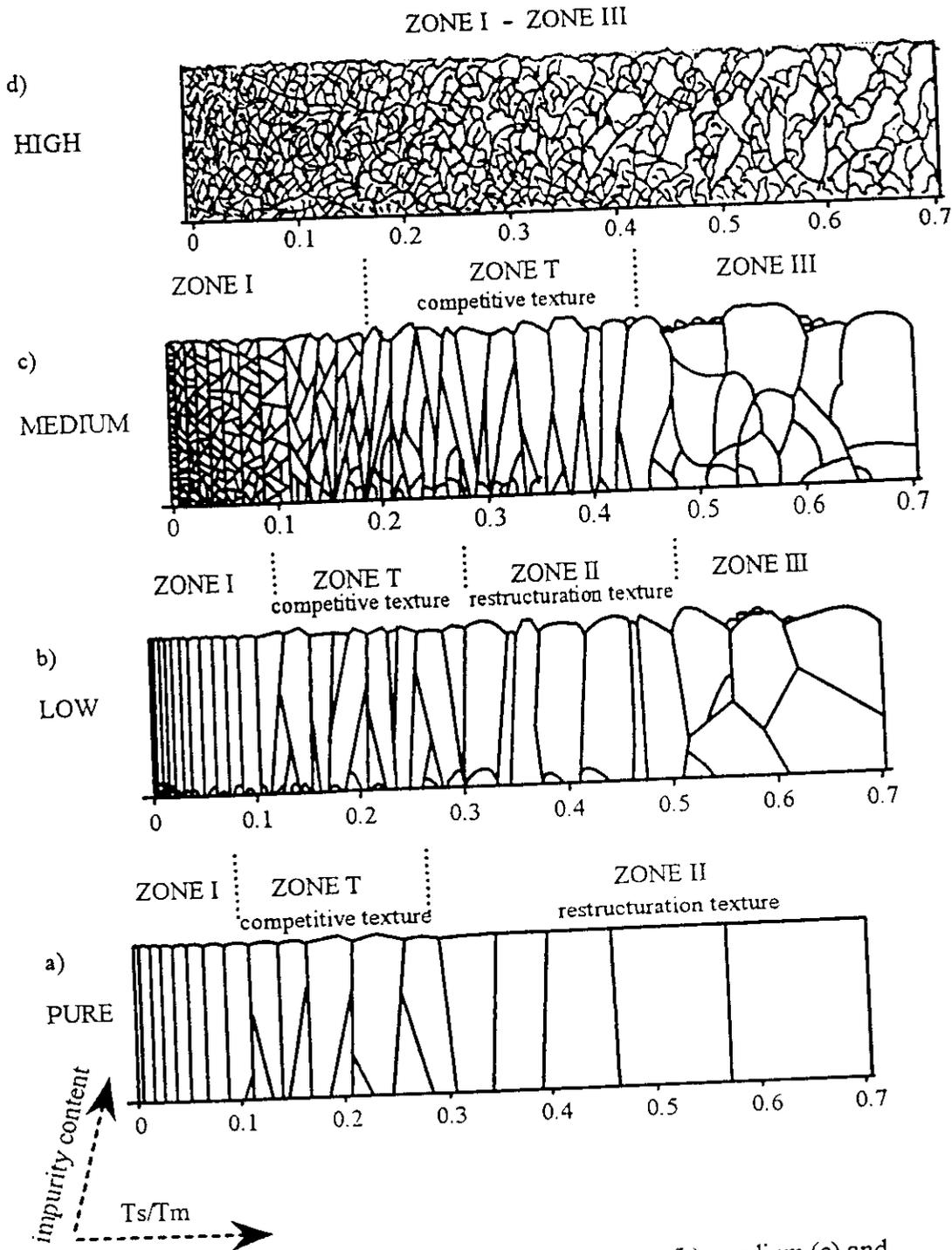
Figure 2. Ideal (a), and real structure zone models of low (b), medium (c) and high (d) impurity concentrations.

material, the growth can proceed in vertical direction uninterruptedly as described by the ballistic models [28], therefore fiber like porous structure develops. The growth structure is mainly determined by the fundamental structure forming phenomenon: nucleation.

In contaminated films the growth of grains follows the phenomena described by the ballistic models and fiber like structure develops. No segregation of the impurity species can take place and they will be incorporated into the growing fibers practically at their impinging sites [28].

The structures related to zone I are frozen in structures both in high purity and in contaminated films. An intensive restructuration can take place by increasing the temperature after deposition.

3.3. ZONE T

At substrate temperatures where the surface diffusion sets in, the fundamental structure forming phenomenon, which becomes decisive in determining the growth structure is the crystal growth. The film formation starts by the development of a small grained structure reflecting the nucleation density, due to immobile grain boundaries. When the film becomes continuous the surface diffusion makes possible the migration of adatoms between neighbouring grains, therefore the crystals having lower surface energy incorporate more material and grow over the neighbouring crystals having higher surface energy [29]. This competitive growth results in the typical cone shaped columnar structure characteristic of this zone. The competitive growth has also influence on the texture of the films by selecting the faster growing directions as texture components [30]. The upper zone boundary is determined by the onset of grain boundary migration.

In contaminated films the lower zone boundary shifts to higher temperatures as described in 3.2. Impurity incorporation can limit the grain boundary migration therefore the upper zone boundary is also shifted to higher temperatures. Impurities can have a peculiar effect on the texture evolution in case of competitive growth. If there is anisotropy in the surface chemical interaction of impurity species with the various crystal faces [31-32], at low or medium contamination level the growth of certain crystal faces can be blocked while others can grow, and this leads to the development of special preferred orientations.

This effect has been shown in case of oxygen contaminated Al films [15,21-23,33-35]. At low or medium oxygen contamination levels the growth of Al films changes from zone II. to zone T, due to the limited grain boundary migration. On the {111} faces of Al the oxygen is segregated while on the {100} and {110} crystal faces the oxygen is incorporated into the crystal lattice. This way the {111} Al crystal faces become covered by oxide impurity phase and their growth is blocked. On the other hand the {100} and {110} crystal faces can grow further. This leads to a competitive growth governed by the anisotropy of the oxygen segregation on the various crystal faces. Due to this phenomenon in oxygen contaminated Al films a <100> + <110> duplex texture coexists with the <111> texture characteristic of zone II.

In highly contaminated films the covering impurity phase can block the growth of all the crystals, consequently the competition can not evolve, zone T does not appear
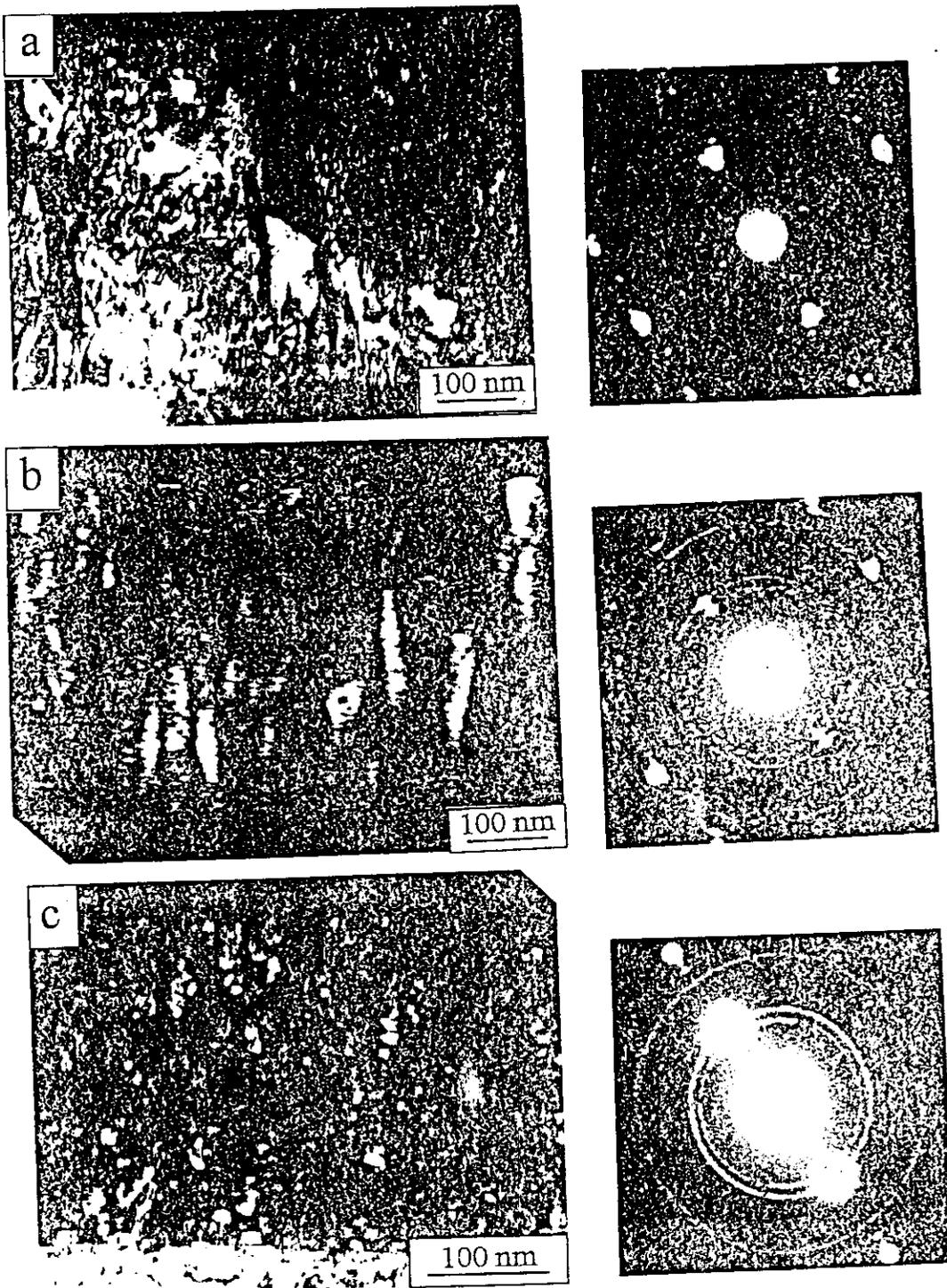
Figure 3. Cross sectional TEM dark field images of NdF$_3$ films deposited by molucular beam deposition at 300 °C substrate temperature on CaF$_2$(111) substrates. (a) single film, (b) stratified by 1 nm thick MgF$_2$, and (c) by 2 nm thick MgF$_2$ interlayers [37-38].
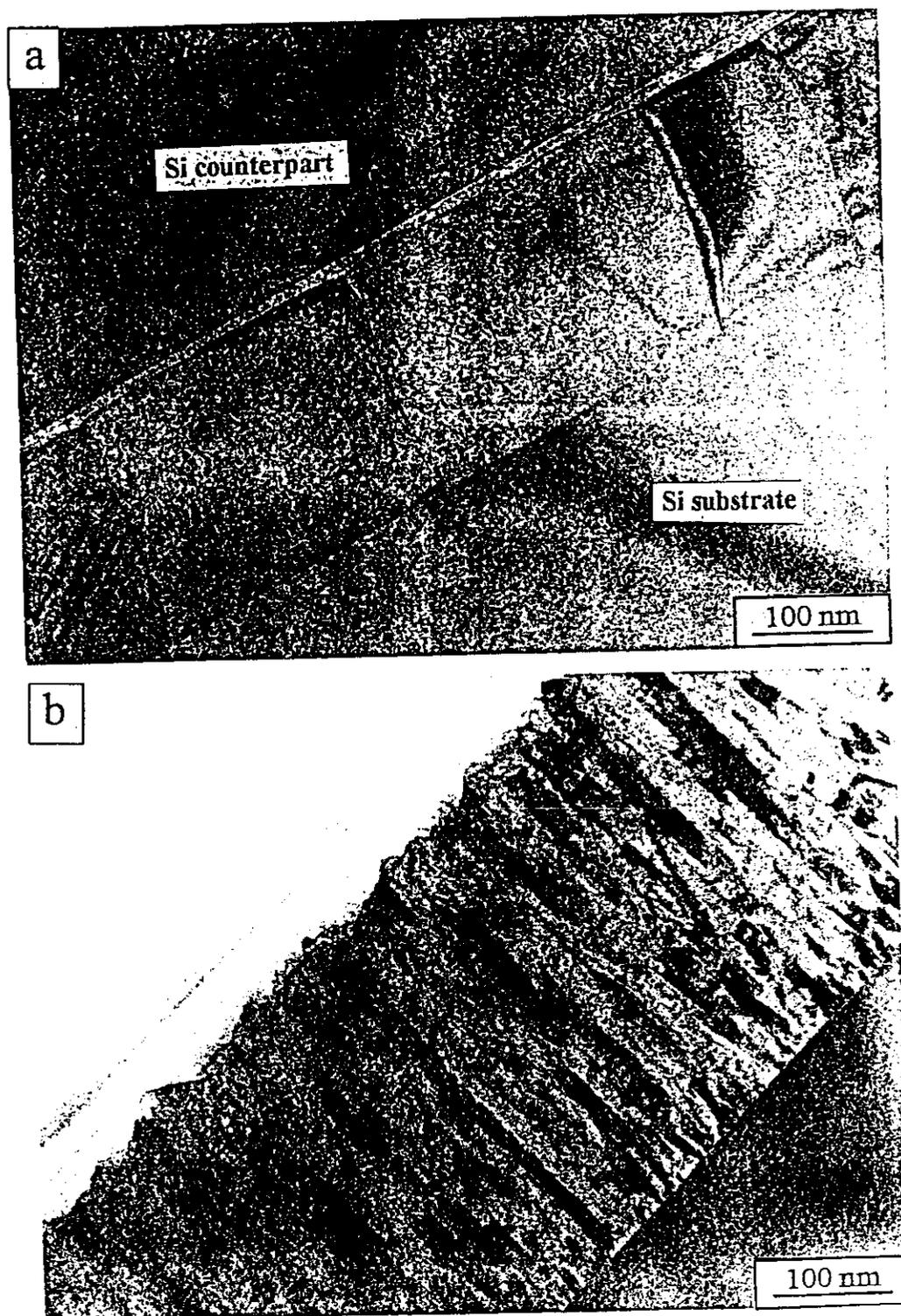
Figure 4. Al films deposited at normal high vacuum (a) and at medium oxygen contamination level (b) at 50 °C substrate temperature on Si.

and globular structure with grain boundaries covered and stabilised by the impurity phase will develop.

The effect of impurities and additives can be clearly shown also in stratified films. Stratification of two materials to control the structure and optical properties in optical coatings has been first applied by Lewis et.al. [36]. This technique utilises the phenomena described above. It has been shown [37] that stratification shifts the zone boundaries similarly to the effect of impurities. Fig.3a . shows the cross section of a NdF_3/MgF_2 stratified multilayer film system deposited in 10/1 nm thick material pairs at 300 °C (0.34Tm) substrate temperature. In this case the NdF_3 forms cone shaped grains instead of columnar morphology of zone II characterising the nonstratified NdF_3 films (Fig.3b). The development of V shaped grains protruding through the multilayer structure can be related to discontinuities in the 1 nm thick MgF_2 interlayers. If the thickness of these is increased to 2 nm the coverage of the NdF_3 crystals is more complete and small grained globular structure will form instead of V shaped crystals (Fig.3c) [38].

