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# Regularities of Formation of the Ordered Structures in Molybdenum at Ion Implantation

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*Is shown, that the character of structural-phase transformations in molybdenum at ion implantation by the elements of the interstitial phase is defined, in the main, by the size factor, i.e. by the ratio of the atomic sizes of implanted elements and atoms of metal. The researches are carried out on molybdenum monocrystals at implantation by ions of Ar, C, N, O, B, Si, P, S.*

*Keywords: Ion Implantation, Structural-Phase Transformations, Kinetic Parameter.*

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## Introduction

One of radiation methods of a surface metals modification resulting in change structures and chemical composition of surface layers is the method of ion implantation. The perspectives of wide practical application of this method depends on the solution of questions as technological character connected to reception of high concentration of an introduced impurity in implanted layers and increase of them thickness, and scientific one, expressing in an establishment of principal mechanisms of rise and disintegration of phases at ion implantation. The majority of experimental works [1-3], directed on the solution of the second sort of tasks, was carried out, in the main, by electron diffraction method "on transmission" in case of thin films or " on «reflection» in case of massive samples. In that and another cases, receive an integrated picture of phase transitions on the top of a surface and in ion implanted volume. In the given work, the researches on ion implanted molybdenum carried out by a method of the X-ray analysis with a use of a glancing beam and photographic method of registration. The using

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of this method, in our opinion, has allowed to distinguish the processes of phase formation directly in implanted volume and to receive rather simple regularities.

## Samples and Research Methods

As an initial material is used molybdenum monocrystals of purity 99.96 %, cut out on a plane (110), by the sizes 8x1,5x1 $mm^3$. After mechanical processing samples were exposed to electrochemical polishing with the purpose of removal of the deformed layers. The ion implantation of argon, boron, carbon, nitrogen, oxygen, silicon, phosphorus and sulfur with energies of 110, 35, 40, 45(140), 90, 100 (300) and 105 keV, accordingly. The implantation with doses of $5x10^{17}$–$10^{18}$ $см^{-2}$ was carried out in vacuum ($1,3x10^{-3}$ Pa) at density of a current not exceeding several $\mu A*cm^{-2}$. The energies of acceleration of ions were chosen so that theoretical profiles of their distribution [4] without the account of effects of sputtering and swelling were about identical for all elements. Thermal isochronal annealing was carried out in vacuum ($6,6x10^{-3}$ Pa) through $100^0$C in a range of temperatures 200-1200 $^0$C during 1hour. The identification of implanted layers structure was carried out on X-rayograms, received with use of a narrow beam monochromatic $CuK_\alpha$ – radiation directed under glancing ($3^0$) corner to a sample surface [5]. At formation of texture phases the additional measurements were carried out at corners of 3, 6, 9 and $15^0$ and the identification was carried out on set of all received reflections. The research of accumulation processes of an implanted impurity was carried out with the help of a RBS-method at energy of protons 500 keV.

## Experiment

**Argon**. X-rayograms received on samples of molybdenum implanted by ions of argon show, that during implantation in researched layers a phase with hexagonal structure (a=3.01Å, c=4.71Å) arises (Fig. 1). Subsequent annealing up to $600^0$C results, simultaneously with the beginning of disintegration of the registered phase, in appearence another hexagonal structure with lattice parameters of molybdenum carbide $Mo_2C$ (a=2.99Å, c=4.72Å) [6]. At $700^0$C, the phase that has arisen at implantation completely disappears. At the further increase of annealing temperature on X-rayograms remain only reflections from a phase $Mo_2C$, to that at $1000^0$C the lines of polycrystalline molybdenum are added.

Most interesting is the fact of appearence, during implantation, of hexagonal structure, that at heating is transformed in molybdenum carbide. It is possible to assume, that it is the phase with structure $Mo_2C$, in that the part of atoms of carbon is substituted by the third element. Atoms of carbon are implanting in researched layers by a method of recoil from an atmosphere of residual gases of the accelerator and adsorbed on a surface of a samples. The third element, taking into account conditions of implantation, can be nitrogen or oxygen (the results of similar character are observed also at implantation of nitrogen ions). Thus, implantation of inert gas does not result in formation of the ordered structures directly with its participation.

