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In Situ Electron Microscopy of Thin Film Growth

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Corresponding to the demands in the investigation of different thin film phenomena, the *in-situ* electron microscopic technique has been developed in different directions. A review of such development is given. Furthermore, experimental conditions ensuring reliable quantitative results are discussed. The phase transitions occuring during thin film growth, i.e. liquid-crystalline, and amorphous-crystalline transitions are dealt with, demonstrations being given by the examples of In, Ge and Sb films. The discussion is focused on the effect of gaseous contamination on the processes.

§1. Introduction

The tasks of work concerning the growth of thin films consist in answering those questions, the knowledge of which enables us to interprete the particular physical properties of a final film. By way of introduction we would like to recall briefly some well-known facts from the wealth of experimental results, which—in our opinion —are decisive from the point of view of understanding the growth processes.

Thin films may have unique properties mainly because they are prepared with peculiar structures, *e.g.* cermets and chalcogenides. If we consider here only those films that are produced by vacuum evaporation or sputtering, they are formed through an atom by atom growth process on the surface of a solid substrate either in liquid phase or in solid phase. It should be emphasized that not only single atoms and/or ions but atom and/or ion clusters can be present in the vapour beam, as has been proved by mass-spectrometric analysis.[1,2]

The structure of a final film is formed through several steps and transitions as far as its phase, crystal structure and composition are concerned. To be able to describe the film growth, it should be investigated theoretically and experimentally how the condensing atoms and atom clusters can move on the substrate surface and on the growing film surface. Furthermore the thermodynamical properties of the forming submicroscopic grains and the laws controlling their coalescence should be revealed. The theoretical and experimental treatment of the processes is rendered more difficult first of all by the large variety and complexity of physical and chemical interaction processes involved. Extremely small quantities of reactants take part in the reactions, which are often surface specific.

The behaviour of single ad-atoms or ad-atom groups—i.e. their movement, adsorption, bonding as well as alloying—on the substrate surface or on the surface of a growing film is determined by the atomic arrangement and chemical composition of the surface. A better understanding of the processes is hindered at present by the lack of knowledge concerning the energies involved in adsorption, binding and diffusion.[3]*

Now, if we try to grasp the roles of parameters determining the processes, we find that still more precise and unambiguous experiments are needed to refine the available theories. What we mean are the experiments in which the composition and the surface properties of substrate and other important parameters such as substrate temperature, impinging vapour flux and residual gas environment are measured and controlled.[4] It is a question which we have to study and control in order that we may investigate a specific phenomenon experimentally.[5]

This paper aims at reviewing the *in situ* electron microscopy from the point of view outlined above and at looking into the future trends suitable to solve our present problems. In the second part of this paper we make an attempt to throw light upon some questions of the *in situ* technique by discussing the formation of polycrystalline and amorphous films

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*D. G. Lord and M. Pruton; to be published.

on the basis of our own results.

§2. Trends in the *in-situ* Electron Microscopic Methods for Thin Film Studies

As is well known, a great advantage of the *in situ* method is that it enables a direct insight into the dynamics of the processes. By ensuring the identity of environmental conditions for each stage of film growth, this method makes it possible to follow the changes in the morphology and crystallography of the individual grains. The same could hardly be expected for those experiments which are carried out in a vacuum evaporator.

A characteristic feature of the present-day *in situ* technique is to try and produce well-defined vacuum conditions at the site of the microscope specimen. Since the contamination in fairly increased in the irradiated area, the required cleanliness can only be maintained by UHV, in which the partial pressures of the hydrocarbons and reactive gases are very low. From this point of view, cryopumps with adequate geometries have proved to be extremely advantageous.[6-10] A considerably large free space for manipulation can be obtained by those technical solutions in which the total object space is under UHV exhausted by separate ion-getter pumps.[5,11]

In different laboratories sophisticated methods have been developed by which investigations have been carried out on different phenomena and processes.

The combination of *in situ* technique and high-resolution TEM using a goniometer stage was worked out for studying the epitaxial overgrowth. In this line the formation of misfit dislocations and the changes in orientation of small crystallites have been followed by moiré-technique.[10-14] Clean single-crystal surfaces have been produced *in situ* either by electron beam-induced cleavage of MgO, ZnS and PbSe crystals,[12] or by evaporation of epitaxial films;[15] ionsputter cleaning of a single crystal surface has also proved useful.[16,17] Clean, amorphous substrates can be obtained also by *in situ* manipulations, *i.e.* by degassing the substrate at high temperatures,[18,19]* or by evaporating an additional amorphous film.[5] These techniques played a

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*J. A. Venables: personal communication.

most important role in the preparation of substrates for *in situ* studies.

An *in situ* arrangement has to be able to control also the substrate temperature in a considerably wide range. Temperature measurement within $\pm 3\,°C$ seems to be satisfactory in most cases; an accuracy of 1/4 K has been achieved by Kramer and Venables.[20] The reproducibility of temperature and the smallest possible temperature gradient along the substrate are of primary importance in measuring the melting point and the crystallization temperature of submicroscopic particles[21-25] as well as in studying nucleation.[18,20,26] The heating effect of the electron beam is to be taken into account in particular in high-resolution experiments: the temperature rise of In crystallites, 500 Å in size, on a substrate at 50 °C amounts to 8–10 °C when irradiated by a 100 kV beam of 10^{-2} A/cm² intensity.

A technique developed in the authors' laboratory enables the *in situ* microscopic study to be conducted simultaneously with the measurement of the electrical conductivity, Hall voltage and magnetoresistance of the film. Such technique is indispensable for the study of amorphous and polycrystalline semiconductor films, which are sensitive to the exposure to atomosphere.[27-29] Structural changes in amorphous chalcogenide alloys resulting from electrical switching have been proved by the *in situ* electron microscope.[30]

The *in situ* study of film formation by sputtering was started recently, widening the range of materials to be investigated.[31,32] The results show that the nucleation density is higher in sputtered films than in evaporated ones. Weissmantel and coworkers investigated by *in situ* SEM the growth of ion sputtered films up to thicknesses which are not transparent in TEM.[33]

A powerful, standardized technique to perform *in situ* electron microscopy with high resolution on clean substrates in a clean vacuum has been worked out by Honjo and coworkers.[10]

Further information on the subject can be found in review papers published recently.[34-36]

The common problem of these experiments is that the real structure of the surface is not known. It turned out in more and more cases that the real structure of a single-crystalline

substrate differed from what we had expected. For instance, Lord and Prutton pointed out by LEED-Auger investigations the role of critical accommodation centres in the epitaxial nucleation.[3]* Venables has found that the growth of rare gas solids on graphite is very much dependent on the cleanliness of the surface. If the graphite is cleaned by heating to about 900°C, the rare gases grow in a layer by layer growth mode,[19]** and not as islands which have been reported before.[13,20] As our invetigations with show, the crystallization of amorphous germanium films (a-Ge films) dependends profoundly on the degassing temperature of the SiO$_x$ substrate.[18]

For a successful study of film growth to be achieved, information as precise as possible is required partly on the substrate, concerning its surface morphology and crystal structure on an atomic level as well as its atomic chemical composition and effective temperature, partly on the intensity and composition of the impinging vapour beam. It is quite clear that stress should be laid on learning the changes in surface properties due to the various *in situ* treatments (*e.g.* heat-treatment, sputter cleaning, etc.). For the investigation of surface structure the LEED-Auger methods are commonly adopted, but useful information on surface properties of single-crystals is hidden also in the nucleation phenomena.[37-39] The answers are awaited for the following questions: What is the real structure of an amorpous substrate surface like?; and how can we obtain information on the arrangement of its surface atoms?

The question in the field of *in situ* TEM is to apply the different methods that have been already developed to various problems, and to develope now methods and their combinations. A direct and efficient method of investigation of the film growth on single-crystalline substrates is the parallel use of LEED-AES and high resolution *in situ* TEM methods, as demonstrated by Poppa and coworkers.[5] A further step forward will be the unification of high resolution *in situ* TEM and LEED-AES systems, which have been suggested by some authors.[5,35] This would furnish direct and quantitative data on the state of substrate

before the deposition and on the occasional contamination of the film surface. This kind of equipment would also prove suitable for following up the chemical processes such as oxidation and corrosion.

A further possibility for doing many-sided investigations would be the unification of *in situ* composition analysis and *in situ* TEM. The knowledge of composition is of great importance for alloy and composite films; it is also useful for the study of one-component films in that it reveals the quality and quantity of contamination built in the film during film formation or annealing. (For instance, the oxygen content of an a-Ge film was found to be quite high, which essentially influenced the physical properties as well as the structure changes that took place during an additional heat-treatment.[28]

For such purposes, the application of an electron probe microanalyser or the analysis of energy-loss of electrons seems to be advantageous; but a full-image analyser which shows the composition distribution in high-resolution[41] is the greatest promiss.

The most important question that remains unsolved is the effects of the high energy electron beam. One used to detect these effects by comparing the final structures found in the irradiated and non-irradiated areas. We have to learn much more on these effects, which are:

temperature increase,

electrical charging of the particles on insulating substrates,

creation of surface defects

and

cathalysis of chemical reactions.