3.4. ZONE II.

At substrate temperatures where grain boundary migration sets in, columnar structure develops with columns proceeding from the substrate to the free surface of the film. The grain boundaries are generally perpendicular to the substrate surface. For this structure the responsible fundamental structure forming phenomenon is the grain growth. Due to grain boundary migration the initially formed small grained structure, characteristic of the nucleation density, is dissolved step by step during coalescence and in the later growth stages. The driving force of grain boundary migration is the grain boundary energy and the surface energy difference of the neighbouring crystal faces due to their orientational relationships. Accordingly the texture evolution is related to the grain growth and the texture axis is related to the lowest surface energy. In the ideal case of pure films this zone represents the upper zone of the structure zone model. As the substrate temperature is increased the lateral size of grains is increased.

In contaminated films the grain boundary mobility is limited, therefore the lower zone boundary is shifted to higher temperatures as discussed in 3.3 (Fig.4). At high temperatures (above 0.5Tm), zone III appears presenting upper boundary for zone II. Due to the limited grain boundary mobility the abnormal grain growth can not be completed, therefore bimodal grain size distribution will characterise the film. At increased contamination level the grain boundaries become immobile and zone II disappears from the structure zone model.

3.5. ZONE.III.

This zone appears only in contaminated films, and the grain size can extend from the globular (nanocrystalline) to the equiaxed micrometer sized range. The responsible fundamental structure forming phenomenon is the process induced segregation of impurities. By increasing the substrate temperature the grain size increases, therefore the surface to volume ratio decreases in the film. In this case the impurity species are segregated on a smaller surface area resulting in a faster development of a surface
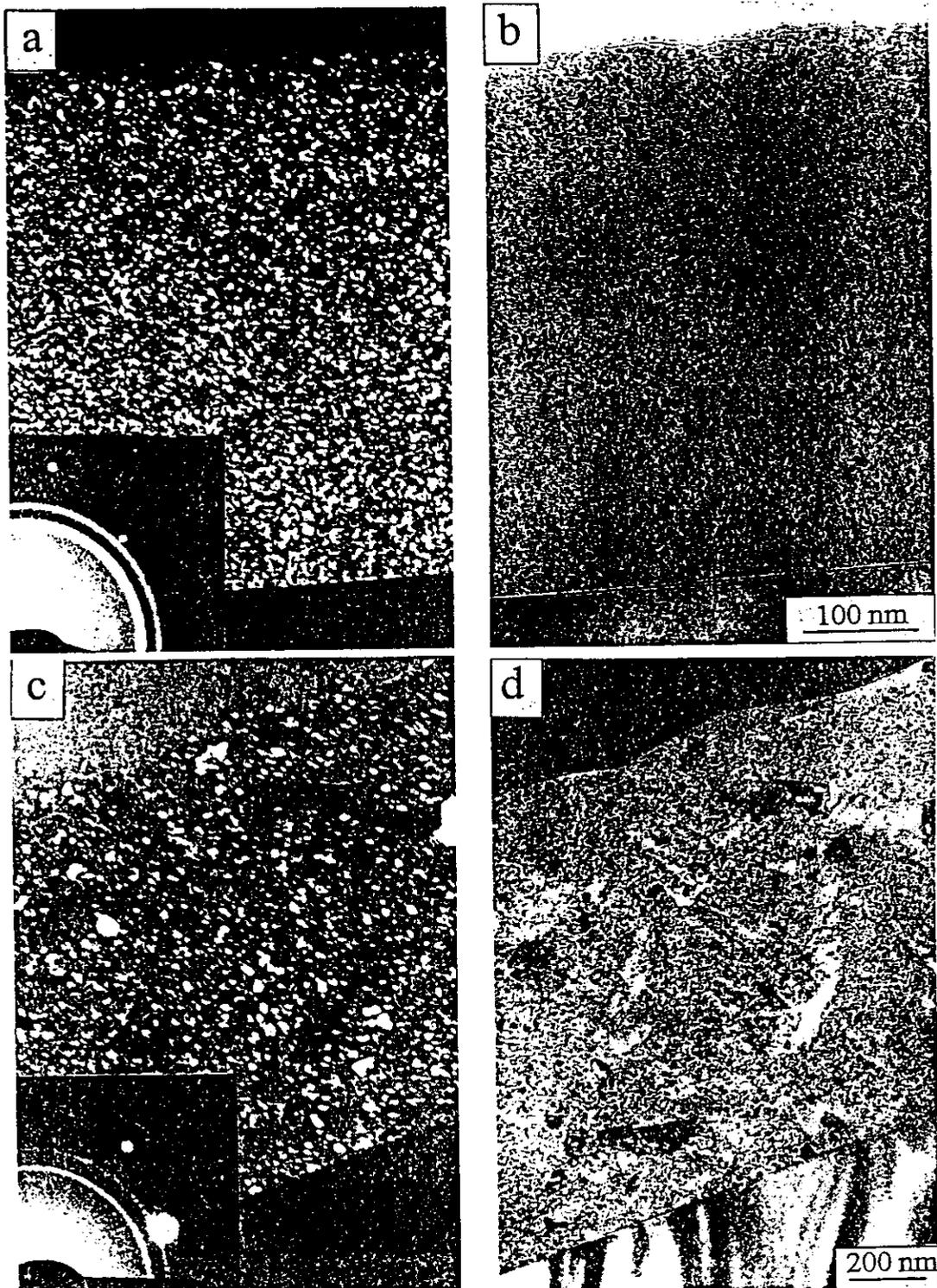
Figure 5. Nanocrystalline structure developed in Al films deposited at high oxygen contamination level at 50 °C (a-b), and 300 °C (c-d) substrate temperature on Si. (a) and (c) are dark field, (b) and (d) are bright field cross sectional TEM images.

covering layer of impurities on the crystal surfaces. Due to this, the growth of the crystals is stopped and the growth continues by repeated nucleation. This leads to the typical equiaxed structure at high substrate temperatures in case of low and medium level of impurity concentration. Since the grain growth is also limited in spite of the high temperature no or only week texture evolution can take place. By increasing the contamination level the lower boundary of Zone III is shifted to lower temperatures while at first zone II and later zone T will disap,ear gradually until the lower boundary of zone III reaches the upper boundary of zone I. In this case the part of zone III at lower temperatures will exhibit the nanocrystalline structure (Fig.5).

4. Summary

The consideration of the fundamental structure forming phenomena and their dependence on the deposition parameters for the description of the structure evolution of thin films at various temperatures and impurity levels makes possible the construction of structure zone models. The fundamental structure forming phenomena are sensitive against orientation conditions of crystals consequently a selection can take place in the course of structure evolution among the randomly oriented nuclei of polycrystalline films developing on amorphous substrates. That is why a strong correlation exists between the grain morphology and the texture of polycrystalline films and protective coatings. The universal nature of the present structure zone models makes possible also the diagnosis of the technological conditions for a wide range of material systems and structures of elements and compounds.

5. Acknowledgements

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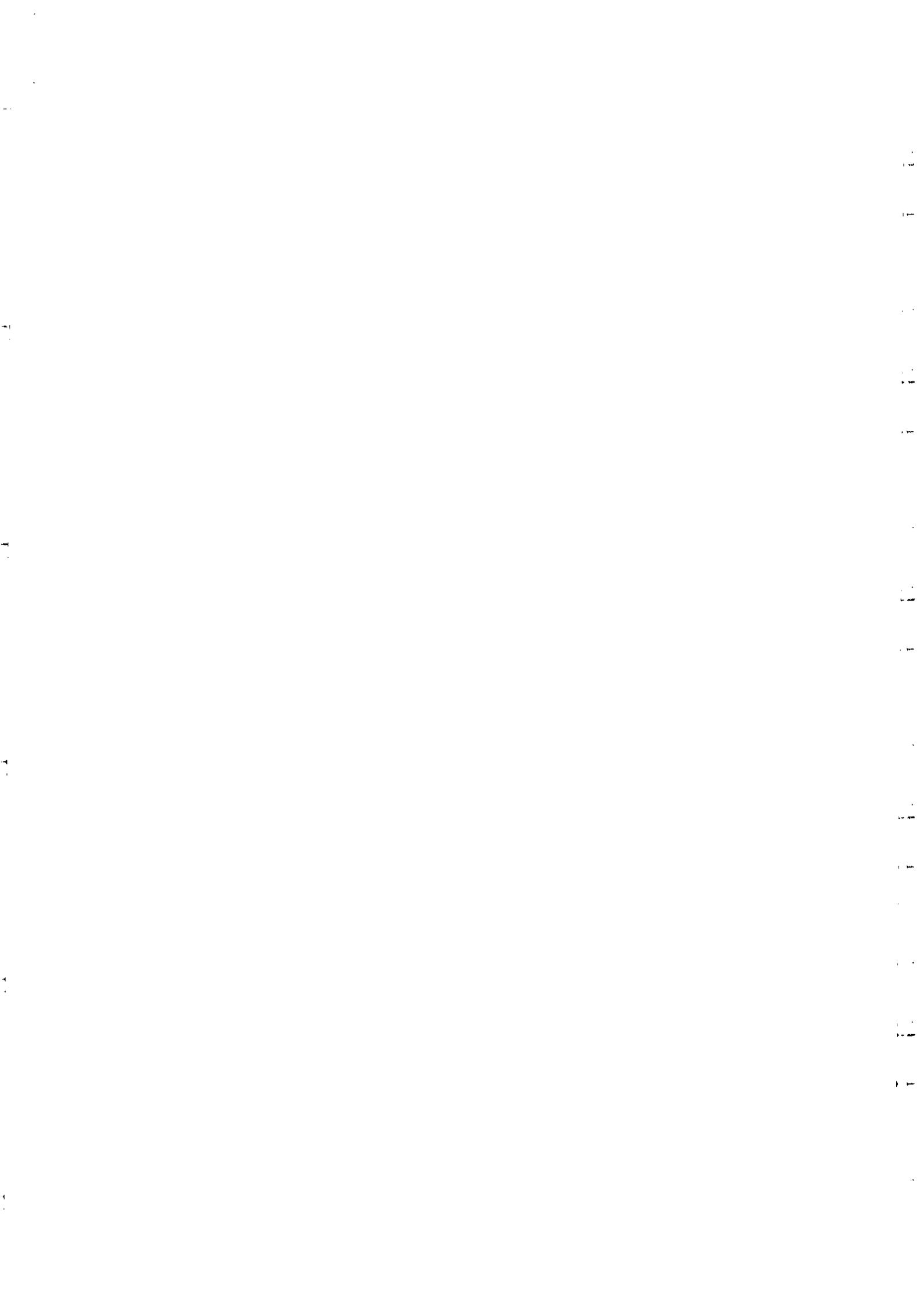
Fundamental structure forming phenomena of polycrystalline films and the structure zone models

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Fundamental structure forming phenomena of polycrystalline films and the structure zone models

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Abstract

Previous structure zone models used for the interpretation of the experimental results were constructed by compiling the various structures found in thick polycrystalline films deposited at different temperatures and parameters. The present paper shows that while the temperature dependence of surface and bulk diffusion can not adequately describe the evolution mechanisms of various polycrystalline thin film structure, the fundamental structure forming phenomena, including the contribution of impurities introduced by the authors make possible the comprehensive description of the structure forming mechanisms. Real structure zone models including also the related textures, are constructed by considering the concentration of impurities (co-deposited additives) in the vapour beam as a new deposition parameter, and the fundamental structure forming phenomena. These are phenomena composed of atomic processes, and can give account for the global effect of the atomic processes and are directly responsible for the structure evolution. Impurities (additives) can promote or inhibit the operation of the structure forming phenomena (promoter or inhibitor resp.). The new structure zone models can be used to tailor polycrystalline film structures of large variety (from large grained through columnar to the micro- or nanocrystalline structures) and to diagnose technologies. © 1998 Elsevier Science S.A.

Keywords: Polycrystalline films; Temperature; Atomic

1. Introduction

Polycrystalline thin films prepared by various techniques at a large scale of parameters exhibit large variety of structures considering the size, morphology and orientation relationship of crystals as well as the microchemistry of the film. Structural inhomogeneity along the film thickness can also be present. The structure zone models (SZM) [1–7], constructed by the compilation of the experimental results, present an important guideline for systematising both the experimental results and the dependence of structures on the deposition temperature (considering the homologous temperature, T_s/T_m, where T_s is the substrate temperature and T_m is the melting point of the film material). It is generally agreed that the surface and bulk diffusion are the most determinant atomic processes of the structure evolution. These can, however, in themselves not explain the evolution of the various, sometimes peculiar structures and the effects of parameters on them completely.

The detailed analysis of the role of impurities in the modification of the conventional film structures and in the development of peculiar structural features [8–12] urged the authors to introduce the pressure or relative impingement rate of active impurities as an additional parameter of the film deposition [13,14]. It has been shown recently that by selecting so called fundamental structure forming phenomena a rather comprehensive and general description of the structure evolution (size and shape of grains together with their crystal orientation) in polycrystalline thin films can be given and an universal SZM can be constructed taking into consideration the effects of co-depositing impurity species [15]. (The co-deposition of some additives and dopants beyond their solubility limit, or component(s) of multicomponent films at concentrations higher than the required stoichiometry have similar effects on the structure evolution as those due to the active impurities, therefore, the expression 'impurity' will be used consistently in general meaning in this paper.)

The present paper is concentrating on some details of the structure evolution of metal thin films by considering the fundamental structure forming phenomena. It will be shown that the active impurities can not only inhibit but also promote the structure evolution in vapour deposited

polycrystalline thin films. The basic concepts of the universal structure zone model, describing both the morphology and texture, will also be discussed.

2. The fundamental structure forming phenomena

It is well known that the growth of thin films proceeds through consecutive stages characterised by specific processes of structure evolution: nucleation, island growth, coalescence of islands, formation of polycrystalline islands and channels, development of continuous structure and thickness growth. The evolution of the structure in polycrystalline thin films is a very complex phenomenon and exhibits different features in different stages of film growth.

The analysis of the structure evolution and that of the effects of the deposition parameters on the structure and on the appearance of peculiar structural features lead to the conclusion that the comprehensive description of the formation of the various structures is possible by selecting the *basic structure forming phenomena* well known in materials science and solid state physics (nucleation, crystal growth, grain growth), and an *additional phenomenon*, the process-induced segregation of foreign species related to crystal growth and grain growth [16–19]. These are the *fundamental structure forming phenomena* active during the structure evolution of real polycrystalline thin films [14]. These phenomena are composed of elementary atomic processes, and can give account for the global effects of the atomic processes on the structure evolution. It is important to note that the atomic processes are controlled directly not only by the temperature but also by the structural conditions characteristic of the actual growth stage (structural preconditions). It has a particular importance that, by considering the fundamental structure forming phenomena, both the evolution of the size and morphology of the grains as well as that of the orientation of crystals can be described.

