

FORMATION OF THIN FILM Cr-N COMPOSITES UNDER ION BOMBARDMENT AT LOW RATES OF CHROMIUM DEPOSITION

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One of peculiar features of the IBA technology consists in that the damage level and concentration of implanted ions are distributed nonuniformly in the depth of deposited material. The calculations, we have done earlier [1], showed that the highest degree of nonequilibrium is realized in the first 50 nm of a coating. However, just in this thickness the nucleation and formation of the material structure is observed. The peculiarities of chromium coating formation without assisted irradiation and under bombarding with nitrogen ions having the energy of 30 keV were studied. The rates of chromium deposition were low, 0,05...0,1 nm/s. During the experiment the vacuum was maintained at a level of $4 \cdot 10^{-3}$ Pa and was determined, in main, by the content of nitrogen molecules arriving from the discharging chamber of the ion source. The thickness within the range from 3 to 10 nm was investigated. The results have shown that at the earliest stages of the film growth solely chromium nitride CrN is formed. Sizes of visible nuclei are in the range from 1 to 4 nm, and their density is $1 \dots 3 \cdot 10^{12} \text{cm}^{-2}$. As the film thickness increases, the nuclei are growing, then their coalescence occurs and a uniform coating is formed. Chromium deposition without irradiation, but at the same nitrogen pressure, resulted in formation of chromium hcp structure with the following crystallographic parameters: $a = 0,315$ nm; $c = 0,492$ nm. The grain size was 3...4 nm. After reaching the coating continuity, the hcp structure was transformed into the bcc structure with the parameter $a = 0,261$ nm.

INTRODUCTION

Computer simulation of the process of coating formation with the use of the ion-beam assisted technology (IBAD method) has shown that the application in this method of ion beams with the energy of several tens keV leads to the distribution of implanted ions with such energies and of point defects created by them in the deposited coating are very nonuniform in depth [1]. As a consequence, the conditions, under which the coating structure nucleation occurs, will be different at the initial stage and at the steady-state stage, although just the peculiarities of coating formation at the first 1...10 nm determine, in many aspects, its adhesion characteristics on the whole. In works, aimed to the study of initial stages of coating formation [2-5], is shown that the ion bombardment in the course of deposition leads to the cardinal changing in the mechanism of film nucleation and growth. The results obtained evidence that the ion bombardment influences on the density of nuclei being formed, their size, crystallographic structure of the coating and its texture.

In the above-mentioned works the ions of inert gases - argon and neon were used as bombarding particles. Their role in formation of the coating structure at the initial stage consists mainly in stimulation of diffusion processes due to the radiation effect. In the process of production of wear resistant and hardening coating one uses, first of all, the ions of active elements - nitrogen, carbon, oxygen, boron. Bombardment with ions of such a kind should influence not only on the structure of the coating being formed, but also on its phase composition.

The goal of the present investigation consisted in the comparative study of the peculiarities of chromium coating formation at the initial stage (thicknesses of 1...10 nm), without ion-beam assisted irradiation and

under conditions of bombardment with nitrogen ions of 30 keV energy at a temperature 200 °C.

EXPERIMENTAL PROCEDURE

Experiments were carried out at the assembly Argon-1 for ion beam assisted deposition [1]. Chromium was deposited onto the NaCl substrate, which was preliminary coated with a carbon layer. The evaporation process was controlled with the use of an electro-resistive transducer. All the substrate area was arbitrary separated into four parts, each of which was successively covered with a blind at regular time intervals. The deposition stopped after appearance of the electrical conduction at the transducer.

