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# ION IMPLANTATION, ION-BEAM MIXING DURING SIMULTANEOUS ION IMPLANTATION AND METAL DEPOSITION

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This article present's researching results of ion implantation Ta in Cu monocrystal with different plane. Also the article demonstrates the processes of ion mixing and deposition of ions $Ta^+$ and $Cu^+$ on polycrystalline Al substrate. Effect of crystalline plane line was found. At the same implantation dose the dose at surface layer is different. Possibilities of the simultaneous ion implantation Ta and Cu and deposition on Al substrate are showed. It causes good corrosion resistance, microhardness increasing of the surface layers.

**Keywords:** ion implantation, ion-plasma deposition, corrosion resistance, microhardness.

## ИОННАЯ ИМПЛАНТАЦИЯ И ПЕРЕМЕШИВАНИЕ ИОННЫХ ПУЧКОВ ПРИ ОДНОВРЕМЕННОМ ОСАЖДЕНИИ МЕТАЛЛА И ИОННОЙ ИМПЛАНТАЦИИ

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В статье представлены результаты исследований процессов ионной имплантации Ta в монокристалле Cu с различной плоскостью. А также процессы ионного перемешивания и осаждения ионов $Ta^+$ и $Cu^+$ на подложку с поликристаллического Al. Обнаружено влияние направления кристаллической плоскости и то, что при одинаковой дозе имплантации в поверхностном слое внедренная доза разная. Показаны возможности одновременной имплантации ионов Ta и Cu и осаждения на подложку из Al, что приводит к хорошей коррозионной стойкости, увеличению микротвердости поверхностных слоев.

**Ключевые слова:** ионная имплантация, ионно-плазменное осаждение, коррозионная стойкость, микротвердость.

## ІОННА ІМПЛАНТАЦІЯ І ПЕРЕМІШУВАННЯ ІОННИХ ПУЧКІВ ПРИ ОДНОЧАСНОМУ ОСАДЖЕННІ МЕТАЛУ ТА ІОННІЙ ІМПЛАНТАЦІЇ

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У статті представлені результати дослідження процесів іонної імплантації Ta у монокристали Cu з різними площинами. А також процеси іонного змішування і осадження іонів $Ta^+$ і $Cu^+$ на підкладинку з полікристалічного Al. Виявлено вплив напряму кристалічної площини і те, що при однаковій дозі імплантації в поверхневому шарі імплантована доза різна. Показані можливості одночасної імплантації іонів Ta та Cu і осадження на підкладинку з Al, що сприяє хорошій корозійній стійкості та підвищенню мікротвердості поверхневих шарів.

**Ключові слова:** іонна імплантація, іонно-плазмове осадження, корозійна стійкість, мікротвердість.

## INTRODUCTION

High dose ion implantation is an effective method of surface modification and improving the servicing characteristics of metals and alloys. This method is developed very intensively due to its advantages in comparison to the traditional methods of surface properties improvement [1]. There are many investigations of processes, which take place in surface layers of metals during ion implantation [2 – 4], but there exist a lot of contradictory results related to intensive and high-dose implantation of a single crystal using multiple-charged ions. By now, there have

been only a few papers on implantation into metal crystals, due to the difficulty of getting good quality surfaces of metal single crystals, and also because of the few research groups having ion sources of high intensity. Such investigations are needed, because processes forming defective profiles and implanted impurities are not well understood.

As is well known, the main disadvantages of ion implantation are (*i*) a relatively low production efficiency, which is determined by the rate of the implanted dose accumulation amounting to << 1016 $cm^{-2}$ over on area of 300 $cm^2$ (1,2) and (*ii*) a small implant concentration for ions with large masses, which is explained by the increasing role of sputtering.

At the same time, the process of implantation by recoil ions (or ion-beam mixing) based on the incorporation of atoms from surface layers to which a kinetic energy is transferred by the primary beam has good prospects as a method for obtaining new structures and compounds with preset properties [2 – 4].