The fundamental structure forming phenomena are summarised in the following.

2.1. The nucleation

Nucleation starting the growth of individual islands takes place on the substrate surface at the very first stage of the condensation (*primary nucleation*) or later on the bare substrate surface area developing upon liquid like coalescence (*secondary nucleation*). A peculiar case of nucleation shows up on the surface of a growing crystal when its growth is blocked by a surface covering layer (SCL) of an impurity phase. This is the *repeated nucleation* [16]. The primary nucleation starts the condensation and the film growth on the whole substrate surface simultaneously, while the secondary and the repeated nucleation initiates the starting of the growth locally in later stages of film formation. It is important to note that on amorphous

substrates the nuclei are randomly oriented. The kinetics of nucleation are discussed in review articles in details [20–26].

2.2. The crystal growth

Crystal growth is the fundamental structure forming phenomenon which incorporates the depositing material into the condensed phase. Two main cases of crystal growth should be considered in case of polycrystalline thin films: the growth of discrete crystals dispersed on the substrate surface (Fig. 1a and b) and the growth of crystals which are parts of a polycrystalline structure (Fig. 1c and d) [14].

2.2.1. Growth of discrete crystals dispersed on the substrate

Crystals growing from the nuclei are randomly oriented due to the random orientation of the nuclei. The complete coalescence of the crystals touching each other is a grain coarsening resulting also in the development of discrete single crystals and connected to some changes in the orientation controlled mainly by the minimisation of the substrate–crystal interface energy. The intersection lines of the crystal side faces and the substrate present a structure precondition specific for the growth of these crystals. The intersection lines can be active or passive in the monolayer nucleation on the side crystal faces. In the first case, the movement of the monolayer growth steps proceeds from the intersection line to the top of the crystal, while in the second case, the movement of the growth steps proceeds to the direction of the intersection line. In the presence of impurities, the direction of the movement of the growth steps will be important in determining the location of the developing second phase, e.g., SCL.

2.2.2. Growth of crystals as parts of a polycrystalline structure

When a crystal becomes part of a polycrystalline structure, it might have various grain sizes and orientations as well as surface conditions. These structure conditions will
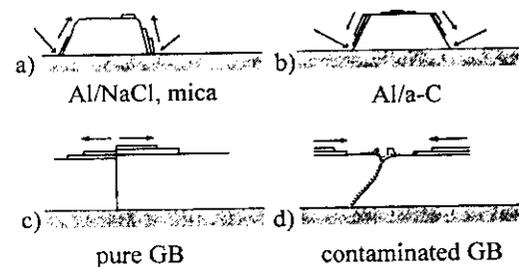

Fig. 1. Types of crystal growth in polycrystalline thin films: (a) and (b) growth of dispersed individual crystals on the substrate surface, the intersection line between the substrate and the side crystal faces are active (a) and passive (b) in the monolayer nucleation; (c) and (d) role of grain boundaries in the growth of crystals as parts of a polycrystalline matrix. pure grain boundary active in the monolayer nucleation (a), contaminated grain boundary passive in the monolayer nucleation (b).

determine its behaviour in the collective crystal growth characterising the polycrystalline film structure.

The growing faces of a crystal are parts of the free surface of the film. These crystal faces correspond to the equilibrium crystal shape and are determined by the orientation of the crystal at high purity conditions. A growth competition can start among the neighbouring crystals in case of different orientation according to the types of their growing faces, i.e., to their orientation [27–29]. The faster growing crystals will grow over the slower growing ones developing V-shaped crystal forms. This competition is terminated when only crystals exhibiting the same type of crystal faces proceed to the free surface. This competitive crystal growth represents an orientation selection among the crystals resulting in the so called *competitive growth texture* in the part of the film away from the substrate. The consequence of this competitive growth is the development of a changing morphology and texture along the film thickness. This is very pronounced at substrate temperatures where grain boundary migration is negligible. In that case, a small grained structure (corresponding mainly to the nucleation density) of random orientation exists in the substrate-near part of the film. It is followed by a part of V-shaped grains accompanied by an increase of the volume of preferentially oriented crystals. This process concludes later in the development of a columnar structure with a nearly unique crystal orientation.

The intersection lines of grain boundaries with the free surface can be active (this is the high purity case) or passive (this is the case of the contaminated grain boundaries) in the monolayer nucleation. Consequently, in the presence of impurities, the property of the grain boundaries will determine the surface area where the segregated SCL will develop [17].

2.3. Grain growth

In the course of structure evolution of polycrystalline films, two kinds of grain growth take place in the temperature interval where the grain boundary mobility has a considerable value. Grain growth takes place at first in the coalescence stage by complete coalescence of the contacting dispersed single crystal islands resulting in a new single crystal. Normal and abnormal grain growth can take place by grain boundary migration in polycrystalline islands and in continuous films.

The grain growth in case of complete coalescence results in a single crystal island on the substrate. The type of complete coalescence might be either a very fast, liquid like process, or a slower one. The type is determined mainly by the sizes of contacting islands, and by the conditions of the contacting surfaces at a given temperature. The complete coalescence of the contacting crystals is a periodic process during the film growth and, beside the increase of grain size, it results also in the changes of crystal orientations due to lowering the free energy of the

developing crystals. This is a restructuration process developing stepwise a texture related to the lowest interface energy. This texture is called as *restructuration growth texture.*

It should be noted that the 'surface recrystallisation' has been introduced by Movchan and Demchishin [1] for the grain growth taking place by complete coalescence on the substrate surface. Unfortunately, this expression has not been used in its original sense consistently in the literature.

Upon liquid-like coalescence, a shrinkage of the coalescing crystals takes place developing bare substrate areas, i.e., places where the condensation proceeds by secondary nucleation. In that case, structures and phenomena of nucleation, island growth and coalescence stages can coexist. This shows up, e.g., in the coexistence of texture and random orientation in the diffraction pattern.

When the film becomes continuous, most of the crystals forming the polycrystalline structure have already participated in a series of complete coalescence during the preceding growth stages. This means that their orientation is already in or near to a preferred orientation corresponding to the minimum of interface and surface energy. Abnormal grain growth [30] takes place in the structure by grain boundary migration [6,7], the direction of which is controlled by the minimisation of the substrate–film interface and free surface energy. This means that the grain coarsening is connected to the strengthening of the preferential orientation. During abnormal grain growth, the grain size distribution is bimodal. When the abnormal grain growth can be completed during the film deposition, the as grown film has a monomodal grain size distribution. This might be realised at high T_s/T_m.

2.4. Formation of new phases by process-induced segregation of impurity species

Impurity species impinging onto the film surface can be adsorbed and segregated on the growing crystal faces or dissolved in the crystal lattice [8,31,32]. According to the experimental results, active impurities can inhibit the operation of the fundamental structure forming phenomena (decrease in grain size, weakening texture) (*inhibitor*) or promote [13,33] them (increasing grain size) (*promoter*). Those inhibitors have the strongest influence on the operation of the structure forming phenomena, i.e., on the structure evolution which are segregated by the atomic processes of the crystal growth and develop bidimensional covering layers on the growing crystal surfaces (SCL) and grain boundaries. Namely, SCL-s covering partly or completely the surfaces of the crystals and grain boundaries can control directly both the crystal growth and the grain growth, which are the most active phenomena of the structure evolution. Impurity segregation can also be related to the migration of grain boundaries [18,19].

The process-induced surface segregation of impurity species stems from the atomic processes of the monolayer
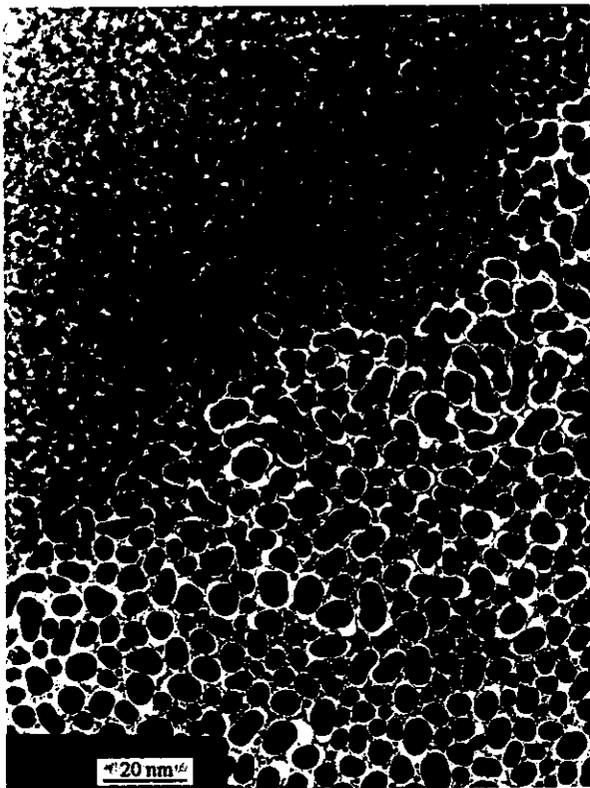
Fig. 2. Co-depositing Sn promotes the coalescence of Al crystals shown in the area marked by (B). Area marked by (A) is the pure Al film. 100-nm thick Al film deposited at room temperature, at 1 nm/s deposition rate on a-C layer supported by a TEM microgrid. Residual pressure was 10^{-4} Pa.

crystal growth discussed in details both in case of individual crystals dispersed on the substrate surface [14] and in case of polycrystalline structures [17] including the role of the activity of the intersection lines. The developing SCL limits the crystal growth on the covered surface areas resulting in the rounding and truncation of crystal shapes as well as in the appearance of dome-shaped surface features in continuous films. In case of complete surface coverage, the growth of crystals is fully blocked and the condensation proceeds by repeated nucleation. In that case, the thick films are composed of three dimensional (equiaxial, globular) overgrown crystals separated by the layers of the impurity phase. Consequently, thin films deposited under the influence of active impurities are two phase systems.

Impurity phase covering either the surface of individual islands or the grain boundaries in the polycrystalline structure can inhibit the grain boundary migration both at the coalescence and in case of grain coarsening. By this way, the processes developing the grain sizes and the restructuration texture are inhibited by the developing impurity phases and result in decreased grain sizes and weak texture or even in random orientation.

The surface chemical interaction of impurity species and, by this way, the segregation conditions might depend

on the type of crystal face as in the case of aluminium and oxygen system [31,32]. In that case, the crystal growth is not inhibited on the crystal faces on which the impurity species are not segregated. Crystals with these types of growing faces can grow continuously in the polycrystalline structure, while the growth of others is inhibited. This is a good basis for the development of growth competition connected to orientation selection among the neighbouring crystals.

Experiments on vapour deposited Al/Sn and Al/In systems revealed that impurities can promote the operation of the fundamental structure forming phenomena by increasing the grain size at the same deposition parameters (Fig. 2) [13,33]. It turned out also that these additives decrease the inhibition effect of oxygen on the structure evolution of Al thin films [33]. Similar effect of additives have been found at electrolytic deposition of Au/Pb system [34].

3. Correlation between growth morphology and orientation of crystals

The analysis of the fundamental structure forming phenomena revealed that the evolution of the crystals morphology is related to the evolution of the crystals orientation through common mechanisms [35]. On this basis, textures can be correlated to the various zones of the structure zone model. On amorphous substrates, the nuclei are randomly oriented and the textures are evolutionary textures due to selection mechanisms. This selection can be related either to the competitive growth of crystals (due to the different growth rates in various crystallographic directions or to the crystal face dependent segregation of inhibitors) or to the abnormal grain growth controlled by the minimisation of the surface and interface energy. In the first case, the texture is *competitive growth texture*, while in the second case, it is the *restructuration growth texture*.

4. Main characteristics of structure zones and construction of new structure zone models

By analysing the structure zone models published in the literature [1–6], the various structure zones can be characterised by the following way (Fig. 3).
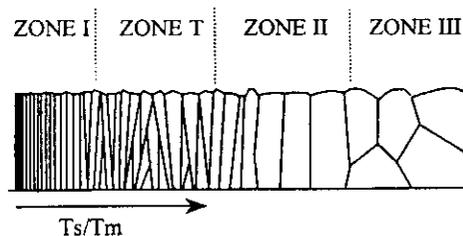

Fig. 3. Main characteristics of structure zones used in the literature [1–6].

In *zone I*, the film is composed of fibres of small diameter (1–10 nm) determined by the nucleation density and statistical fluctuation. The crystalline fibres grow out of the primary nuclei and proceed to the top of the film. The fibres are often collected into bundles. This is a rather homogeneous structure along the thickness of the film with increasing diameter of fibres by increasing T_s/T_m. The crystals contain probably high density of defects and the grain boundaries are porous. This structure belongs to the temperature interval $0 < T_s/T_m < 0.2$ where neither the bulk diffusion nor the self surface diffusion has remarkable value.

In *zone T*, the structure is inhomogeneous along the film thickness. It is fine crystalline at the substrate, composed of V-shaped grains in the next thickness range while can be columnar in the upper part of thick films. This zone belongs generally to the temperature interval $0.2 < T_s/T_m < 0.4$ in which the self surface diffusion is remarkable, however, the grain boundary migration is strongly limited.

Zone II represents a homogeneous structure along the film thickness composed of columns penetrating from the bottom to the top of the film. The grain boundaries are nearly perpendicular to the film plane. This zone is characteristic for high substrate temperatures ($T_s/T_m > 0.4$).

In *zone III*, the structure is characterised by equiaxed (globular) three dimensional grains, which is a direct indication that the crystal growth has been blocked periodically. This kind of structure is generally attributed to the high substrate temperature range. It will be shown, however, in the next paragraphs that the development of this kind of structure is the consequence of the presence of inhibitors and can exist at every substrate temperature with different grain sizes.

4.1. Concept of the basic structure zone model

The structure evolution in polycrystalline thin films can be discussed universally on the basis of the fundamental structure forming phenomena by considering the dependence of these phenomena on the temperature and on the actual structure preconditions existing in the film. Considering the basic structure forming phenomena (nucleation, crystal growth and grain growth), a basic structure zone model can be constructed. This model interprets the structure evolution at various temperatures and when no effects of co-depositing foreign species have to be considered.

Fig. 4 illustrates the structures at the various temperature intervals at increasing film thickness. In the temperature interval $0 < T_s/T_m < 0.2$, the nucleation density determines the lateral sizes of the fibres which are growing uninterruptedly side by side binding the adatoms at their impinging sites described by the ballistic models [36]. The orientation of fibres follows the random orientation of the nuclei. This is the structure of *zone I*.

