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# EFFECT OF IONLY-PLASMA IMPACT ON THE ELEMENT COMPOSITION AND STRUCTURAL PHASE STATE OF THE SYSTEM OF Cu-Ti

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The results of the investigations of the elemental composition and phase state of the Cu-Ti system after high-ion implantation and electron annealing by high-current electron beam (HCEB) are presented. It has been established that the use of high dose ($(5…8)\cdot10^{17}$ ions/cm$^2$) implantation and the subsequent effect of HCEB leads to a reduction in the concentration of titanium, and the use of a small dose to $1\cdot10^{17}$ ions/cm$^2$ until it diffuses in depth from the surface. Investigation of the structural-phase state showed a partial evaporation of layers of carbide-titanium and the formation of a substructure.

## INTRODUCTION

According to the literature [1–20], high-dose ion implantation of copper and α-Fe leads to the complex changes in the elemental and structural-phase state of the surface. Due to the features of high-dose implantation, the surface structures, which are formed under this influence, are nonequilibrium. Therefore, it is reasonable to expect a change in the distribution of the implanted elements, structure, and phase composition upon further annealing of copper samples implanted by titanium. We used a pulsed low-energy high-current electron beam (NCEB) for studying such transformations in implanted copper layers for the surface during thermal annealing. The change in the energy of the electron beam makes it possible to study the influence of heating of surface sample in a wide range. Furthermore, NCEB surface treatment have additional and independent interest, since pulsed irradiation mode is accompanied by high local temperature gradients and cooling rates (about 109 K/s) regions, which greatly affects to the formation of defect structure in the surface regions.

This paper presents the results of studying of elemental composition and the structure-phase composition of copper monocrystals with orientations (100) and (111), which are implanted with titanium in the range of $1\cdot10^{17}…8\cdot10^{17}$ ion/cm$^2$ after treatment with a low-energy high-current electron beam at a flux density energy from 2.5 to 5 J/cm$^2$.

In addition, for studying the features of structure formation and phase composition in the Cu-Ti system under ion-plasma treatment the technology of simultaneous deposition of coatings (ion-precipitated deposition of coatings (IAP)) and high-dose ion implantation were used. The number of works devoted to such complex processing is limited, although this process has great prospects.

## SAMPLES AND METHODS OF INVESTIGATIONS

Samples of single crystals of Cu, which are cut in parallel with the (111) and (100) planes with electrochemically polished surfaces measuring 14×14×3 mm were studied. Polishing was carried out in a solution of 15 ml of $H_2CrO_4$, 90 ml of $H_2O$ and 3 drops of HCl.

Also, for the investigations, α-Fe samples were used in the form of pellets with a total impurity content of $10^{-3}$ wt.% (the C content did not exceed $10^{-4}$ wt.% ). In a vacuum arc furnace, ingots with a mass of 200 g, 150 mm in diameter and 15 mm in length were smelted. The ingots were subjected to diffusion annealing at 1200 °C during 5 hours in a vacuum, which facilitated their homogenization. Further ingots were cut to 130 mm in length. The samples were thermally annealed in vacuum ($10^{-5}$ mm Hg V.) at 950 °C during 2 hours, followed by the formation of fine grains with an average size near 20 μm.

The diameter of the ion beam is 5…50 cm. Such parameters provide a rate of dose $10^{16}$ ion/cm$^2$ min on targets with an area of $\sim 10^2…10^3$ cm$^2$. For high-dose implantation of metal ions, as well as the production of multilayer, multi-element ion-mixed structures, the universal wide-range ion-plasma source was used.

The electron microscopic studies using microdiffraction were carried out for studying the phase composition and defect structure of the samples.

The analysis of the concentration profiles of titanium was carried out by the Rutherford backscattering method of $^4He^+$ ions with an initial energy of 2 MeV. To obtain a profile of oxygen atoms in the near-surface layers of the samples, an elastic resonance of the $^{16}(^4He, ^4He)^{16}O$ reaction in the region of 3.045 MeV was used. The spectra were recorded at an angle $\varphi = 60°$ and angular dispersion $\theta = 170°$.

## RESULTS AND DISSCUSIONS

The irradiation modes with the electron beam energy density between 2.5 and 3.5 J/cm$^2$ were used for studying the effect of a low-energy high-current electron beam on the redistribution of implanted elements and the change in the structural-phase state of the surface of copper monocrystals irradiated with titanium.