At present we have to clear up these effects for every single experiment, taking into consideration that these are also temperature-dependent. The phenomena to be studied by *in situ* electron microscopy are restincted first of all, by the electron beam effects.

§3. **Amorphous and Polycrystalline Films, Amorphous-Crystalline Phase Transitions**

During the film growth, the condensed mass determines the properties and structure of the film as well as their changes; whereas for the final film the time as independent variable is the decisive factor at given parameters. Investigations to be presented here are concerned

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*D. G. Lord and M. Pruton: to be published.

**J. A. Venables: personal communication.

with both growth processes and changes in the final film. Dealing with the growth of polycrystalline In films on amorphous substrates we describe the liquid-crystalline phase transition and the influence of gaseous contaminations on the processes. Furthermore, description will be given of the formation of amorphous structures, with the examples of Ge and Sb, and of the structure changes in the amorphous Ge during heat-treatment.

3.1 Growth of indium films

The growth of indium films can be regarded as the model of the growth of metal films with low melting points.[23,42-44] The advantage of selecting indium lies in its low vapour pressure at the melting point and its selective sensitivity to oxygen. The films were deposited onto evaporated carbon films, which are not wetted by indium.

The growth processes are summarized in Table I. Nucleation takes place in liquid phase at substrate temperatures above +30°C at pressures lower than 10^{-6} Torr. By increasing the condensed mass, the liquid droplets grow on and coalesce. After reaching a critical size they may crystallize if they contain a seed inducing crystallization. From this stage on, liquid and crystalline grains coexist and take part in the coalescence irrespectively of their phase. It is to be noted that randomly oriented crystallites come into being from the liquid droplets. The orienting effect of the substrate does not work in this process because the droplet-substrate interface is small due to the large contact angle and the orientation of the seeds is independent of the substrate. It is well known that the role of the interfacial energy shows up only when coalescing crystallites recrystallize either via partial melting or in solid phase. The oriented texture of the film (generally with (111) preferred orientation) is formed step by step through coalescence of grains and recrystallization.

The absorption of residual gases, especially for indium films the absorption of oxygen, has an important effect on the surface tension of the particles and thereby influences the crystallization and coalescence. This manifests itself in the increase in melting and crystallization temperatures of the individual droplets as well as in the disappearance of regular crystal habit. Since the contamination accumulated by this means on the surface hinders the liquid-like coalescence and the accompanying recrystallization, crystallites tend to remain in random orientations; and the interfaces between the adjacent grains are easily stabilized, resulting in films with small grain size. Provided the growing crystallites be

Table I. Phenomena taking place during the growth of vacuum deposited In films at substrate temperatures above +30°C. L: liquid droplets /L/: hypothetic transition through liquid phase; C: crystallites.

| PHASE STATE	STAGE OF GROWTH	PROCESSES		STRUCTURE
Liquid	Nucleation	Formation of nuclei		Liquid
				Crystalline /Random/
	Post nucleation	Growth of nuclei		
	Coalescence of the particles	L + L → L L + L → L → C L + C → L → C Contraction of area	Secondary nucleation on the empty surface, and repeating the growth process	
		C + C → /L/ → C Contraction of area		
		C + C → C C + C → /L/ → C $d_2 > d > d_1$ Recrystallization		Crystalline /Texture/
		C + C → C $d > d_2$		
	Formation of the islands, channels	Grain boundaries		Crystalline /Texture/
Solid	Continuous	Filling of the channels		
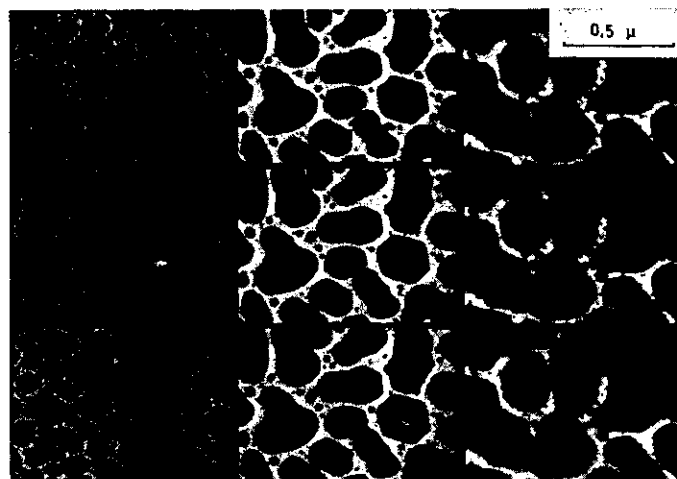
Fig. 1.   The effect of cracking products on the growth of In films. $T_s=30\,°C$; vacuum environment: 5.10^{-6} Torr without cooling trap in JEM 6 A TEM; deposition rate: 3 Å/s.
The growth of larger crystallites is stopped by the building up of contamination cover; new nucleation starts on these covered grains.

covered by a continuous contamination layer, new nuclei would appear on this layer (Fig. 1).

If one knows the melting point, the crystallization temperature and the formation temperature of texture orientation as functions of the particle size (see[23]) one can determine the phase state corresponding to a given substrate temperature and a certain stage of growth (i.e. particle size). It should be noted again that the contamination raises considerable the temperature of melting and crystallization.

3.2   Formation of antimony film

The formation of Sb films has been studied extensively, because Sb has been widely employed as photocathode material.[45,46] Its condensation in amorphous phase in a wide range of temperature has been described, and the spherulitic crystallization at thicknesses above a critical film thickness is also well known. According to Palatnyik and coworkers observation,[47] the crystallization of thin Sb films is a slow process whereas films thicker than 1000 Å crystallize like an explosion.
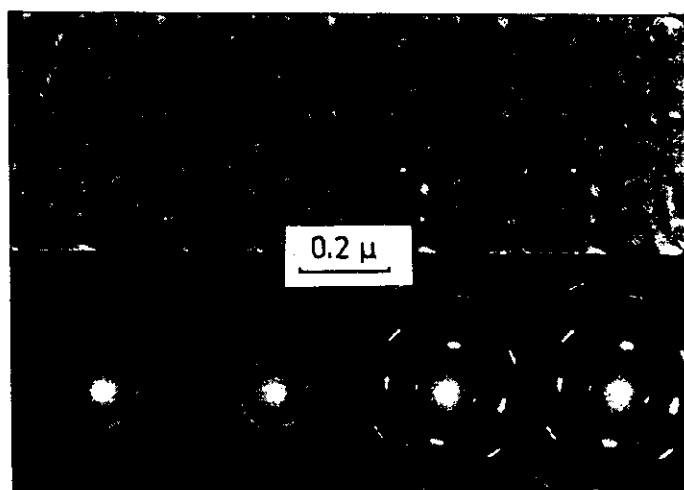
We have investigated *in situ* the formation of

Fig. 2.   Sudden crystallization of Sb film during the condensation. Substrate temperature: 75 °C; deposition rate: 10 Å/s; thickness at the crystallization: about 300 Å.

Sb films in the 20–150 °C temperature range. This process starts with nucleation in amorphous phase, and goes on with the growth of adjacent particles into a network. The crystallization takes place very suddenly (Fig. 2): *e.g.*, on a substrate at 60 °C, a film of 5 μ^2 area turned crystalline in a time less than 1/50 seconds, resulting in a single-crystal. It is remarkable that the grains that are not connected with the network remain amorphous, as one can see in Fig. 3; after some hours, even the "lonely" gains and chains of grains crystallize, but such films are found to be polycrystalline. At a substrate temperature of 150 °C, the saturation density of nuclei is low enough for the amorphous particles, about 250 Å in size, to grow without forming a continuous network. When the deposition is stopped, only very few (1–2 in 500 μ^2 area) crystallized grains can be found.

Since the crystallization occurs extremely rapidly in films of continuous network, it would be possible only with amorphous Sb films containing separate particles to investigate the nucleation rate. Experiments of this type are in progress in cooperation with I. Rechenberg (Humboldt University, Berlin). In connection
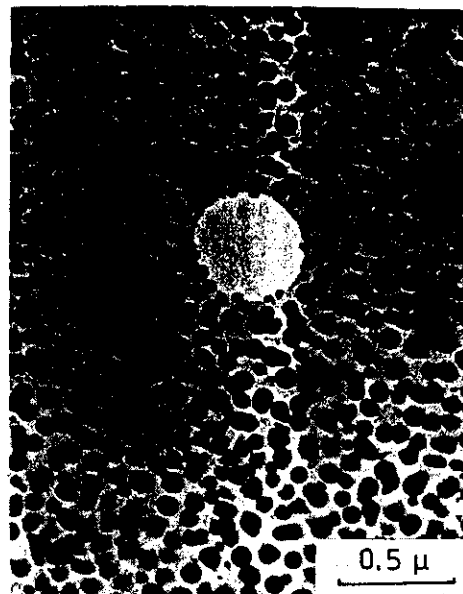

Fig. 3. Structure of an Sb film deposited *in situ* and crystallized just before finishing the condensation. Substrate temperature: 150 °C; deposition rate: 10 Å/s. The amorphous particles, not connected with the network, did not crystallize.

