# Modification of Materials Surface Layers by Low-Energy Ion Irradiation in Glow Discharge

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***Abstract*** **– Possibility of increase of welded connections reliability in the electronic devices elements consisting of the materials, which vary by mechanical, physical and chemical properties and have a limited or unsatisfactory weldability, is considered. It is shown, that prior modification of a chemical composition of metal-environment interface by method of introduction of recoil atoms from the sputtered thin metal films in the glow discharge at energy of ions to 1 keV make an effective impact on diffusion processes of solid-state welding of metals by pressure and elevate connection durability on 20 … 40%.**

***Keywords – components of electronic devices; modification of surface layers; metal films; diffusion mass transfer; pressure welding; ion bombardment***

## I. INTRODUCTION

In technological processes of electronic devices production, first of all, chips, sputtered thin metal films with use of magnetron atomizer systems is widely used. A basic element of such systems is the cathode assembly consisting of the sprayed material (target) and a shunt to it. The surface of a target is bombarded by the concentrated stream of the accelerated positive ions of working gas that leads to its heating and need of cooling. Besides, for decrease in power losses in a shunt-target transition it is necessary to achieve decrease in electrical resistance of this contact. Fulfillment of both specified conditions can be reached by quality ensuring connection of cathode assembly elements. Such connection can be reached by pressure welding methods without fusion, the main among them is diffusion welding.

For shunt in cathode assembly, the copper with high thermal and electrical conductivity is used. As the sprayed material, in particular for creation of ohm contacts in semiconductor devices, refractory metals – niobium, tantalum, molybdenum, chrome, tungsten are often used. These metals significantly differ from copper by physical, chemical and mechanical properties that limits their weldability with copper and, respectively, possibility of receiving reliable connection. The similar problem arises at production of anode assembly of x-ray tubes and some other powerful electrovacuum devices in which copper with refractory metals connections are also representing.

Strong welded connections are formed by metals and alloys which consists of the elements possessing unlimited mutual solubility not only in liquid, but also in a solid state, i.e. forming continuous number of solid solutions. Mutual solubility of elements is defined by similarity of crystal lattices of solvent and soluble component, a difference in nuclear radiuses of components and by the size of the electronegativity characterizing binding energy between two elements. According to the rule of Hume - Rothery [1] elements with identical type of a crystal lattice form a continuous number of solid solutions only at small differences between nuclear radiuses (in limits ± 15%) and electronegativity (no more than ± 0.4) of components. Outside the specified admissions, valent and dimensional factors are adverse for formation of solid solutions and reliable welded connection.

According to this when the metals, significantly different by physical properties, are welding, an intermediate element which satisfies to the rule stated above for both connected metals-solvents into a zone of connection are entered. In particular, as such element at diffusion welding of copper with refractory metals (tungsten and molybdenum) nickel [2] in the form of a foil or the thin film, applied in any way on the connected surfaces, is applied. In the same time, rather low coefficient of diffusion of nickel in these metals limits development of a transitional diffusive zone thereby reducing connection durability.

Recently the effect of penetration of metal atoms from a surface on macroscopic distances deep into of a substrate at low temperatures (to 473 K) in the conditions of ionic bombing of a surface in the glow discharge was found. In the research [3] is shown that depth of diffusion of the cesium atoms which is in a type of a thin coat layer on a surface of nickel and aluminum was tens micrometers.

At that time coefficients of diffusion of cesium atoms in nickel and aluminum on 1…2 orders exceed the similar values, received in the conditions of isothermal annealing.

## II. EXPERIMENTAL PROCEDURE

In this work the effect described above was used for researching of technology of receiving diffusive and welded assembly of chrome with copper which weldability is complicated because solubility of chrome in copper does not exceed 0,0021% at a temperature of 1173 K [4]. In the work bombing influence by ions of inert gas on a blanket of a chromic sample in the glow discharge on diffusion of nickel atoms in chrome for the purpose of increasing of a diffusive zone and, respectively, durability of welded connection was studied.