Fig. 1 shows the profiles of the change in the concentration of implanted titanium for Cu (100) samples, which are implanted with a dose of $8\cdot10^{17}$ ion/cm$^2$, under further processing of HCEB with different energy flux density.

It can be seen (from Fig. 1) that the increased energy flux density of HCEB from 2.5 to 3.5 J/cm$^2$ leads to decreasing in the peak of the titanium concentration in the surface, which are implanted copper by 20% and 30% relative to the initial state. In this case, irradiation of the surface of copper (implanted with titanium) by an electron beam also leads to a shift of the maximum and the entire concentration profile to the surface of the sample.

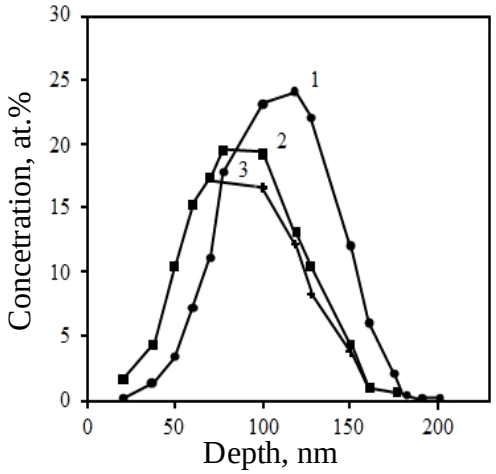


*Fig. 1. Concentration profiles of implantation of Ti in the surface layer of a Cu (100) single crystal: 1 – initial state (implantation of Ti with a dose of $8\cdot10^{17}$ ion/cm$^2$); 2 – further annealing by HCEB with an energy flux density of 2.5 J/cm$^2$; 3 – annealing by HCEB with an energy flux density of 3.5 J/cm$^2$*

The influence of a high-current electron beam on the copper surface (titanium implanted) with an energy density of 2.5 and 3.5 J/cm$^2$ leads to the melting of the copper matrix and the formation of a mixed phase (solid and liquid). The presence of such a zone is due to the presence of more refractory, in comparison with copper, CuTi and TiC compounds in the structure. Increasing the energy flux density of a low-energy high-current electron beam leads to an increase the depth of the molten layer. At the same time, as shown in [15–19], the formation of a molten layer upon irradiation of HCEB is accompanied by its partial evaporation. Preservation of a significant concentration of titanium in the near-surface layers of copper after irradiation of HCEB (Fig. 1 (curves 2 and 3)) is due to the most of the titanium implanted during implantation is bound in the intermetallic phase of CuTi, which melts only partially, as well as in the refractory phase of TiC, which practically does not melt under energy flux density of 2.5 and 3.5 J/cm$^2$.

Similar results were obtained in the case of irradiation of single crystals of copper with orientation (111) with a low-energy high-current electron beam, which were previously implanted with titanium with a dose of $8\cdot10^{17}$ cm$^{-2}$ (Fig. 2). The difference in the position of the concentration peaks of titanium in the samples of the implanted Cu (111) surface, after irradiation of the HCEB in comparison with the case of Cu (100) (see Fig. 1), is obviously due to the difference in the thicknesses of the oxidized films on the surface of Cu (100) and Cu single crystals (111) after implantation with titanium with a dose of $8\cdot10^{17}$ ion/cm$^2$. More refractory oxidized film partially prevents the evaporation of copper and titanium, which leads to the above mentioned difference in the position of the concentration peaks and their values for different orientations of the surface of copper single crystals (see Figs. 1, 2).

The effect of the oxidized film on the distribution of titanium in the surface of copper is particularly evident during irradiation of samples by HCEB with small doses.