**Oxygen**. X-ray researches that have been carried out on molybdenum samples implanted by oxygen show (Fig.2) that during implantation arises a bcc-structure with parameter of a lattice a=3.46Å, that differs from similar parameter of molybdenum (a=3.14Å) almost on 10 %. Subsequent isochronal annealing up to $500^0$C does not bring in essential changes to an observable picture. At $600^0$C, the bcc-structure disappears and instead of its a polycrystalline phase $Mo_2O_3$ arises, to that at $800^0$C the

small quantity of a polycrystalline phase $MoO_2$ adds. The formed structures is stable up to temperature $1200^0$C, annealing at that results in their complete disintegration.

The analysis of the results, received on oxygen, in view of the known data on system Mo-O [7] allows to make the following conclusions relatively of observable processes. Despite of the high chemical activity, the atoms of oxygen in process of implantation do not form chemical compound with molybdenum, and only, being placed in an initial lattice, form superstructure. The appearence superstructure with increased, in relation to molybdenum, parameters of a lattice causes a pressure in a crystal that partially relaxes by transition in a polycrystalline state.

Annealing results in to diffusion of oxygen from implanted layers and segregation it in separate regions (most likely on borders of crystallites) with the subsequent formation of chemical compound. It is possible also, that segregation occurs directly at implantation. This conclusion follows from composition of an arising phase $Mo_2O_3$. As to a phase $MoO_2$, appearing in small quantities after annealing, it arises at achievement of threshold temperature ($700\text{-}800^0$C) in those regions of an initial material, where owing to diffusion and segregation processes is created necessary composition. Thus, the time of annealing at temperatures exceeding threshold value in this case can render essential influence on formation of oxides.

As to literary data of other authors relatively processes of phase formation in molybdenum at implantation of oxygen, in them it is possible to find various results. For example, in work [8] in result of implantation by various dozes of mono- and polycrystalline samples of molybdenum are received low ($MoO_2$), intermediate ($MoO_x$, where $2<x< 3$) and highest ($MoO_3$) oxides. At the same time, results received in work [8] at implantation by oxygen of molybdenum films well correlate with results submitted in the given section, except the fact of appearence of superstructure after implantation and formation of phase $MoO_2$ at annealing.

**Carbon**. At introduction of ions of carbon in molybdenum arise a texture phases of carbide ($Mo_2C$) and monocarbide molybdenum (γ′-MoC) with hexagonal structures. Subsequent annealing up to $1200^0$C results in disintegration of the monocarbide molybdenum ($800\text{-}900^0$C) and increase of the particles sizes of the carbide molybdenum. At the same time at temperatures $800\text{-}900^0$C appearence of a phase $Mo_2C$ in not texture, but in a polycrystalline state, is marked. As have shown additional experiments on annealing of unimplanted samples, this phase is formed on a molybdenum surface at the expense of carbon presenting in an atmosphere of residual gases of the furnace at annealing.

The analysis of the received results, that have been carried out in view of the known data on system Mo-C [7] allows making conclusions concerning observing processes. In works [9,10] by an electron diffraction method investigated mono- and polycrystalline film of molybdenum, implanted by ions of carbon ions. Is shown, that during implantation in researching layers polycrystalline phases carbide ($Mo_2C$) and monocarbide (γ-MoC) of molybdenum of hexagonal structure appears. Subsequent thermal annealing at $1000^0$C resulted in strengthening of intensity of the reflexes. The results of the given work also show the formation of similar phases at implantation. However, alongside with appearence of molybdenum carbide is formed not low-temperature γ-, but high-temperature γ′-MoC phase, that disintegrates at annealing in a range of temperatures $800 – 900^0$C. About a γ′-phase is known only that it is formed in process of carboning at low temperatures and transforms with increase of temperature to a usual γ-phase [11].