with the sudden crystallization of the continuous network, it is worthy of note that a shock wave passes through the film when crystalliza-
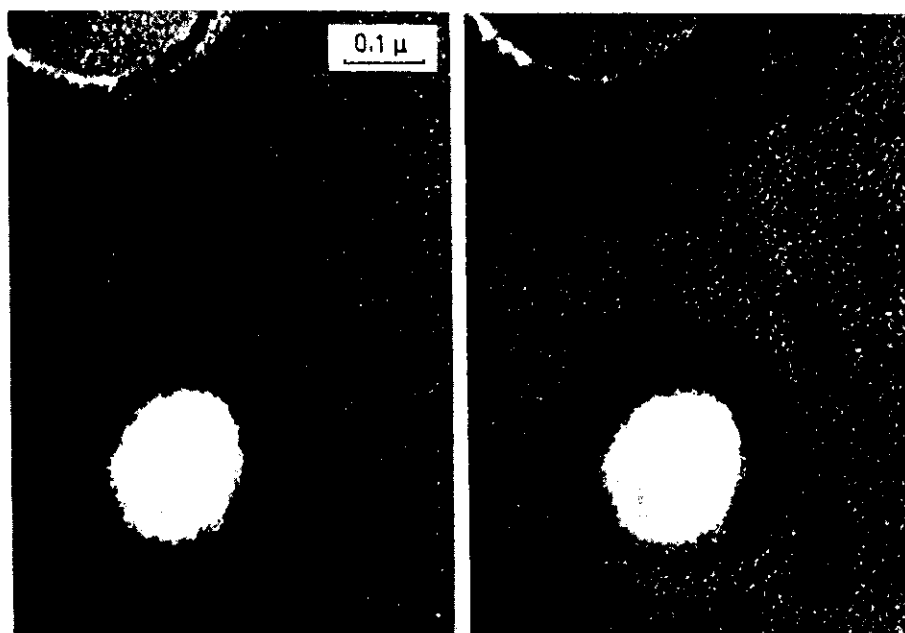

Fig. 4. Stereo pair of electron microscopic images showing bubbles formed during the *in-situ* heat-treatment of an a-Ge film deposited at 100 °C in a vacuum of 10^{-9} Torr. The bubbles are in the low density transition regions. Film thickness: 1300 Å, heat-treatment at 350 °C for 10 min.

tion takes place, which may a result in a sudden defocus in the ciné film taken by the imaging electrons.

3.3 Structure, ordering and crystallization of a-Ge films

There are inconsistencies in the experimental results in the field of research of amorphous materials.[48] The structural ordering of very pure a-Ge films during heat-treatment and the effect of gaseous contamination on the crystallization have been directly observed by means of UHV *in situ* electron microscopy.[18,28]

For the time being the formation of a-Ge films is to be regarded as a process starting with nucleation. The nucleation density is determined solely by the substrate temperature if well degassed substrates are used under UHV conditions. The amorphous structure builds up similarly to the Polk model,[49] starting from the nuclei. No coalescence of the contacting particles can be observed; low density transition regions are formed between the particles. In this way a continuous uninterrupted structure is formed in the final a-Ge film. However, there is a periodic fluctuation of the film density along the film plane. The film consists of so to say "rods", oriented perpendicularly to the substrate, which are separated by lower density regions. The existence of such structure has been proved both by electron microscopy and small angle electron diffraction.[28] The formation of lower density regions can be explained by taking into account the low surface diffusion rate on the amorphous particles and the fact that about 1/5 of the Ge vapour beam consists of atom clusters containing 2–8 atoms.[1,2] It is quite clear that these clusters can "sit" in atomic voids larger than their own sizes, the voids being covered and remaining vacant. This effect shows up especially at the connecting surfaces of the growing particles.

As a result of heat-treatment at above 350 °C, ordering takes place first in the low density region, provided the built-in contamination is very low (Fig. 4). The ordering results in the diffusion of invisible atomic voids; these are accumulated in the form of bubbles. The disappearance of rod-structure can be demonstrated by fading-out of the intensity of low-angle diffraction. If the film is contaminated by residual gases, *e.g.* by raising the pressure up to
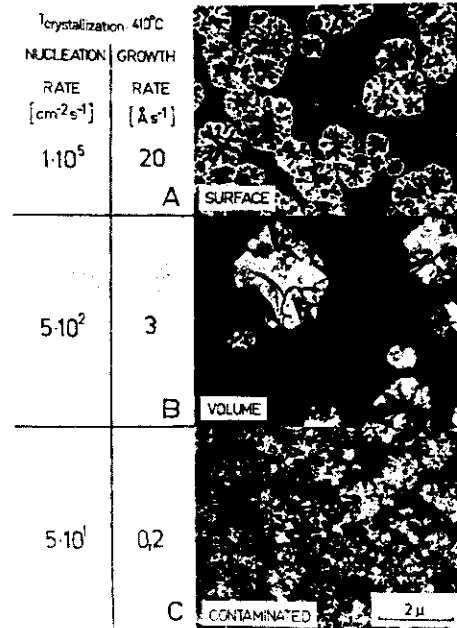
Fig. 5. Three types of crystallization of UHV deposited a-Ge films as affected by the gaseous contaminations.

A: Substrate: SiO_x layer degassed in-situ at 500 °C; deposition and heat-treatment at 5.10^{-9} Torr;

B: Substrate SiO_x layer degassed in-situ at 350 °C; pressure during deposition 5.10^{-9} Torr, during heat-treatment increased for 10 min. up to 10^{-7} Torr;

C: The same as in A, but the film was exposed to air between deposition and heat-treatment.

10^{-6} Torr for 5 min, this structural ordering does not occur: the original rod-like structure does not dissappear in the course of heat-treatment.

The forms of crystallites and the nucleation rate of a-Ge films are very sensitive to the gaseous contamination.[18] In a-Ge films of high purity, nucleation starts on the film surface and results in spherulites of small grain size; films contaminated on the surface crystallize first in the bulk, leading to the formation of large, flat single-crystals. In amorphous films exposed to the atomsphere, the crystallization is a very slow process (Fig. 5).

The effect of contamination on the crystallization can also be shown by the *in situ* electrical measurements of conductivity and Hall-voltage. The conduction mechanism and the temperature-dependence of the mobility of charge carriers can be accounted for by the effect of barriers generated by contamination at the grain boundaries.

Acknowledgements

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IMPURITY EFFECTS IN THE STRUCTURAL DEVELOPMENT OF VACUUM DEPOSITED THIN.FILMS

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Many results of thin film studies prove that impurities are accumulated at the surface of crystals or at the grain boundaries, and are responsible for the structural, physical and chemical properties of films. The accumulated form of impurities enables to understand why impurities can be extremely active in determining the structural development also at very low concentration. The paper reviews some of these results and point to the situation that the various structural peculiarities of crystalline and amorphous films can be understood better when films are considered as multicomponent systems. Models proposed to describe the participation of impurities in the growth processes of crystals, amorphous grains and in their coalescence are discussed. It is shown that these processes can accumulate the impurity molecules. The present work seems to provide a somewhat unifying effect to the various concepts on the mechanisms of structural formation. What the present work illustrates is that the better understanding of the surface chemical interactions and the role of foreign species in the surface processes is an urgent need to get a progress in our thin film studies.

I. INTRODUCTION

The very high number of parameters and effects controlling the structural developments of thin films is one of the principal problems both of thin film research and application. Beside certain parameters which can be determined (monitored) with higher or lower accuracy (e.g. substrate temperature, rate of impinging species of film material, film thickness, etc.) there are other ones 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 and explanation of the various peculiarities or apparent anomalies in the structural and physical properties found in numerous experiments (e.g. /1-9/). In spite of many results, however, very few are known on the facts, where the impurities are coming from and how they really affect the properties of the films and how they participate in the structure forming processes. In this respect a major problem in most experiments is until now not only to monitor the kind and quantity of impurity species present either on the substrate surface or in the beam of impinging species but to detect, if they exist at all. According to recent results /10-14/ impurities can also be active if their quantity is near to or under the detectability limit of the analytical methods available at present.

Too often, models of thin film formation are idealized without considering the role played by the nonavoidable presence of impurities. However, the question could be raised whether a minimum of impurity concentration exists under which their effect can be left out of consideration and whether the UHV conditions allow to neglect them. (In any case, impurity effects must be considered e.g. in the "so called" UHV studies in which an increase in the total pressure can be detected during the experiment). We have to refer also to the very strong interactions between the deposition parameters. These interactions are unknown in most cases. They make the evaluations and interpretations of experimental results in terms of models difficult and need often speculations.

For the moment, the opinion can be expressed that one has to be cautious in this sense and consider the effect of impurities on the phenomena studied as long as the absence of impurities cannot be proved at very high accuracy. This opinion relates first of all to the long term experiments or to the judgement of the state of purity of substrate surfaces and interfaces. Further quantitative infor-

mation on the possible nature of surface chemical interactions and carefully prepared experiments revealing the very fine effects of impurities are necessary to answer the questions mentioned above. By this way one can also expect to understand phenomena which seemed to be "misterious" yesterday.