Simultaneously with deposition, one part of the substrate was bombarded with 30 keV nitrogen ions at the dose production rate of $2 \cdot 10^{14}$ ions/cm².s. The second part was covered against the ion beam action. The rate of chromium deposition was maintained rather low, 0.1...0.15 nm/s. The exposition time was selected so that each of four parts was irradiated up to doses 1.2, 2.4, 3.6, $4.8 \cdot 10^{16}$ ions/cm² respectively. Before the experiment, the working chamber was evacuated up to the pressure of $5 \cdot 10^{-4}$ Pa. In the course of the experiment the vacuum in the working chamber was worsened up to $4 \cdot 10^{-3}$ Pa at the expense of nitrogen leakage from the discharge chamber of the ion source. The substrate temperature was 200 °C.

After fulfillment of the experiment, the carbon film together with deposited chromium was separated from the substrate and examined in the electron microscope JEM-100CX.

RESULTS AND DISCUSSION

In the process of ion beam assisted deposition at the surface and inside of the substrate the complex physical-mechanical phenomena occur related to the modification of the structure and the component composition of the substrate itself, as well as, to the coating building up. Most part of the primary processes, occurring in this case, is described in [6]. Taking into account low rates of chromium deposition, being used in our investiga-

tion, and a relatively high nitrogen pressure in the working chamber is should be expected that in the process of coating build up the most part of nitrogen molecules will be captured by the atomic-molecular chromium flow. In order to study the influence of the residual atmosphere on the chromium coating structure, a part of the substrate in the course of the experiment was screened from the ion beam by the fixed blind.

Table 1

The interplanar distances for chromium films as deposited without ion bombardment

HKL	$h \approx 3 \text{ nm}, 4 \cdot 10^{-3} \text{ Pa}$	$h \approx 90 \text{ nm}, 4 \cdot 10^{-3} \text{ Pa}$	$h \approx 90 \text{ nm}, 5 \cdot 10^{-4} \text{ Pa}$
Cr hcp, 10.0	0,278		
Cr hcp, 00.2	0,253		
Cr hcp, 10.1	0,237		
Cr hcp, 10.2	0,209		
Cr bcc, 110		0,203	0,206
Cr hcp, 11.0	0,188		
Cr hcp, 10.3	0,162		
Cr hcp, 20.0	0,147		
Cr bcc, 200		0,140	0,144
Cr hcp, 11.2	0,139		
Cr bcc, 211		0,115	0,118
Cr bcc, 220		0,096	0,101
Cr bcc, 310		0,089	0,092

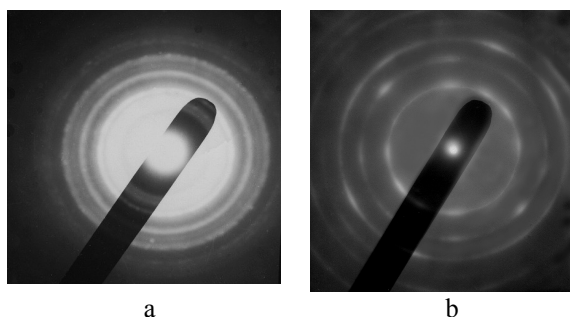


Fig. 1. Diffraction patterns for non-assisted chromium deposition: $h \approx 8 \dots 10 \text{ nm}$ (a); $h \approx 90 \text{ nm}$ (b)

Table 1 presents the interplanar distances obtained after counting the electron diffraction patterns of the chromium film deposited without ion beam assistance. Analysis has shown that at the initial stage of deposition there formed are hcp chromium structures with the parameters: $a=0,325 \text{ nm}$, $c=0,512 \text{ nm}$. The hcp phase remains stable up to the thicknesses from 20 to 30 nm at which the film becomes continuous. In the same table are given the results of structure analysis of the chromium coating, with the thickness exceeding 50 nm. It is

seen that the hcp structure is transformed in the bcc structure. Here also the interplanar distances of the bcc phase of chromium deposited at an initial pressure of $5 \cdot 10^{-4} \text{ Pa}$ are given.