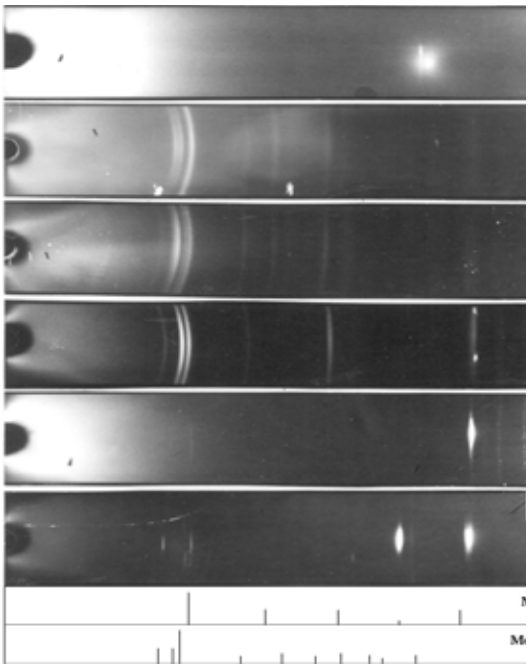

Fig. 1 X-rayograms of a molybdenum surface before (1) and after implantation (2) by argon ions, and annealing at temperatures 900(3) and $1200^0$C(4) at angles $\alpha$ $3^0$ (1-3) and $15^0$ (4).

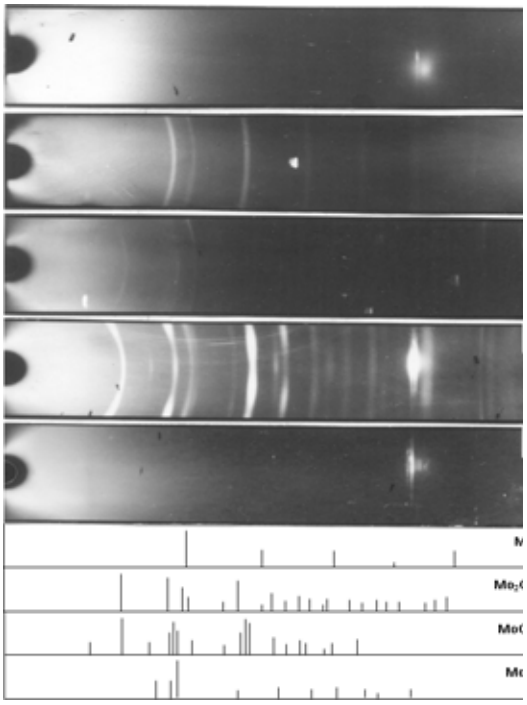

Fig.2 X-rayograms of a molybdenum surface after implantation by oxygen ions (1), and annealing at temperatures $600^0$ (2), 800 (3) and $1200^0$C (4). $\alpha = 3^0$.

**Regularities of phase formation**

Analyzing the received experimental data (Table 1), is possible to notice, that character of processes, proceeding at implantation, depend on the atomic sizes of introduced elements only. In process of their increase occurrence superstructure (oxygen), formation of introduce phases (nitrogen, carbon) and, at last, disordering of researched layers (boron, phosphorus, silicon, sulfur). The synthesis of the compounds in last case is observed only at the temperatures exceeding certain threshold values. As to inert argon, it has propensity at an irradiation to segregate and to form a bubble; therefore, the disordering of a molybdenum lattice is not observed.

The revealed regularities well correlate with a rule of Hagg [12], according to that if the ratio of radius of nonmetal atom ($r_X$) to radius of metal atom ($r_M$) is less than the critical value (~ 0.59), the simple structures are formed. They represent introduce phases, in that nonmetal atoms is possible to consider as inserted in an atomic lattice of metal. Thus the introduced atoms or fill an insignificant part of interstices (austenite, introduce solutions on a basis of bcc – lattice), or, at the large concentration of an impurity, the lattice of the metal – solvent suffers polymorphic transformation, more often in a sequence bcc-hcp/fcc [13]. Comparing peculiarities of introduce phases formation with the regularities of structural – phase transformations at ion implantation, revealed in the given work, it is possible to note, that a decisive role in researched processes at a stage of implantation plays the size factor. If radius of introduced nonmetal atoms correlates with a Hagg rule, the solid solutions or compounds of introducing having simple close packed structures are formed. Thus composition of compounds will be determined by the achieved concentration of implanted atoms and presence of such compounds

