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Models of Structural Zones for Sputtered and Evaporated Thin Films.

Kameneva AL*.

Perm National Research Polytechnic University, Department of Innovative Engineering Technology, Komsomol'skii pr. 29, Perm, 614990, Russia.

ABSTRACT

It is established that forming conditions and structural evolution of polycrystalline films may be simultaneously presented as structural zone models (SZM). The paper analyzed SZM of the films deposited by DC magnetron sputtering in inert and reactive media, by RF magnetron sputtering, and cathodic arc evaporation. The structural evolution of films in SZM is studied as a function of temperature, technological and physical parameters of the deposition process: a relation of the substrate temperature to the film melting point, working gas Ar pressure or its mixture with a reaction gas, relations of impurity and metal input flow intensities, relations of ion and metal flow intensities, substrate bias voltages. The author of the paper developed a SZM for the deposition of polycrystalline films in the low-temperature zone 1 by cathodic-arc evaporation. The heating rate of the film during its deposition is determined – $V_{heat.}$=3.7…4.1 K/min, that allows to increase the velocity of formation of polycrystalline films.

Keywords: model of structural zones, low-temperature zone 1, polycrystalline films, temperature and technological conditions, magnetron sputtering, cathodic arc evaporation.

**Corresponding author*

INTRODUCTION

Possibilities to produce films with a stable structure are limited. The actual film structure characterized by shape, volume, crystallographic orientation of the polycrystalline phase, its internal structure and mutual position against the X-ray amorphous phase, is unstable. The issue how to forecast and to stabilize the film structure draws a growing attention of various scientific schools worldwide. The evolution of polycrystalline films is established to be presented as a structure zone model (SZM) as a function of formation conditions. Scientific trials undertaken to describe, analyze and forecast the evolution of film structure in different intervals of technological and temperature parameters, are aimed at the study of regularities of their influence on the film structure formation, the search for new possible ways to describe fully events related to the development of different film structures.

The present paper analyzes SZM of polycrystalline films deposited by DC magnetron sputtering in inert and reactive media, by RF magnetron sputtering, and cathodic arc evaporation. The evolution of film structure in SZM was studied as a function of temperature, technological and physical parameters of the deposition: a relation of the substrate temperature (T_s) to the film melting point (T_m), working gas Ar pressure or its mixture with a reaction gas, relations of impurity and metal input flow intensities, relations of ion and metal flow intensities, substrate bias voltages (U_{bias}). The author of the paper determined that the evolution of structure and velocity of film structure formation, complementary to the substrate temperature, is affected by its heating rate in the deposition.

STRUCTURE ZONE MODELS FOR SPUTTERING

DC magnetron sputtering in the inert media

Thornton updated Movchan-Demchishin model [1] using the additional introduction of the second axis with technological parameters –pressure of the working gas Ar and the fourth structure zone for metal films with a thickness of 20…250 µm formed by magnetron sputtering at the rate of 50 to 20 000 Å/min (Fig. 1, a) [2].

Zone 1. The film structure at the cross-section is cone columnar crystallites with intermediate pores due to the low substrate temperature and low surface diffusion coefficient of atoms adsorbed. High roughness of the film surface is caused by anisotropic conditions of nucleation and formation of crystallites. It is shown that in Thornton model at 523°K (zone 1 – Ts/Tm = 0.14…0.25) for Cr film used in the production of magnetic recording media, a structural transition from the nucleation to the first formation stage of textured layers Cr (200), which correspond to the zone T, takes place [3].

Zone T – a transition between zones 1 and 2 characterized by the surface diffusion and columnar structure similar to the structure of the zone 1, but with less fibrous crystallites and dense enough boundaries, which provide good film mechanical properties [4,5]. This is explained by the fact that the atoms evaporated usually possess the energy about 0.1 eV, while the atoms sputtered – some eV, therefore in the condensation of atoms from the evaporator and sputter, films with different density are formed [6]. The authors of [7] believe that for this reason, the zone T is observed only in the deposition of films by the magnetron sputtering. The width of the zone T increases with the energy increase of condensing particles. Structure of the zone T of generally preferred zone 1, since solid films are usually characterized with a high level Tm (3223 K for TiN), while the Ts often remains relatively low (i.e. below 823 K for the stainless steel substrate) [8,9]. For this reason, at Ts/Tm = 0.2…0.3, both porous films with a low microhardness, reflectivity and tensile stress (zone 1), and dense films with a high low microhardness, reflectivity and tensile stress (zone T) may form. Dense films with extraordinary properties, which correspond to the zone T of Thornton model, may be obtained if the sputtering is performed at low pressure about 0.1 Pa and lower (Fig. 1,b) [10]. The low pressure sputtering moves the transitional zone T to the low-value region Ts/Tm and, thus, allows producing dense films, which correspond to the zone T, at low Ts.