In the temperature interval $0.2 < T_s/T_m < 0.4$, the surface diffusion has a considerable value. A structure at-
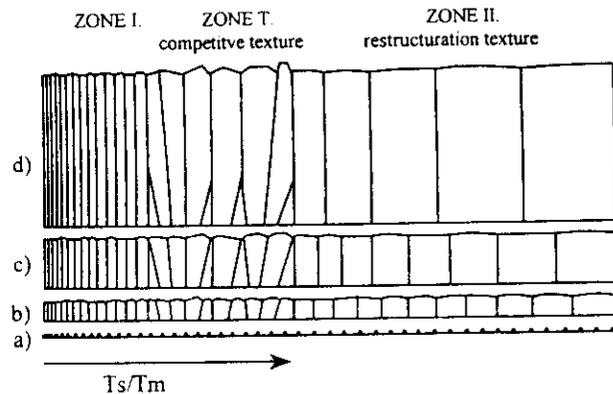

Fig. 4. Basic structure zone models at various film thickness.

tributed to *zone T* develops by competitive growth of differently oriented neighbouring crystals [28,29]. In the lower part of this temperature interval, no grain boundary migration can be expected. Therefore, the lateral size of competing crystals at the substrate is determined by the nucleation density. These crystals are in random orientation. At higher temperatures more and more grain boundaries become mobile resulting in the lateral growth of grains situated on the substrate. Due to this process, a weak preferred orientation develops strengthening gradually with temperature (Fig. 4b). The development of V-shaped crystals is a result of the competition taking place among the differently oriented neighbouring crystals (Fig. 4c) which concludes in a columnar morphology at higher thickness (Fig. 4d).

The texture is changing with the thickness in this zone. In the lower temperature range, the substrate-near part shows random orientation, while moving away from the substrate, the competitive growth texture is increasing. In the higher temperature range, the substrate-near part shows a weak restructuration texture controlled by the surface energy minimisation. Moving away from the substrate, the restructuration texture can diminish and the competitive growth texture increases when these two are different.

In the temperature interval $0.4 < T_s/T_m$, the effect of grain boundary migration becomes decisive. The first structure of randomly oriented small grains is dissolved gradually by the coalescence and grain coarsening (Fig. 4a–d). This strong restructuration is controlled by the minimisation of the interface and surface energy and develops the *restructuration growth texture*. Being the grain boundaries mobile, the minimisation of the grain boundary energy can also take place resulting in grain boundaries perpendicular to the film plane. The film is composed of columnar crystals with similar orientation. The lateral size of the grains increases with increasing temperature.

4.2. Concept of the real structure zone models

In the case of real films, the co-deposition of active impurity species is hardly avoidable. The additional struc-

ture forming phenomenon, the process-induced segregation of active impurity species and the formation of SCL becomes active already at very low, sometimes hardly detectable impurity concentration of the impinging vapour beam.

The real structure zone models representing the temperature dependent structures at various levels of impurity concentration are given in Ref. [15]. In Fig. 5, the changes of the structure and the orientation conditions with increasing impurity concentration is shown for aluminium oxygen system deposited at room temperature, which corresponds to zone II in the basic structure zone model.

At low level of oxygen concentration, the grain growth in the coalescence stage is not limited remarkably, and the restructuration texture can develop. The growth of oriented grains develop the columnar structure according to zone II (Fig. 5a), however, the decreased mobility of contaminated grain boundaries limits the further grain growth. The width of columns (Fig. 5b) will be smaller than those according to the basic model, but the texture is still the restructura-

tion texture, but weaker than in the case of the basic model.

At medium level of oxygen concentration, the grain growth is limited already in the coalescence stage. Because of the random orientation of the first crystals, a growth competition will start related to the different segregation property of oxygen on the different Al crystal faces [9,10,31,32]. A structure corresponding to zone T and competitive growth texture is developing (Fig. 5c).

At high level of oxygen concentration, the growth of crystals is blocked periodically by the developing SCL covering the whole surface of the crystals. It means also that no grain growth can take place hindering also the development of the restructuration growth texture. The film is composed of three dimensional equiaxial (globular) grains with random orientation according to zone III (Fig. 5d).

5. Conclusions

The identification of the fundamental structure forming phenomena (nucleation, crystal growth and grain growth as basic phenomena and the process-induced segregation of impurity species as an additional phenomenon) present a good basis for a coherent view to understand and describe the structure evolution of polycrystalline films. This involves that when investigating the correlation between the applied technology (e.g., CVD, PVD including biased sputter deposition, ion assisted deposition) and parameters (e.g., ion energy, incidence angle) and the structural characteristics one has to analyse and understand how the technology and parameters alter the structural preconditions and the kinetics of the structure forming phenomena related to the basic structure zone model.

Considering only the basic structure forming phenomena, the basic structure zone model can be constructed which describes the structure evolution of pure metal films on amorphous substrates. Taking the additional phenomenon, the process-induced segregation of co-depositing impurity (additive) species into account, the structure zone model of real polycrystalline films can be constructed.

The correlation between the grain morphology and texture of the films can be understood on the basis of the fundamental structure forming phenomena. This correlation made possible to complete the structure zone models by relating the growth textures to the specific zones.

It has been recognised that impurities or additives can inhibit or promote the operation of the fundamental structure forming phenomena. This presents new possibilities for tailoring stabilised artificial (nanocrystalline or extremely large crystalline) thin film structures and to interpret the results published recently on the role of parameters in the development of nanocrystalline structures [37,38] and in changing the grain size and texture [39–41].
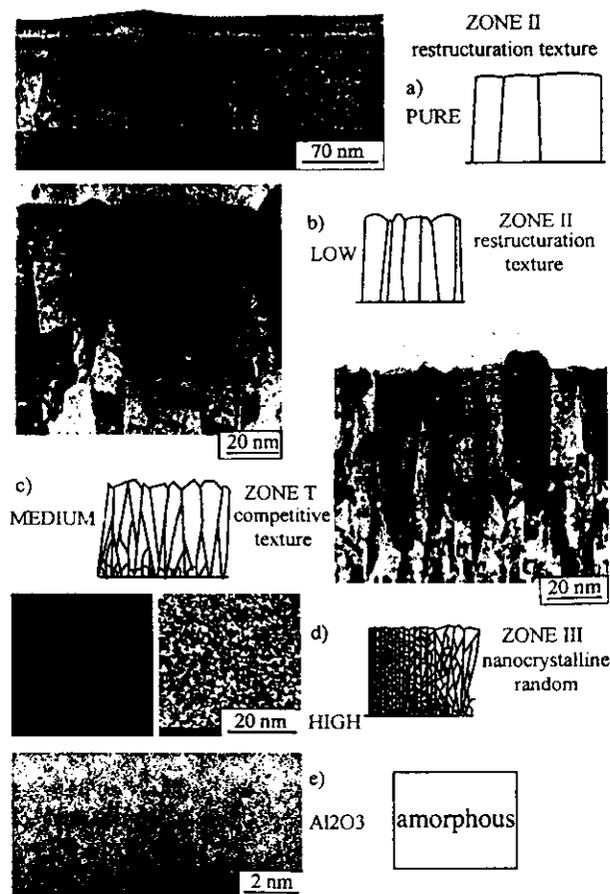

Fig. 5. Structural characteristics of Al thin films deposited by thermal evaporation at room temperature at normal high vacuum condition (a), at low (b), medium (c), high (d) and very high level of oxygen contamination.

Acknowledgements

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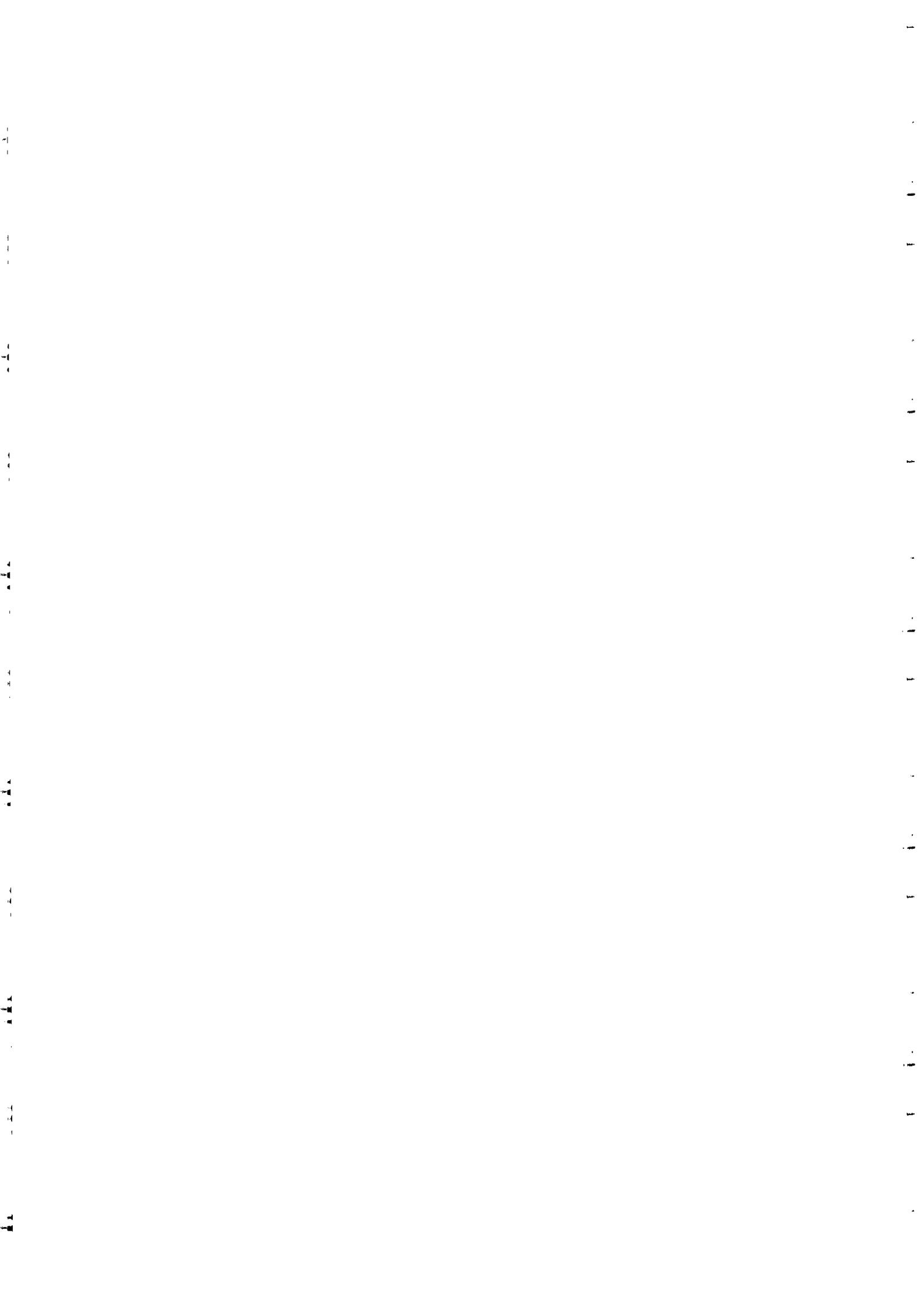
SCIENCE AND TECHNOLOGY OF THIN FILMS

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28

GROWTH MECHANISMS OF POLYCRYSTALLINE THIN FILMS

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ABSTRACT

The structure evolution in polycrystalline thin films and the related structure zone models are reviewed. Fundamental structure forming phenomena are used to describe the evolution of the various morphologies and textures. It is shown that by introducing the content of impurities as a primary preparation parameter beside the temperature the structure formation can be treated comprehensively. A basic structure zone model is proposed describing the temperature dependence of the structures at pure growth conditions. Real structure zone models have also been constructed taking into account the effect of impurities.

1. Introduction

Polycrystalline films received a rapidly growing interest in the past decades due to their increasing area of application in advanced technologies. The production of information storage materials[1-6], various types of surface coatings (hard or soft coating, protective coatings etc.[7-16]), optical coatings and multilayer systems[17-21], active and passive layers of various generation of microelectronic devices[22-25], etc. are all based on thin film technologies. Some materials and new material structures came also into the focus of interest, e.g. the diamond films[26], the micro- and nanocrystalline material structures[15,27-30,4], which have specific properties. The reason of the interest both of thin film research and application in the structure of polycrystalline thin films has been clearly discussed already by E. Bauer in the introduction of his review paper on textures of thin films presented at the Ninth National Vacuum Symposium of the American Vacuum Society[31], in 1962. This introduction can summarise and express also our present interest in this topic:

"Many crystallisation phenomena lead to crystal aggregates in which a crystallographic axis of the individual crystals is more or less aligned along a preferred direction. The resulting preferred orientation of the crystals, called fiber texture, can strongly influence the physical properties of the crystal aggregates. This can be due to a dependence of the physical properties of the individual crystals upon

1

crystallographic direction (crystal anisotropy), upon the shape of the crystals (shape anisotropy)), or, in the case of asymmetrically shaped crystals, upon their arrangement (order anisotropy)). To control the properties of the whole aggregate we have to study the conditions leading to fiber texture and to try to understand the mechanism responsible for its formation. It is the purpose of this paper to review the work which has been done in the past on the fiber structure of thin evaporated films, and to discuss the present status of the subject. Although the ideas presented here are derived for evaporated films, they may, with minor alterations, also be applied to fiber textures formed in other deposition processes, e.g., sputtering, vapour decomposition and reduction, chemical displacement or electroplating."

The task of the present authors to fulfil the purpose of this paper seems to be easier at the first view, while, it is also more difficult, than it was 33 years ago. The task is easier, because a very intensive research has been carried out in this area during this period, building up a very rich resource of experimental results and experiences, of their possible interpretations and that of ideas on models explaining the structure development. However, one can come to the conclusion soon that only few systematic experiments have been carried out giving a more or less comprehensive view on the mechanisms and on the correlation between the applied deposition techniques, the parameters and the structural properties of the films, and that many contradictory results and interpretations exist even today. This is partly because of the neglect of the simultaneous effect of the many deposition variables as it was stated by Chopra in his book[32] long time ago, partly because beside certain parameters which can be determined (or monitored) with higher or lower accuracy (e.g. substrate temperature, impinging rate of adatoms, film thickness, etc.) there are others which cannot be (or are not) identified and determined in the experiments. Among the latter ones the presence of various kinds of impurities (environmental or doping ones) has to be considered as that which, as much as the substrate temperature, strongly affect the structure evolution[33-39,18,40-45,25]. The present results of Toyoda et.al[45] clearly show that environmental impurities can be present, affect and alter the structure evolution also in case of UHV deposition techniques. This is in accordance with the conclusions of Barna[41] when reviewed the results of the related literature namely that impurities of a quantity near to, or even below the detectability limit may affect significantly the structure formation. This high sensitivity can be explained by the possible process induced segregation of impurity species taking place during growth and coalescence of crystals as well as during the grain growth by grain boundary movement in the continuous films[46,39,47-50].

Among the important results of the last decades which could be used to understand the mechanisms responsible for the structure formation, the results of the in situ transmission electron microscopic (TEM) experiments and the compilation of the structure-zone models have to be mentioned here.

The in situ TEM experiments revealed the growth stages and the elementary processes of the structure evolution (nucleation, crystal- or grain growth, coalescence, grain coarsening by grain boundary (GB) migration, phase transformations), and the possible effects of deposition parameters on them[51,36,52,38]. These experiments revealed

clearly also the segregation of codepositing impurity species to the surface of growing crystals and the repeated nucleation on these surfaces covered by the layer of this impurity phase[53,38,54].