The BX-2K chrome alloy, which surface was previously processed mechanically, was used as samples. By thermal vacuum evaporation on a surface of a chromic alloy, a 1 - 2 micron thick layer of nickel was spattered. Then bombing of this layer by the argon ions received in plasma of the glow discharge was carried out. Processing was made by the abnormal glow discharge with a tension on electrodes 600 V and argon pressure 13,3 Pa. Duration of ionic bombing was 900 sec. After that, the diffusion welding of the received chrome sample with copper (copper M1) was made. The surface of a copper sample was also previously processed mechanically with the subsequent washing with acetone. Diffusion welding of samples was carried out on the following mode: temperature of welding 1193 K, effort of pressing 6 MPa, time of isothermal endurance 900 sec. The durability of the received samples was compared with the durability of the samples, received by welding through the nickel layer, which was evaporated on a surface of a chromic sample without ionic processing. Quality of welding was estimated by results mechanical tests for cut of samples.

## III. RESULTS AND DISCUSSION

Durability of samples with processing was 160…170 MPa, for the samples without processing durability did not exceed 120…122 MPa. In both cases, destruction was observed on chrome, most likely, owing to its higher fragility. Nature of destruction thus differs a little. In the samples with an evaporated layer, the zone of destruction looks like the layer of chrome scales on a copper sample surface. Samples with an evaporated layer and ionic processing have considerable separations from a chrome surface. It can be evidence of more depth of a diffusion zone towards chrome. The research of elements distribution in a transitional zone were carried out with usage of the micro x-ray spectral analyzer "Comebax" SX-50 with a diameter of probe 1 micron.

They showed that in samples with only the evaporated nickel layer the last intensively diffuse towards a copper sample (Fig. 1a) owing to a high coefficient of diffusion of nickel in copper ($4 \cdot 10^{-14}$ m/s$^2$ at T=1273 K). As a result, the diffusion zone towards copper was rather big (17…19 microns).

Diffusion of chrome in nickel is much worse that can be associated as with existence on its surface of the oxide layer, which complicate diffusion, and with its lower coefficient of diffusion. As a result, the diffusion zone near chrome was insignificant, not exceeding 3…4 microns. Distribution of nickel in a contact zone considerably changes when elements are welded with a spattering and ionic processing (Fig. 1b). Preliminary introduction of nickel atoms in chrome surface layer allows to reach its uniform distribution in the connection zone during the welding process. That leads to significant increase of a transitional zone towards chrome (to 9…10 microns).

Research of micro hardness of a transitional zone were carried out with usage of the micro durometer M–400 LECO. Research showed that on chrome-copper border a layer with hardness differing from the connected metals is present. Width at the first case is 10…20 microns, at the second – 30…40 microns that agrees with the results of the micro x-ray spectral analysis (Fig. 2).

Movement activation mechanism of nickel atoms in depth of chrome under the influence of ionic bombing in the conditions of the glow discharge cannot be explained with the applied methods of metals structures change with ionic implantation [5] and ion-beam hashing [6] by the bombarding ions which are carried out at the energy, reaching above 100 keV.

Energy of ions when processing in the glow discharge does not exceed 0,2…3 keV. As a result, saturation with a near-surface layer of a detail initially displaced atoms from the film, which is on a surface, when bombing it by ions of inert gases is actual [5]. Such atoms receive quite high energy at impact with the accelerated ions and can move in a solid body on distance of several nanometers. This effect arises in processes of ionic implantation at big concentration of the dopant impurity in the ionized steam phase, so in a number of sources [6, 7] it is called recoil atom implantation. In a case when energy of initially displaced atom is slightly higher than a certain