The author came to the opinion that to fulfill the real need of studying the formation of this film "in their entity"—as formulated by Robins /15/—to get a new progress in thin film research and technologies, the systematic investigation of impurity effects is basically necessary.

At this point it can be instructive to call to our mind some results illustrating that very low concentration of impurities can have a high importance in explaining the growth phenomena, and properties:

1.1. Binding of adatoms and admolecules at active surface sites

Active surface sites binding the adatoms (e.g. ledges, kinks, vacancies) are the most active ones both in binding the impurity species and/or catalysing surface chemical reactions /16/. These active sites are reproduced by the atom-by-atom structure building processes in the course of film formation. Consequently, the surface of a growing film has to be considered as one of the highest activities in the sense of surface chemistry. The very strong influence of adsorbed foreign species on surface physical processes has also been proved e.g. by blocking the source of surface self-diffusion /17-19/ and changing the surface free energy. That is the reason why the understanding of surface chemical processes taking place on the growing film surface and the knowledge of their crystal face unisotropy are of great importance in explaining the structural development of thin film /20/.

1.2. Accumulation of impurities

An important phenomenon, the accumulation of impurities to the surface of growing crystals has been proved directly by in situ electron microscopic experiments /21,22/. Impurity layer can develop and cover the surface of crystals partly or completely and block their growth, as indicated by the appearance of secondary nuclei on the surface of large crystals (Fig. 1). Barna /21/ has studied this phenomenon in indium films and found that the thickness of the In_2O_3 covering layer exceeds three atomic layer thickness. He used the spherical-granula model and a value of 0.3 for the sticking coefficient of oxygen in his calculations.
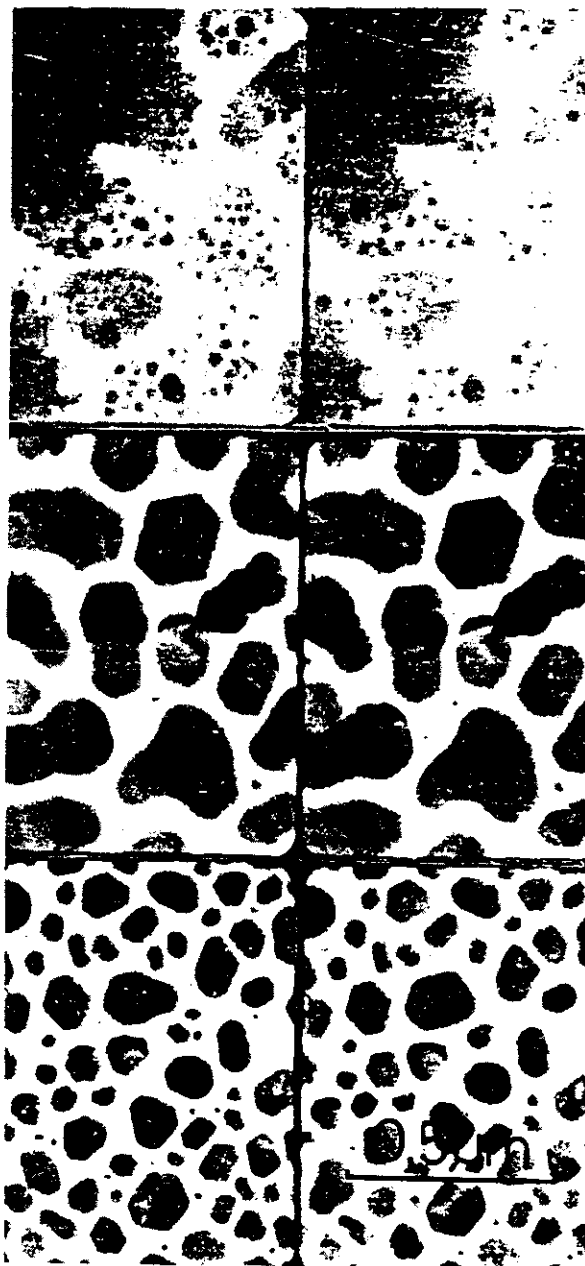

Figure 1.
Various stages of the growth of In film deposited at 10^{-4} Pa and $60°C$ substrate temperature. The presence of secondary nuclei indicates that the large crystals have been covered by an impurity layer completely. (In situ electronmicroscopic experiment without cooling trap. Frames of a cine film /6, 22/).

1.3. Crystal face anisotropy in the surface chemistry

The surface chemical studies revealed already that crystal phase anisotropy can exist both in the adsorption of species and in their situation on the surfaces /23-27/. Experiments carried out on Al-oxygen system demonstrated a correlation between this anisotropy in the surface microchemistry

and impurity-affected anisotropy in the crystal growth /9,28,30/.

I.4. Impurities accumulated at the grain boundaries

There are arguments indicating that impurities insoluble in the growing lattice are accumulated at the grain boundaries in polycrystalline films or at the intergrain area (supernetwork) in amorphous films. The same occurs also when films are exposed to gases or vapours. The following results have been interpreted by considering these effects:

Stress in films, due to grain boundary interaction, could be reduced or changed from tensile to compressive one by incorporation of a small amount of gaseous impurity or some doping elements /7,8,31-36/.

The structure and impurity content of grain boundaries are decisive in determining the *electrical properties* of thin films /37,38/. Zimmermann et al. /39/ found that the very small quantity of oxygen detected in Al films can be responsible for the changes in the superconducting properties of Al films only when oxygen is considered to be concentrated at the grain boundaries. They used spherica-granula model to determine the thickness of oxide barrier. Oikawa /40/ concluded that the effect of lattice imperfections in the grain boundry on R (reflection coefficient of conduction electrons at grain boundaries) is small in comparison to the effect of impurities on R in oxygen contaminated Mo films. Thomas and coworkers /41/ could interpret the changes in the electrical conduction of a-Ge films upon oxygen exposure by considering the diffusion of oxygen into the supernetwork area.

The grain boundary barrier model could be used to describe the electrical conduction mechanism also in polycrystalline semiconducting (Ge and Si) films prepared either by deposition /42, 43/ or by the crystallization of amorphous samples /44/. In a very recent paper a direct correlation between the electrical resistivity of the grain boundary and its oxygen content in polycrystalline Si film have been proved /45/.

Recent experiments demonstrated that the effective *optical properties* of fine-grained films can be satisfactorily explained by considering an inhomogeneous film structure and the existence of grain boundary material without assuming any anomalous behaviour of the crystalline grain interiors /46-48/. Nestell et al. /49/ assumed that the electron density is smaller in the grain-boundary area than in the crystals.

The behaviour of the film during post-deposition heat treatments indicates that impurities are accumulating at the grain boundaries during the film preparation, and these contaminated grain boundaries limit the recrystallization (grain coarsening). Müller and coworkers /50/ presented an excellent example for this effect by depositing $Bi_{1-x}Sb_x$ films at various hydrocarbon partial pressures for heat treatment experiments.

I.5. Crystallization of amorphous films

Structural reordering and crystallization of amorphous films proved to be very sensitive against small amounts of impurities /51-55/. Barna et al. /56/ demonstrated that various types of crystallization of a-Ge films can be realized by changing the grade of their contamination during or after the deposition. They determined also the activation energies of nucleation and growth of crystalline phases for the various types of crystallization.

I.6. Structural defects

More and more evidences are presented on the facts that impurities being present in the substrate surface or incorporating during the film preparation are responsible for the formation of structural defects /57,58/.

The reader can find very excellent books and review papers discussing the phenomena and processes of the various stages of film formation e.g. /59-67/. Effects of impurities are referred also in many respects. However, the recent result of surface and thin film studies can give a better insight into the possible roles of impurities and how far they can influence the phenomena and make possible to develop new ideas on the structural development of various kinds of films used in our daily work.

The paper is going to compile the growth stages, phenomena and processes of the structural developments as well as the ideas on the interaction of impurities with these. Among the parameters the effects of substrate surface conditions and the ion bombardment will be reviewed. Phenomena of the growth of crystals and amorphous grains, their coalescences as well as the development of structural zones in thick films seemed to be interesting for discussion focused to the influence of impurities. Regarding the problems of nucleation excellent reviews can be referred /14,66-69/.

The expression impurities is used throughout the discussions both for occasional contaminations and doping elements. Effects of impurities not dissolved in the growing lattice are in the focus of interest. Effects of doping elements come into consideration in our discussion when their concentration exceeds their bulk solubility at the growh temperature. K-impurity (the ratio of impurity species to the vapour atoms striking the growing film surface) introduced by Caswell /70/ will be used to characterize the quantity of impurities participating

in the condensation phenomena. The expression atom will be used for species of the vapour beam of film material while molecules for the species of impurities consequently.

II. PROCESSES, PHENOMENA AND GROWTH STAGES OF FILM FORMATION

The very early experiments, mainly the in situ electron microscopic experiments /1,6,61,71/ revealed the elementary phenomena and growth stages of film formation compiled in Table I.