With increasing the substrate temperature, the structure of the zone T is transformed to the structure of the zone 2, for which a well pronounced columnarity is typical.

In the zone 2, due to the surface diffusion and control of the forming process, the film has a dense columnar structure with a smooth surface. Due to the surface energy anisotropy, with increasing the film temperature columnar grain size increases and then, on their surface a faceting appears. The formation of columnar structure is observed in the ion deposition of iron-chrome films [7]. The columnarity of ion condensates TiN is also indicated in [11].

Zone 3 – the zone of equiaxial crystallites, formed at high substrate temperatures and in the dominance of lattice diffusion. The hardness of the metal thin film in zones 2 and 3 is higher than in zones 1 and T. If the pressure of working gas is increasing, the boundary of zone 3 is moved to the low temperature region [4].

Thornton′ SZM is a classical structural model [12-15] and reproduced in many handbooks on PVD [16,17]. Thornton′ SZM developed to produce single-layer thick films by the magnetron sputtering, hold for multilayer films, formed by other vacuum methods, for example, cathodic arc evaporation or chemical vapor [18]. There are various examples for the structure monitoring of films based on oxides, nitrides and fluorides of solid and gaseous elements, obtained by a number of vacuum methods, using Thornton′ SZM [11]. Records on the research of films obtained by the cathodic arc evaporation, are very limited.

The limitation of the use of Thornton′ SZM is shown, for example, for thin films AlN. To work on the model, it is difficult to determine Ts/Tm of this composition, which does not proceed from liquid state to solid one, but resolves incongruently at 2573 K [19-21].

Thornton′ SZM is reproduced the most frequently in the review part of [7,10,18,22-25], used to analyze the structure of films to be formed [3,6,8,19-20,26-28] or is taken as the base for advanced models for cathodic arc evaporation [30], arc discharge from the gas mixture to produce diamond films [31] and sol-gel method [32].

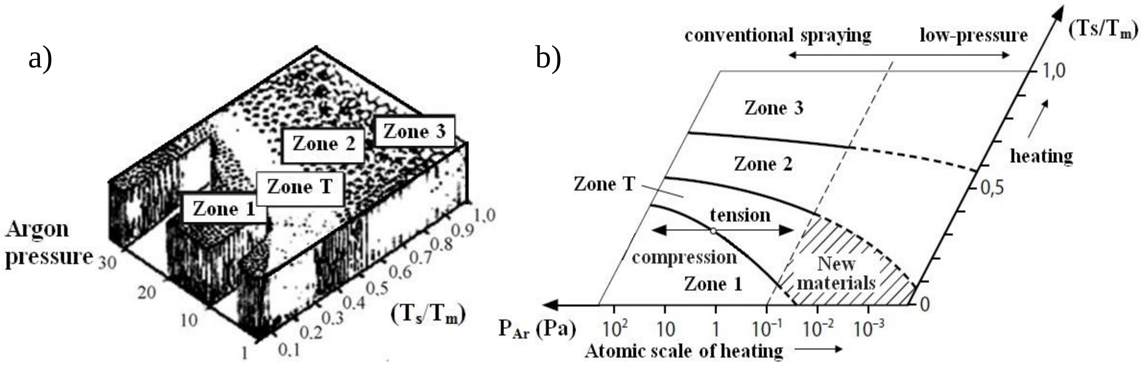

Fig. 1. Model of Thornton (1977): DC magnetron sputtering

At the first stages, Thompson etc. modeled the structure of the film formed on semiconductors, metals with regard of impurities, ion bombardment and fast thermal annealing, as well as other treatment conditions. Further research was directed to the simulation of continuous grain forming and structurized film, experiments on the epitaxial grain forming.