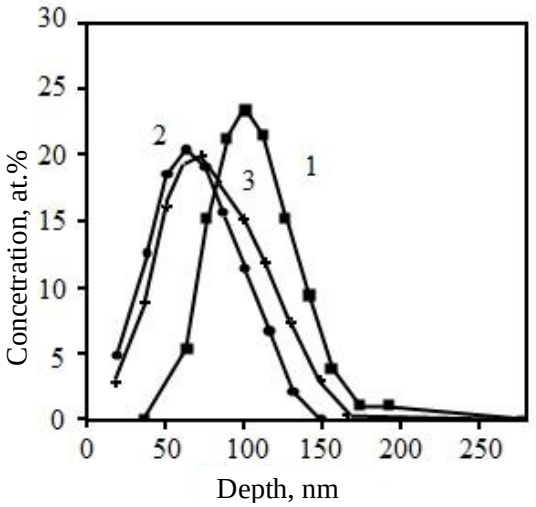


*Fig. 2. Concentration profiles of the introduction of Ti in the surface layer of a Cu (111) single crystal: 1 – initial state (implantation of Ti with a dose of $8\cdot10^{17}$ ion/cm$^2$); 2 – further annealing by HCEB with an energy flux density of 2.5 J/cm$^2$; 3 – annealing by HCEB with an energy flux density 3.5 J/cm$^2$*

Fig. 3 shows the distribution profiles of titanium ions in the Cu (111) surface after implantation of titanium with a dose of $1\cdot10^{17}$ ion/cm$^2$ (curve 1) and with subsequent annealing by a low-energy high-current electron beam with an energy flux density of 3.3 J/cm$^2$ (curve 2). It was shown that irradiation leads, as in the case of high doses (up to $8\cdot10^{17}$ ion/cm$^2$), to a decrease in the peak of the titanium concentration in the copper liner, compared to the initial implanted state. However, in the case of a small dose of implantation of copper monocrystals of titanium ions after HCEB, the peak concentration and the profile of the titanium distribution shift in depth from the surface. At high ($5\cdot10^{17}$…$8\cdot10^{17}$ ion/cm$^2$) doses of implantation, this film is practically sprayed, and at low doses, the effect of sputtering is decreased. In this connection, the initial oxidized film even grows due to oxygen from the residual atmosphere of the accelerator chamber.

Fig. 3 shows the concentration profiles of oxygen in Cu (100) samples implanted with titanium with a dose of $1\cdot10^{17}$ ion/cm$^2$ (curve 1) and after irradiation of HCEB with an energy flux density of 2.5 J/cm$^2$ (curve 2). After irradiation with a low-energy high-current electron beam, the oxygen concentration in implanted titanium single crystals of copper increases (about 3 times), in comparison with the initial state (see Fig. 4). This indicates that in this case a thick oxidized film does not penetrate and evaporate, but rather grows and acts as a protective layer against the evaporation of the liquid

layer of the copper liner. Redistribution of titanium in copper samples (irradiated by HCEB) occurs by its diffusion in the liquid and solid phase into the depth of the copper matrix, which causes a decrease in the peak concentration of titanium and the displacement of its profile in depth from the surface.

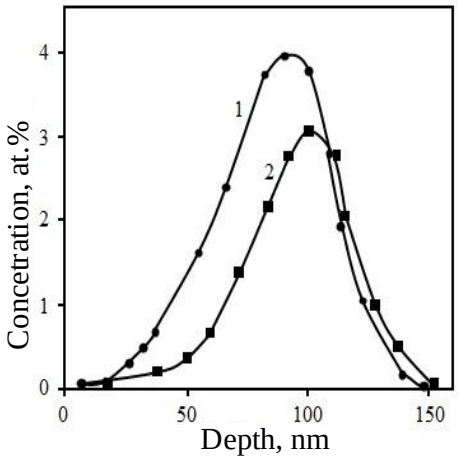


*Fig. 3. Concentration depth profiles of implantation of Ti in a single crystal Cu (111): 1 – initial state (implantation Ti with a dose of $1 \cdot 10^{17}$ ion/cm$^2$); 2 – further annealing of HCEB with an energy flux density of 3.3 J/cm$^2$*

