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Role of Energy and Composition of Film-Forming Species in Formation of Composition and Structure of Compound Films

L. R. SHAGINYAN

Institute for Materials Science Problems of National Academy of Sciences of Ukraine,
Krzhizhanovsky str., 3, Kiev-03142, Ukraine

Abstract

Effect of bombardment of the growing film by energetic particles on its properties is know over many years and is widely used for modification of the film properties. Despite of this there are no final answers on such questions as: what is the mechanism of compositional changes that take place for some compound films deposited under the ion bombardment, how the ion bombardment influences the epitaxial growth, what mechanisms govern the growth of the film on its early stages during deposition under the ion bombardment. The role of composition of film-forming species in formation of film structure is barely investigated or even not investigated at all. Experimental evidence and discussion of the influence of ion bombardment and composition of film-forming species on structure and composition of compound films are briefly considered in the review.

1. Introduction

The irradiation of the growing film by energetic ions and fast neutral particles has been shown to be useful for controllably altering the microstructure and some physical properties of the layers. In a lot of investigations in which bombardment of the growing film was used to modify film structure the following effects were observed: densification and increased oxidation resistance in optical films; reduction or elimination of columnar microstructure in metallization layers; altering the average grain size, preferred orientation and state of residual stress in the film; increased film-to-substrate adhesion; decreased temperature of epitaxy, etc.

Despite of extensive studies of above effects over many years, the mechanisms of influence of ion bombardment on: early growth stages of the film; on composition of compound films; on epitaxial growth, are still not completely clear. Thus, in[1] during the investigation of initial growth of In film using low-energy ($E_i \leq 300$ eV) ion irradiation it was established that the average island size increased, while the island density per square decreased rapidly with increasing of E_i. At the same time in quite similar investigations it was shown that the size of islands decreases and their surface density increases with increasing of E_i[2] that is just opposite to observations described in[1]. To the best of our knowledge such questions as: how the ion bombardment influences the temperature of epitaxial growth of the film; in what cases and by what means the bombardment of growing film is able to change film composition, also have no clear explanations.

The composition of the film-forming species (atoms, molecules, larger clusters) is another factor that can noticeably influence the film structure. Nevertheless there are no recent reports devoted to this problem.

In this review some mechanisms of influence of ion bombardment and composition of film-forming species - these important physical factors of plasmous deposition process on film structure and composition are considered.

2. Role of fast particle bombardment in formation of film structure and composition

2. 1 Effect of ion bombardment on the initial stages of film growth

Indium films were deposited by ion-plating system, where the indium vapors generated by thermal evaporation passed throw the r.f.-inductor (copper coil connected to a r.f.-generator) and condensed onto the room temperature substrates. A negative controllable d.c. voltage was applied to the substrate holder relatively the crucible. The argon at a pressure of 5×10^{-2} Pa was used as a ballast gas.

Argon and indium vapors were ionized by r.f.-gas discharge and were accelerated toward the substrate by the substrate voltage. Copper grids for TEM with thin carbon films placed on them, polished ceramic plates, NaCl single crystals (both with and without metal film contacts) served as a substrates. The composition and morphology of the deposited films (4-200 nm thick) were studied using ESCA and TEM.

For the films deposited with various substrate voltages (U_s= -600, -300 and 0 V) the number of islands per unit surface (the island density) was calculated as a function of the substrate voltage and is plotted in Fig. 1. It is seen from this plot that the density of islands increases and their average size decreases with increasing of the voltage (the energy of ions bombarding the growing film). This tendency found for the initial stages (4-12 nm) of film growth also holds for thicker condensates (Fig. 2 a, c).