One of the possible ways of eliminating the aforementioned disadvantages is to use a combined setup including an arc plasma source for the coating deposition and an additional source for the ion implantation. In such a system, the process may be conducted using the two sources operating either simultaneously or sequentially [4]. The combined process involves mutual diffusion of atoms from the coating and substrate as a result of the atomic or ballistic mixing. This results in the smearing of a sharp interface between the materials and increasing the adhesion, which allows the deposition-implantation process to be used for predicted modification of the working properties of articles and materials.

In the case of high dose (up to $10^{16}$ $cm^{-2}$ per pulse) ion implantation the sputtering processes is of great importance. There have been almost no investigations on surfaces after high-dose ion implantation in a carbon-containing medium, which is used to produce the *C*-film and carbides in the surface layer [5]. This paper deals with analysis of the changes in the surface layer of Cu (100), (111) which result from high dose ($10^{17}$ $cm^{-2}$) $Ta^+$ ion implantation.

Mainly three different types of experiments are presented here, in which the influence of ion implantation on material changes has been investigated. These are: 1) studies of element distribution after $Ta^+$ implantation and its dependence on the plane of the ion treatment; 2) microhardness measurements of samples surface; 3) corrosion resistance studies for treated and untreated samples.

The purpose of our experiments was to study the process of ion-beam mixing during simultaneous deposition and implantation of Cu and Ta ions into Al substrates.

## EXPERIMENT

We investigated Cu single samples cut out in parallel to the surface (100) and (111). The single crystals had surfaces of 10×10×3 mm in dimension. The $Ta^+$ ion implantation was carried out with an "Diane-2" implanter. The parameters of the ion treatment are presented in tabl. 1.

Table 1

Parameters of the ion-beam treatment

| Ion source | Arc-type |
|---|---|
| Ions | $Ta^+$ |
| ions energy | 40 keV |
| frequency of pulses | 50 Hz |
| pulse duration | 200 мs |
| ions current | 10 mA |
| ion beam diameter | 200 mm |
| implantation dose | $10^{17}$ $cm^{-2}$ |
| Residual pressure | $10^{-3}$ Pa |

The samples were cooled by water and their temperature during the implantation didn't exceed 473 K.

The experiments were performed with 200- or 500-μ-thick Al samples, the surface of which was preliminary cleaned by sputtering with $Ar^+$ ions. Then $Cu^+$ or $Ta^+$ ions were either plasma-deposited with or without additional implantation of the same ions at an accelerating voltage of 60 kV.

The samples were prepared in the following regimes (subscripts "*i*" and "*d*" indicate implantation and deposition, respectively):

$Al(Ta_d^+ + Ta_i^+ + Ta_d^+)$, implantation dose $\approx 8\cdot10^{15}$, Ta film thickness ≈40 nm; (1)

$Al(Ta_d^+ + Ta_i^+ + Ta_d^+) + (Cu_d^+ + Cu_i^+ + Cu_d^+)$ implantation dose $\approx 8\cdot10^{15}$, Ta film thickness 25 nm, Cu film thickness ≈30 nm; (2)

$Al(Ta_d^+ + Ta_i^+ + Ta_d^+) + (Cu_d^+ + Cu_i^+ + Cu_d^+) + (Ta_d^+ + Ta_i^+)$, implantation dose $\approx 10^{16}$, first Ta film thickness ≈45 nm, Cu film thickness ≈55 nm; second Ta film thickness ≈70 nm; (3)

Regime 3 + $Ta_d^+$. (4)