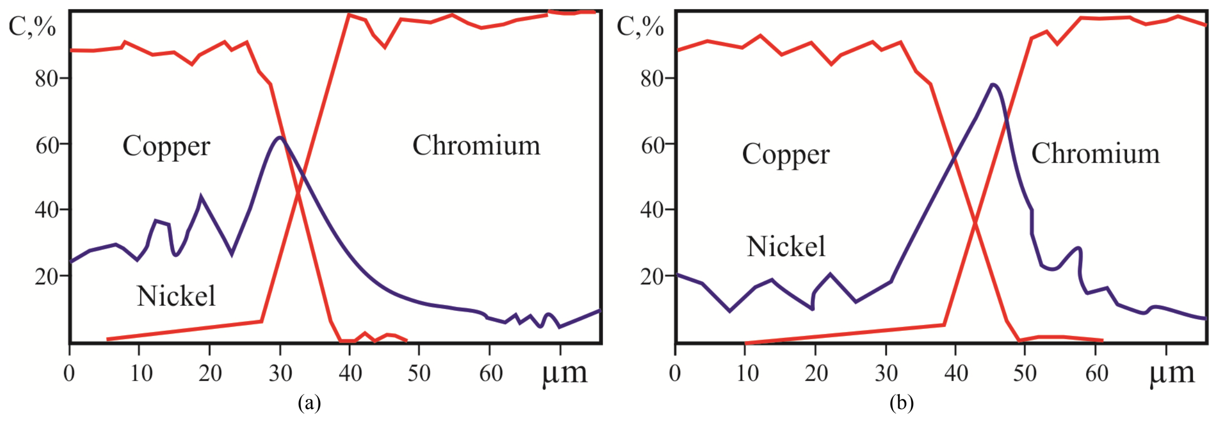


Fig.1. Distribution of elements in the transition zone of chromium-copper joint through the deposited (a) and additionally treated with argon ions (b) an intermediate layer of nickel

threshold energy of displacement ($T_d$ = 10…30 eV), this atom can displace also other atoms. The average of such atoms [5]:

$$Nd = \frac{0{,}42\nu}{Td} \qquad (1)$$

Where ν – energy of initially displaced atom which as a first approximation can be accepted as drop of potential value in cathode region of the glow discharge.

In the abnormal glow discharge with gas pressure p <<133 Pa the drop of potential value is 0,9…0,95 of tension on discharge electrodes value [8].

According to this, single impact of the accelerated ion on the films surface atoms leads to successive displacement of tens or hundreds of atoms in the direction of blow. In the conditions of the small thickness of a film, this can lead to introduction of film atoms in a substrate (sample) due to the displacing and replacing nuclear collisions. Long dynamic impact of the accelerated ions on the moved atoms transfer them energy and an impulse in the direction from a surface and promotes them migrate from a film deeper into of a substrate.

Ionic processing is characterized by several key parameters: accelerating ions tension, density of discharge current and processing time. It is important to specify their role in the process of an ionic alloying and, respectively, further formation of a diffusion zone, and also, determinate of optimum range of change of their values.

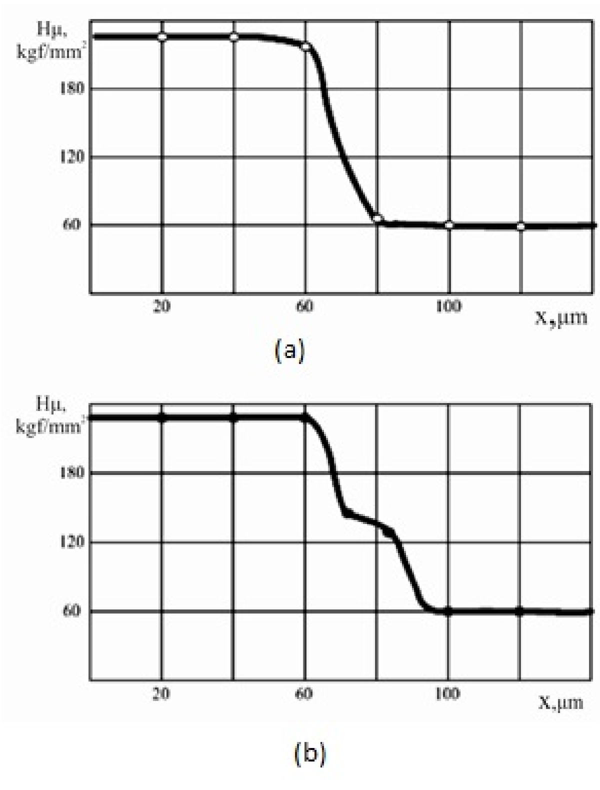


Fig. 2. The character of microhardness changes in the chromium-copper joint zone through the nickel layer without bombardment (a) and argon ions bombardment of this layer (b)

Influence of these factors on welding quality was evaluated by the results of mechanical testing of welded samples. To determine the optimal range of bombarding ions energy tension on the electrodes was varied in the range of 200 to 1500 V.