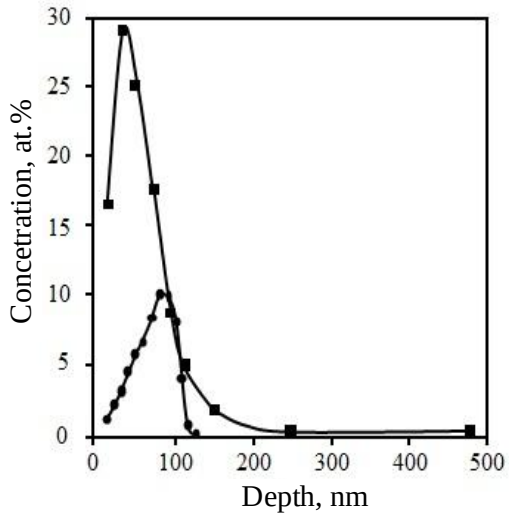


*Fig. 4. Concentration depth profiles of oxygen after titanium implantation of Cu (100) samples with a dose of $1 \cdot 10^{17}$ ion/cm$^2$: 1 – initial state; 2 – after the influence of HCEB with an energy flux density of 2.5 J/cm$^2$*

Electron microscopic studies indicate that the treatment by low-energy high-current electron beam of samples of copper single crystals, implanted with titanium, besides redistributing the implanted elements, also leads to a significant change in the structural-phase state of the surface.

Fig. 5 shows typical electron microscopic images and diffraction patterns of the most characteristic regions of near-surface regions of copper (111) single crystals implanted with titanium with a dose of $5 \cdot 10^{17}$ cm$^{-2}$ with further treatment by a low-energy electron beam with an energy flux density of 5 J/cm$^2$.

Attention is drawn to the fact that, in comparison with the initial state (implantation without the treatment of HCEB), the samples of copper single crystals with (111) orientation, implanted with titanium after HCEB treatment, are characterized with a much smaller amount of titanium carbide interlayers and a virtually complete absence of an amorphous carbon film in the near-surface regions.

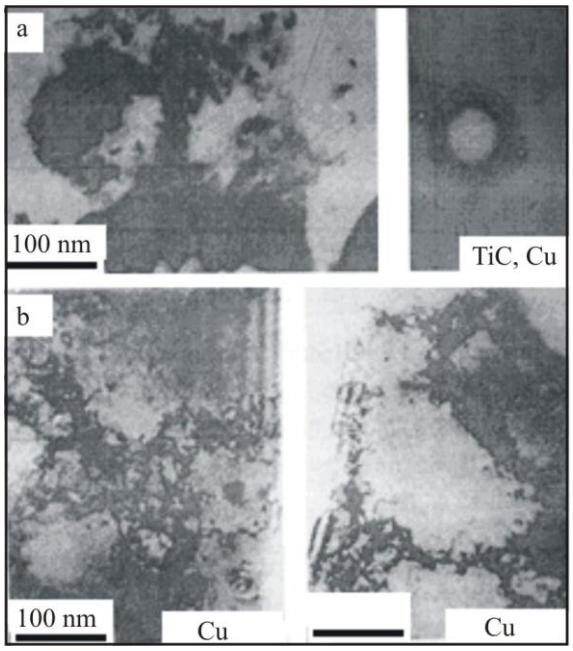


*Fig. 5. Diffraction structure of a single crystal Cu (111) implanted with Ti ions with a dose of $5 \cdot 10^{17}$ ion/cm$^2$ with further pulsed annealing of HCEB (5 J/cm$^2$): a – surface layer; b – near-surface layer*

This demonstrates the partial evaporation of these structural constituents during the treatment by an electron beam in the melting mode and agrees with the data of the elemental composition studies (see Fig. 2), namely decreasing in the peak of the titanium concentration, in its integral content in the surface and displacement of the entire profile to the surface.

In addition, high temperature gradients and cooling rates during surface treatment by a pulsed low-energy high-current electron beam in the melting mode lead to a significant change in the scale levels of the structural components and defect structure of the near-surface regions implanted with copper titanium.

So, for example, surface treatment by pulsed HCEB leads to a significant dispersion of the structure of the TiC interlayer. The dimensions of the minimum scale level of the interlayer of titanium carbide are 2…4 nm, which is much less than in the case of implantation by titanium of Cu (111) single crystal samples without treatment by HCEB.

Electron beam irradiation of titanium implanted samples also leads to significant changes in the structure of the copper liner, and in particular of the copper layer, which directly contacts with the interlayer of titanium carbide. These areas of copper due to the treatment of HCEB have acquired a nanoscale structure with an average crystal size of 50…70 nm.