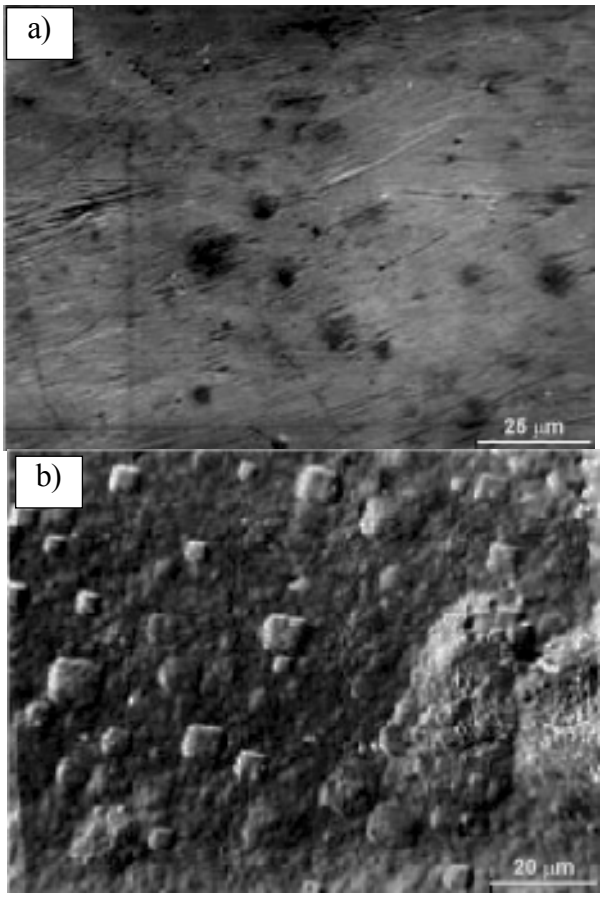
The implantation and deposition processes were carried out using an accelerator with an implantation

pulse duration of about 200 |tm and a deposition pulse duration of 0.8 –1 ms; the process was conducted in a vacuum of >>$10^{-3}$ Pa. The experimental regimes are described in more detail elsewhere [2]. The experimental conditions were varied by controlling the implantation dose, substrate temperature, pulse repetition rate, and the film deposition rate. The elemental compositions were studied by Auger electron spectroscopy (AES) and secondary ion mass spectrometry (SIMS) [5, 6]. The ion sputtering was performed either with an $Ar^+$ beam with the parameters $E = 2$ keV, $j = 5 \cdot 10^{-5}$ A/cm$^2$ (dynamic sputtering mode) or with an $N^+$ ion beam with $E = 2$keV, $j = 1 \cdot 10^{-7}$ A/cm$^2$ (static sputtering mode). The experimental setup was equipped with an energy analyzer that allowed the energy distributions of secondary ions (EDSI) to be measured.

## RESULTS AND DISCUSSION

### MORPHOLOGY CHANGES

Ion implantation leads to the certain changes in the surface morphology of the crystals. The pictures of the sample surfaces before and after implantation are shown in fig. 1. (In picture c) we can see drops of metal, which are typical for high-dose ion implantation. This picture corresponds to the plane of irradiation (111). The more interesting is the fig. 1b. In this picture the surface of copper single crystal (100) after implantation is shown. As we can see there are many crystallites on the surface



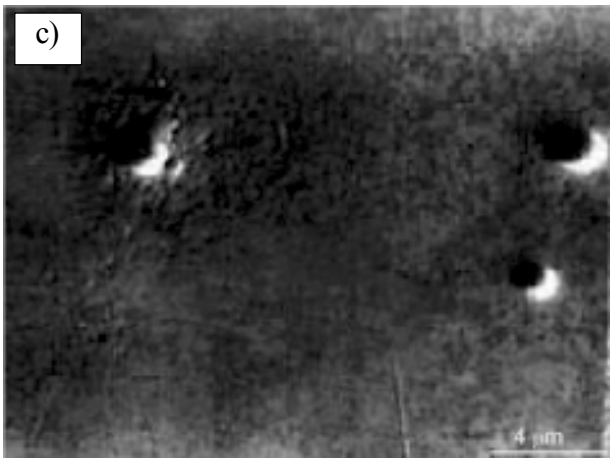
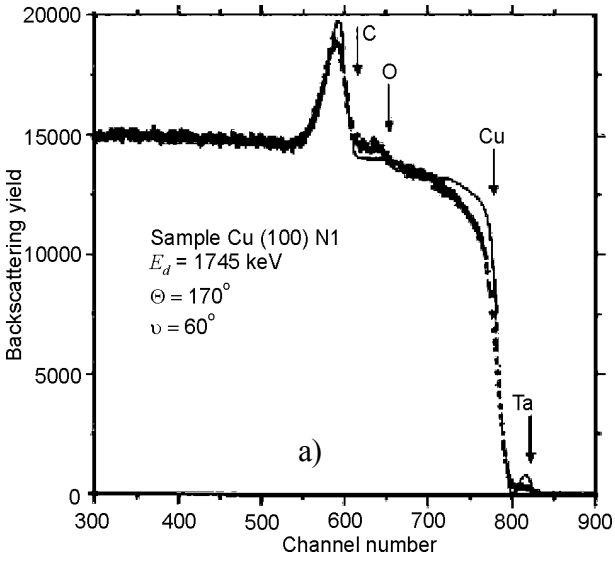