The treatment of the sample surface with nickel deposited film produced for 900 sec. at the argon pressure 13.3 ... 15.9 Pa. The pressure range was selected according to the condition which limits the cathode sputtering effect of film during the bombing, which manifests itself most visibly at gas pressures less than 13.3 Pa [7].

Results of tests of welded samples show (Fig. 3) that in the range of discharge tension 200…400 V energy of ions is insufficient for moving atoms of a film to chrome surface layer. It is expressed in the lowered durability of connection, which is slightly exceeding durability of the samples, which are welded without application of ionic bombing. At the same time, at voltage of discharge more than 1000 V connection durability also decreases. With other things being equal (pressure of gas and duration of processing) it can be caused by three times increasing [6] of the nickel dispersion coefficient by argon ions at change of discharge tension from 200 to 1200 V that leads to decrease its concentration on a substrate surface.

As results show, the most optimum range of discharge tension for a chrome surface alloying nickel lie within 600…900 V.

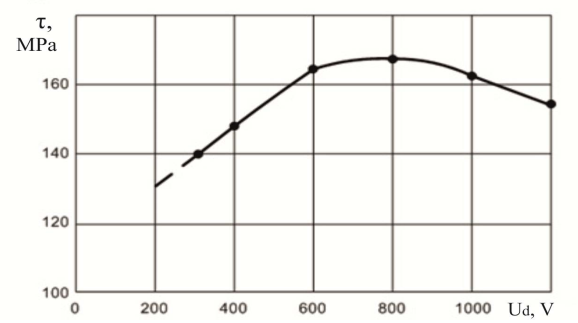


Fig. 3. The dependence of the copper-chromium joint strength on voltage at the electrodes of a glow discharge during ion treatment of deposited intermediate nickel layer (the gas pressure 13.3 ... 15.9 Pa, the treatment time 900 seconds)

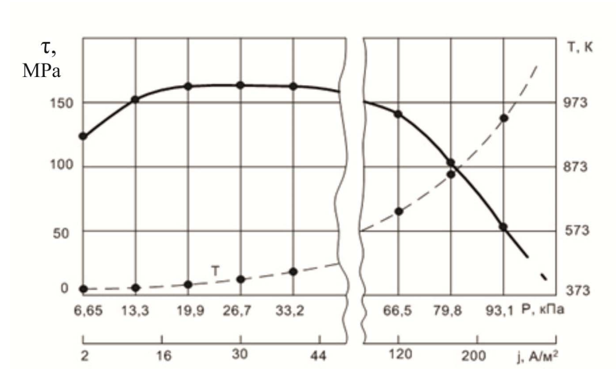


Fig. 4. Dependence of chrome-copper joint strength on current density and gas pressure during ion pretreatment of intermediate nickel layer (T - temperature of heating specimen during ion treatment)

Other parameters of processing, such as density of the discharge current *j* and duration of bombing τ define a radiation dose $Q = j\tau$, i.e. quantity of the particles that fall on surface unit during time unit and, most likely, can be coordinated with each other. The research showed that current density on a surface of details changes slightly. Increase of current density leads to heating of details that in the conditions of the rarefied gas atmosphere can lead to emergence on its surface of the thin oxide layers interfering process of a mass transfer. Durability of such connection significantly falls (Fig. 4) and samples destruct by welded seam. Thus, an alloying of a samples surface with use of glow discharge plasma must be carrying out at a temperature of samples no more than 423 K that excludes surfaces oxidation.

Influence of the ionic bombing duration of a sputtered nickel film on the chrome sample on durability of welded chrome with copper was made at a tension of discharge 600 V and pressure of gas 13,3 Pa. Duration of processing was varied from 300 to 3600 sec. It is established (Fig. 5) that with these parameters connection durability smoothly increases with increase of bombing duration, reaches a maximum in 212…223 MPa approximately for 2000…2400 sec and then practically does not change. Micro x-ray spectral research showed that in this case the extent of a transitional zone towards chrome reaches 12 microns.