The results on the grain morphology of as-deposited thick films prepared in the characteristic temperature ranges (Ts < 0.3 Tm, 0.3 Tm < Ts < 0.5 Tm, Ts > 0.5 Tm, where Ts is the substrate temperature, Tm the bulk melting temperature of the film material) have been compiled in the structure-zone models[55,57,42,38]. The attempts made time after time to describe and understand the mechanisms responsible for the development of these morphologies in the various temperature intervals contributed to the correction of the different models, and urged researchers to include new possible mechanisms into them for the better understanding of the problems, and give a more comprehensive description of the phenomena responsible for the development of the various structures. The surface diffusion and its dependence on the temperature, incidence angle of the vapour beam, adsorbed impurities, as well as the "surface recrystallization" (more precisely surface-energy-driven recrystallization introduced in ref. 55) were at first the main arguments in general terms to explain the formation of various structures[55,59-61]. Grovenor et.al[42] stated that "it has not been clearly demonstrated however that surface diffusion and surface recrystallization can completely determine the grain structure of deposits". Therefore GB migration has been introduced into the description of the development of grain structure as a decisive element and confirmed by recent investigations[42,62,58,63] pointing also to the situation that both the mobility and the activation energy for migration of GB-s depend on their crystallography and on the level of contamination. Barna[41] and Barna et.al[18] have shown that the process induced segregation of impurity species taking place on the growing crystal surfaces[18] can accumulate the contamination at specific GB-s of polycrystalline films and change their properties. On the basis of these results impurities should be considered as one of the key parameters controlling the structure evolution in the various zones of the structure zone models.

Codeposition of impurities might have also specific effects both on the grain morphology and on the texture when a crystal face anisotropy in the surface chemical interaction exists. This effect has been shown for oxygen and Al system[64-65] and made possible to explain the formation of growth hillocks with tops of truncated octahedrons in Al films[46,39], the rounding of the edges formed by (111) faces of Al crystals, and the different growth topography of Al (111) and (100) faces[47] as well as the changing of the usual <111> texture to the coexistence of the <111> and <100> textures in the presence of oxygen[66-67,44].

The present paper reviews the fundamental structure forming phenomena which control the structure formation in polycrystalline films and their role in the evolution of characteristic structures (morphology, texture and structure of GB-s). Impurity content is introduced as a fundamental parameter of the film deposition, and the influence of active additives and impurities on these phenomena, and consequently, on the developing structure will be considered in details. It is shown that an basic (ideal) structure zone model (BSZM) incorporating also the texture properties can be developed on the basis of the fundamental structure forming phenomena in the absence of impurities. This model

during the formation of the film. The analysis of the problem leads to the conclusion that, because of its complexity, the structure formation can not be described only by single atomic processes like surface diffusion and bulk diffusion, but we should find the the fundamental structure forming phenomena which give account for the global effect of the atomic processes and are directly responsible for the various features of the structure evolution.

TABLE 1. THE FUNDAMENTAL STRUCTURE FORMING PHENOMENA

OCCURRENCE NATURE	PHENOMENA	PLACE
time to time at activation	*NUCLEATION* clustering	**on the substrate**
continuous	*CRYSTAL GROWTH* monolayer crystal growth	**on crystal faces**
time to time at activation *time to time at activation*	*GRAIN GROWTH* coalescence grain boundary migration	**on the substrate** **in continuous film**
continuous *time to time at activation*	*PROCESS INDUCED SEGREGATION of IMPURITY SPECIES* * due to monolayer crystal growth * due to grain boundary movement	**on crystal faces** **in the bulk of film**

2.1. The Fundamental Structure Forming Phenomena

The fundamental phenomena are the phenomena which

a.) start the condensation on the substrate:
    it is the nucleation;

b.) incorporate the impinging (deposited) adatoms[a] into the growing individual units of the film structure:
    it is the crystal growth;

c.) reorganise the unit structure of the film:
    it is the grain growth by coalescence and by abnormal grain growth due to GB migration;

d.) develop the phases of impurities or additives:
    it is the process induced segregation.

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[a] The terms "adatom" will indicate the species of the main component, while "impurity species" the impurities and additives.

enables the construction of real structure zone models (RSZM) for the various preparation conditions and the description of the development of these real structures by the fundamental structure forming phenomena and by the dependence of these on the active impurities or additives (impurity species). The results could contribute to the interpretation of various experimental results, and also to the tailoring of defined polycrystalline film structures.

2. The Fundamental Structure Forming Phenomena and their Role in the Evolution of the Characteristic Structural Features

The growth stages of the polycrystalline film formation are schemed in Fig.1.[1] This structure evolution (i.e. nucleation, grain growth, coalescence of impinging grains by complete (liquid like) coalescence leading to single crystals, or by incomplete coalescence, leading to polycrystalline islands, thickness growth) is valid at substrate
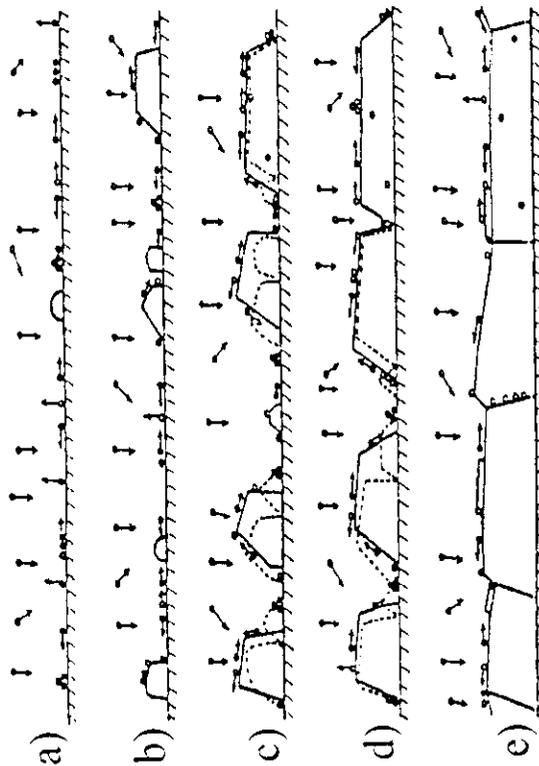
Fig.1 Growth stages of polycrystalline film formation a nucleation, b: crystal growth; c: coalescence; d growth by filling of the channels; e thickness growth of the continuous film. Dark circles mark adatoms; light circles impurity species; crystals before coalescence are marked by dashed line

temperatures Ts ≥ 0.3 Tm, i.e. when the bulk diffusion is effective. Codeposition of impurities, or additives is also considered, and their species are schemed by open circles. From this picture it is clear that the final structure of the film is a result of the creation and growth of the structural units (like grains) and their periodic reorganisation

The fundamental structure forming phenomena are continuously effective (the crystal growth, the segregation of impurity species by the crystal growth) while others are occasional (the primary, secondary or repeated nucleation, the restructuration by GB migration, the segregation of the impurity species by GB migration). These phenomena manifest diversely in the various growth stages because they are controlled by the actual structural conditions existing in the given growth stage. It is also easy to understand that these structural conditions (called structural preconditions) are developed by the growth phenomena being active during the growth stage preceding the considered one.

In this section the fundamental structure forming phenomena will be discussed except the primary and secondary nucleation on the substrate in which we refer the reader to the reviews given in ref. 68-74. Codepositing impurity species have a direct influence both on the crystal growth and the GB migration therefore it is practical to discuss at first the process induced segregation of impurity species and the formation of their phases.

2.1.1. The Process Induced Segregation of Impurity Species

According to the experimental results those impurities play an active role in the structure formation which are segregated by the structure building and restructuration processes and develop three dimensional segregates or a bidimensional covering layer on the free surface or on the grain boundaries (active impurities). In this section the possible atomic processes of segregation and the formation of impurity phases are discussed. Segregation can take place either on the free surface by the atomic processes of crystal growth or in the volume of the film by GB migration.

In situ transmission electron microscopic experiments carried out on In and codepositing carbon as well as on Al and oxygen systems clearly demonstrated the segregation of impurities during the crystal growth and the development of a surface covering carbon or oxide layer resulting in the rounding of the crystals and in repeated nucleation on them[38,43,55]. The development of three dimensional segregates has been found in codeposited Al-Ni and Al-Sn thin films[46,75]. The small grained structure with an oxide phase at the grain boundaries detected in magnetic recording thin films[4] can also be attributed to the segregation phenomenon.

The process induced segregation of impurity species stems from the atomic processes of the monolayer crystal growth[48,53]. Impurity species are preferentially adsorbed at the kink sites, i.e. at the same sites where the adatoms are sticked and incorporated into the growing crystal lattice and generally bonded in precursor state at these first with low binding energy. The segregation of impurity species can proceed at these sites as the impurity species are replaced by an impinging adatom, or remain adsorbed and migrate along the step. This process can be repeated and by this way the moving growth step will roll all the adsorbed impurity species along the crystal face and nuclei of a solid phase of impurity or its compound will develop at some sites of growth steps later. Three dimensional segregates will form at these nuclei if the impurity has high self

surface mobility, while at low self surface mobility the growth steps can be covered by the impurity phase. The next growth step arriving at this site will be also stopped. Bunches of growth steps decorated by pinning sites develop in that case. Typical surface topography related to this proposed mechanism are shown in oxygen contaminated thick Al films (Fig.2a).

This model indicates that the sites of monolayer nucleation and the direction of the movement of the growth steps will determine the surface areas where the phases of segregated impurities will develop. This phase of impurities will hinder the incorporation of adatoms, i.e. the crystal growth in that area showing up as the truncation of crystals (area marked by B). The different growth directions and their effect will be discussed in the following sections in connection with the particular stages of film formation Higher concentration of impurities in the vapour beam extends of the coverage of the crystal faces and can result in the full coverage of the crystals. In that case the growth of these crystals will be completely blocked and the condensation will proceed by repeated nucleation[46,39] Fig.2b.(area marked by A).

The growth morphology of crystals will be more complicated when the surface chemical interaction of codepositing impurity species with the growing crystal surface is different on the different crystallographic faces. It has been shown that oxygen species can in detail for the Al and oxygen system. penetrate into the topmost layer of the crystal lattice on the {001} and {110} faces while they are situated on the {111} faces[64,65]. As a consequence of this the crystal growth will segregate the oxygen species on the {111} faces while they can be incorporated into the {001} and {110} faces. Therefore the {111} faces will be covered by the phase of an impurity layer, while the other faces remain uncontaminated. This anisotropy in the segregation shows up on one hand in the different growth topography on the various crystal faces of Al crystals (bunches of growth steps develop only on the {111} crystal faces)[47,76] Fig.2c, and on the other hand in the different truncation of edges formed by the different crystal faces (truncation of edges formed by {111} faces, no truncation of edges formed by {111} and {100} faces)[47].

Moving GB-s can segregate the solute impurities both to GB-s[49,50], and in case of coalescence to the surface of developing crystals.

2.1.2. The Crystal Growth Phenomena in Polycrystalline Films

The deposited material is incorporated into the condensed phase by the crystal growth processes. Two main cases of crystal growth should be considered in polycrystalline thin films: the growth of discrete crystals dispersed on the substrate surface and the growth of crystals which are parts of a polycrystalline structure. The effects of the temperature and impurities on the crystal growth will be considered.

Growth of Discrete Crystals Dispersed on the Substrate Surface

The discrete crystals dispersed on the substrate surface are growing independently of each other disregarding the fact that their adatom collection areas may overlap (Fig1.a

and b.). The defect structure of the crystals as well as their orientation on the substrate together with their coverage with possible phases of segregated impurities will control the crystal growth processes. Their growth takes place by joining the adatoms impinging directly from the vapour beam onto their surface and by the flux of the adatoms adsorbed on the substrate and migrating to them. In case of small crystals and low nucleation density, the later process dominates.

The substrate can affect the monolayer growth of the crystal according to the nature of the intersection lines between the substrate and its side faces. If the intersections are active in the nucleation of monolayers, the growth steps will move across the crystal faces from this intersection to the top of the crystals. In the other case the nucleation of the bidimensional monolayers can take place on the top of the crystals and the growth steps will move across the side faces to the substrate.

This has been demonstrated in codeposited Al-Sn system[75] and in oxygen contaminated Al films[47]. The segregation of Sn to the top surface of the Al crystals on mica and NaCl (100) surface indicated that on these substrates the intersections were active in the nucleation. This have shown up also when the epitaxially grown Al crystals were deposited in the presence of oxygen impurity. In that case the truncation of the edges between the top {111} and the side {111} faces indicated that the growth steps moved on both crystal faces to this edge segregating the oxygen also to this area. On amorphous carbon or SiO_2 substrates Sn was segregated to the substrate, i.e. the growth steps moved on the side faces downwards to the substrate, i.e. the intersections were not active in the nucleation of monolayers in these cases.

At a given impurity level the extent of coverage by the impurity phase on the various crystal faces is determined by their orientation and by the activity of their intersection with the substrate. Therefore it influences the coalescence and determines the purity of GB-s developing at first by coalescence[54].

The self surface diffusion of adatoms plays a crucial role in the growth of discrete crystals. If the self surface diffusion of adatoms is high (at high substrate temperatures), well faceted crystals can grow at high purity conditions. The self surface diffusion of adatoms is reduced by lowering the temperature. In that case the oblique incidence of the vapour beam will strongly influence the crystal growth because of the different impinging rate on the various crystal faces will not be compensated by the self surface diffusion.

The Growth of Crystals as Parts of a Polycrystalline Structure

The growth of crystals as parts of a polycrystalline structure generally starts when the coalescence stage is completed, i.e. the film is continuous. In that stage the film is composed of crystals developed during the coalescence stage with sizes and orientations determined both by the temperature and impurity content (Fig.3).