The defect structure is represented by a disoriented strip structure, when the distance is 0.05…0.1 μm from the copper interface with the titanium interlayer. The

discrete misorientation between the bands is approximately 6…7°. In the middle of the bands, a dislocation structure is observed. The scalar density of dislocations in the copper matrix after processing of the implanted samples by a pulsed low-energy high-current electron beam, in comparison with the initial state, increased to $0.5 \cdot 10^{12}$ ion/cm$^2$.

Also, the treatment by HCEB of the titanium-implanted surface of samples of copper single crystals leads to a significant increase of the depth (near 1 μm) of the transformation of the single-crystal state of the copper into a coarse-grained structure, compared with the initial state.

Analogical results were also obtained for electron-microscopic studies of a surface samples of copper single crystals with the (100) orientation implanted by titanium and after irradiation by a pulsed low-energy high-current electron beam.

Thus, electron-beam irradiation in the melting mode of copper single crystals implanted by titanium leads to significant changes in the elemental state and the structure of the near-surface layers. These changes due to the partial evaporation of the surface amorphous carbon film and titanium carbide layers, the dispersion of the structure of the constituents (TiC, copper matrix), the formation of the cell dislocation structure and the increasing of the density of dislocations at depths that significantly exceed them for the initial (without HCEB treatment) state.

## CONCLUSIONS

1. It was shown that the irradiation of the surface of copper single crystals implanted with titanium with high implantation doses ($(5…8) \cdot 10^{17}$ ion/cm$^2$) by HCEB leads to a decrease in the peak of the titanium concentration in the copper matrix and a shift in the concentration profile to the surface and a decrease in the total content of titanium due to partial evaporation material surface in the process of its electron-beam processing.

2. It was shown that the presence of a thick oxidized film on the surface of copper samples implanted with a titanium with a low dose ($1 \cdot 10^{17}$ ion/cm$^2$) leads to a significant shift of the evaporation effect of the copper liner with the next irradiation by the HCEB and as a consequence to the displacement of the titanium concentration profile due to the diffusion into depth from the surface.

3. From electron microscopic studies, it has been established that irradiation of a copper with titanium implanted by HCEB leads to the removal of the surface of an amorphous carbon film and the partial evaporation of titanium carbide interlayers, to a greater dispersion of structural components, to the formation of a cell substructure and to an increase in the dislocation density in lining at depths.

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## ВЛИЯНИЕ ИОННО-ПЛАЗМЕННОГО ВОЗДЕЙСТВИЯ НА ЭЛЕМЕНТНЫЙ СОСТАВ И СТРУКТУРНО-ФАЗОВОЕ СОСТОЯНИЕ СИСТЕМЫ Cu-Ti

***А.Д. Погребняк, Аид Куссей Джаруллах, А.Д. Михалев, Л.В. Маликов***

Представлены результаты исследования элементного состава и структурно-фазового состояния системы Cu-Ti после воздействия высокодозной ионной имплантации и электронного отжига импульсным низкоэнергетическим высокотоковым электронным пучком (НВЭП). Установлено, что применение имплантации с высокой дозой ($(5…8)\cdot10^{17}$ ион/см$^2$) и последующим воздействием НВЭП приводит к уменьшению концентрации титана, а применение малой дозы до $1\cdot10^{17}$ ион/см$^2$ к его диффузии в глубину от поверхности. Исследование структурно-фазового состояния показало частичное испарение прослоек карбида-титана и формирование субструктуры.

## ВПЛИВ ІОННО-ПЛАЗМОВОЇ ДІЇ НА ЕЛЕМЕНТНИЙ СКЛАД І СТРУКТУРНО-ФАЗОВИЙ СТАН Cu-Ti

***О.Д. Погребняк, Аїд Куссей Джаруллах, А.Д. Міхальов, Л.В. Маліков***

Представлені результати дослідження елементного складу та структурно-фазового стану системи Cu-Ti після впливу високої дози іонної імплантації та електронного відпалювання імпульсним низькоенергетичним високострумовим електронним пучком (НВЕП). Встановлено, що застосування імплантації з високою дозою ($(5…8)\cdot10^{17}$ іон/см$^2$) і подальшим впливом НВЕП призводить до зменшення концентрації титану, а застосування малої дози до $1\cdot10^{17}$ іон/см$^2$ до його дифузії в глибину від поверхні. Дослідження структурно-фазового стану показало часткове випаровування прошарків карбіду-титану і формування субструктури.

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