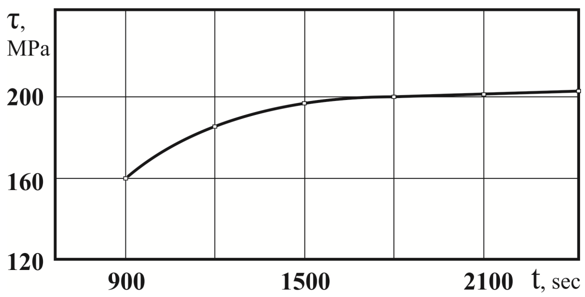


Fig. 5. The dependence of the chromium-copper welded joint strength on the duration of the ion bombardment of intermediate nickel layer: P= 13,3…15,9 Pa; Ud=600 V.

The influence of ionic bombing of a nickel film on character and depth of its introduction in chrome was studied by radioactive isotopes method. The radioactive isotope of Ni63 which was sputtered on a chrome surface electrolytically in the form of a film about 0,5 microns thick was used. Results of research of depth dependence of nickel penetration into chrome from the accelerating tension size and ionic processing duration of a nickel layer are given on Fig. 6. In both cases the dependences have almost linear character, thus depth of a nickel penetration zone increases for several times in comparison with the raw layer.

In the considered cases, quality indicators of welding was reached by usage of an intermediate nickel layer, which possesses solubility with both connected metals – chrome and copper. Additional ionic bombing of a nickel layer served as the tool providing the accelerated compulsory introduction of nickel in near-surface chrome layers. It is necessary because the thermal coefficient of nickel diffusion to chrome is two times lower, than in copper. The nickel which is forcibly introduced in chrome promotes copper, thanks to its high coefficient of diffusion in nickel ($9{,}58\cdot10^{-14} m^2/sec$ at 1273 K [9]), to get into chrome, expanding a diffusive zone and increasing, thereby, connection durability.

However, in some technical cases presence of the third element in connection chrome-copper influence on the different properties (conductivity, heat conductivity, etc.) [6] of a product and is prohibitive. Welding of this materials through the copper layer received by a thermal vacuum spattering and the punched copper layer [10] did not provide rather high mass transfer. Durability of this connection was at the level of no more than 110…130 MPa. Temperature of welding was 1273 K, squeeze pressure of samples - 24 MPa. Such result can be explained by significantly low solubility of chrome and copper in each other that is caused, agrees to given above Hume-Rothery rule, essential distinction of physical properties of metals. However, this distinctions are less considerable for ionic metallurgy. According to the empirical rule formulated by D. Sud [12], metastable replacement alloys are formed at ionic implantation if the radius of implanted impurity atoms lies within 85 … 140 % of radius of solvent atoms, and their electronegativity differ less, than on ± 0,7. It gives the chance to create homogeneous mixes of substances, insoluble in equilibrium conditions by ionic processing.

Possibility of durability increase of chrome-copper

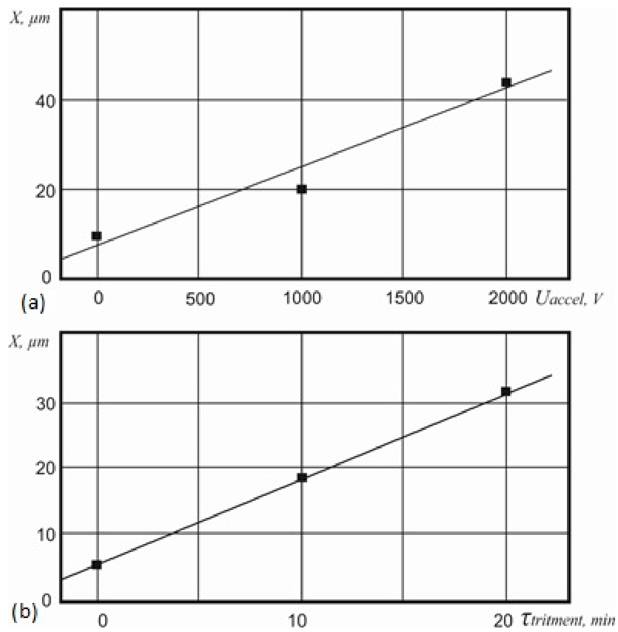


Fig. 6. Dependence of the depth 63Ni implantation in chromium on the acceleration voltage (a) and the duration of ion nickel layer treatment (b)

connection by means of preliminary introduction of copper atoms from the copper film is studied in this work. Copper film with thick 1…2 microns was thermal spattered on chrome and then bombed by argon ions in the glow discharge. Bombing was made, as well as in the previous case, at a tension of discharge 600 V, gas pressure 13,3…15,9 Pa during 900 and 1800 sec. Samples was welded at a temperature of 1193 K, squeeze pressure of 16 MPa during 1200 sec, i.e. on significantly "softer" mode, than in work [7]. Durability of the welded samples received after ionic bombing of a film during 1800 sec. reached 161 MPa that is 15% higher, than in work [7], with much smaller deformation of samples.