The electron-microscopic images and the electron-diffraction photographs of chromium films are presented in fig. 1a, b. The "thickness" of the first of them corresponds to the thickest of four covered parts of the substrate ($\approx 8 \dots 10 \text{ nm}$), the thickness of the second one is 90 nm. In fig. 2 given are the histograms of nuclei grain distribution by sizes in the films deposited on each of four areas of the substrate. It is seen, that as the film thickness increases, the maximum position gradually shifts towards large sizes.

The interplanar distances of the crystalline structure being formed in the process of chromium deposition under ion bombardment are given in Table 2. Analysis has shown that the dominant phase at the initial stage of deposition is chromium nitride CrN (Fig. 3,a). Later on, while forming the continuous coating and increasing its thickness, the nucleation of chromium grains was observed. At thicknesses higher than 50 nm (Fig. 3,b) the material structure looks as a mix of Cr and CrN nano-size grains, the size of which does not exceed 10 nm.

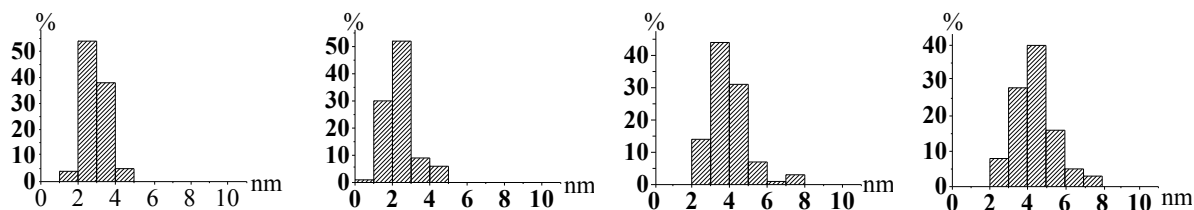


Fig. 2. Evolution of chromium cluster density as deposited without ion bombardment

The histograms of CrN grain distribution and the percentage of substrate surface coverage for different deposition times are presented in fig. 4. The material structure at the given stage looks as a system of grain nuclei, the distribution function of which changes with deposition time and irradiation dose increasing. If for the first two films a monodimensional distribution with a rather narrow peak in the range of sizes $\approx 2 \dots 3$ nm is characteristic, then, beginning already from the third film, the appearance of nuclei with a size of $\approx 5 \dots 8$ nm is observed. This tendency manifests most distinctly in the fourth film. It should be noted, that the increase of the main grain size occurs not at the expense of peak distribution shift towards large sizes, as it was observed for films deposited without ion irradiation (see fig. 2), but due to the appearance of the second peak in the area of coarse nuclei. A number of small-sized nuclei remain practically unchangeable. It means that we can speak about the coalescence of fine grains into coarser ones and about appearance of a new population of nuclei on the free sites.

Table 2
The interplanar distances for chromium films as deposited with ion bombardment

HKL	D_{bulk} , nm	$h \approx 3$ nm	$h \approx 50$ nm
CrN, 111	0,240	0,238	0,235
CrN, 200	0,207	0,203	-
Cr, 110	0,205	-	0,207
Cr ₂ N, 112	0,163	-	0,161
CrN, 220	0,147	0,145	0,144
CrN, 311	0,126	-	0,128
Cr, 211	0,117	-	0,117
CrN 400	0,104	-	0,102

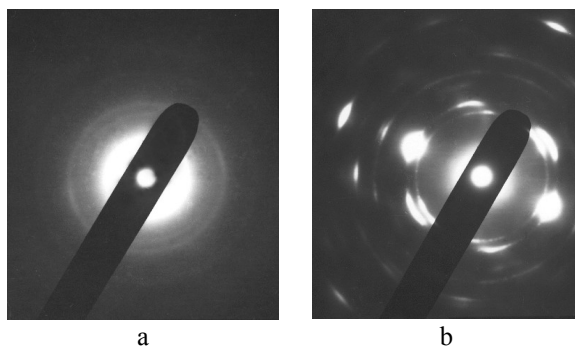
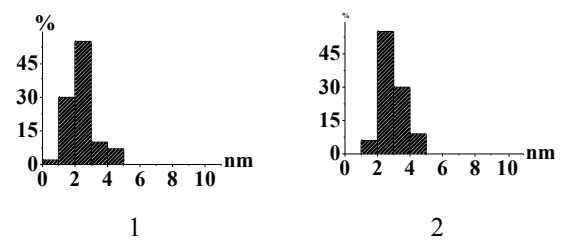