Fig. 1. Surface morphology of a copper single crystal irradiated with $Ta^+$ atoms in different planes: a) untreated surface; b) Cu(100); c) Cu(111).

### ELEMENT COMPOSITION

The RBS spectra are given in the fig. 2. Fig. 2 demonstrates the energy spectra of back-scattered protons for Cu samples (100) and (111) implanted by the $Ta^+$ ions with a $10^{17}$ cm$^{-2}$ dose. There are two peaks on the both spectra. The first one is in the region of the 590 channel, corresponding to the protons output scattered on the carbon ions. The second one is in the region of 830 channel and corresponds to the resonance output of $H^+$ scattered on implanted Ta atoms. Also on both spectra one can see the shelf in the region of 640 channel. This shelf is a sign of oxygen atoms presenting in the near-surface layer [6]. Ion implantation was accompanied



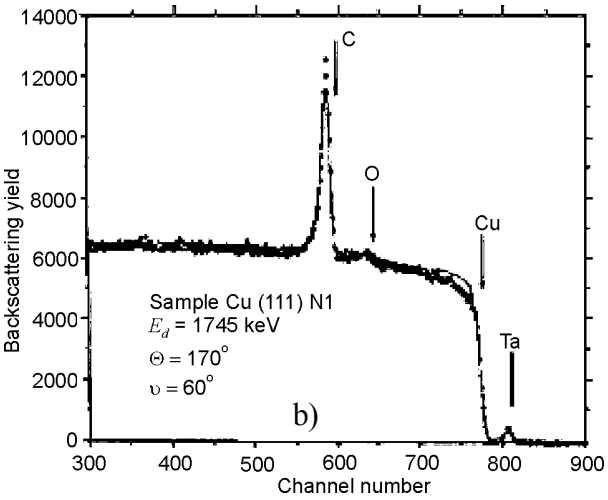



Fig. 2. RBS spectra for single crystal of copper implanted with $Ta^+$ ions in planes: a) Cu (100); b) Cu (111).

by carbonization and oxidation of the sample surfaces due to poor vacuum
($10^{-3}$ Pa) [7].

In fig. 3 concentration profiles of elements in surface layer calculated from the RBS spectra are presented.