The specific surface elements of polycrystalline surfaces which control the monolayer growth of the individual crystals are the intersections of GB-s with the surface. The condition and structure of GB-s determine their role in the crystal growth phenomena[48,51]. The intersection of pure GB-s with the free surface present a line of

0.5 μ

0.5 μ

2 μ

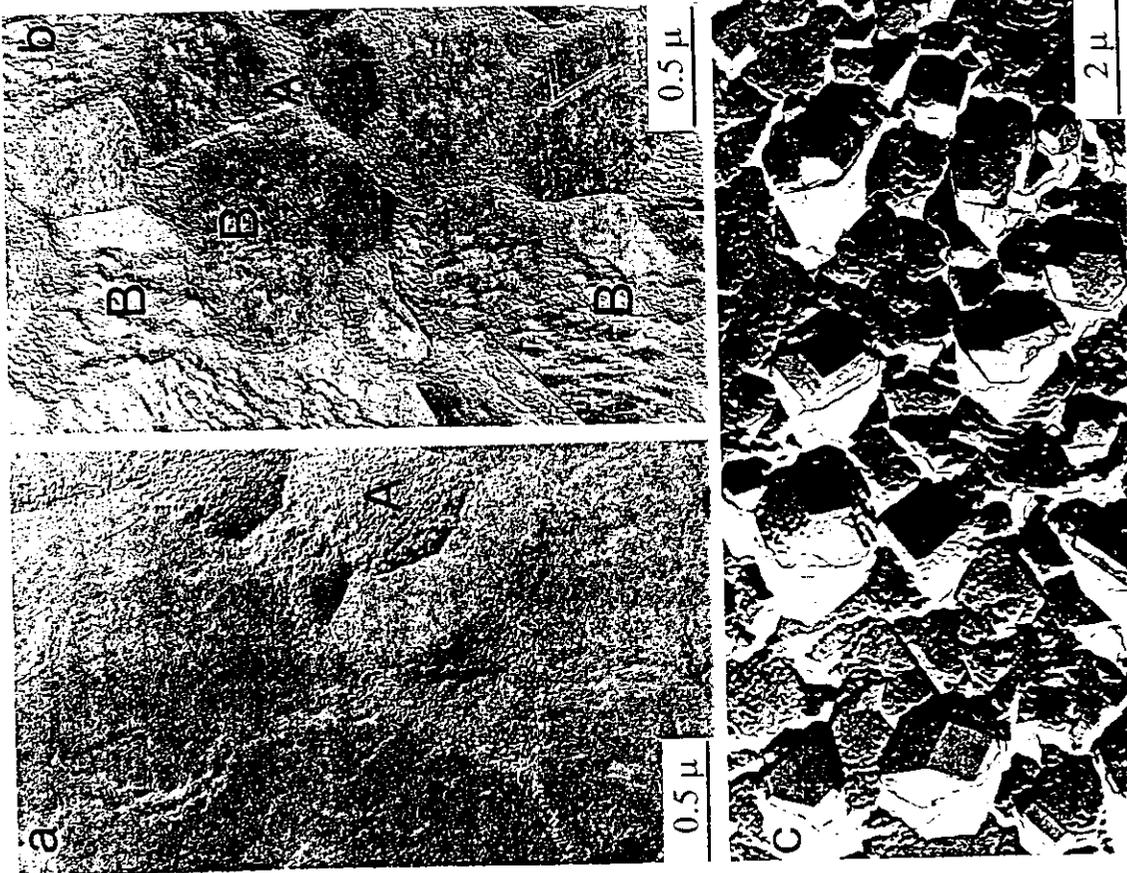Fig.2 Surface topography of 1 μm thick Al films deposited at 2 nm/s deposition rate. a) and b), Ts = 0.6 Tm low level of oxygen contamination, bunches of growth steps, repeated nucleation on contaminated crystal surfaces (marked by A) and truncated crystals (marked by B). c) Ts = 0.4 Tm medium level of oxygen contamination smooth {100} crystal faces, steps due to lamellar growth on {111} crystal faces
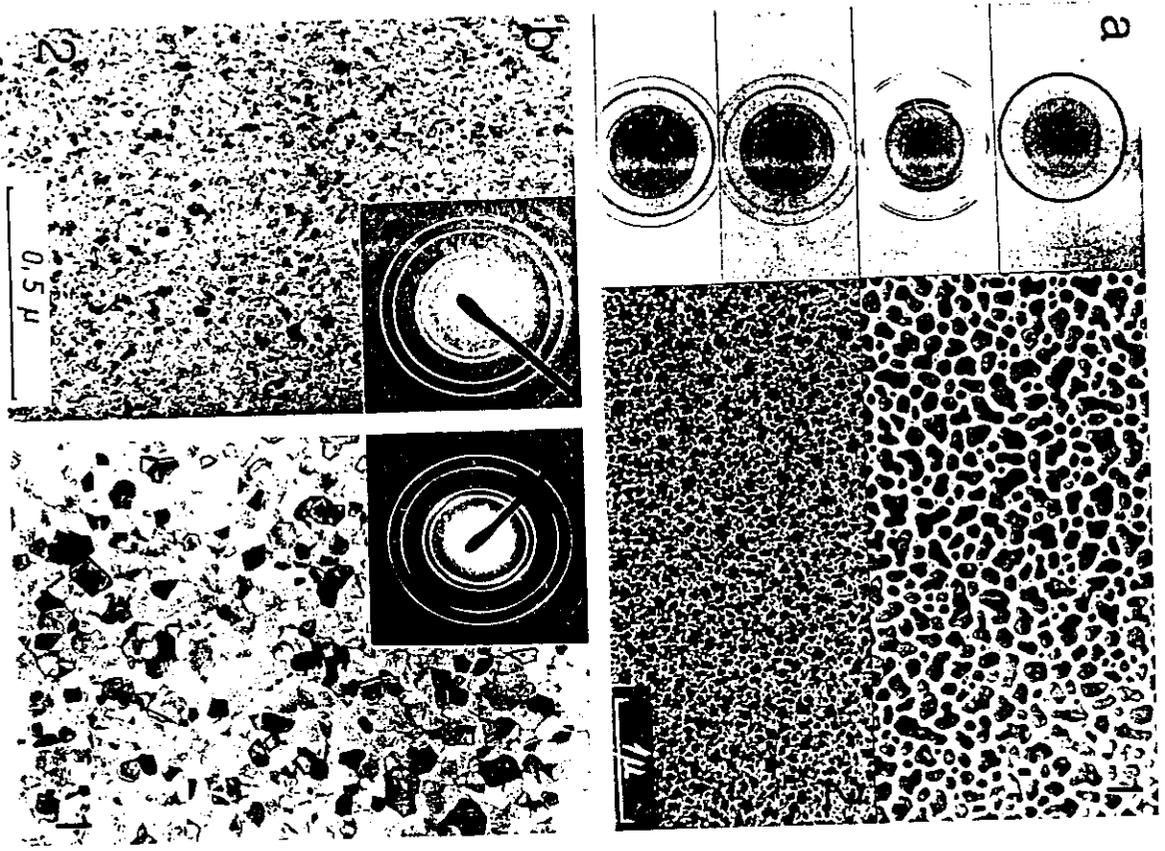
Fig.3. Transmission electron microscopic images and the corresponding electron diffraction patterns of films deposited on amorphous substrates at different impurity level of oxygen contamination a) 50 nm thick In film deposited at 1 nm/s deposition rate, at Ts = 0.67 Tm, level of oxygen contamination: 1) low, 2) high; b) 50 nm thick Al film deposited at 1 nm/s deposition rate, at Ts = 0.4 Tm, level of oxygen contamination 1) low, 2) medium.

defects which can be active in the nucleation of monolayers. Consequently the monolayers will preferentially move from the GB-s to the centre of crystal faces. In case of contaminated GB-s their intersection line is not active in the monolayer nucleation, but it might be active in the binding of impurity species. Consequently the monolayers are nucleated in that case mainly within the crystal faces and the growth steps move to the GB-s. Therefore the codepositing impurity species will be segregated to the centre of the grains in the first case and to the GB-s in the second one.

At high purity conditions and noticeable self surface diffusivity of adatoms smooth crystal faces can develop. The parts of these crystals protruding over the surface are faceted which reflect the orientation of the crystals. In case of textured film the whole surface is smooth and built up of crystal faces according to the orientation of the texture. GB grooves shaped according to the thermodynamic equilibrium can be present on the surface.

The growth of the crystals can be interrupted at noticeable value of the bulk diffusion (Ts > 0.3 Tm) by a restructuration developing larger grains. The crystal growth is however continued on the new surface of the developed grain and controlled by the new surface conditions. In that case single crystals proceeding from the substrate to the surface grow permanently during the film deposition (Fig.4.).

At temperatures Ts < 0.3 Tm where the volume diffusion is not effective and therefore the restructuration (coalescence) is negligible, a growth competition can develop between the neighbouring crystals of different orientations when the growth rates of the different crystal faces are different due to the surface energy anisotropy[7]. In this case the faster growing crystals will survive forming a cone like columnar structure.

At substrate temperatures Ts < 0.2 Tm where the sticking coefficient is unity and the surface diffusion is negligible, the crystals developing in the nucleation and growth stages will grow in the continuous film uninterruptedly with the same growth rate independently on their orientation. In that case a fibrous structure develops.

Impurities dramatically change the crystal growth phenomena also in continuous films. In that case, depending on the impurity content, a lower or larger number of GB-s are contaminated from the beginning. This means that the crystal growth will segregate the impurities mostly to the contaminated GB-s contributing to the growth of the impurity phase in that area[48]. One should consider here the situation that both the sticking probability of impurity species and their segregation depends on the temperature.

By increasing the concentration of impurities, the surface area covered by the impurity layer increases. At first the impurity phase will grow only at the GB-s. In that case columnar structure with thinner columns and contaminated GB-s will develop (Fig.5). At higher impurity concentration the impurity phase will grow over the surface of the neighbouring crystals and by this way broader and deeper GB grooves will develop. Further on the surface of the growing crystals could become completely covered and the growth of the crystals stopped. In that case the condensation proceeds by repeated nucleation on the covered surface of crystals. These films might contain GB-s also parallel to the substrate, and build up from three dimensional equiaxed grains or from grains of bimodal size distribution. These grains are separated by contaminated GB-

s. At high impurity concentration globular, or even microcrystalline or nanocrystalline structures can develop by these mechanisms[s4].

The phenomena are the same at various substrate temperatures, however the sizes of grains will decrease by decreasing temperature, and the size distribution may become more bimodal.

The anisotropic segregation of impurities related to the anisotropic chemical interaction on the different crystallographic faces results in a peculiar growth competition between crystals with different orientation. Those of the randomly oriented crystals will survive which are growing with faces not segregating impurities. The development of growth hillocks in oxygen contaminated Al films exhibiting tops of truncated octahedrons could be explained also by this competitive growth[78,41,39]. At given deposition parameters the segregation of oxygen on the {111} Al crystal faces can induce the lamellar crystal growth on these faces[76] (Fig.2c.).

The oblique incidence of the vapour beam has an influence on the grain growth in continuous films when the surface diffusion and the GB migration are limited or blocked. In that case the impinging rate of adatoms on the various crystallographic faces is influenced by the oblique incidence of the vapour beam according to their situation relative to the incidence plane of the vapour beam. As a consequence both the growth rate of the various crystal faces and their contamination rate are be different. Channels between the crystal planes perpendicular to the vapour beam incidence plane can develop because of the shadowing while coalescence or competitive growth of grains can take place at crystal faces lying in the plane of the vapour beam incidence. This leads to the development of elongated grains with long axis perpendicular to the vapour beam incidence plane. The columns are tilted to the direction of the vapour beam incidence[79,44,80-81]. At temperatures Ts < 0.2 Tm when the surface diffusion of adatoms is negligible a fine fiber structure tilted to the direction of the vapour beam incidence develops. This situation is described by computer simulations on the basis of the ballistic model[82,83].

2.1.3. Grain Growth by Grain Boundary Migration

This phenomenon takes place during two stages of the formation of polycrystalline films: during the coalescence stage and during the thickness growth (in polycrystalline island and continuous film).

Coalescence

Coalescence takes place when the growing adjacent discrete crystals approach and touch each other. During this process the previously isolated grains interact by interfusing their structure. At the coalescence an intergranular area develops and the coalescing crystals mutually influence the reorganisation and growth of their structure.
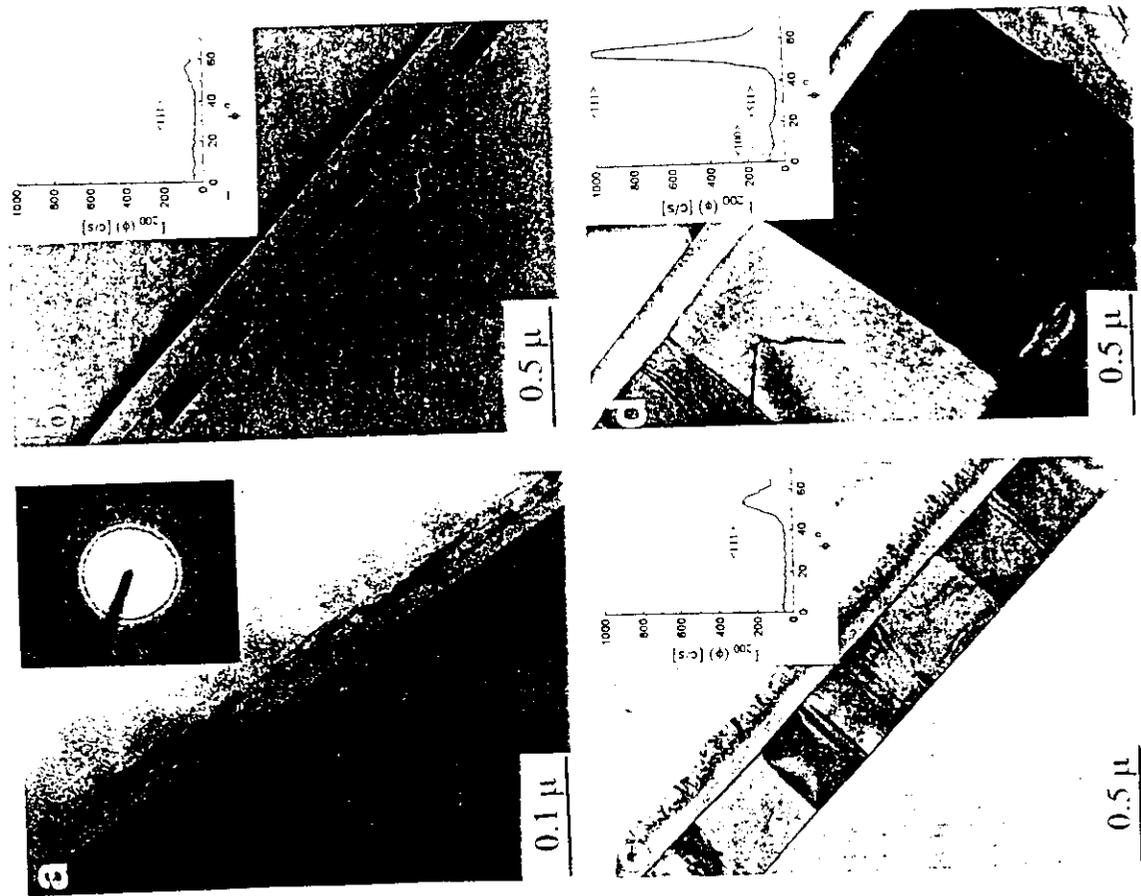