Following the long-term developments in the field of building of SZM and forming of continuous films, Thompson etc. simulated a process of grain formation for continuous films [33-34]. It is shown that deposition conditions of the almost and full «bamboo»-structure differ significantly, the transition to the fully bamboo structure is exponential in time, and the transformation velocity is inversely proportional to the square band width [33]. The researchers determined conditions, under which a fully bamboo structure is formed, and earlier structure evolution models of polycrystalline compounds were changed to the «bamboo»-structure (Fig. 2, a) [34]. Thompson etc. found that if the simulation is applied to the models of grain boundaries reinforced through free surface crossings, they are complied with a maximum band width-to-thickness ratio (about 3), beyond which the transformation to the bamboo structure does not go to its end.

Later, Thompson etc. established that such structural properties as grain size and shape, distribution and crystal-lattice orientation are affected by the technological conditions, under which grain nucleation, growth, coarsening, coalescence, and thickening occur [35-36]. In particular, relative rates of nucleation and island formation control grain size to its coalescence. The nucleation rate, diffusion rate of adatoms on the substrate surface and desorption rate of adatoms strongly depend on the T_s, and the nucleation rate and island formation – on the deposition rate. The grain size (up to the coalescence) increases with increasing the T_s and does not depend or decreases with increasing the deposition rate. The processes of concurrent coarsening, which take place before, during and after the coupling, affect the film grain size [36].

In 2000, Thompson etc. simulated a two-dimensional forming process of the continuous film from planar grains, following which the movement direction of boundaries is in the film plane, and the movement of grain boundaries is strongly limited in the plane of boundary curvature (Fig. 2,b,c) [36]. If grain boundaries are mobile, the granular film structure develops during the coalescence and continues its development during the forming of the solid film, resulting in more equiaxial structures, in which the grain size in the plane is usually almost comparable with the film thickness. The actual two-dimensional grain formation in thin films rarely takes place.

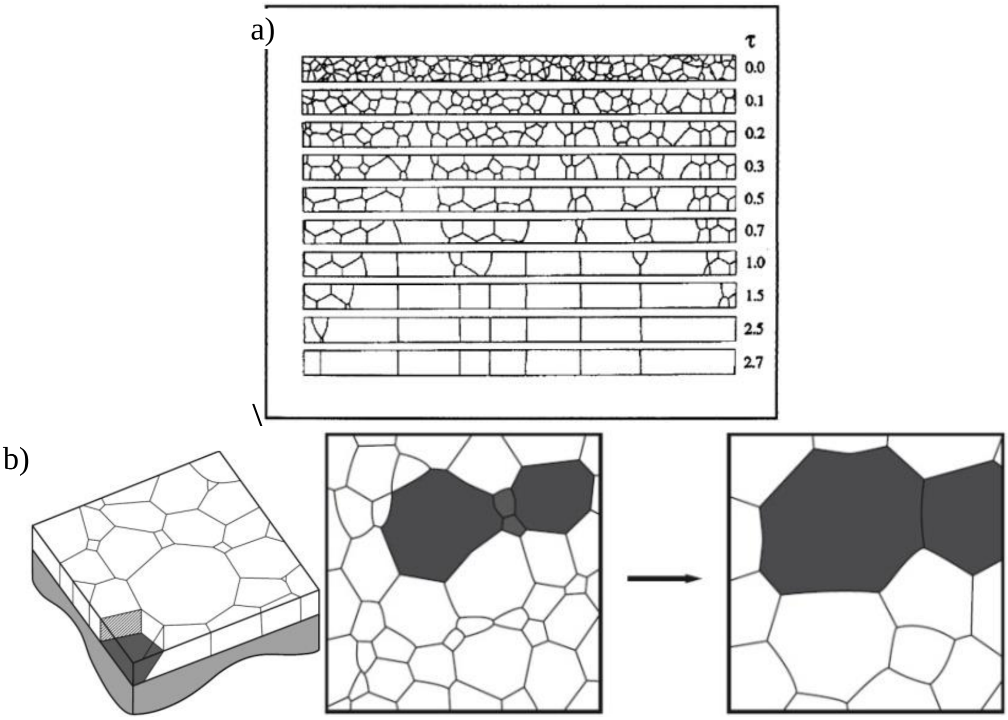

Fig. 2. Model of Thompson: magnetron sputtering, a) (1992), b) (2000)

DC magnetron sputtering in the reactive media

Control of film structure and texture and, as a consequence, smoothing of typical irregularities and undense structures (zones 1 and T) of refractory materials deposited at the low ratio T_s/T_m, are performed by Petrov etc. through the ion-assisted deposition process [36]. Under appropriate deposition conditions, the ion bombardment increases nucleation velocity and film density; decreases mean grain size; suppresses the formation of columnar structures related to the high surface roughness, and controls defect density and film orientation. Due to the practical importance as model systems, Petrov etc. selected films TiN and related nitrides of transition metals.