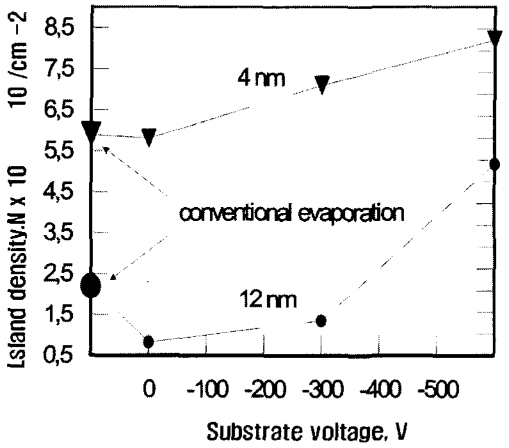
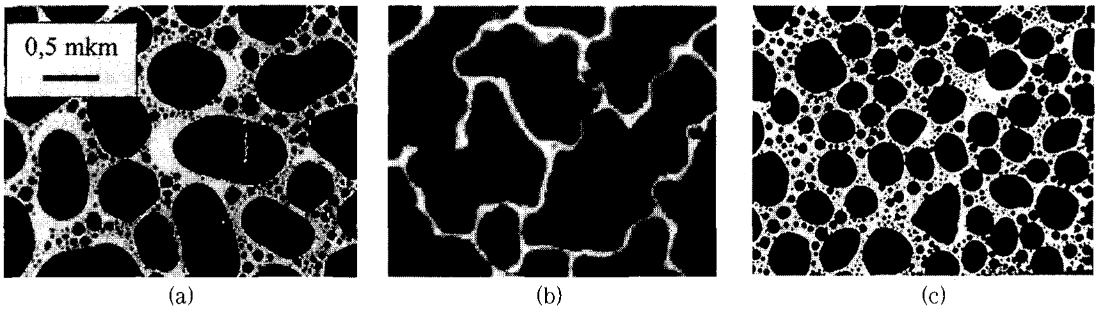


Fig. 1 The island density of In films as a function of the substrate voltage. The data obtained for two (4 and 12 nm) values of effective film thickness.

At the same time, the films deposited in discharge without accelerating voltage (U_s=0 V) in contrast with those prepared at U_s= -600 V, become continuous earlier than do films deposited by conventional evaporation under the same conditions (Fig. 2 b). All the features mentioned above are observed over a wide range of the film deposition rates (0.5 - 6 nm/s).

The obtained results may be explained on the basis of accepted concepts. When highly energetic



(a) (b) (c)

Fig. 2 Microstructure of 120 nm thickness In film deposited in different conditions:
a) film deposited in Ar without discharge (conventional evaporation);
b) film deposited in a discharge in Ar with U_s=0 V;
c) film deposited in a discharge in Ar with U_s= -600 V.

ions bombard the condensation surface, additional nucleation centers appear, leading to a higher density of islands. However bombardment promotes also the sputtering of growing islands and migrating indium adatoms. This process hinders the growth of island and blocks their coalescence. As a consequence, the films grown under the ion bombardment were composed initially of fine islands (compare micrographs on Figs 2 a and c) and later of fine grains. The films with fine grain structure had a 1.3-1.5 times higher resistivity than those deposited without ion bombardment.

Another particularity of the films deposited under the ion bombardment is a substantially lower concentration of impurity atoms in them. A 2-3 times decrease in an oxygen content was observed in films deposited at a highest (-600 V) substrate voltage. One more easily observed effect of ion bombardment is the increase of the temperature of condensation surface. The islands of films deposited by conventional evaporation frequently had a faceted form while those deposited at -600 V had a round shape (Figs. 2 a and c), which indicates an increase in the surface temperature, although the substrate temperature was held constant within ±5 K. Conventional deposition of In film on the substrate heated up to the indium melting point resulted in a decrease in the island density and in an increase of their size. However, the trends revealed for the films deposited under the ion bombardment at a room temperature were similar to those observed for the films deposited at elevated substrate temperature.

Comparing the results considered above with those presented in[1)] we can see that they are opposite. This effect has following reasons. Firstly, the thermal conductivity of Si_3N_4 substrates used in[1)] is lower than that of carbon films placed on copper grids in our experiments. Secondly, the ion fraction in our experiments was not higher than 12-15%, while this value was about 3 times higher in[1)]. Therefore, it is reasonable to suggest that the substrate surface temperature in the experiments described in[1)] was noticeably higher than that in our experiments. Taking into account that increasing of the substrate temperature results in a decrease in the island density and consequent increasing of their average size one can assume that the data obtained in[1)] mostly relate with the effects of the temperature of the condensation surface. The earlier continuity of the films deposited in a discharge without ion bombardment in comparison with those deposited in other deposition conditions relates with the form of the islands of these films. The characteristic feature of islands of such films is their planar form, while the islands of the films deposited in other deposition conditions have a convex shape (Figs. 2 a, b, c). Planar islands cover the condensation surface much better than those with convex shape. Planar form of the islands indicates their good wetting of the substrate surface. The reason of changing of wettability can be the impurities in the film. In fact, during the structure investigations of thick (120 nm) films deposited in a discharge without ion bombardment a pronounced line of indium dioxide in electron diffraction pattern was revealed. A gas discharge activates oxygen from the background gas that forms an indium oxide on the surface of indium islands.

