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# Deposition of metal layers on carbon assisted with the same metal's ion radiation

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## Abstract

The depth distribution of metals inserted into graphite by means of clean ion beam assisted deposition displays a dependence on the energy density deposited in the atomic collision cascade. Qualitative and quantitative element, phase and chemical analyses of (Cu, Co, Mo, W)/C structures have been conducted with Rutherford backscattering and X-ray photoelectron spectroscopy (XPS) methods. In experimental conditions which satisfy a "global" spike model chemical forces such as the heat of mixing, cohesive energy and probably other effects may be employed for the explanation of experimental data. XPS analysis shows that in the Mo/C system near 60% of metallic molybdenum and 40% of oxide MoO<sub>x</sub> ( $x \approx 2$ ) are formed while in the W/C system almost every atom of tungsten is oxidized.

**Keywords:** Metal; Deposition; Ion; Radiation; Mixing

## 1. Introduction

Energetic ions which are used in a number of ion beam techniques are able to influence different physical and chemical properties of solids. There are well-known advantages and disadvantages of ion implantation (II) in the modification of materials. Because of a sputtering effect there are limitations on the introduction of a desirable element into a target. According to Ref. [1], the maximum concentration  $N_{\max}$  of the ion-implanted element usually does not exceed 10–15 at.%. A number of experiments have proved this statement [2,3]. The above-mentioned limitations of II may be neglected when semiconductors are implanted, but for modification of corrosion, mechanical, adhesion properties etc. of metals it becomes a substantial disadvantage.

Since 1970 ion beam mixing (IBM) has been successfully applied for substrate–thin film intermixing and modification of surfaces [4]. The IBM technique is free of II's limitations. However, when the coating on the substrate is thicker than 0.1  $\mu\text{m}$  one has to use for IBM experiments gas ions (Ar, Kr, Xe) with energy above 100 keV. In such regimes of ion radiation according Ref. [5] the amount of average deposited energy density (DED) in the atomic collision cascades may be estimated

often to be from 0.01 to 0.1 eV atom<sup>-1</sup>. Relatively, high doses of gas ions (several times  $10^{16}$  cm<sup>-2</sup>) are used in IBM. Therefore a sufficiently large Ar concentration (about 10–20 at.%) in the  $R_p$  region may be obtained. We consider the effect obtained to be a negative feature of the IBM method.

The relatively new ion beam assisted deposition (IBAD) technique uses simultaneous material deposition on a target and ion radiation of a forming structure [6,7]. The estimated DED when Ar ions with energies of 3–15 keV are used for radiation is often 0.5–2 eV atom<sup>-1</sup>. Unfortunately a large concentration of gas introduced into the target is a disadvantage of the IBAD method. The original "clean" IBAD (CIBAD) method suggested here is expected to be able to provide IBM during surface layer deposition without introducing into the target an admixture of noble gases (Ar, Kr, Xe). Secondly, the amount of DED can increase to 1–20 eV atom<sup>-1</sup>. Both effects can influence synergetically the mechanisms and processes of atomic mixing and accompanying processes, such as phase transformation and chemical compound creation in the coating–substance transition region.

We introduce here preliminary results of investigation of Me/C structures which have been formed by means

of CIBAD of Co, Cu, Mo and W metal on the carbon base.

## 2. Experiment

CIBAD experiments were performed using a resonance vacuum arc ion source which is described elsewhere [8]. It provides deposition of a thin metal film on a target and simultaneous radiation of it with ions of the same species. Deposition and irradiation of Co, Cu, Mo, W on graphite and partly on glassy carbon were performed. The vacuum in the target chamber was about  $10^{-4}$  Torr, and the energy of ions was 7, 15, 20 keV. Sigmund's approximation [5] was used for estimation of DED in IBM experiments.

The Rutherford backscattering (RBS) technique was employed for the investigation of target composition and for depth profiling of components in prepared structures. The energy of  $\text{He}^+$  ions was 1.5 MeV, scattering angle  $\theta = 160^\circ$ , and angles of entry and escape were  $50^\circ$  and  $70^\circ$  correspondingly. The energy resolution of the analysing system was 15 keV. Concentration profiles of components were evaluated using computer simulation [9].