Despite the relatively high ion energy (E_i=100 eV), the microstructure in zone 1 is columnar and very porous with inter- and intra-columnar voids along the boundaries of well-pronounced dendrites, such a porous structure is caused by the limited surface diffusion.

Effects of the ion radiation were characterized by the relation of intensities of ion and metal flows I_i/I_{Me}, which fall onto forming film surface, and by the mean ion energy E_i: effects of increasing the ion energy, while $I_i/I_{Me} \leq 1$, effects of increasing I_i/I_{Me} with $E_i \leq 20$ eV [36]. Figure 3(1) is bright-field XTEM micrographs from TiN films deposited by reactive magnetron sputtering with low-temperature film growth with low-energy ion irradiation at general pressure P = 0.665 Pa with I_i/I_{Ti} ~ 1 and E_i ~ 20 eV. The grain size with the increase of film thickness (TiN) increases gradually, and boundaries of columns become opener to a great extent. The self-organized columnar structure of the zone T is formed in the disordered nucleation, limiting the coarsening in the coupling and concurrent formation of the columnar structure. The dense structure obtained is described using the lattice kinetic Monte Carlo model [37-38].

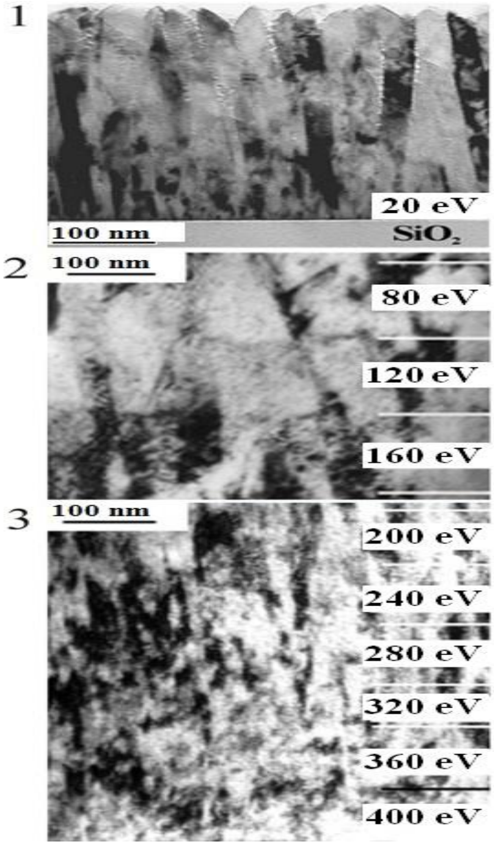

Fig. 3. Model of Petrov (2003): reactive magnetron sputtering

During the growth of the film the mean ion energy E_i was varied in steps of 40 eV from 400 to 0 to 400 eV at P = 0.745 Pa (Fig. 3,2). It is established that the layer structure at $E_i \leq 80$ eV is composed of dense columns with open boundaries, if the ion energy increases to 120 eV, voids along the boundaries of columns disappear, and the film becomes denser, which is however accompanied by the combination of intragranular residual defects (on Fig. 3(2), at E_i = 120 eV they appear as a darker region being distinct from the mean sublayer section), the concentration of which increase at higher stresses (at E_i = 160 eV, the mean sublayer has an even darker region) [36].

Figure 3,3 is bright-field XTEM micrographs from TiN films deposited by reactive magnetron sputtering at P = 0.745 Pa with E_i = 200…400 eV. A common factor in the regions with high-energy ion radiation (over 160…200 eV) – the disordered local formation of crystallites on individual columns due to the renucleation, which is accompanied by forced compaction and formation of the highly defective equiaxial structure under the further impact and form of the high-energy ion radiation (E_i = 200…400 eV) (Fig. 3,3) [36].

The film structure contains a thin phase, being formed due to the segregation of reactive components. Following X-ray and electron-diffraction patterns, the change in the preferred orientation from incompletely dense 111 to dense 002 was shown to take place with increasing E_i.