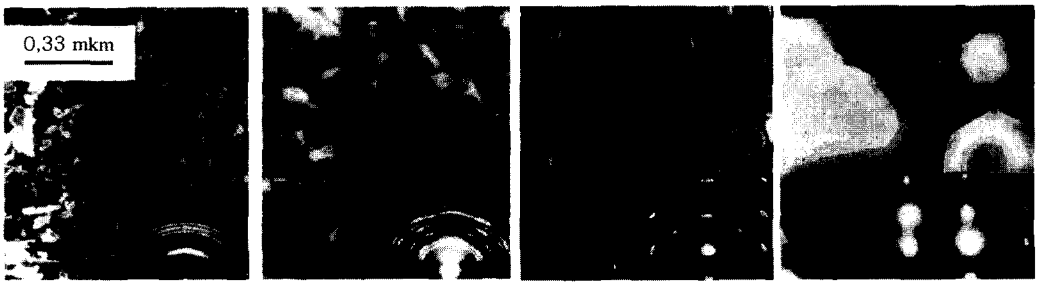
2. 2 Effect of ion bombardment on the epitaxial growth

In this section the epitaxial growth of GaN films deposited by reactive ion plating onto different types of substrates is considered. The deposition facility was the same as in case of deposition of In films. GaN films were deposited simultaneously onto (0001) of 6H-SiC, (0001) and $(01\bar{1}2)$ of sapphire, (111) of Si polished planes of corresponding single crystals. A series of depositions with different substrate temperatures and different

Table 1. Structure types of GaN films forming during the deposition onto different substrates and at different temperature ranges (ion bombardment is absent)

Ts, K / Substrate	300 - 450	450 - 650	650 - 850	850 - 1050	1050 - 1250
Carbon film	A	PC	TPC		Not investigated
Ceramic	A	PC	TPC		
α-Al_2O_3	A	PC	[illegible]	[illegible]	[illegible]
6H-SiC	A	PC	[illegible]	[illegible]	[illegible]
Si	A	PC	TPC		

Abbreviations: A, amorphous; PC, polycrystalline; TPC, textured polycrystalline; SC, single crystal.



(a) (b) (c) (d)

Fig. 3 Evolution of microstructure of GaN film deposited onto (0001) 6H -SiC single crystal with increasing of the substrate temperature T_s. Deposition without ion bombardment (U_s= 0 V). a) T_s=530 K; b) T_s=680 K; c) T_s=780 K; d) T_s=980 K.

voltages, applied to the substrate holder were carried out. Nitrogen was used as a working gas.

Temperature dependence of structure perfection of GaN films deposited without ion bombardment is presented in Table 1 and can be explained by the following processes. At a low substrate temperature the surface mobility of film-forming species is low that facilitates the nucleation process. In this case each occasional surface defect or impurity along with the energy surface of crystallographic plane serve as a center of nucleation. This results in appearance of high density nuclei with occasional crystallographic orientations that favors the growth of fine-grained or amorphous film. With increasing the substrate temperature the adatom mobility increases and simultaneous thermo-desorption of impurity atoms takes place. In these conditions the nucleation occurs predominantly at a sites corresponding to the energy surface of crystallographic plane. In this region of substrate temperature epitaxial growth of the film is observed. Disruption of epitaxial growth at a higher temperature (>1000-1100 K) is caused by the accumulation of structure defects like nitrogen vacancies in these films. This follows from the fact of lower nitrogen content in the films deposited at these temperatures. The evolution of microstructure and crystallographic structure of GaN/6H-SiC with the substrate temperature is shown in Fig. 3 a-d. The epitaxial film with a single crystal structure is formed from uniformly oriented tree-dimensional separate monocrystalline blocks of different size (Fig. 3d). The growth of the film occurs mostly owing to accretion of separate monocrystalline grains without their coalescence.