Fig.4 Grain growth and texture evolution in Al films with increasing thickness at low level of oxygen contamination. Substrate Si(111) covered by oxide. Deposition rate: 2 nm/s, Ts/Tm: 0.35. Inserts are the selected area transmission electron diffraction pattern in a), the 200 pole figures in b),c) and d).
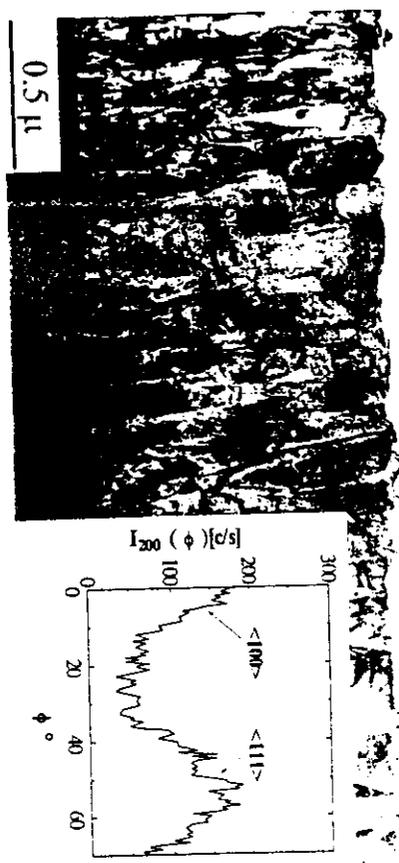
Fig.5. Cross sectional TEM image of an Al film deposited on naturally oxidized Si wafer at Ts = 0.36 Tm. at 2 mm/s deposition rate and medium level of oxygen contamination. The morphology is changing along the cross section : small crystals are at the substrate and V shaped columns are growing out of the small grains. Coexistence of <111> and <100> texture shown by the X-ray pole figure.
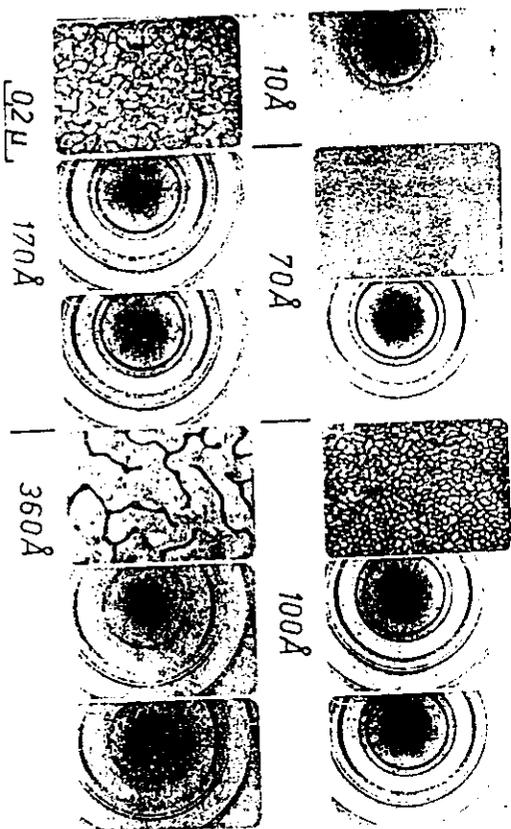

Fig.6. Development of texture in In film deposited at Ts = 0.47 Tm at low impurity level. Images taken from in situ TEM experiments[11,12].

According to the theory of sintering, the main processes of coalescence are: (I) neck formation, (II) filling of necks by surface self diffusion, (III) formation of GB-s upon joining the lattices of the crystals, (IV) moving out of the GB by diffusion controlled GB migration (recrystallization)[51]. The coalescence is considered *complete* when all the above mentioned processes take place and a single crystal develops, or *incomplete* when the recrystallization is not accomplished and a polycrystalline island containing intergranular area (defects, large or small angle GB-s) is formed[54]. When the complete coalescence is liquid like, it is accompanied by a strong contraction of the coalescing crystals leaving free area on the substrate. In these areas the condensation results in secondary nucleation growing new grains, the secondary crystals.

The presence of impurities through the development of segregated covering layers on the surface of the growing discrete individual crystals (discussed in 2.1.2.) strongly modify their coalescence. The contamination of the contacting surfaces can hinder not only the realisation of the complete coalescence but also the filling up of the necks. Pores can develop in the areas of these necks and the GB-s will be covered and stabilised by the impurity phase[54]. This effect of impurities limiting the coalescence is clearly shown in the difference of grain sizes of In and Al films deposited at low (Fig.3a.1. and b.1.) and high level (Fig.3a.2. and b.2.) of oxygen contamination. Mostly pure GB-s are present in the first case and contaminated GB-s in the second.

Grain Growth in Continuous Films by GB Migration

The restructuration discussed in connection with the coalescence proceeds further in continuous films by the movement of GB-s. At a given temperature the mobility of the GB-s depend on their type and level of contamination. The two driving forces for GB migration are the GB energy and the anisotropy of the free surface energy of the neighbouring crystal faces. In thick films where the free surface to volume ratio is low, the main driving force is the GB energy, while in thin films where this ratio is high the anisotropy of the free surface energy of the neighbouring crystal faces can drive the GB migration[42,63,58,84,88].

If there are mobile GB-s abnormal grain growth takes place leading at first to the development of bimodal grain size distribution[87]. At high purity conditions and at high Ts the bimodal grain size distribution can be transformed into a monomodal distribution during the film preparation. If a part of GB-s are contaminated, the abnormal grain growth cannot be completed and a bimodal grain size distribution will be stabilised. At high contamination level abnormal grain growth cannot be realised because all or most of the GB-s are contaminated and stabilised when the film becomes continuous.

3. Structure Evolution

The structure evolution of polycrystalline films can be followed in Table 2. The fundamental structure forming phenomena which were discussed before and the

elementary atomic processes of these phenomena together with the structural preconditions determining the processes and the developing structures are summarised for the subsequent stages of film formation[24]. One has to remember that the structure forming phenomena and the involved atomic processes are different and characteristic to each stage of the structure evolution. This is because the structural conditions of each growth stage are unique and the elementary processes in each stage are determined by the structural conditions.

4. Texture Evolution

In many cases all or a part of the grains of polycrystalline films is oriented in a preferred direction with respect to the substrate. This property of thin films is called texture (macrotexture). As a consequence of the development of macrotextures other crystallographic properties of thin films can be identified. If one considers the texture on a small scale i.e. a few hundred grains, one can find that the distribution of the preferentially oriented grains might be inhomogeneous i.e. the film might have a microtexture[x]. This inhomogeneity of the texture might be related to substrate inhomogeneities and to their effects on the fundamental structure forming phenomena. In textured films the grain boundaries have also a preferential geometry which is called misorientation texture (mesotexture)[x].

There are extensive reviews and books on the different kind of investigation methods applied for the determination of textures. The most general techniques are the X-ray diffraction methods[91,92], which give an overall information of the texture in the whole thickness of the film. For the description of preferred orientations pole figures and more recently orientation distribution functions (ODF) are used. Textures can be characterised by the high resolution as well as selected area transmission electron diffraction and the reflection electron diffraction methods[x]. The determination of micro- and mesotextures is carried out by grain by grain orientation measurement in TEM[95] or SEM[96].

In this section the characterisation of the textures will be given and their origin and development will be reviewed in the light of the fundamental structure forming phenomena discussed above.
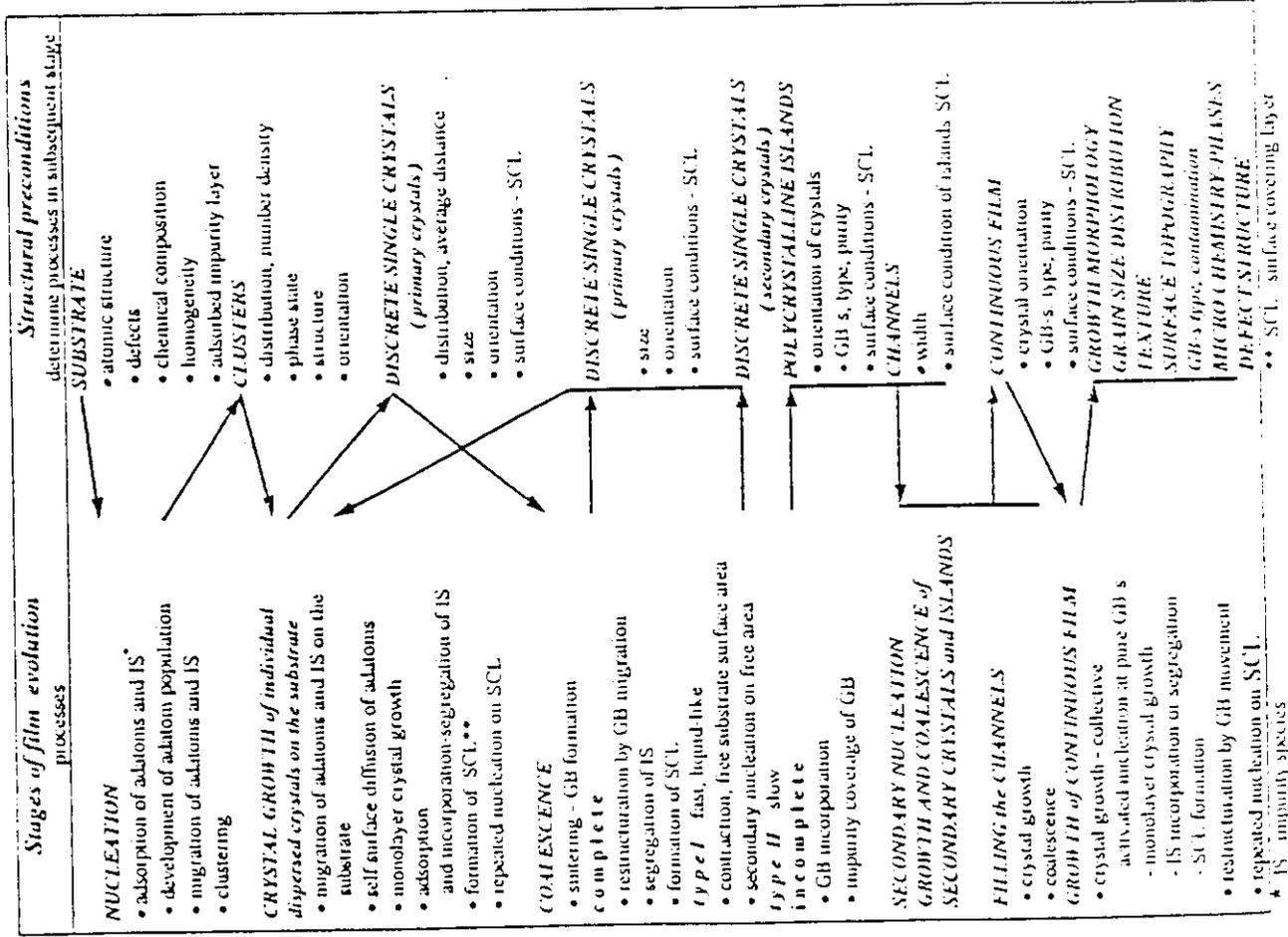
4.1. Classification of Textures

E. Bauer[x,x] classified the textures according to the *kind of orientation* of the crystals as follows:

One degree orientation (1-O) (fiber texture) means that only one crystallographic axis of most crystals points preferentially in a given direction, which is the orientation direction, or fiber axis. The random orientation of all crystals is the limiting case of the 1-O texture for increasing deviations from the preferred direction.

In case of *two degree orientation* (II-O) two axes of most crystals point in preferred orientations. The single crystal orientation is the limiting case of II-O texture for

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TABLE 2. STRUCTURE EVOLUTION IN POLYCRYSTALLINE FILMS

Stages of film evolution processes	Structural preconditions determine processes in subsequent stage
NUCLEATION • adsorption of adatoms and IS* • development of adatom population • migration of adatoms and IS • clustering	**SUBSTRATE** • atomic structure • defects • chemical composition • homogeneity • adsorbed impurity layer
CRYSTAL GROWTH of individual dispersed crystals on the substrate • migration of adatoms and IS on the substrate • self surface diffusion of adatoms • monolayer crystal growth • adsorption and incorporation-segregation of IS • formation of SCL** • repeated nucleation on SCL	**CLUSTERS** • distribution, number density • phase state • structure • orientation **DISCRETE SINGLE CRYSTALS (primary crystals)** • distribution, average distance • size • orientation • surface conditions - SCL
COALESCENCE • sintering - GB formation **complete** • restructuration by GB migration • segregation of IS • formation of SCL *type I* fast, liquid-like • contraction, free substrate surface area • secondary nucleation on free area *type II* slow **incomplete** • GB incorporation • impurity coverage of GB	**DISCRETE SINGLE CRYSTALS (primary crystals)** • size • orientation • surface conditions - SCL
SECONDARY NUCLEATION **GROWTH AND COALESCENCE of SECONDARY CRYSTALS and ISLANDS**	**DISCRETE SINGLE CRYSTALS (secondary crystals)** **POLYCRYSTALLINE ISLANDS** • orientation of crystals • GB s, type, purity • surface conditions - SCL **CHANNELS** • width • surface condition of islands SCL.

FILLING the CHANNELS
• crystal growth
• coalescence
GROWTH of CONTINUOUS FILM
• crystal growth - collective
  activated nucleation at pure GB s
  - monolayer crystal growth
  - IS incorporation or segregation
  - SCL formation
• restructuration by GB movement
• repeated nucleation on SCL.
	CONTINUOUS FILM
	• crystal orientation
	• GB s, type, purity
	• surface conditions - SCL
	GROWTH MORPHOLOGY
	GRAIN SIZE DISTRIBUTION
	TEXTURE
	SURFACE TOPOGRAPHY
	GB s type, contamination
	MICRO CHEMISTRY-PHASES
	DEFECT STRUCTURE

* IS impurity species

** SCL surface covering layer

decreasing deviation of all crystals, which can be realised completely only on single crystal substrates in case of epitaxy.

The universal validity of this classification has been supported by the large number of experiments. The fiber texture is the general case in polycrystalline films and the coexistence of two fiber textures in a film (e.g. <111>, <100> in Al films[67,44,66]) is also common and mainly related to the preparation conditions. The development of II-O texture is mainly related to oblique deposition in the presence of impurities[44].

The classification of textures according to their *origin* can promote the understanding of their evolution and the interpretation of the textures of films prepared by different techniques at various parameters[97]. The following types of textures according to their origin can be identified:

- *activated nucleation texture*
- *evolutionary growth texture*
  - *restructuration growth texture*
  - *competitive growth texture*

This classification involves already the mechanisms of their evolution.

Experiments have shown that on amorphous substrates the nuclei are randomly oriented[98,99]. From these results one can conclude that initial or nucleation textures are due to the orienting influence of the singlecrystalline or polycrystalline substrates (e.g. underlayer) therefore the nucleation texture can be only an activated one. This is illustrated in experiments applying textured underlayers[100,4]. In the following we intend to discuss the conditions and the operation of the fundamental structure forming phenomena leading to the development of evolutionary growth textures.

4.2. Development of Evolutionary Growth Texture

The evolutionary growth texture means that the preferred orientation of the crystals develops during the evolution of the film structure. In that case one has to reveal and understand which of the fundamental phenomena are active in the development of the crystals with preferred orientation and how the deposited material or a part of it is accumulated into those crystals.