In the formation of 002 texture and grains with open directions of channels, for example 001, and a high probability of survival due to the anisotropy of intensifying effects, the ion energy supplied to open channels, results in a lower sputtering yields and less lattice distortion. The ion energy required to complete the transition is established to exceed 800 eV and result in an unacceptable big stress level, the use of high energy, and low-energy ion radiation is therefore not a real approach to control film texture. The ion energy increase at low I_i/I_{Me} is effective only in the narrow range (100…200 eV), at which a compaction takes place with allowable damage threshold by radiation and gas introduction.

The residual stress remains low in the atomic movement of the volume lattice in transition metals nitrides, and the impact on the texture and structure is significant if $I_i/I_{\mathrm{Me}} \geq 5$ at $E_i \leq 20$ eV, which are below the threshold value. Based on the independent control of the energy and ion flow fall onto the forming film, it is established that in the independent change of E_i and I_i/I_{Me}, impact directions change, even when the mean kinetic energy accounted for by the atom $\langle E_i \rangle = E_i(I_i/I_{\mathrm{Me}})$, remains constant. The actual change in I_i/I_{Me} in a wider range with $E_i \approx 20$ eV, which results in a negligible concentration of residual ion induced effects and residual stress, in the magnetron sputtering is an effective method to control the evolution of polycrystalline NaCl structures $Ti_{0.5}Al_{0.5}N$ [36].

Finally, Petrov etc. showed that a particular relation of ion to metal flows may be used for the selective and control-based film preferred orientation of transition metals from preferred 111 to 002. The above behavior is explained by authors with a concurrent formation of grains with a low thermal diffusivity, which uncover planes to the forming surface, and grains with a high thermal diffusivity, which are affected by the high-intensity ion radiation and balance between directions 111 and 002. In addition to the controlled texture change from 111 to 002, the increase of ion flow corresponds to the increase of layer density and decrease of surface roughness from underdense layers (δ–TaN) with intra-columnar voids and self-organized forming of columns separated by deep surface channels, to fully dense layers with smooth surfaces. The compaction is attributed to the less pronounced kinetic roughing due to the ion radiation, which increases the surface movement and results in smoother surfaces with a less atomical screening. The specific texture evolution causes a disordered nucleation on the amorphous substrate. So, the texture inheritance may be used to select a preferred orientation at the nucleation stage. This concept is used to produce dense highly-oriented transition metal films (TiN and TaN) relative to the plane 111 [36].

According to Petrov etc., the above kinetic and thermodynamic parameters should be incorporated into multiscale (planar and spacial) models of the first-stage structure evolution, which contain island formation and coalescence. Structure evolution models should be based on a combination, for example, functional theory of density measurement, molecular dynamic simulation, kinetic Monte Carlo simulation and a continuum of methods with the accurate output information, and drive every next scale in the simulation. The most complicated part is always the transition to a continuum. The model prediction should be controlled additionally with in-situ procedures, which use the dynamics of film forming, for example, scanning tunnel microscopy, low-electron velocity microscopy and TEM. Experimental results should be compared to model predictions, and if it is necessary to return to the further model improvement. Latest achievements in electron microscopy with the deviation adjustment using new generation devices, most applicable for such experiments, will provide large effective volumes between pole pieces (magnet) to perform in-situ film formation while maintaining the atomic resolution, imaging and providing the ultra-speed record.

RF magnetron sputtering

Many researchers in the field of film formation showed the existence of principal distinctions in the structure and mechanism of film forming [18], change in morphology (and, finally, in Thornton model) by applying a negative bias voltage Ubias to the substrate during the ion bombardment [19]. For example, increasing the Ubias during RF-magnetron sputtering can result in transition of the zone 1 microstructure to the zone T microstructure [8]. Messier [5] changed Thornton′ SZM by replacing the axis «pressure» with the axis, which characterizes the ion energy. In the model development, he assumed that in the consideration of ion energy, variables of the ratio of incoming ions and atoms are not accepted, the mass of ions is not equivalent to the mass of atoms, and that ions may have a non-uniform energy distribution. Basically, Thornton′ SZM in the new models is preserved and covers both similarity of the morphology of different levels and the developmental morphology of film forming, it is however believed that in the model generated, the transition zone T is formed only with the ion assistance (Fig. 4,a) [36].