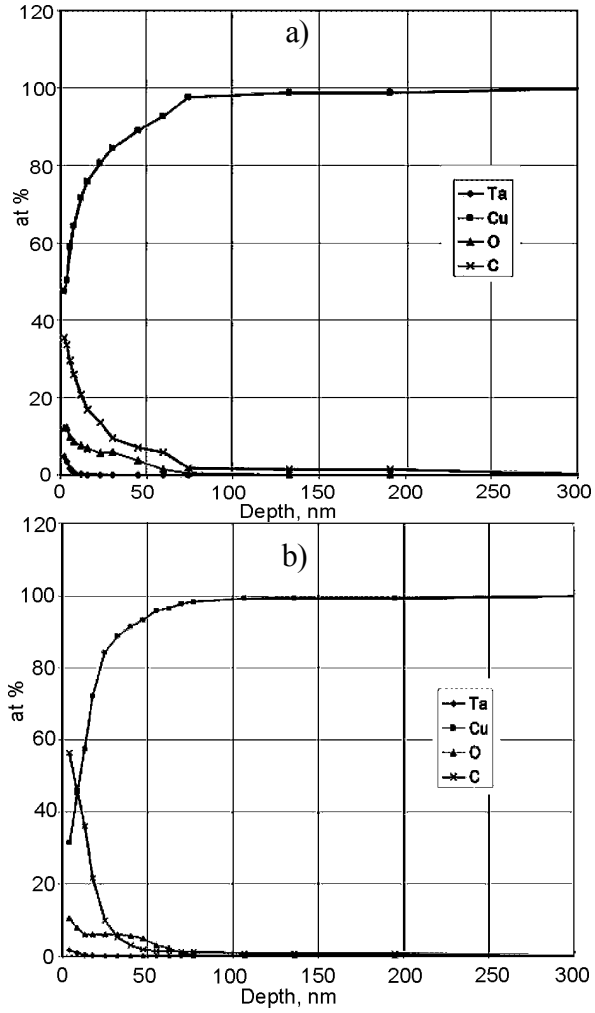



Fig. 3. Concentration profiles of copper single crystals implanted with $Ta^+$ ions in planes Cu(100) (a) and Cu(111) (b).

As we can see the maximum of the concentration of $Ta^+$ atoms is observed on the surface but not in the depth of a sample.

## HARDNESS TESTS

The results of hardness tests are shown in the tabl. 2.

Table 2

Microhardness measured by indentation techniques of mono crystal of copper (100) and (111) with and without $Ta^+$ implantation

| Sample | Values of microhardness MPa |
|---|---|
| Non-implanted surface of Cu | 346 |
| Cu (100) | 458 |
| Cu (111) | 446 |

It may be seen that hardness improvement was observed for both of the implanted samples. For planes (100) and (111) enhancement of hardness was 32,4% and 28,9% respectively.

The surface microhardness of ion-implanted samples is determined by assuming the creation a uniform layer in the material.

It is thought that the increased microhardness is due to the radiation damage, leading to the creation and pinning a big number of dislocations.

## CORROSION RESISTANCE

Tabl. 3 presents the results of the corrosion studies for the single crystals of copper (100). We can see that ion implantation enhance corrosion resistance properties of the surface of single crystal of copper. The mass coefficient of corrosion for implanted sample is one order lower than for untreated one.

This enhancement occurred due to the formation of carbon and oxide thick film on the surface of sample. The presence of such film is shown in fig. 3, where the concentration profiles of elements are

Table 3

Results of the corrosion studies of single crystal Cu (111) in $H_2SO_4$ acid

| Sample | Non-implanted | Implanted |
|---|---|---|
| Surface area of etching, $mm^2$ | 46,33 | 150,44 |
| Mass before etching, g | 0,99231 | 1,59569 |
| Mass after etching, g | 0,80412 | 1,40455 |
| Loses of mass, g | 0,18819 | 0,19114 |
| Mass coefficient of corrosi- | 0,001015487 | 0,000317635 |

presented. This film protects underlying regions from being chemically attacked by aqueous exposure.

## ION-BEAM MIXING AND METAL DEPOSITION

A comparison of the changes in the EDSI pattern measured on the Cu and Ta films on Al obtained by deposition without mixing (fig. 4a) and by a combined deposition-implantation process in regime 3 (fig. 4b) shows evidence of a change in the character of chemical bonds as a result of the ion-beam mixing. The EDSI peak position changes only slightly (by 10 eV) toward greater energies. The width of the energy distribution exhibits a more pronounced variation, considerably increasing upon the onset of sputtering of the film-substrate interface (fig. 4b, curves 1, 4, 7, and 9 for Cu, curves 2, 5, 6, 8 for Ta. and curves 3 and 10 for Al). The most significant changes in the width of energy spectra are observed for Cu and Al ions. In addition, an interesting feature is revealed by curves 8 and 10 in fig. 4b showing several peaks instead of one, which is evidence of an additional interaction with the residual atmosphere components-probably, with oxygen, leading to the formation of oxides ($Ta_2O_5$-$Al_2O_3$) at the interphase boundary. All these changes in the EDSI curves (width, main peak position, appearance of additional peaks) are indicative of an increase in the binding energy and the work function. This, in turn, is evidence of the interaction between target components at the film-substrate interface (caused by ballistic mixing and recoil ion implantation) with the formation of a complex system of intermetallic phases