Processes, controlling the phenomena, are surface processes taking place on the substrate surface and/or on the surface of the growing film. They are characterized by activation energies and are, consequently, very sensitive to the temperature and surface conditions (orientation and structure, composition and quantity of absorbed impurities). Substrate surfaces are considered as static ones in the first approximation. They can be however modified by the condensing species blocking the active sites by nucleation, reorganizing, desorbing or even incorporating the adsorbed or chemically

bounded impurity species. Superstructures existing in the surface layer of crystals can be modified also by the condensing adatoms /72/. The surface of growing film, however, is changing very dynamically. The atom-by-atom building process and the coalescences of grains, as will be shown, reorganize not only the surface defect structure, but also the distribution of impurities. The surface sites being active both in binding adatoms and in the chemical interactions are reproduced permanently.

Surface processes of impurity molecules striking the substrates or film surface should be considered additionally to the processes of atoms as schemed in Table I. Impurity molecules affect however the surface processes of atoms directly by the following ways:

(1). They can be adsorbed in various states and block the surface sites being active in binding atoms or being sources of atoms contributing to the surface self-diffusion.

(2). Impurity admolecules can form complexes with the migrating or already bounded adatoms. These complexes can have activation energies different from that of the atoms and can promote or even hinder the surface processes.

(3). Impurity molecules can be adsorbed and

ADSORPTION, DESORPTION, DIFFUSION OF ATOMS AND MOLECULES

PROCESSES

on the SUBSTRATE surface

on the FILM surface

on the FILM surface covered by CONTAMINATION LAYER

BINDING, SEGREGATION, RELAXATION of ADATOMS and ADMOLECULES

SURFACE SELF-DIFFUSION of ADATOMS

VOLUME DIFFUSION

SURFACE CHEMICAL INTERACTIONS on the SUBSTRATE SURFACE

on the FILM SURFACE

PHENOMENA

NUCLEATION on the SUBSTRATE

on the FILM SURFACE

on the FILM SURFACE covered by CONTAMINATION

GROWTH of CRYSTALS or AMORPHOUS GRAINS

COALESCENCE TYPE I - liquid-like

COALESCENCE TYPE II

RECRYSTALLIZATION

NUCLEATION of IMPURITY PHASE

GROWTH of IMPURITY LAYER on substrate and film surfaces or at grain boundaries

BLOCKING of cryst.growth, coalescence, recryst. by CONTAMINATION LAYER

GROWTH STAGES

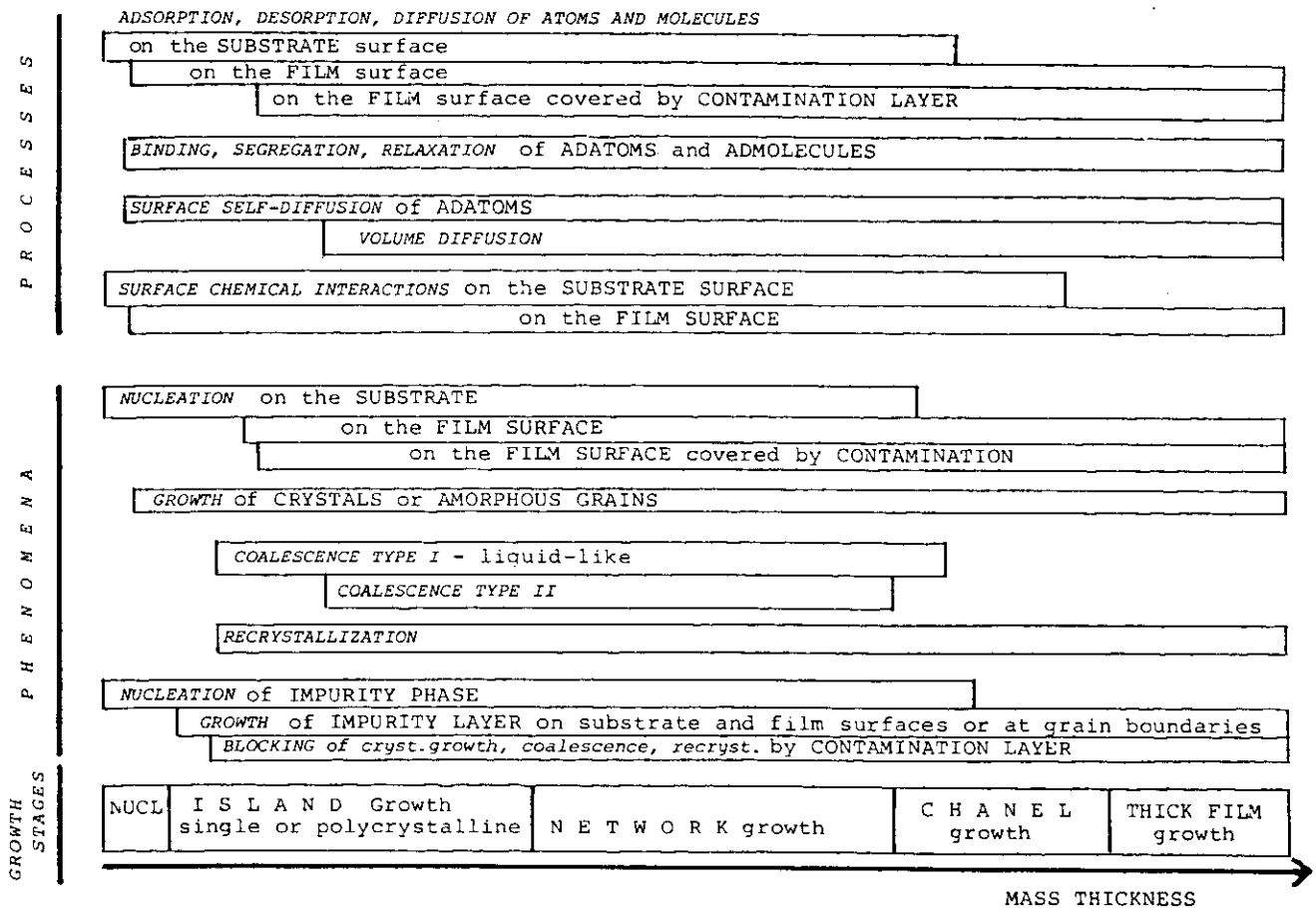| NUCL	ISLAND Growth single or polycrystalline	NETWORK growth	CHANEL growth	THICK FILM growth

MASS THICKNESS

Table I.

Processes, phenomena and stages of thin film growth.

accumulated and by this way they can develop their own two or three dimensional phases, or those of their compounds. In such a case impurity phases present new local surface conditions both for the condensation of adatoms and impurity admolecules. They can orient or even block the continuous building of the crystal lattice or amorphous network of film material.

We can conclude that impurity molecules striking the substrate or film surface can control the nucleation and growth of crystals or amorphous grains directly. The coalescence is affected only by those impurity molecules which have been adsorbed and accumulated by the growth on the surface of crystals. The same can be stated for the recrystallization of considering the coverage of grain boundaries by the accumulated impurities.

Impurities besides the substrate temperature will determine the effectivity of various processes and phenomena in the structural development. The liquid-like coalescence e.g. can be limited or completely suppressed by choosing very low substrate temperature or a high value of K-impurity, as is shown in Sec. V. The development of texture structure illustrates this conclusion very well. Namely, the texture is very weak, or even missing in films deposited at rather high value of K-impurity at $T_s/T_m > \frac{1}{3}$ or low T_s/T_m. (T_m is the bulk melting temperature).

III. IMPURITY EFFECTS RELATED TO SUBSTRATE SURFACE CONTAMINATION AND TO THE BOMBARDMENT OF THE FILM BY HIGH ENERGETIC IONS

These two effects may have special interest. The contamination of substrate surface affects not only the very first stage of film formation (the nucleation and the structural modification of the nuclei or small crystals) but may have influence also on the grain growth and, indirectly, on the structural development of thicker films. The bombardment of the growing film by ions is an additional effect in the sputtering process affecting the contribution of impurities to the development of the various film structures.

III.1. Contamination of the substrate surface

According to Mittal /73/, the contamination of substrate can originate from a number of sources: (i) Adsorption of impurities from the ambient (e.g. hydrocarbons, water vapours); (ii) Reaction of the surface with active species (e.g. oxygen) which results in reaction layer; (iii) Preferential diffusion of one component (in case of multicomponent substrate) can give rise to variable composition type of surface contamination; (iv) Residues of cleaning or other pretreatment. We have to count

with the interaction of these sources and products, too. The polarizability of contaminations play also an important role in determining the phenomena /66,74,75/. Substrates are usually pretreated at higher temperature in the vacuum system before starting the film deposition. There is however, a time interval long enough between these two processes to develop an absorbed layer of gases and vapours.

The main effects of substrate surface contaminations can be summarized as follows.

The sticking and surface diffusion coefficients of adatoms and admolecules can be increased or decreased by the various kinds of substrate surface contaminations e.g. /4,17,66,76/. Joyce and co-workers /77/ have found that a higher supersaturation of Si vapour was necessary to initiate the condensation on Si(111) single crystal surface covered by an oxide layer than in the case of a clean one. Numerous experiences proved that a small amount of one material adsorbed on a surface can influence the adsorption kinetics of other gases considerably /78-82/. Winkler /81/ has found that the sticking coefficient of oxygen on Ni changes with coverage. There are experiments /51,57,58,83-85/ illustrating that the incorporation of environmental impurities and their contribution to the defects formation depends on the grade of substrate surface contamination. Such observations suggest an idea that islands of contamination can act as preferential sites for binding impurity admolecules (see the discussion in Secs. V and VI).