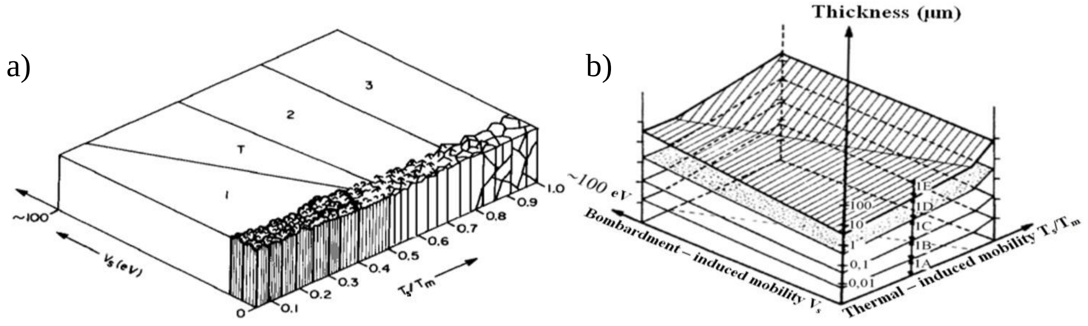

Fig. 4. Model of Messier (1984): RF magnetron sputtering

The updated SZM model proposed further by Messier etc. is the first to address to the film thickness in the development of structural zones **(**Fig. 4,b) **[**5,30,39-41**]**. For the zone 1, levels of the physical structure column/void are considered and assigned subzones lA, lB, lC, 1D and 1E **[**5**]**. The smallest subzone (1–3 μm) is designated by 1A, and the biggest one – 1E (with column size 300 μm). The dimensions increase from lF, lG etc. These structural zones were found in all films deposited from the vapor-gas phase, as well as in cathodic arc evaporated films **[**39.41**]**. The common origin of thin film forming is denoted by generality of the physical structure of different materials and self-similarity in the structure development **[**30, 39-41**]**. Models **[**4,5**]** were improved by other authors **[**8,33,42**]**.

STRUCTURE ZONE MODEL FOR CATHODIC ARC EVAPORATION

The structure evolution of TiN ($Ti_xZr_{1-x}N$, $Ti_{1-x}Al_xN$) films was investigated in the temperature range T_s/T_m =0.194…0.234, belonging to the zone 1. Compared to previous models, it is established that the pressure of gas mixture Ar and N_2 (P) in the zone 1 results in an increase of film heating rate in its deposition ($V_{heat.}$) from 2.5 K/min to 4.1 K/min. The following parameters are determined: T_s/T_m, $V_{heat.}$ and P for all formation stages of polycrystalline TiN ($Ti_xZr_{1-x}N$, $Ti_{1-x}Al_xN$) films, caused by the change in gas mixture pressure from 0.6 Pa to 1.4 Pa in increments of 0.2 Pa **[**43-50**]**. Figure 5 shows formation stages of polycrystalline films as a function of gas mixture pressure. The increase of P, T_s/T_m and $V_{heat.}$ have been shown to affect the structural and deformed state of TiN ($Ti_xZr_{1-x}N$, $Ti_{1-x}Al_xN$) films.

Globular stage – formation and integration of globules in compositions: 0.6 Pa – limited wetting and failure of the surface continuity; 0.8…1.4 Pa – increase of diameter and decrease of globule height

↓

Primary order of surface structure of globules: 0.6 Pa – it does not proceed; 0.8…1.4 Pa – increase in size of globular compositions

↓

Formation of 3D- compositions with granular structure: 0.6 Pa – it does not proceed; 1.0…1.4 Pa – elementary seeds of the polycrystalline film component on the surface of granular compositions

↓

Nucleation of polycrystalline film component: 0.6 Pa – it does not proceed; 0.8…1.4 Pa – increase in number of facets on the surface

↓

Coarsening / coalescence of germinal polycrystalline compositions: 0.6 Pa – it does not proceed; 0.8…1.4 Pa – increase in size of crystallite

↓

Island formation of the polycrystalline film: 0.6 Pa – 3D-compositions with non-ordered structure; 0.8…1.4 Pa – 2D-polycrystalline islands with ordered structure

↓

Formation of the solid polycrystalline film with inequigranular (0.6 Pa) and equigranular structure with equiaxial grains (0.8…1.4 Pa)

↓

Formation of microcompositions with granular substructure on the solid film surface with irregular (0.6 Pa) and ordered structure (0.8…1.4 Pa)

Fig. 5. Formation of the polycrystalline film TiN at P=0.6…1.4 Pa, T_s/T_m =0.194…0.234 and $V_{heat.}$= 2.5…4.1 K/min

The structure evolution of TiN ($Ti_xZr_{1-x}N$, $Ti_{1-x}Al_xN$) thin films investigated and presented as special SZM, reflects their structural changes as a function of P, T_s/T_m and $V_{heat.}$ (Fig. 6). Figure 7 shows micrographs of TiN film surface at different formation stages at optimal parameters: P=1.0 Pa, T_s/T_m =0.200…0.225 and $V_{heat.}$= 3.7 K/min.