Table 1. Phase transformation in ion implanted molybdenum

| Ions | E, keV | Phases | Structures | Temperature, $^0$C | | $r_x/r_{Mo}$ [24] |
|---|---|---|---|---|---|---|
| | | | | Formation | Decay | |
| O | 50 | Mo(O)<br>$Mo_2O_3$<br>$MoO_2$ | bcc<br>rhombohedr.<br>monoclynic | at implant.<br>600<br>800 | 600<br>>1200<br>>120 | 0.43 |
| N | 45 | δ-MoN<br>γ-$Mo_2N$ | hexagonal.<br>fcc | at implant.<br>at implant. | 700-800<br>800-900 | 0.51 |
| C | 40 | γ′-MoC<br>$Mo_2C$ | hexagonal.<br>hexagonal | at implant.<br>at implant. | 800-900<br>>1200 | 0.55 |

in the corresponding phase diagrams. So, for example, the implantation of oxygen in interstices of a molybdenum lattice results in appearence of the ordered solid solution without formation of compounds. In a case implantation of nitrogen or carbon, compounds of introducing with simple close packed structures arise. They can be received by usual methods at increase of an impurity concentration up to values determining polymorphic transformation of a lattice of the metal – solvent. Thus, because of wide diapason of homogeneity, the formation of the compounds should be observed in the rather large range of dozes.

It is necessary to note, that, as the method ion implantation is thermodynamically nonequilibrium, the synthesized structures can be metastable, as is observed in experiments. At using of usual methods they are received by hardening, that has resulted, in our opinion, in appearence of models of ion synthesis containing idea of formation along a track of an implanting particle or at the end of its high-temperature ranges, cooling down with the large speed (thermal peaks or peaks of displacement [14, 15]). Other reason of arising of this models is stipulated for receipt of a lot of experimental data showing of formation during implantation at room temperatures and lower not only simple, but also rather complex structures.

Such approach to mechanisms of ion synthesis from the point of view of thermal peaks or peaks of displacement apparently is not right on several reasons. First, on our data during introduction arise only simple close packed structures, that formation proceed by polymorphic transformations at the expense of pressure created in a lattice of the metal by introduced particles. Secondly, any correlation between mass and energy of bombarded particles determining temperature of peaks, on the one hand, and arising of most probable from phase diagrams structures – with another, was not founded. Transition to heavier ions, that should create more high-temperature peaks of displacement at the expense of increase of losses of energy at elastic collisions in smaller volume, do not result to ion synthesis, and cause disordering of implanting layers only. It is observed in a case of implantation of boron, sulfur, phosphorus and silicon, that size factors ($r_X/r_M$) much more exceed critical value determined by Hagg (Table 1).

The received results give the occasion to conclude, that, the process of disordering in this case is caused not by fast cooling of high-temperature peaks, but accumulation of the structural defects formed at the expense of effect of presence of introduced atoms with the rather large atomic radiuses in a lattice of metal. The concentration of these defects in metal is determined not kinetic parameters of implanting atoms, but their quantity and atomic sizes.

To answer a question, why on the data of other authors at ion implantation frequently arise complex structures, for formation of that it is necessary to involve models of peaks, it is necessary to pay attention first of all to objects of researches, used techniques for structural researches and conditions of experiments. During ion implantation the surface of an sample is exposed to sputtering; swelling; implantation by recoil method of uncontrollable impurity, adsorbed on a surface from an atmosphere of residual gases of the accelerator; ion-stimulating chemical processes on top layers of the surface etc. Among them is necessary to distinguish last process that has been not connected directly with implantation of concrete kinds of ions, however capable to render essential influence on interpretation of results on structural – phase transformations. The speech goes about ion – stimulated chemical reactions of atoms of metal on a surface of a sample with adsorbed elements or appeared on a surface implanted atoms owing to effect of sputtering, that proceed on other laws, rather than in volume. At the same time the main part of works performed in this direction, is carried out by an electron diffraction method. The thickness of researched layers in this case not exceed 10 nm at measurements on «reflection» and 100 nm – at measurements on "transmission". At measurements on "transmission" is registered an integrated diffraction picture, independently of a site of an arising phase – on top layers of the surface or in implanted volume of a material. In result, the processes of phase formation in the top layers of a surface frequently attribute to the phenomena caused by ion implantation in deeper implanted layers. At using of a method on «reflection», the uncertainty grows, as is sounded only upper layers in some nanometers. The same concerns and to the phase analysis by a method of Mosbauer on conversion electrons, where the integrated picture is observed and the depth of sounding is not more 100 nm.