Results of micro x-ray spectral research show (Fig. 5a) noticeable increase in width of a transitional zone towards chrome as a result of ionic bombing of an intermediate layer. The coefficient of copper diffusion in the chrome determined by Matano's method on welded samples was $D=2,1\cdot10^{-8}$ m/s$^2$ against $D=3,9\cdot10^{-9}$ m/s$^2$ on the samples which were not exposed to ionic processing. The ionic etching of a connection zone was executed on the ION SPATTER JFS-1100 of JEOL also shows increasing of transitional zone width.

samples showed that the processing of a nickel layer by argon ions at a tension of discharge 600 V during 900 sec. promotes increase of a transitional zone width in 1,5…2 times. Durability of welded connections by a cut increased from 122 MPa on the control raw samples to 143 MPa, i.e. almost for 15%. This gives the reason to recommend use of the offered technique at diffusion welding of a wide range of the diverse metals that considerably differ with physicomechanical properties.

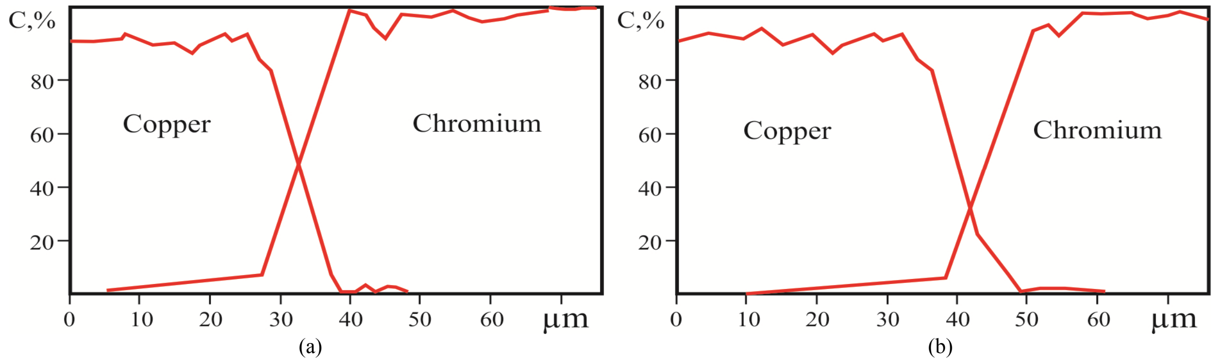


Fig. 7. The element distribution in the transition zone of chromium-copper joint through the sputtered (a) and additionally treated by argon ions in the glow discharge (b) copper layer deposited on the chromium surface

## IV. Conclusions

It is established that one of the most effective ways of influence on diffusion mass transfer processes in the production of diffusion-welded joints of magnetron sputtering systems is the use of pre-modification of the chemical composition of metals surface layers. This is accomplished by introduction of recoil atoms deposited on their surface, in any way, thin films of metals and their subsequent treatment with inert gas ions in the glow discharge with an energy of about 600 - 1000 eV.

The test results of the diffusion-welded copper-chromium and copper-titanium joints have shown possibility of regulating the values of the diffusion zone length by applying of ion bombardment less activated metals surfaces during the welding. So, the width of the diffusion zone after ion modification in the glow discharge at welding of metals increases by 1.5 - 2 times as compared to specimens without any processing, which leads to an increase of joints strength characteristics is 15 - 40%.

The most effective application of the proposed method of the surfaces modification in pressure welding without melting of metals significantly different physical and mechanical properties, and have limited mutual solubility in the solid state.

The offered technique of activation of a mass transfer processes was also used at diffusion welding of the titan with copper through the intermediate layer of nickel applied with vacuum evaporation on a surface of the titan. Welding of samples was made during 900 sec. at a temperature of 1123 K, squeeze pressure of 8 MPa. Results of researches of welded

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