Fig. 3. Diffraction patterns for ion-assisted chromium deposition: a – $h \approx 8 \dots 10$ nm; b – $h \approx 90$ nm

So, the investigation performed showed, on the one hand, that the existence of the increased nitrogen content in the residual atmosphere, in combination with the low chromium deposition rate, leads to the formation, at the initial stage, of a hcp structure being no characteristic for the “bulk” chromium. The ion beam assisted deposition stimulates the nucleation of a nanocrystalline structure of chromium nitride CrN. At the initial stage, the forming of such a structure proceeds via the process of nucleation and coalescence.

In the scientific literature the polymorphism is often described by researchers, which studied the formation of thin films at the stage of their nucleation. As a rule, there occurs the formation of crystallographic structures packed closer than these observed in the “bulk” material. In the case of chromium one observed the formation of a hcp structure or a complex cubic structure [7, 8]. This phenomenon was explained in work [8] where the authors have supposed a changing of thermodynamic equilibrium conditions in thin films.

Chromium deposition at the increased nitrogen content in the working chamber occurs under conditions of continuous absorption of nitrogen molecules by the substrate surface. And the rate of nitrogen absorption higher by several folds than the rate of chromium condensation. The nitrogen dissociation energy is rather high, 205,5 kcal/mol. [9], and therefore nitrogen dissociation and formation of a chemical compound with chromium is improbable. Its blocking on the substrate surface seems more probable. Under such conditions, even though the deposition occurs at increased temperature, the surface diffusion of chromium adatoms to the grain nuclei is hampered. Thus, the main mechanism of grain growth will be the grain build-up at the expense of vapor deposition. The growth at the expense of surface diffusion will be less preferential. As a result, a mass nucleation of grains takes place.



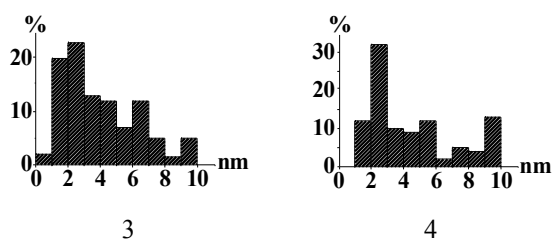


Fig. 4. Evolution of chromium cluster density as deposited with ion bombardment

If chromium is deposited under conditions of irradiation with nitrogen ions, then the mechanism of nucleation is appreciably changing. At the initial stage of film deposition the most important will be the influence of ion bombardment on desorption of gas molecules, on sputtering of chromium atoms, on their mobility. Furthermore, it should be noticed once more phenomenon not described in work [6], namely, ion-stimulated dissociation of nitrogen molecules being sputtered and a subsequent repeated nitrogen sorption on the substrate, but then in the atomic form. Just atomic nitrogen undergoes a reaction with chromium resulting in formation of chromium nitride CrN.

So, the mechanism of chromium coating nucleation under bombardment with nitrogen ions can be presented as follows. The ion beam destroys the layers of sorbed gas molecules, including nitrogen, and creates, on the one hand, an increased concentration of defects on the substrate surface, and thus forms conditions for more intensive nucleation of chromium grains, on the second hand, it creates, at the expense of nitrogen molecule dissociation, preconditions for sorbing nitrogen in the atomic form, and, on the third hand, it stimulates a surface diffusion of both the chromium atoms and the nitrogen atoms. The latter process leads to the formation of chromium nitrides CrN.