Substrate surface contamination can influence also the interface energy between the growing crystals and the substrate /86/, the orientation relations /4,10,66,74/, shape /14,87,88/ and the melting temperature /6,66,89/ of the small crystals.

Both the adsorbed layer and solid phase contaminations affect the nucleation very sensitively. The complete nucleation can be transformed into uncomplete one when the surface is contaminated /6, 59,67,77,79,90-92/. Local high number density of nuclei on substrates might decorate the islands of impurities. Two ideas can be used to interpret the development of the high number density of nuclei: the impurity phase can contain numerous active sites for nucleation or the high concentration of adsorbed gases due to a higher adsorption energy of the contamination layer can promote the nucleation as in the case of NaCl /74/.

Impurities adsorbed on the substrate surface can be built in the structure and contribute to the development of a distorted or modified structure as well as to the formation of amorphous phase in the layer on the substrate /51,93-97/.

III.2. Impurity effects related to high energetic ion bombardments

Systematic experiments indicated that pronounced

differences can occur between the structures, properties and impurity contents of film prepared by evaporation or by sputtering. Sputtered films have usually a better ordered structure, lower grade of contamination and their physical properties approach rather the bulk properties than evaporated films. These differences are attributed mainly to the following effects of ion bombardment: creation of defects, implantation, selective resputtering, promoting the desorption or chemical reactions and momentum transfer /35,36,91,98-102/.

The very recent studies of Greene and Barnett /103/ presented important results on the impurity incorporation under ion bombardment. They have found that in the case of GaAs deposition the incorporated quantity of oxygen decreased when the bias potential was increased from 0 to −75 V. A further rising of the negative bias potential increased the built-in quantity of oxygen.

Sugiura /58/ has found that ion bombardment improved the epitaxial growth of Si films and suppressed the production of stacking faults. One can speculate that besides the energy transfer /58/, the preferential desorption of weakly bounded oxygen by the high energetic ions can promote these phenomena.

Species sputtered from the walls and other parts of the working chamber can increase the impurity effects and make them more complicated than in the case of vapour deposition /104/.

IV. GROWTH OF INDIVIDUALS CRYSTALS

The value of K-impurity falls into an internal of 10^{-4} and 10^{-1} in most of the experiments carried out in the high or ultra high vacuum range. This situation initiates the idea to complete our picture on the atomic processes responsible for the crystal growth in thin films and consider also the participation of impurity species in them (Table I and Fig. 2). By following the model of Venables and Bermond /14,105/, we have to count with a population of codepositing impurity admolecules both on the substrate surface and on the crystal faces. The admolecule population develops also by the same processes as the population of adatoms.
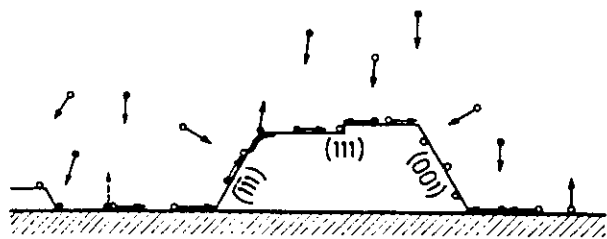

Figure 2.
Schematic diagram of processes in nucleation and growth on surface considering impurity molecules too. and a contamination layer covering the edge between 111 faces.

However, the concentration of impurity admolecules can be different on the various crystal faces by many reasons. The crystal faces are inclined to the vapour beam of atoms by different angles. This results in the various values of K-impurity when considering the flux coming from the vapour phase. Faces of different Miller indices can have different values of the adsorption and diffusion energies for the atoms and molecules /106/. The same can hold also for the transfer coefficients of edges. Besides these, the side faces of crystals are in a particular situation in the early stages of film formation. The biggest part of the net flux of atoms and molecules arriving to these faces originates namely from the bare substrate surface area. And, consequently, the composition of this net flux will be determined by the substrate surface properties. This last phenomenon can contribute to the development of different growth shapes of crystals growing simultaneously on substrate areas of different surface properties (e.g. pure and contaminated areas).

Recent surface studies revealed that crystal faces of different Miller indices may have different chemical activity and the adsorbed molecules can penetrate into the surface layer or they are sitting on it /23-27/. Due to the crystal face anisotropy in the surface micro chemistry, in the case of a given material-impurity system, the growth of various crystals will depend on their orientation /9,20,28-30/.

The following effects of impurities on the growth of crystals can be assumed considering the model used by Venables and Bermond /14,105/.

(a). Individual admolecules may bind to the kink sites and decrease both the creation rates and trapping probability of adatoms.

(b). Complexes can develop upon impingement of adatoms and admolecules on the substrate and film surfaces having activation energies different from that of adatoms and admolecules.

(c). Admolecules or their complexes can develop islands of their own stable phases or compounds both on the bare area of the substrate and on the crystal faces /51,58,85,107,110/.

(d). Admolecules on their complexes can penetrate into the surface layer of some crystal faces and be dissolved in the crystal lattice /9,20,27-30,23,24,25/.

(e). The growth steps can sweep on the admolecules bounded in precursor state on crystal faces where the admolecules cannot penetrate. One can assume that a change-of-place mechanism can take place between the weakly bounded admolecules and impinging atoms and can be responsible for the accumulation of impurities by the growth front. The concentration of admolecules at the steps increases by this way and a stable phase of impurities can start to

develop by nucleation /9,20,28-30/. These nuclei can form the pinning sites decorating the experiments, e.g. in Si films /107;110-112/;in Al films /9,28-30,109/ and in GaAs films /113/. One can understand that the surface of growing crystals can be covered also completely by this accumulation mechanism resulting in a structure shown in Fig. 1. This mechanism leads to the development of the spherical-granula structure in thin films as indicated by Ziemann et al. /39/ and Barna et al. /108/.

(f). Islands of impurities can act as preferential trapping centres of impurities while the adsorption energy of adatoms can be decreased. The local condensation coefficient of impurities will be increased by this way while that of adatoms is unchanged or even decreased.

(g). The growth of crystals is hindered in the surface areas covered by an impurity layer. When the inpurity layer develops at the edges, they will be rounded /20,29,30/.

The effects of impurities, discussed above, can select the crystals of different orientations with respect to their growth and coalescence conditions /28,30/.

We can assume that the change-of-place mechanism between the weakly bounded admolecules and impinging atoms as well as the accumulation of impurities by the growth front can take place also in the case of amorphous structures /114/.

V. COALESCENCE OF GRAINS

The coalescence of grains plays a very important role both in the formation of structural features (orientation of crystals, grain size, defect structure, morphology) and consequently in the physical properties especially in the development of mechanical stresses /7,8,31-36/ in films. Coalescence takes place when adjacent grains approach and at least touch each other. This means a process during which the previously isolated grains start a "cooperative life" by contacting and interfusing their structures. At this moment a new structural element, the intergranular area appears and the coalescing grains begin their mutual influence on their structural developments.

The phenomenon of sintering is used to describe the coalescence /2,66,71/. Accordingly, the main stages of coalescence are: (i) the neck formation, (ii) filling up of the necks by surface self-diffusion including also diffusion of adatoms, (iii) formation of intergranular structure (grain boundary) upon joining of the different lattices of grains, (iv) moving out of the grain boundaries by diffusion controlled grain boundary migration (recrystallization).

One has to understand that the characteristics of the coalescing grains will control the processes

(surface and bulk diffusion, release of surface energy) being active in the coalescence. This holds also when the crystals are melted partly or completely during the coalescence due to the energy released by the reduction of the total surface area /21,66/.

The main characteristics of the grains getting at the moment of coalescence are the following: orientation; size; mechanical stresses; defects structure; morphology; surface energy; state and location of impurities on the surfaces of grains.

These characteristics, as discussed in the previous section, are determined by the growth phenomena of isolated grains and also by the fact, whether the grains have participated already in coalescence(s) or not. Inhomogeneities in the substrate surface properties (e.g. domains of various kinds of crystal structures, bulk or surface impurities as well as various kinds of defects) may have also a strong influence on the coalescence.

However, the characteristics of the grains and the local properties of the substrate surface are hardly known and cannot be determined in the experiments at present. One can infer on these only by studying the structure and morphology of the grains developed during the preparation as well as from the preparation parameters, when these are well controlled. In situ experiments applying high resolution surface analytical techniques (e.g. high resolution SAM) and facilities to image the details of surface topography (e.g. high resolution SEM, reflection EM or high resoltuion dark field TEM) would be necessary to provide the information necessary for elaborating a quantitative and more comprehensive description of the elementary phenomena of coalescence.

We are now going to analyze the various types of coalescence to get insight how far and by which way the impurities can affect the structural development at this growth phenomenon. We shall consider the coalescence as "complete" one when all the stages mentioned above are completed, while it is "incomplete" when the recrystallization is not realized. According to this definition, the complete coalescence reorganizes the structure, and morphology of crystals as well as the distribution of bulk and surface impurities. The moving grain boundaries can sweep the bulk impurities to the surface. By this way the surface coverage of grains by impurities can be increased upon coalescence. The complete coalescence results every time in the formation of unique and homogeneous (uninterrupted) structure. In that case the structures of the coalescing grains are interfused by recrystallization or could be joined without defects tracing the coalescence area. This last process characterizes the perfect epitaxial growth. The "incomplete coalescence" leads to the formation of some kinds of intergranular area containing various types of defects, large or small angle grain boundaries as well as impurities.