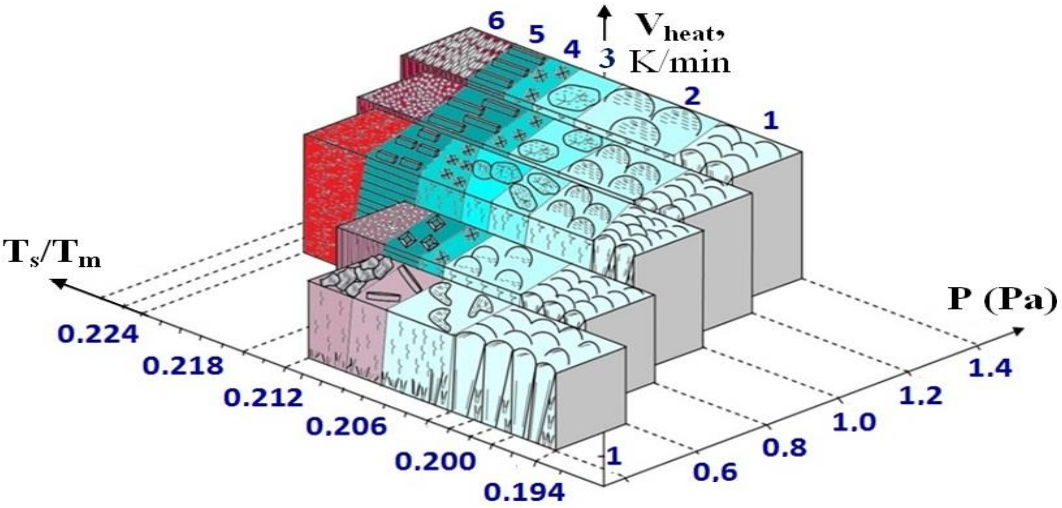

Fig. 6. Model of Kameneva (2013): cathodic arc evaporation [49]

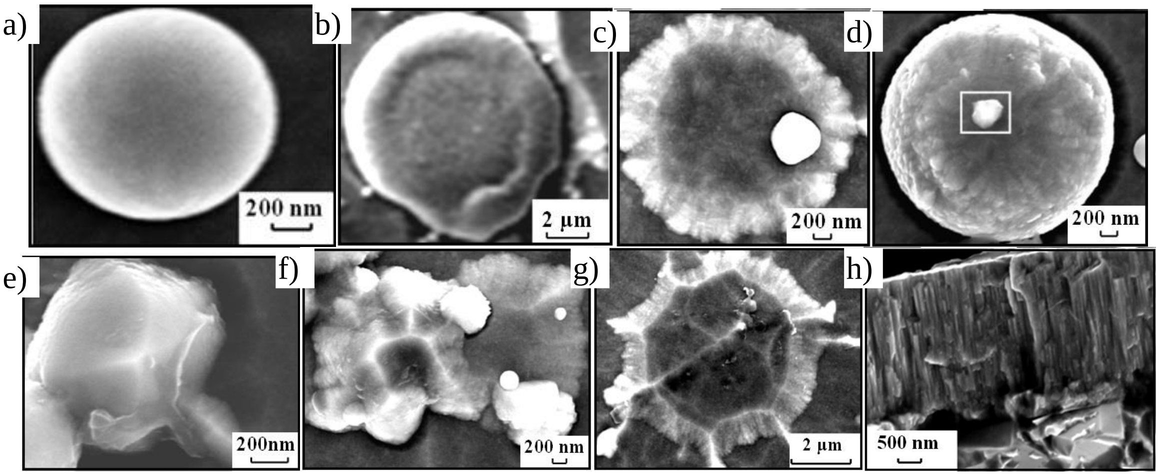

Fig. 7. Micrograph of the surface of polycrystalline TiN film at different formation stages at optimal pressure 1.0 Pa

Using SZM, optimal temperature parameters T_s and $V_{heat.}$, at which the film structure formation stabilizes, the diameter of primary nanocrystallites decreases to 5 nm, the velocity of formation stages of the polycrystalline film increases, and finally its structure formation moves to the area of lower temperatures, are determined.