An analysis of the elemental depth-concentration profiles observed for the samples obtained in two regimes (fig. 5) shows, in addition to the complicated shape of Ta and Cu profiles (multipeak structure), the presence of a high concentration of carbon on the surface and at the film-substrate interface. Oxygen also exhibits a complicated profile and an increase in concentration at the film-substrate interface. The shapes of the Auger electron spectra of oxygen and carbon indicated that these elements could be present in the form of oxides and carbides, as well as in the free state.

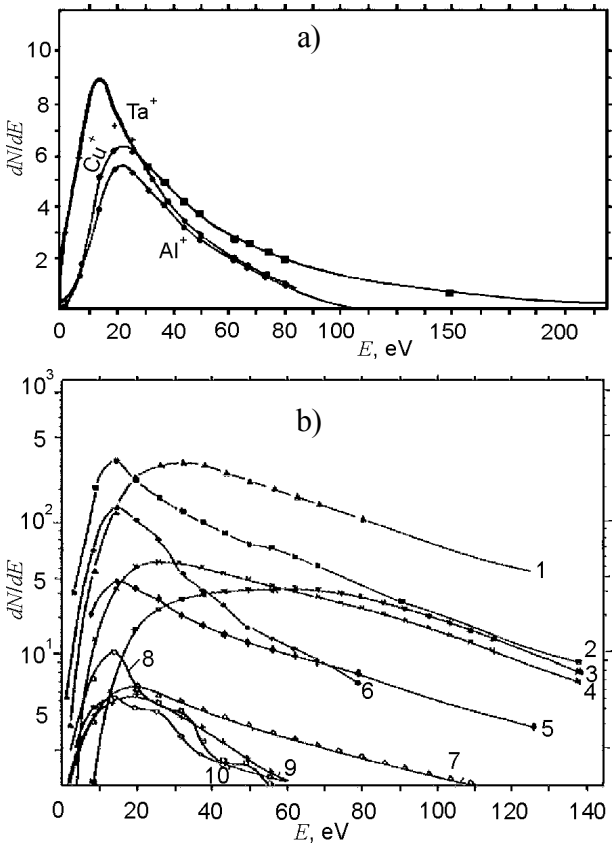



Fig. 4. (a) Energy profiles of secondary ions for the surface of (a) Al substrate after deposition of Cu and Ta and (b) Al substrate after deposition and implantation of the same ions in regime 3 (in various regions of the coating).