The results of in situ electromicroscopic experiments (Refs. 6,61,71) revealed two types of coalescence. The type I is a very fast phenomenon like the coalescence of liquid droplets and called "liquid-like" coalescence consequently. This coalescence is "a priori" a complete coalescence and results in the development of three-dimensional single crystals. It is also characterized by a strong contraction of the coalescing grains leaving bare area behind, which initiates a new nucleation. The bare area is purified by the contracting crystals in many cases. In the case of coalescence type II, the phenomenon proceeds very slowly. This can be either complete or incomplete. Incomplete coalescence is taking place when the grain boundary cannot move out before the island participates in the next coalescence developing unfavourable geometry for the grain boundary migration, or the grain boundary migration is very limited either because the very low temperature or because the presence of impurities. The coalescence type II develops two-dimensional islands, resulting in a very pronounced change in the morphology of the grains. Its incomplete form is responsible for appearing of grain boundaries already before continuity, for the characteristic changes in the physical properties, and for the development of tensile stress. The statistical evaluation of Pócza carried out on In films /115,116/ proved the change of morphology of island from equiaxed to flat at a critical mass thickness. According to the in situ observations, this is the moment, when the coalescence type I changes to type II. Pócza has found that by increasing the partial pressure of oxygen during deposition, this critical mass thickness decreases and the islands become to be polycrystalline from that moment (incomplete coalescence). This indicates now directly that the oxygen contamination suppresses the coalescence type I and makes the coalescence incomplete at smaller grain sizes.

The complete coalescence in both types results also in the reorientation of crystals. It has been proved that the liquid-like coalescence and the complete type II coalescence are responsible for the development of the texture orientation of crystals in films deposited onto amorphous substrates, while in the case of epitaxial growth they contribute to the improvement of epitaxy at a great extent /66,71,77/.

Examples taken from the results on Al films deposited on mica can illustrate the effects of impurities on the coalescence. In Fig. 3 islands, developed by complete coalescence of type II in films are shown. Very flat and defect-free smooth islands of <111> orientation (marked by A) are developed upon the coalescence of well oriented crystals of pure surface. However one can find also three-dimensional crystals (marked by B) developed by liquid-like coalescence as indicated by the bare substrate surface left around this crystal. This kind of crystals have an orientation of <312>. It is very probable that the crystals having participated in this liquid-like coalescence had different orientation due to local contamination or to a domain of the mica surface. It is remarkable that a very high percentage of the shape of this crystal is destroyed. This indicates that impurities are accumulated to its surface at high extent. We can understand that the next coalescence of this crystal will be now controlled by these surface conditions.

In Fig. 4 islands developed by incomplete coaslescence type II in Al films deposited at higher rate of oxygen incorporation are presented. Epitaxially grown crystals are coalesced also in that case. However grain boundaries and macrosteps at the grain boundary areas can be identified. Grain boundaries exist also in the islands the geometry of which promoted the movement of the grain boundary. Both of these facts indicate that the coalescing surfaces were contaminated: the diffusion in the grain boundary areas was limited and the macrosteps were inactive in the crystal growth.

On amorphous substrates the phenomena are the same with the difference that the coalescing grains have usually different orientations and consequently different degree of contamination of the contacting faces. Depending on these, the coalescence of various groups of crystals can be completely different mainly at higher degree of contamination as detected by Reicha and Barna /28/. They have shown that there are groups of grains with pure contacting faces. These groups coalesce by liquid-like coalescence while other groups contaminated surfaces participate in an incomplete coalescence type II. Single crystals of large size can develop by this way on one hand, and small crystalline groups on the other hand simultaneously. The large crystals developed by liquid-like coalescence will accumulate material in surplus also by coalescing crystals grown from secondary nuclei in the channels. The crystals in the other groups are however limited in their growth by the surface contamination layer and are covered completely by this. The process shown in Fig. 1 repeats itself and a spherical-granula structure develops in that area. One can conclude that crystals (or crystal groups) are selected during the impurity controlled coalescence from the point of view of their further growth and the structural and thickness inhomogeneity developing at this stage will be reinforced when the film growth proceeds. A basis can be found in this structure and phenomenon for understanding the development of the very rough surface structure, detected many times in thicker films at which the columns are completely separated /9,30,117,118/.
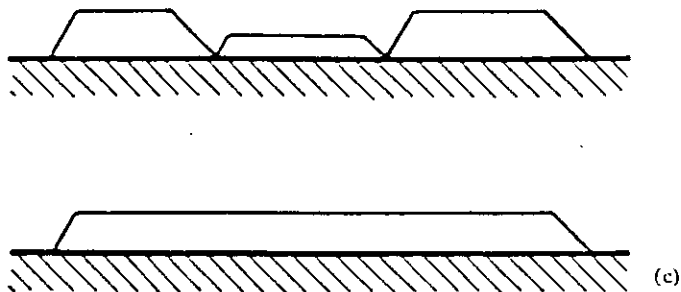
We have to deal also with the coalescence phenomena in amorphous thin films, namely because the formation of the amorphous structures starts also by nucleation in the most cases /52,114,
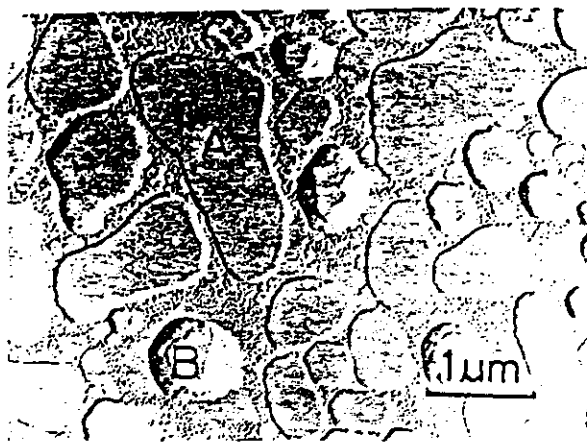
(a)　　　　　　　　　　　　　　　　　　　　(b)

(c)

Figure 3.
Islands developed by complete coalescence type II of epi-
taxially grown crystals (marked by A) and by liquid-like co-
alescence (marked by B). A film deposited on mica at $550°$ C,
$K_{oxygen} \sim 10^{-3}$. (a): Pt-C replica; (b) TEM imagen; (c): The
scheme of the coalescence.

119-121/. As a consequence, the coalescence of grains has a very high importance in the development of the structure of continuous films. This phenomenon is but neglected in most of works discussing the structural development of these films /7,122/. Because of the very limited surface and bulk self-diffusion in amorphous structures, the interfusion of the structure in the contacting area is a very complicated atomic process. Numerous atomic voids can develop and many atomic bonds becomes to be distorted which can serve as source of stress too. It seems that the mobility of adatoms control the perfectness of this interfusion and inter-grain structure mainly /114,121/, however the discussion and simulation of these processes are completely missing untill now. The coalescence of amorphous grains can be considered as a fully incomplete coalescence type II. One can conclude that the inhomogeneous structure accepted generally for amorphous films /114,123/ can be attributed to the incomplete coalescence. The relaxation of built-in straining stress can contribute to create further defects concentrated mainly in intergrain area and by this way reinforce them /114,120,124/. Impurities may increase or decrease the surface and bulk self-mobility of adatoms and by this way promote or hinder the structural reorganization during or

after the film formation. Oxygen and water vapour proved to hinder the diffusion in the case of a-Ge films /51,52/, while hydrogen promotes the adatom diffusion probably by forming Si-H complexes in the case of a-Si:H film preparation /114,125,126/. The hydrogen contributes to the formation of a very homogeneous structure in that case definitely.

The role of impurities in the phenomena during the coalescence stage can be summarized as follows:

—Impurities accumulated to the surface of crystals during their growth control the kind of coalescences (complete or incomplete, liquid-like or type II) at a very high extent besides the deposition temperature, orientation, size and defect structure of coalescing grains, as well as beside the local properties of the substrate. A selection of crystals take place from the point of view of their further growth in the presence of impurities at this stage. The anisotropy in the surface micro-chemistry for the given impurity results in a further orientation selection because of the anisotropic accumulation of impurities to the various crystal faces. Coalescence of amorphous grains is an incomplete coalescence.