Chemical analyses of surface layers were conducted by X-ray photoelectron spectroscopy (XPS) in an electron spectrometer (model LHS-10, Leybold, Germany). The analysis was performed with  $\text{Mg K}\alpha$  X-ray radiation ( $h\nu = 1253.6$  eV) and an applied pressure of about  $10^{-9}$  Torr. Bombardment by Ar ions at 3 keV energy and ion current  $10 \mu\text{A cm}^{-2}$  was also carried out to clean the surface and to obtain data about the chemical bonding states of carbon, oxygen and metal atoms at selected depths below the phase interface after sputtering. Detailed scans, for chemical state identification, from C 1s, O 1s, Mo 3d, W 4f regions were obtained. The Au 4f signal was used as a line position to calculate binding energies.

## 3. Results and discussion

The samples used in this study were prepared by deposition of thin Co, Cu, Mo, W films onto polished graphite with irradiation of the same metal ions. These chosen bicomponent systems facilitate RBS and XPS analysis and are characterized by a large (more than one order of magnitude) difference in DED. The interval of ion energies employed is also enough to obtain a many-fold difference in DED for the same system. System configuration and parameters are presented in Table 1.

RBS spectra of Co deposited and irradiated samples are shown in Fig. 1. The observed changes in the spectra are the appearance of a cobalt signal and signals of

Table 1

System configuration, mass ratio  $M_{\text{Me}}/M_{\text{C}}$ ,  $Z$  and  $E$  of ions, and deposited energy density

Constructed structure	$M_{\text{Me}}/M_{\text{C}}$	$Z_{\text{Me}}$	DED ( $\text{eV atom}^{-1}$ ) for the following $E$		
			7 keV	15 keV	20 keV
Co/C	4.92	27	0.32	0.07	0.04
Cu/C	5.29	29	0.49	0.12	0.06
Mo/C	7.99	42	1.89	0.88	0.66
W/C	15.31	74	3.80	1.76	1.33

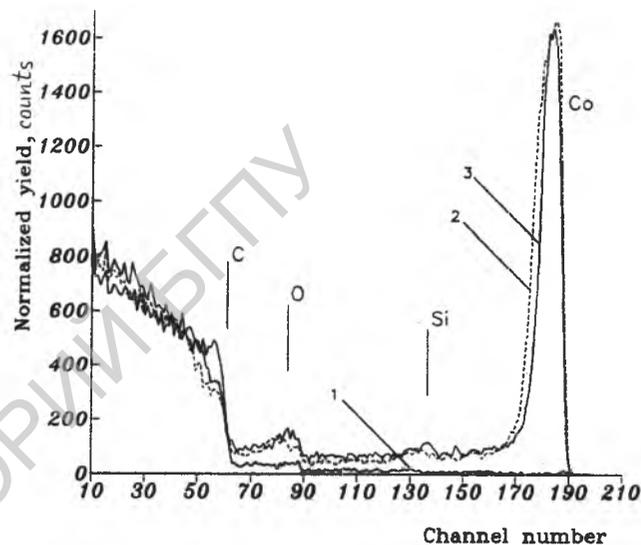


Fig. 1. RBS spectra of graphite before (spectrum 1) and after Co treatment with the following  $\text{Co}^+$  ion energies: spectrum 2, 7 keV; spectrum 3, 15 keV.

oxygen and a minor quantity of silicon and a decrease in the yield of carbon in the surface region. These reflect the deposition of Co on graphite with associated impurities of O and Si and penetration of all these components into the sample as a result of ion assisted mixing processes. The presence of oxygen in modified layers of graphite may be explained as a result of interaction of oxygen (from residual gas in the chamber) with metal. The appearance of Si in the treated samples is probably connected with the effect of a small amount of sputtering of isolators from the ion source. No other admixture, e.g. noble gases etc., has been observed. The difference between curves 2 and 3 in Fig. 1 reveals a deeper penetration of components into graphite when a small (7 keV) energy of  $\text{Mo}^+$  ions is used in spite of the projected length data quoted in Table 2. This effect is more pronounced in Fig. 2(a) and less in Fig. 2(b), where depth distributions of carbon, molybdenum, tungsten, oxygen and silicon are presented.