Quite different growth mode is observed for the films deposited in the same conditions but under the ion bombardment. In this case qualitatively new processes take place on the growth surface. At a nucleation growth stage the ion bombardment removes the impurities or other occasional sites of nucleation on the growth surface ; increases the surface mobility of adatoms. These processes facilitate the proper nucleation, "prepare" the sites for epitaxial growth and stimulate the growth process. At a later growth stages the ion irradiation facilitates the coalescence of is-

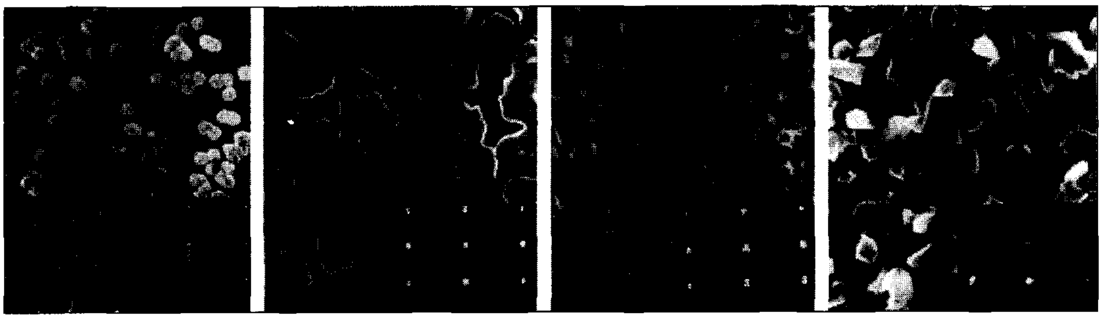


Fig. 4. Evolution of microstructure of GaN film deposited under the ion bombardment onto (0001) 6H -SiC single crystal at T_s=780 **K** with increasing of the effective film thickness.

a) film thickness 30-50 nm, substrate voltage U_s= -130 V ;
b) film thickness 100 nm, substrate voltage U_s= -130 V ;
c) film thickness 200 nm, substrate voltage U_s= -130 V ;
d) film thickness 200 nm, substrate voltage U_s= 0 V.

lands by transferring of portion of ion energy to the crystallization surface and increases the surface mobility of adatoms that favors the orienting influence of the substrate. In other words, the ion bombardment intensifies the action of the substrate temperature. Due to this effect it is reasonable to expect the lowering of the temperature of epitaxial growth in the presence of ion bombardment.

All these effects were experimentally observed during the epitaxial growth of GaN/SiC. Character features of these films are high density and small dimensions of islands on the initial growth stage, uniformity of their form and dimensions, two-dimensional shape (Fig. 4a). Average diameter of the islands is ~5-8 times larger than their height. The growth of such film occurs mainly by accretion of islands in a substrate plane with subsequent coalescence of the islands (Fig. 4b). Such films become continuous at a relatively low (~100 nm) thickness and have a flat surface and low porosity. These results show that the ion bombardment changes the mechanism of epitaxial growth of GaN film from three-dimensional that is intrinsic for the film growth without the ion bombardment, to two-dimensional.

Another effect of ion bombardment is the existence of an optimal ion energy (100-130 eV) at which the temperature of epitaxial growth of GaN film decreases in 100-120 K (Table 2). If the ion energy exceeds the optimal value the epitaxial growth disrupts and film growth rate decreases up to complete stopping of the growth. Further increase of the ion energy promotes the sputtering of the growing film and film growth rate decreases up to complete stopping of the growth. Optimal combination of the substrate temperature and the ion energy provides the growth of the film with perfect structure.

2. 3 Effect of ion bombardment on the film composition

The effect of ion-bombardment-induced compositional changes was mainly observed in alloy films[3, 4] and almost was not described for compound films. Our investigations of the influence of ion bombardment on the composition of $A^{III}B^{V}$ nitrides and indium oxide films deposited by reactive ion plating and that obtained by sputtering of (W-30Ti) alloy allow understanding the mecha-

Table 2. Substrate temperature at which transition from one structure type to another has occurred in GaN films, as a function of substrate voltage and substrate type.