—The coalescence recrystallization collects the impurities to the surface of crystals or to the grain boundaries. The percentage of the crystal surfaces

(a)
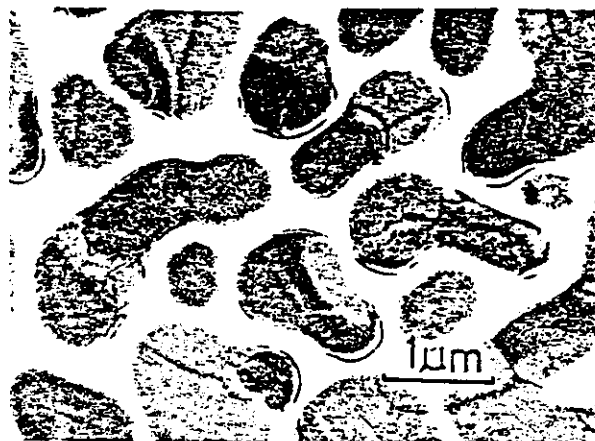
(b)
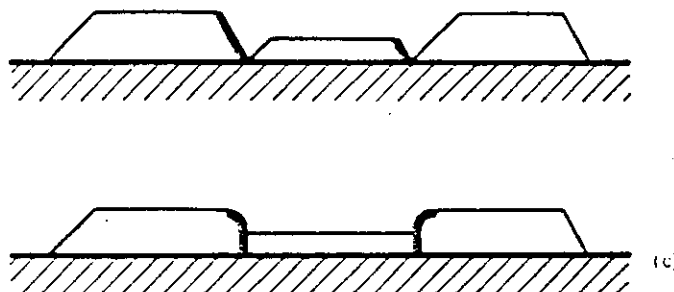
(c)

Figure 4.

Islands developed by incomplete coalescence type II of epitaxially grown crystals. Macrosteps and grain boundaries are formed due to the contamination of contacting faces. Al film deposited film on mica at $500°C$. $K_{oxygen} \sim 10^{-1}$. (a) Pt-C replica; (b) TEM image; (c) scheme of coalescence indicating the contamination layer (thick line).

covered by impurities increases by this way upon coalescence, on one hand, and on the other hand intergranular areas (grain boundaries) incorporate various amounts of impurities. The grain boundary contamination can limit the further recrystallization (i.e. the growth of grain size) during the growth of films or during a post-deposition heat treatment. The contamination can be also very active in binding and incorporating the impurity species during the further growth of the film. Pronounced and usually decorated growings at the grain boundaries found in continuous films can be attributed to the growth of grain boundary impurity layer over the crystals surfaces.

VI. GROWTH PHENOMENA IN THICK FILMS

The growth phenomena controlling the structural development of thicker films are determined by the structure, composition and morphology of the continuous film surface developed by the last coalescences. Focusing our interest again to the problems of the participation of impurities in the

growth processes and their effects on the structural development, we can conclude the following:

Grain boundaries, first of all those having solid phases of impurities can act as preferential sites for binding and incorporating the molecules of impurities migrating or having been swept by the monolayer growth to these areas. The impurity coverages of grain boundaries persist by this way and columns with impurity stabilized boundaries can develop. In that case the sizes of columns will be determined preferentially by the grain sizes developed upon the last coalescences of type II making the film continuous. The orientation of columnar crystals will mainly follow the orientation of the "basic" crystals.

At a low level of contamination, grain boundaries will be less contaminated and an effective recrystallization can take place during the further growth of film resulting either in an increase of the diameters of columns or in the development of a large-sized, equiaxed grain structure according to zones 2 and 3 of the structure zone model /127/. Some changes in the orientation of grains can be expected too.

At a higher level of contamination the impurity layers developed at the grain boundaries can persist their growth also along the surfaces of the growing

crystals. The whole surfaces of one or the other crystals can be covered at least completely according to the phenomenon shown in Fig. 1. Then the growth of such crystals will be interrupted and new crystals start to grow on their surfaces by new nucleation and coalescence, or adjoining crystals can overgrow them. A spherical-granula structure can be formed by this mechanism.

The very inhomogeneous structures developed on amorphous substrates upon the last coalescence of very high degree of contamination (discussed in Sec. V) can be a basis to initiate the development of a structure with completely separated columns (or even whiskers) /9,30,117,118/. Among the processes the low value of local condensation coefficient of atoms in the fine-grained areas can be responsible for the development of this very peculiar structure. The significant decrease of the condensation coefficient can be due to the high percentage of crystal surfaces covered by impurity layer.

The adsorpion and surface diffusion of impurities, their chemical activity and binding state on various crystal faces are sensitively determined by the deposition temperature too. This is also a reason why the deposition temperature can play primary role in the formation of various zones of the structure zone model /36,127/. However only by changing the oxygen partial pressure at the deposition of Al films without changing the other parameters (vapour beam intensity, substrate temperature), Barna et al. could get the characteristic structures of different zones /108/.

In connection with the interpretation of the structural zone model some remarks can be made:

(1). The experiments used to develop this model were carried out at rather moderate vacuum conditions (10^{-3} — 10^{-5} Pa), consequently the adsorption, binding and incorporation of impurities controlled by the given temperature could play an important role in the development of various zones.

(2). Thornton used the cathode sputtering in his experiments and analyzed the influence of sputtering gas pressure on the development of the various structural zones /127/. Recent results /35,58,103/ proved however that the quantity of incorporated gases depends on the gas pressure and on the energy of ions bombarding the film during deposition. Consequently, uncontrolled effects of impurities could not be excluded also in the case of Thornton's experiments.

(3). At very low temperattures a large quantity of weakly bounded gaseous impurities can be incorporated because of their very high sticking probability. The very fine "botryodal" structure in these films /128/ of zone 1 can be due to the development of small crystals which were interrupted in their growth by the

adsorbed impurities already at very low sizes. One can assume that the intergrain boundaries are filled by these weakly bounded games, and by this way the coupling between the grains is very weak.

The presence of impurities play a decisive role in the development of columnar structures inclined to the direction of the obliquelly incident vapour beam in metallic films as proved by Nakhodkin and Shaldervan /129/. By considering the differences in the conditions on the various sides of crystals created by the obliquelly impinging vapour beam (on Fig. 2) the pronounced differences in the effect of impurities turn out immediately. Crystal faces having different orientation to the vapour beam will have different level and kind of contamination and in consequence of this, different growth conditions as well as different structures and strength of grain boundaries. Pócza has shown the existence and intensification of the anisotropy in the shapes of grains and in the width of channels between the grains from the very beginning of Al film formation and their dependence on the incidence angle of the beam /130/.

The columnar structure proved to be a common characteristic of thick amorphous films too /52,114, 120,121/. The columnar structure in thick films might be determined also by the structure developed upon coalescence in the first continuous stage of film formation. This structure will persist and develop the columns and intergrain boundaries. Relaxation of straining stress incorporating as the thickness increases can contribute to the intensification of this supernetwork structure too /114,120, 124/. One can speculate that the network structures of larger diameters described by Messier et al. /120/ could be attributed to a step-wise relaxation of the straining stress increasing with the film thickness. This large-sized network structure can be similar in the sense of its origin to the crack network detected by Nordlander in thick Cr films /36/ and in thick NiCr films by Tóth and Sáfrán /131/. Impurities can be concentrated during the film formation into the supernetwork structure mentioned above by the change of place process or by diffusion from the atmosphere after deposition.

Structural reordering has been detected directly in high purity a-Ge films leading to the homogeneization of the structure in the supernetwork /52/. However the inhomogeneous structure can be stabilized by impurities of very low concentration /51,52/.

Finally another effect of impurities has to be mentioned in connection with the growth phenomena in thick epitaxial films. Changes in the value of K-impurities during the film formation can alternate the growth conditons and morphology. The case of the epitaxial growth of <111> oriented Al films can be mentioned in this context as an example. Barna and coworkers have found that the

2D monolayer growth transforms into 3D one when the K_{oxygen} increases from 10^{-4} to about 10^{-1} /132/. The roughening of the originally smooth surface occured during to the formation of three dimensional islands upon increasing of K_{oxygen}.

VII. SUMMARY

The analysis of the experimental results and the processes of film formation indicates that the various structural characteristics and physical properties of films can be understood better when considering the development of the films as the formation of multicomponent systems. Here the codeposition of unavoidable impurities should be considered at the first place. The effects of doping elements is very important when their concentration exceeds the solubility limit at the given temperature.

Codepositing impurity molecules influence the surface processes directly and by this way the growth and coalescence of crystals or amorphous grains. In the case of impurity insoluble in the lattice, a change-of-place mechanism between the adsorbed impurity molecules and impinging atoms can be proposed to explain the accumulation of impurity component by the growing surface. A solid layer of impurity can develop by this way on the surface of grains or at the grain boundaries. The impurity layer can present local inhomogeneities for the surface and interface (grain boundary) processes.

It has been shown that the structural development and the effects of impurities on these can be analyzed on the same basis both in the case of crystalline and amorphous films. The nucleation, the growth and coalescence of grains as well as the recrystallization or structural reordering in the grain boundary area should be considered in this respect. In thicker films the relaxation of stress into a network of defects is an additional phenomenon determining the structural inhomogeneities and the morphology.

The analysis of the possible processes in the presence of impurities revealed that certain growth morphologies (e.g. rounded crystal shapes, bunches of growth steps decorated by pinning sites) can correspond to the interference of impurity molecules with the growth processes. The appearance of growth peculiarities (e.g. growth hillocks, whiskers) in thick films seems to be due to the effects of "active impurities". Their activity is produced by the crystal face anisotropy in the surface micro-chemistry of deposit crystals.

ACKNOWLEDGEMENTS

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