4.2.1. Restructuration Growth Texture

It has been shown in the previous sections that restructuration can be active when the grain boundaries are mobile, i.e. at $T_s > 0.3$ T_m and at low impurity content. The restructuration is effective in the development of texture, when the driving force of the GB migration is related to the difference in the surface energy of the neighbouring crystal faces at the free surface and at the substrate. This consideration concludes that faces can develop in a thickness range where the surface to restructuration growth texture can develop in a thickness range where the surface to volume ratio is large. The most effective in this respect is the coalescence stage. This is illustrated in Fig.6, by the results of in situ TEM experiments, in which In was deposited

on amorphous carbon layer at -70 °C. It is shown that the crystals formed by nucleation are randomly oriented. The texture develops mainly during the growth of grains by coalescence. This is the general condition for the restructuration growth texture. The coalescence. This is the general condition for the restructuration growth texture. The further grain growth in thicker films, i.e. the completion of the restructuration occurs in the whole increases the strength of the texture. In that case the restructuration occurs in the whole thickness of the films dissolving also the initially formed randomly oriented small grains increases the strength of the texture. In that case the restructuration occurs in the whole The films have a homogeneous structure along the thickness from the beginning of the film formation and the singlecrystalline grains (columns) proceed from the substrate to the film surface.

In case of restructuration growth textures the crystal faces of lowest free energy are parallel to the substrate and the axis of the texture is the respective crystallographic axis (in f.c.c. metals this is the <111> axis).

The development of restructuration growth texture is shown on cross sectional TEM images in Fig.4, in case of Al film deposited at 50°C and at low impurity content, o SiO₂ covered Si wafer. The film growth starts by the formation of a very large number of discrete small crystals of random orientation. By increasing film thickness the <111> preferred orientation develops simultaneously with an increase of the grain size.

By increasing impurity content in continuous films, both coalescence and grain growth are more and more limited because of the increasing contamination level of the crystal surfaces and of the surface of coalescing crystals and of the grain boundaries. The complete coalescence is more and more limited and the film will be composed of small grains with increasing part of random orientation when it becomes continuous. This shown in Fig.3a.2. and b.2. From this structure, containing contamination stabilised GB either a columnar, or globular structure of randomly oriented grains or at given conditions also a texture can develop due to the competitive growth of random grains, be discussed in the next section.

The oblique incidence of the vapour beam will not influence the development of the restructuration growth texture when the restructuration is strong i.e. at substra temperatures higher than a critical value which is about 0.3 T_m at low impuri concentration[79,44]. By increasing the impurity concentration this critical temperatu increases. Below the critical temperature the texture axis together with the colum becomes tilted to the direction of the vapour beam incidence[80,44,81]. In case of impuri with anisotropic surface chemical interaction a II-O texture can develop as illustrated oxygen contaminated Al films[44]. The development of this structure seems to be impurity controlled competitive growth texture discussed in the next section.

4.2.2. Competitive Growth Texture

The origin of competitive growth is different at high purity conditions and wh impurities are present. Competitive growth of randomly oriented crystals can take pl at the end of the coalescence stage when the GB movement is limited either because the low temperature or the presence of impurities.

Fig.7 Structure zone models published in the literature a) Movchan-Demchishin[55], b) Thornton[16], c) Messier et al[57], d) Grovenor et al[42]

Left column

At low impurity concentration the competitive growth takes place at Ts < 0.3 Tm where the migration of pure GB-s is negligible. The driving force is the surface energy difference of the neighbouring crystal faces at the free surface leading to the preferred migration of adatoms[37].

At higher impurity concentration the GB migration is limited by the adsorbed impurities and the developing impurity phase can grow over the free surfaces of crystals hindering their growth. The small grained structure of randomly oriented crystals formed in the first stage of the film formation on the substrate is preserved till the end of the continuous film. A competitive growth of these crystals starts during the growth of the coalescence stage and a competitive growth of these crystals develops when an anisotropy exists in the surface chemical interaction of impurities on the various crystal faces. Only those crystals can grow continuously which are growing with faces not segregating the impurity species. The growth of crystals of other orientation will be blocked by the developing surface covering layer of impurities at different growth stages. By this way the preferentially oriented crystals grow over the others. The development of <100> texture in oxygen contaminated Al films was described by impurity controlled competitive growth[34,37] (Fig.5). In case of mixed <111> and <100> textures the <111> part probably develops by restructuration and the <100> part by competitive growth controlled by impurities.

5. Structure Zone Models

The structure zone models constructed so far are compiling the morphologies of thick films prepared in the various laboratories at different circumstances[55,58,42] (Fig.7). Sometimes structures related to some specific preparation conditions are also incorporated[42]. It has been shown in the previous discussions that the substrate temperature, and the impurities (concentration, kind) are the two main parameters which directly control the fundamental structure forming phenomena and the structure of the films itself. The systematisation of the fundamental structure forming phenomena, and their dependence on the two main parameters enable the construction of structure zone models describing both the morphologies and textures of films prepared at different conditions. These models synthetize the existing structure zone models and provide a tool for the classification of structures of real thin films and for the interpretation of their development.

In the following a basic structure zone model will be introduced at first, which considers only the temperature dependence of the fundamental structure forming phenomena if impurities are not present. Other structure zone models are also constructed for the different levels of impurity concentration as parameters[101].
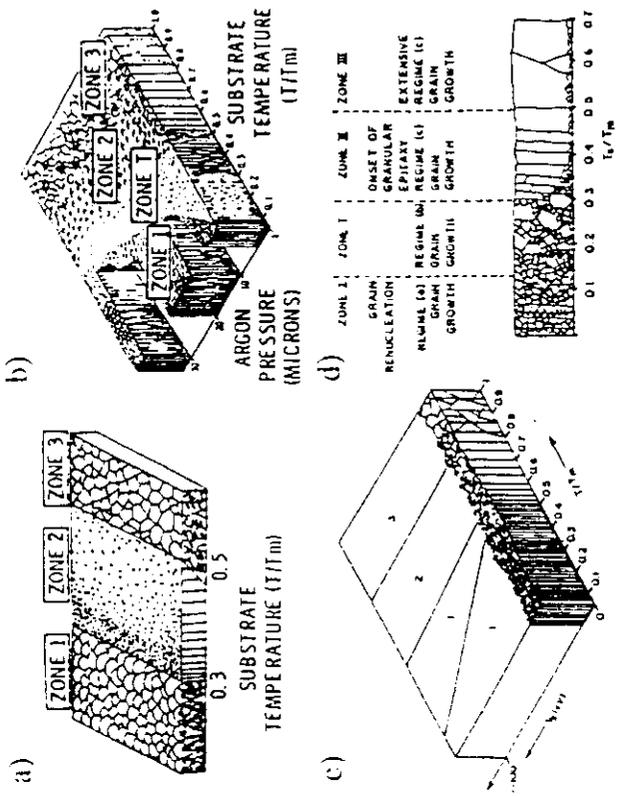
Right column

5.1. The Basic Structure Zone Model

The proposed basic structure zone model[101] is shown in Fig.8. At very low temperatures, Ts < 0.2 Tm (zone I.) no bulk diffusion exists and the surface diffusion is very limited. The grain structure is composed of fibers and most of them proceed from the substrate to the film surface. The size and orientation of fibers follows practically the size and the random orientation of the primary crystals developed in the first stage of the deposition. The size of the fibers increases with increasing temperature following mainly the temperature dependence of the nucleation density.

In the temperature range 0.2 Tm - 0.3 Tm (zone T) surface diffusion becomes effective inducing a possible competitive growth of the primary crystals of random orientation[9,102]. The driving force is the surface energy difference of the neighbouring crystal faces at the free surface leading to the anisotropic migration of adatoms between them (as discussed in section 2.1.2). This competitive growth results in an inhomogeneity both in the morphology and in the crystals orientation across the film thickness. At the substrate surface small primary crystals of random orientation exist. At higher thickness the crystals having higher growth rates develop into cone like grains due to the

competitional. Texture with orientation related to the fastest growing direction of crystals is monomodal. Texture evolved moving away from the substrate

In zone II and zone III, both the evolution of morphology and texture is controlled by restructuration. The film is composed from singlecrystalline columns with increasing diameter at increasing temperatures. The texture is determined by the lowest free surface energy of crystals. The films are homogeneous in the whole thickness.
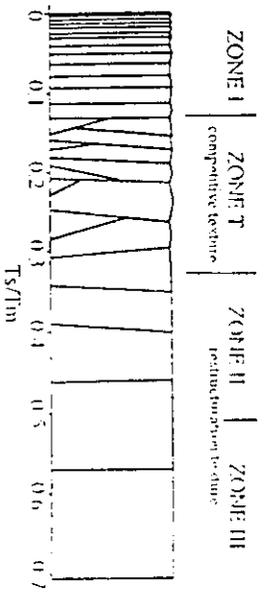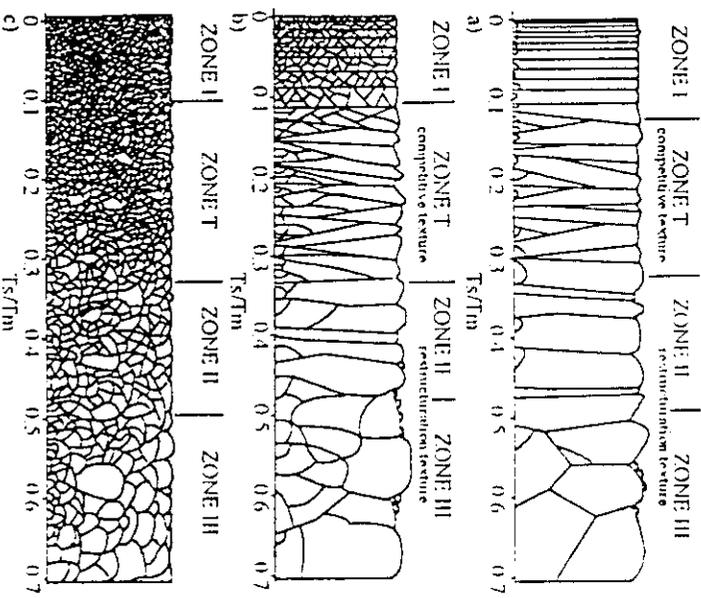

Fig 8 The schematic figure of the basic structure zone model[??]

Fig 9 The real structure zone models at low a), medium b) and high c) impurity content[??]

At high substrate temperatures the grain size distribution of as deposited films is monomodal. As the temperature is decreased it becomes bimodal because the GB is migration rate becomes lower and the abnormal grain growth can not be completed during the film deposition

The surface morphology of the film in the various zones is described in section 2.1.2.

5.2. Real Structure Zone Models

The structure evolution of real films is basically influenced by the second most important parameter, by the impurity content as explained before. The effect of this parameter was not considered in the previous structure zone models. In this section the real structure zone models are introduced for low, medium and high impurity concentration (low: $C_{imp} < 0.5\%$, medium: $C_{imp} \sim 1\%$, high: $C_{imp} > 10\%$) as well as for medium concentration of impurity with anisotropy in the surface micro chemistry

Low Impurity Level

The structure model at low impurity concentration is shown in Fig 9. At very low temperatures (zone I) the process induced segregation of impurities can be negligible and the impurity species could be incorporated into the growing lattice of fibers. The density of nucleation could be primarily influenced by the impurities and consequently the diameter of fibers could be smaller compared to BSZM.

In zone T the segregation of impurity species by the crystal growth increases by increasing temperature and the impurity phase is expected to be segregated mainly at the grain boundaries. This will decrease the diameter of grains and can contribute to the competitive growth of crystals in addition to the driving force related to the surface energy difference of neighbouring crystals. Both the morphology and the texture are inhomogeneous along the film thickness. Randomly oriented small grains can be found at the substrate while the fraction of the films apart the substrate is composed of cone like grains having competitive growth orientation. Exciting examples of this structure have been published in the literature for polycrystalline Si films[103,104,25].

In zone II a part of the first developing GB-s will be covered by the segregated impurity phase. Consequently the diameter of the developing columns will be smaller than in zone II of the BSZM, and the segregated impurities will be accumulated preferentially at these GB-s during the film growth. Because of the presence of contaminated GB-s, the developing columnar structure will have a bimodal grain size distribution. The texture is determined by the surface and interface energy minimisation but will not be as strong as that in zone II of the BSZM.

In zone III. the segregation of impurities by the GB movement becomes effective with increasing temperature and by this way a contamination layer can develop covering completely the surface of growing crystals. This results in the development of three

dimensional large grains which are separated by contamination stabilised GB-s. The grain size distribution is impurity stabilised bimodal. Texture due to the surface and interface energy minimisation can be present because in the coalescence stage of film formation the restructuration could be effective. The texture however will not be as strong as in zone III. of BS/M.

The surface roughness of the films in every structure zone will be higher than in case of the BS/M. This is related to the situation that the texture is not so complete. The features of the surface topography are the truncated parts of the crystal shapes protruding over the film surface. Dome shaped surface features as well as broad-deep GB grooves decorated with small grains, developed by repeated nucleation can be also present.

The role of segregated impurity phase in the crystal growth and restructuration increases by increasing the level of impurities. This results in decreased grain size destroying the texture. In case of impurities with anisotropy in the surface chemical interaction, duplex fiber textures will develop[64] (Fig.5.) or the texture orientation will be completely changed.

High Impurity Level

In that case the structure is globular in every zones with different grain sizes and mainly monomodal grain size distribution. The GB-s are covered by the impurity phase and mainly randomly oriented grains develop by repeated nucleation. Working at very high impurity content the volume of the impurity phase becomes comparable with that of the deposited material and microcrystalline, nanocrystalline and finally amorphous structures develop. The surface topography is composed of dome shaped features with sizes related to the actual size of the grains.

6. Summary

The introduction of the impurity content as a primary parameter of the film preparation beside the temperature makes possible the comprehensive treatment and analysis of the formation of polycrystalline film structures. It has been shown that the same mechanisms are responsible both for the development of the morphology and the orientation (texture) of crystals, and that is the reason why a good correlation between the morphology and texture could exist. These mechanisms can be compiled in the fundamental structure forming phenomena.

Structure zone models (SZM) proved to be advantageous since long time for the interpretation and classification of thick film structures prepared by different methods. The analysis of the fundamental structure forming phenomena, their dependence on the temperature and impurity content, and their role in the evolution of the various structural units enable the construction of phenomenological structure zone models. Considering only the temperature dependence of the phenomena, a basic structure zone model (BSZM) could be constructed and proposed. On the basis of this model the consideration

of impurity effects in the elementary processes enables the development of structure zone models representing the structures of thin films prepared at various preparation conditions.

By the application of these models one can conclude that the three dimensional grain morphology (sometimes with equiaxed grains or bimodal grain size distribution) found in many experiments in zone III. is due to impurity effects like the small grained structure near to the substrate shown in Fig.7. It is clear that one has to consider the effects of impurities on the structure evolution when the structures of films prepared at the same temperature show different morphologies in the different experiments. The opinion of the authors is that further systematic experiments are necessary to clarify the finer details of the correlation between the structure, the fundamental structure forming phenomena and the preparation parameters as well.

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