Substrate voltage, U_s	Substrate type The temperature of formation of different structure states, K		
	α-Al_2O_3	6H-SiC	Si
0	460⇒PC ; 600⇒TPC ; 980⇒SC	460⇒PC ; 580⇒TPC ; 900⇒SC	460⇒PC ; 700⇒TPC ; No
-100	460⇒PC ; 600⇒TPC ; 980⇒SC	280⇒PC ; 480⇒TPC ; 780⇒SC	280⇒PC ; 530⇒TPC ; No
-200	460⇒PC ; 600⇒TPC ; 980⇒SC	280⇒PC ; 460⇒TPC ; No	280⇒PC ; 530⇒TPC ; No
-400	460⇒PC ; 600⇒TPC ; 980⇒SC	280⇒PC ; No	280⇒PC ; No
-600	460⇒PC ; 600⇒TPC ; 980⇒SC	500⇒ No condensation	500⇒ No condensation

Notes: 《460⇒PC ; 600⇒TPC ; 980⇒SC》 - temperatures of formation of: polycrystalline ⇒PC), textured polycrystalline ⇒TPC), single crystal films. At $T_s < 460$ K films were amorphous. 《No》 - no changes in film structure occurred with further increasing of substrate temperature ; 》No condensation》 - at these conditions the film did not grow.

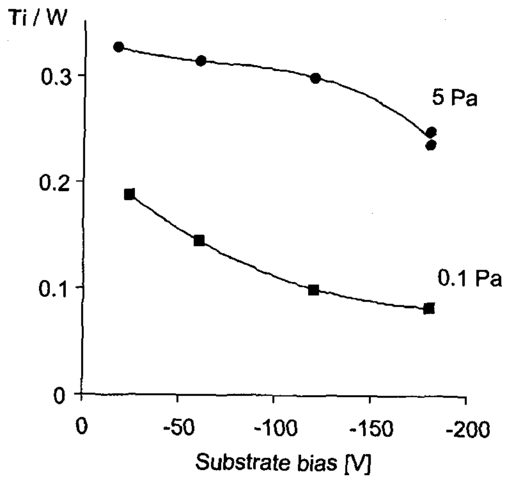


Fig. 5 Dependence of relative titanium content ⇒ Ti/W) in the film deposited by magnetron sputtering of W-30Ti alloy on the substrate voltage.

nism of this effect[5-9].

Facility and deposition conditions of InN, In_2O_3, AlN films deposited by reactive ion plating were similar to those described above for In and GaN films. Investigation of series of InN films deposited at different substrate voltages (0; -100; -600 V) and at different substrate temperatures (300 K; 570 K) has shown that the microstructure and composition of the films strongly depend on these parameters. The films deposited without ion bombardment have stoichiometric InN composition, while the increase of the ion energy accompanied by depletion of the film by nitrogen. The films deposited with $E_i = 600$ V were formed of pure indium[5].

Similar to those results were obtained during magnetron sputtering of W-30Ti alloy. On Fig. 5 the dependence of film composition on the substrate voltage is displayed. As it is seen from the plot, relative titanium content Ti/W in the film decreases with increasing of the ion energy[9].

At the same time the composition of AlN[7] and In_2O_3[8] films deposited by reactive ion plating in conditions similar to those for deposition of InN films, or composition of BN films obtained by r.f.-magnetron sputtering[10] did not change with changing of the ion energy.

The depletion of InN films in nitrogen and W-Ti films in titanium can occur by two mechanisms: via re-sputtering of N or Ti migrating adatoms from the condensation surface ; via selective ⇒ preferential) sputtering of these elements from the bulk of the film. Special experiments have shown that the depletion of InN films in nitrogen and W-Ti films in titanium proceeds via re-sputtering of migrating adatoms. The question arises: why similar depletion for AlN, In_2O_3 or BN films deposited under the ion bombardment was not observed?

The composition of the film forms mainly due to chemical reaction between separate atoms on the condensation surface. At the same time it was shown that the depletion of the film proceeds via re-sputtering of migrating atoms. Thus it is reasonable to assume that the higher is the rate of chemical reaction between the atoms, the lower the probability of re-sputtering of atoms is.