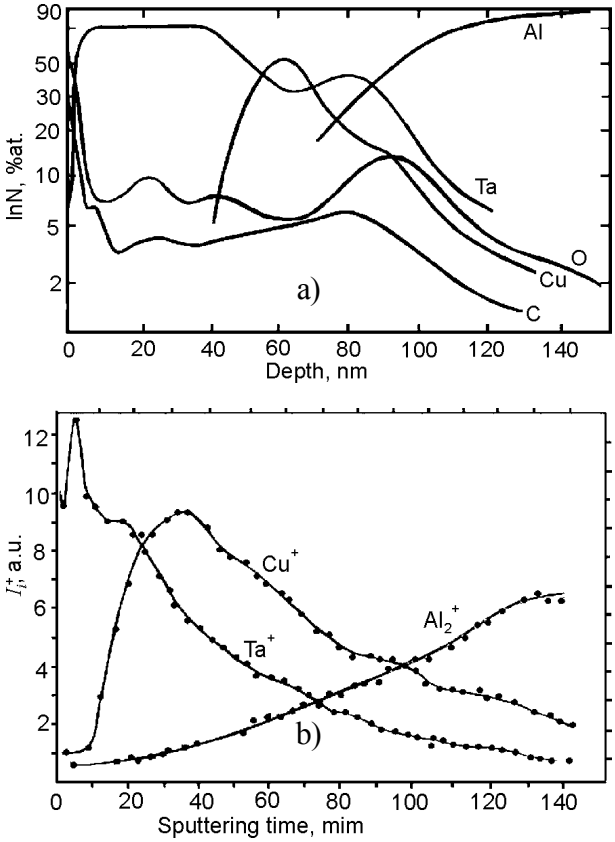



Fig. 5. (a) Elemental depth-concentration profiles obtained by SIMS for the surface layers of Al after implantation of Cu (20 min) and deposition – implantation of Ta (10 min, regime 2). (b) Elemental depth (sputter time)-composition profiles abtained by AES for the surface layers of Al after deposition – implantation of Ta and Cu (15 min, regime 3).

The measurements of microhardness of the coated samples, performed with the aid of the Knoop pyramidal indenter with variable load, showed that the ion-beam mixing leads to an increase in microhardness up to $153 \pm 6$ kg/mm$^2$. This gain in microhardness was markedly greater than that in the case of pure implantation with Cu or Ta, where the resulting microhardness was $96 \pm 4$ kg/mm$^2$. It must be noted that the thickness of the hardened layer in the case of the combined deposition – implantation process is also greater than that in implanted aluminum.

The results of adhesion testing showed that the combined deposition – implantation process increases the adhesion of coating to the aluminum substrate above $120 \pm 8$ kg/mm$^2$. The corrosion resistance of the coated material also markedly increased by almost two orders of magnitude as compared to the initial material.

Element composition and its depth distribution were analyzed by means of Rutherford Backscattering Spectrometry (RBS) of protons with energy of 1745 keV. The spectra were recorded at $\upsilon = 60°$ (the angle between the beam and the target) and the scattering angle $\Theta = 170°$. The concentration depth profiles of the elements were obtained under energy spectra processing using special computer program.

Changes of morphology of samples surface were observed with the help of transmission electron microscopy technique.

Microhardness measurements were performed with nano-indenter PMT-3, where four-faced diamond pyramid was used. The load on the pyramid was 7 g. Microhardness was measured for implanted and non-implanted surfaces of single crystal that made it possible to determine the relative improvement of surface hardness as a result of ion implantation.

Corrosion tests were carried out by means of etching implanted and non-implanted samples in a 2 M solution of $H_2SO_4$ acid. The crystals were exposed to the aggressive environment for four hours. Then the mass coefficient of corrosion was calculated for both implanted and non-implanted samples using following expression:

$$K_{\text{mass}} = \frac{m_B - m_A}{S \cdot t},$$

where $m_B$ – mass before corrosion test, $m_A$ – mass after corrosion tests; $S$ – sample surface area; $t$ – time of corrosion test.

## CONCLUSIONS

Tantalum ion implantation in a copper single crystal (100), (111) has been studied. The element distribution dependence on the direction of irradiation was observed. The highest concentration of $Ta^+$ was for copper single crystal (100). This plane is a plane of the closest packing, so penetration of $Ta^+$ ions in this direction is the most difficult.

As microhardness tests showed ion implantation induced microhardness enhancement of the copper surface for both of the samples.

A carbon and oxide-containing film formation was observed. This film defends the surface from being attacked by aqueous exposure. So it leads to the increasing of the corrosion resistance of the surface.

Thus, the deposition Ta and Cu ions accompanied by their simultaneous implantation into Al substrates results in the formation of coatings with complicated elemental profiles revealing mutual penetration of elements from the film into the substrate and vice versa. All these factors suggest that the combined deposition – implantation process is more effective than ion implantation alone. This is also manifested by increasing microhardness and adhesion values and by a two-order increase in the corrosion resistance of aluminum.

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