COMPARISON OF SZM OF FILMS OBTAINED BY DISPERSION AND EVAPORATION

Morphological changes and structural evolution of the film at its formation stages in low-temperature zone 1 depend on the deposition method and its assistance mode. In the zone 1, a columnar porous film is only formed by magnetron sputtering both in inert and reactive media with a low energy and low ion radiation flow. In the RF magnetron sputtering with increasing value of U_{bias}, the zone 1 is replaced by zone T. The ion bombardment increases the nucleation rate and film density, decreases the grain average size, provides the formation of columnar structures related to the high surface roughness and allows to affect defect density and film orientation under control.

In the zone 1 a dense defect-free polycrystalline film can be provided by cathodic arc evaporation, regardless of the fact that sputtered atoms possess a higher energy than evaporated ones. The formation of the polycrystalline film is moved to a lower temperature area through the high average energy of ions generated – 40…100 eV, the ionization level of cathode substance, which exceeds 90%, Ar and N_2 pressure increase, and finally the increase of $V_{heat.}$ in the deposition. The author of the paper determined the value of $V_{heat.}$=3.7…4.1 K/min, providing to increase the velocity of formation of polycrystalline films based on nitrides of transition metals in zone 1 by cathodic-arc evaporation.

Table I. Structure of sputtered and evaporated thin films in the zone 1.

Method	T_S/T_m	$V_{heat.}$,K/min	P,Pa	J_i,eV	Ion assistance	Structural characteristics
DC magnetron sputtering in inert media[1]	0.14… 0.25	-	-	-	-	Cone-shaped columnar crystallites with interstitial pores
Reactive magnetron sputtering[36]	0.24	-	5.0	100	Low-energy, low-flux ion irradiation during growth at J_i/J_{Ti}=0.5	Columnar and high-porous structure with inter- and intra-columnar voids at the interface of well pronounced dendrites
RF magnetron sputtering[18]	<0.3	-	-	100	By increasing value of U_{bias}	Zone 1 is replaced by Zone T
Cathodic arc evaporation[46]	0.19…0.23	3.7… 4.1	1.0… 1.4	-	By increasing value of P and $V_{heat.}$	Zone 1 is replaced by Zone T at optimal T_S/T_m and $V_{heat.}$

SUMMARY AND CONCLUSIONS

The evaluation of Russian and foreign dissertations, contributions and scientific papers over a period of 1969 to 2015 showed that one of major ways to stabilize the structure and operational properties of polycrystalline films is the study of the evolution of film structure in the deposition as a function of temperature and technological conditions, and finally the design of SZM.

The discrepancy of the first Movchan-Demchishin model with the next ones is explained by the fact that it considers the structure of T_S/T_m only, and was obtained based on the data of a relatively low optical resolution and not always satisfying results of SEM. As a basis of most SZM developed later, a dependence of films structural changes on T_S/T_m and technological parameters for different deposition methods of the films, which control its structure, was taken. These parameters include: T_S/T_m, the pressure of working inert gas or its mixture with a reactive gas, the relation of impurity and metal input flow intensities, the relation of ion and metal flow intensities, substrate bias voltage.

It is important to note models, which allowed to determine formation conditions of the solid defect-free film in the low-temperature zone 1 by the low-pressure dispersion;4 ion-assisted film deposition [11]; and film structure formation acceleration in the deposition through the increase of film heating rate [46-54].

The SZM [49] for the zone 1 includes formation stages of the polycrystalline film by cathodic arc evaporation: formation of globules, primary order of surface structure of globular, 3D granular compositions, nucleation of polycrystalline film component, coarsening / coalescence of germinal polycrystalline compositions, island formation, coalescence, formation of the solid polycrystalline film, secondary island formation.

SZM under investigation are a useful tool to describe semi-quantitatively and forecast the film structure evolution as a function of technological and temperature parameters of film formation.

The SZM [49] for the zone 1 developed to produce single-layer thin films by the cathodic arc evaporation, hold for multilayer films with different structure and composition of the layers formed using cathodic arc evaporation and other methods such as magnetron sputtering.

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