Thus it is reasonable to assume that the higher is the rate of chemical reaction between the atoms, the lower the probability of re-sputtering of atoms is. The rate of chemical reaction between the elements depends on their mutual chemical activity. The indicator of this is the difference of electronegativities ⇒X_{A-B} of elements. As long as the difference of electronegativities in a row $\Delta X_{In-O} = 1.8$, $\Delta X_{B-N} = 1.7$, $\Delta X_{Al-N} = 1.6$, $\Delta XI_{n-N} = 1.3$ decreases it is reasonable that the probability of re-sputtering of nitrogen atoms during the formation of InN is higher, than that for In_2O_3, BN, or

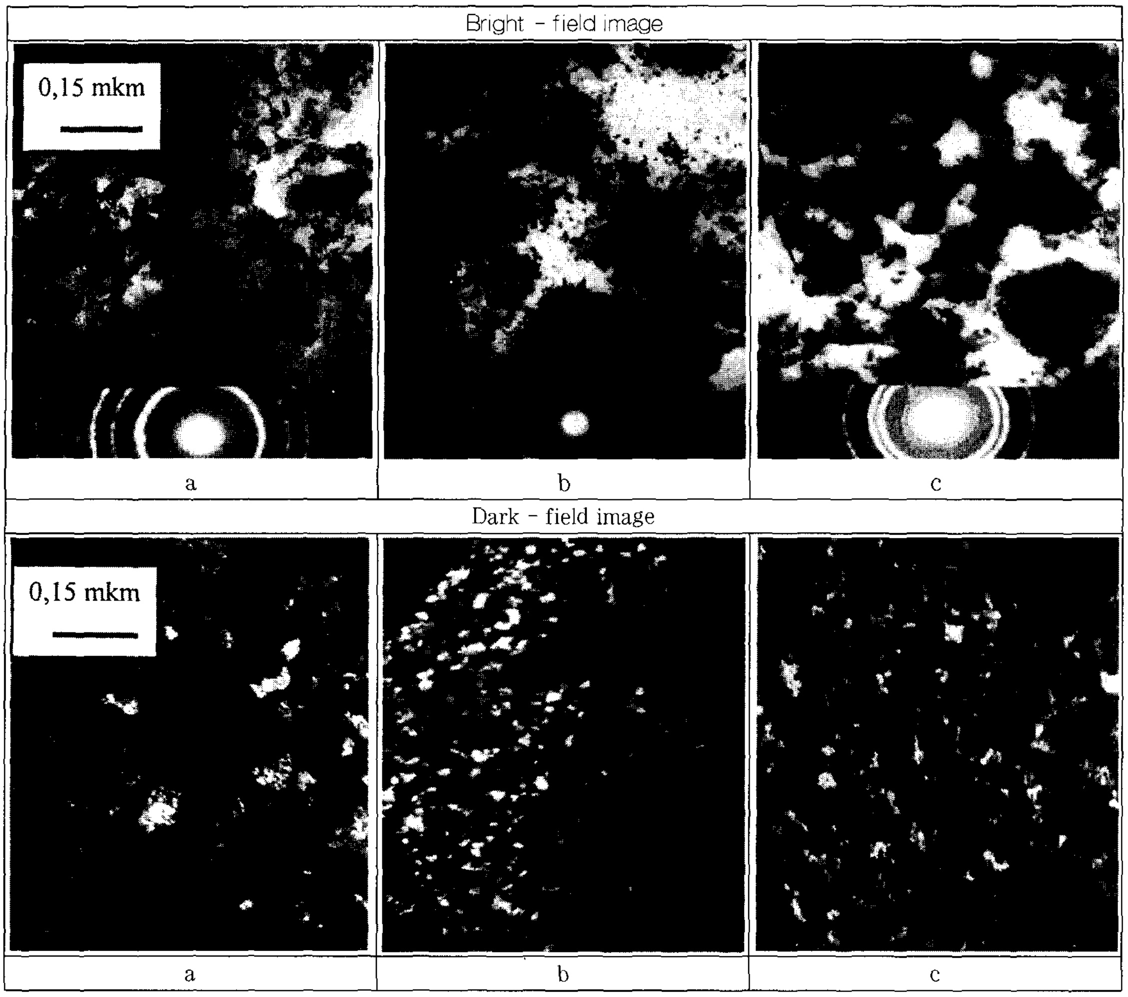


Fig. 6 Structure of (W, Ti)N films deposited by reactive magnetron sputtering of (W-30Ti) alloy at a different nitrogen concentrations in Ar-N_2 working gas.
a) nitrogen concentration 0% ; film composition ($W_{0.88}Ti_{0.12}$) ; grain size (50-100) nm
b) nitrogen concentration 16% ; film composition : ($W_{036}Ti_{0.2}$)$N_{0.28}$+$W_{0.16}$; grain size ~ (10-20) nm
c) nitrogen concentration 40% ; film composition : ($W_{0.4}Ti_{0.15}$)$N_{0.45}$; grain size (20-40) nm

AlN. Just this effect was observed experimentally.