CONCLUSIONS

ФОРМИРОВАНИЕ ТОНКОПЛЕНОЧНОГО Cr-N-КОМПОЗИТА В УСЛОВИЯХ ИОННОЙ БОМБАРДИРОВКИ И НИЗКИХ СКОРОСТЕЙ ОСАЖДЕНИЯ ХРОМА

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Проведено сравнительное исследование начальных стадий формирования хромового покрытия в условиях бомбардировки ионами азота с энергией 30 кэВ и без ассистированного облучения, но при повышенном содержании азота в рабочей камере. Скорости осаждения были выбраны небольшими – 0,05...0,1 нм/с. Вакуум в камере был на уровне $4 \cdot 10^{-3}$ Па и определялся в основном азотом, который напускался в разрядную камеру ионного источника. Толщина исследуемых объектов была в интервале 3...10 нм. Результаты показали, что при ионной бомбардировке происходит образование нитрида хрома CrN, начиная с самых ранних стадий роста пленки. Размер видимых зародышей находится в диапазоне 1...4 нм, плотность – $3 \cdot 10^{12}$ см⁻². С увеличением толщины пленки происходит коалесценция малых зародышей, образование свободных зон и зарождение на них новой популяции зерен. Осаждение хрома без ионного облучения приводит к формированию ГПУ-структуры с параметрами решетки $a=0,315$ нм и $c=0,492$ нм. При достижении сплошности у пленки происходит трансформация ГПУ-структуры в ОЦК с параметром $a=0,261$ нм.

ФОРМУВАННЯ ТОНКОПЛІВКОВОГО КОМПОЗИТУ Cr-N В УМОВАХ ІОННОГО БОМБАРДУВАННЯ ТА НИЗЬКИХ ШВИДКОСТЕЙ ОСАДЖЕННЯ ХРОМУ

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The comparative investigation of initial stages of chromium coating formation at 200 °C under condition of the increased nitrogen content in the working chamber and of assisted irradiation with 30 keV nitrogen ions has shown that the nitrogen presence leads to changing in the mechanism of chromium deposition and creates preconditions for the formation of a nonequilibrium hcp structure, which transforms into the bcc structure with film thickness increasing. Bombardment of the chromium film during deposition with nitrogen ions initiates a sputtering of adsorbed nitrogen molecules and their dissociation. During the secondary sorption of nitrogen in the atomic state the ion irradiation stimulates surface diffusion of both the chromium atoms and the nitrogen atoms. The results of the action of the above-mentioned processes is the formation of a chemical compound in the form of CrN nuclei, their surface diffusion with subsequent coalescence leading to the formation of a nanocrystalline structure of chromium nitride CrN having a grain size of $\approx 3 \dots 5$ nm.

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Проведено порівняльне вивчення початкової стадії формування хромового покриття в умовах бомбардування іонами азоту з енергією 30 кеВ та без асистуючого опромінення, але при підвищеному тиску азоту. Швидкості осадження були підбрані невеликі – 0,05...0,1 нм/с. Вакуум у камері був на рівні $4 \cdot 10^{-3}$ Па та обумовлювався азотом, який напускався в розрядову камеру іонного джерела. Товщина досліджених плівок – 3...10 нм. Результати показали, що при іонному бомбардуванні має місце створення нітриду хрому CrN починаючи з самих початкових стадій. Розмір зародків знаходиться у діапазоні 1...4 нм, щільність – $3 \cdot 10^{12}$ см⁻². Зі збільшенням товщини має місце коалесценція зародків, створення вільних зон та зародження на них нової популяції зерен. Осадження хрому без іонного опромінення призводить до формування ГПУ-структури хрому з параметрами ґратки $a=0,315$ нм та $c=0,492$ нм. При появленні сполушної плівки має місце трансформування ГПУ-структури у ОЦК з параметром $a=0,261$ нм.