In this respect X-ray method of register with glancing x-ray beam practically does not feel upper layers in some nanometers and gives the data only about the volumetric phenomena. As the proof it is possible to adduce the unpublished data on research of molybdenum, implanted by ions of carbon, with electron diffraction method «on reflection». They showed appearing, alongside with molybdenum carbides, number of structures that are not registered by an X-ray method. At the same time, the differentiation of top surface and volumetric effects allows to explain appearing of observed structures without attraction of models of thermal peaks not only at ion implantation, but also at other kinds of radiation.

Thus, in the given work is not revealed of obvious dependence of character of ion synthesis from physical-chemical properties of implanted elements, that begin to act only at transition formed by ion implantation metastable structures in an equilibrium state at heating. In result, arise, in the main, expected from the phase diagrams, structures. Synthesized high-temperature interstitial phases (superstructure, carbides, nitrides) at annealing are disintegrating with formation of low-temperature phases. In case of other elements (boron, silicon, phosphorus, sulfur) are observing formation of low-temperature phases with various structures (Table. 1), kind of that is determined by concentration of the implanted atoms, and processes of their diffusion and segregation. Last conclusion follows from consideration of composition of received compounds that can differ from expected ones. Thus, for ion synthesis of the compounds with necessary composition the performance of the following conditions is necessary. First, – the receipt in ion implanted layers of the appropriate concentration of implanted impurity taking into account processes of sputtering and swelling of implanting layers, that in this case can become restriction of a used method. Secondly, it is necessary to take into consideration the

diffusion processes that in most cases do not give possibility to keep of the achieved concentrations of the implanted impurity at heating up to temperatures of phase transitions. One of ways of the solution of a problem in the latter case is the creation of diffusion barriers behind of implanting layers.

The main regularities of formation of the ordered structures at implantation of molybdenum by elements forming an interstitial phases (B, C, N, O, Si, P, S) are revealed. According to them the character of structural – phase transformations in molybdenum at ion implantation is determined not kinetic parameters of bombarding particles and their chemical activity, but the size factor $r_X/r_M$ (ratio of atomic radiuses of implanted elements and atoms of a matrix). At change of its values, can be observed: formation of superstructures ($r_X/r_M < 0.43$), polymorphic transformations with arising simple close packed structures ($0.43 < r_X/r_M < 0.69$), disordering of a lattice of an initial matrix up to amorphisation of implanted layers ($r_X/r_M > 0.69$).

## Conclusions

2. The direct dependence between mechanisms of structural – phase transformations and processes of accumulation of an implanted impurity in researched layers is established. For example, at implantation of nitrogen in molybdenum, leading to formation of nitrides in process of implantation ($r_N/r_{Mo} = 0.51 < 0.59$), its concentration in implanted layers rises with dozes up to a certain level. The superfluous atoms of nitrogen are forced out in the neighboring regions with smaller concentration, owing to what the phenomenon of disordering is not observed. Implantation of phosphorus ($r_P/r_{Mo} = 0.77 > 0.59$) leads to continuous increase of its concentration in implanted layers with a doze and disordering initial lattice of molybdenum.

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# Закономерности формирования упорядоченных структур в молибдене при ионной имплантации

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*Показано, что характер структурно-фазовых превращений в молибдене при ионной имплантации элементами фазы внедрения определяется в основном по размерному фактору, т. е. отношением атомных размеров внедренных элементов и атомов металла. Исследования проводились на монокристаллах молибдена при имплантации ионами Ar, C, N, O, B, Si, P, S.*

*Ключевые слова: ионная имплантация, структурно-фазовые превращения, кинетические параметры.*

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