The depletion of W-Ti film in titanium under the ion bombardment is also conditioned by the absence of chemical bonding between the tungsten and titanium. Complete immiscibility of these metals almost up to 700 K confirms this assertion. The depletion of the film in titanium relates with easier re-sputtering of titanium adatoms due to substantially lower atomic mass of titanium in comparison with that of tungsten.

3. Role of film-forming species in formation of film structure

To the best of our knowledge the type of film-forming species (atoms, molecules or larger clusters) was not considered in literature as a factor that may noticeably influence on the film structure. Meanwhile as an indirect confirmation of this effect may serve the fact that DLC-films can be deposited only from uniform flux of carbon atoms[11].

In the investigation of film formation during reactive magnetron sputtering of W-30Ti alloy in Ar-N_2 gas mixture[12] has been made an attempt to find out the correlation between the composition of film-forming species and the film structure. The structure of films deposited at different nitrogen concentration in Ar-N_2 mixture is presented in Fig. 6, and the composition of species revealed in the substrate region as a function of the same parameter is shown on Fig. 7. The microstructure of W-Ti film deposited without nitrogen is dense and formed from relatively large (50~100 nm) grains. Substantial decrease of the grain size up to about 10 nm occurred with addition of 16% N_2 to Ar (Fig. 6). This film consists of two phases, β-W and $(W,Ti)_2N$. Further increase of the nitrogen concentration in working gas results in formation of monophase $(W,Ti)_2N$ condensates with grains a little larger (~20-40 nm) than in previous case.

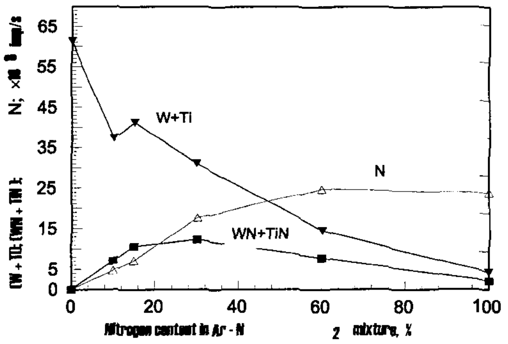


Fig. 7 Composition of film-forming species generated during reactive magnetron sputtering of (W-30Ti) alloy as a function of nitrogen concentration in working gas.

The described evolution of film structure with increasing of nitrogen concentration in working gas can be explained basing on corresponding changes in composition of film-forming species. In the region of nitrogen concentrations below 20 $\%N_2$ the prevailing film-forming species are W and Ti atoms, while the concentration of WN and TiN molecules is lower. At the same time the total concentration of WN+TiN molecules in these conditions is higher than the portion of N atoms (Fig. 7). Therefore one may consider that the main portion of nitride phase in condensate deposited at this nitrogen concentrations is formed from WN and TiN molecules, but not due to the reaction between the metal (W and Ti) atoms and N atoms on the condensation surface. The presence of a large and stiff WN and TiN molecules on the growth surface limits the mobility of metal atoms that results in growing of small grains of metal phase (Fig. 6). Let us note that the films with such microstructure have had a maximal microhardness. The increase of nitrogen concentration in working gas over 20% is accompanied by increasing in concentration of nitrogen atoms and simultaneous decrease of portion of MeN molecules on the growth surface (Fig. 7). Synthesis of nitride phase in such conditions occurs mainly by means of reaction (Me+N=MeN) between metal and nitrogen atoms on the condensation surface. Some enlargement of the grains in this film (Fig. 6) relates with the enhancement of the temperature of condensation surface due to its heating by heat of chemical reaction.

Thus, this example clearly shows that the composition of film-forming species can noticeably affect on the film microstructure.

4. Conclusion

A brief review of experimental facts clearly shows, that the energy and composition of species arriving at the condensation surface can substantially transform both the composition and the structure of the film.

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