A significant difference regarding the carbon concentration is observed in the Mo/C system with respect to DED, which reveals the difference between transport

Table 2  
Projected length and straggling of ions in graphite [10]

Ion	Cu			Co		Mo			W			
Energy (keV)	7	15	20	7	15	20	7	15	20	7	15	20
$R_p$ (Å)	78	130	160	80	135	167	77	122	147	75	113	133
$\Delta R_p$ (Å)	20	30	36	23	37	45	17	25	30	13	18	20

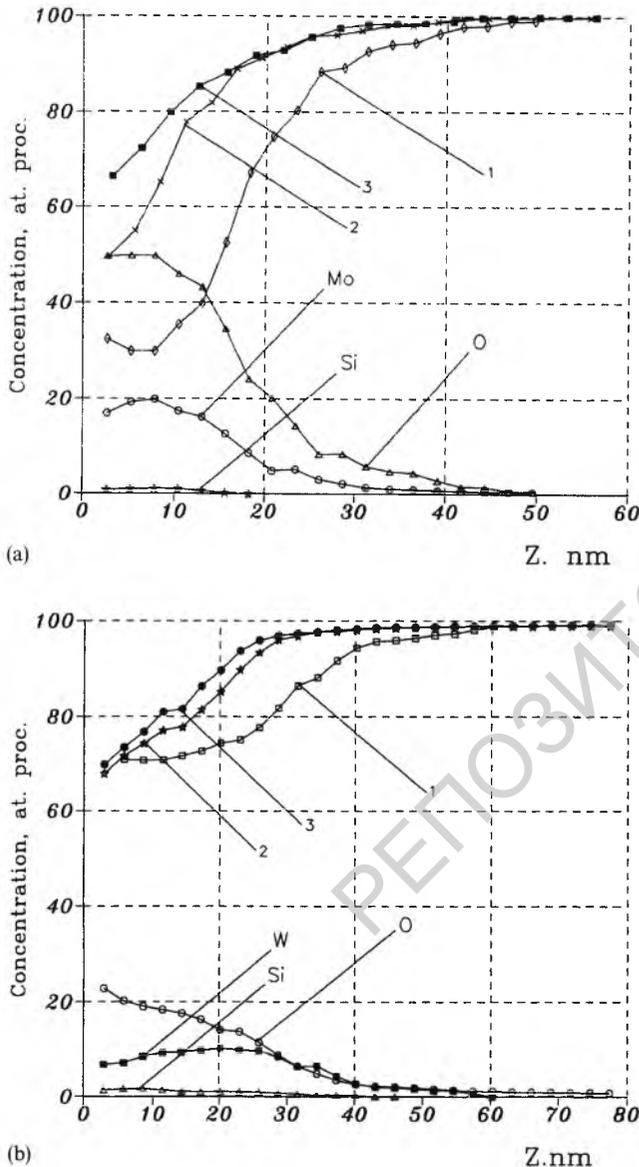


Fig. 2. Component profiles in graphite after deposition and irradiation of (a) Mo and (b) W: curves 1, 7 keV; curves 2, 15 keV; curves 3, 20 keV. Profiles of Mo, W, O, Si are shown in samples irradiated with 7 keV ions.

processes in graphite and in the W/C and Co/C systems. In our measurements of the layer concentration of components in targets it was estimated that approximately 1.5–2 atoms of oxygen accompany one atom Co or W, while each Mo atom goes with 2.5–3 or more

atoms of oxygen. In the Cu/C system the amount of O is so small that less than one atom of O may be counted per metal atom.

We parametrized the obtained energy dependence of the depth distribution of components in the treated graphite using the concept of DED in the atomic collision cascade. As a whole, the factor DED revealed an evident dependence of atomic transport efficiency on the incident energy of ions in the investigated systems. However, the DED factor was not invariant but dependent on the system applied and probably on the concentration of impurity and its chemical state. The absolute values of the DED varied from  $0.32 \text{ eV atom}^{-1}$  to  $3.80 \text{ eV atom}^{-1}$  for 7 keV ions and from  $0.04 \text{ eV atom}^{-1}$  to  $1.33 \text{ eV atom}^{-1}$  for 20 keV ions (Co, Cu, Mo, W). There was only a 3-fold difference in DED for Me/C systems when the energy of the ions was changed from 7 keV to 20 keV.

Chemical analysis of the modified graphite has been conducted also by means of XPS. Table 3 presents the chemical composition of the sample which has been modified using 15 keV  $\text{Mo}^+$  ion irradiation. These data are only in a qualitative agreement with RBS results. For example, the content of Si is several times overestimated in the XPS study. However, it is important that XPS analysis confirms a relatively deep penetration of Mo and O into the irradiated graphite.

XPS spectra obtained from the C 1s region show that carbon at depths of 125, 225 and 425 Å is in the graphite phase. Evaluation of the signal from the Mo 3d region shows that a high contribution of metallic molybdenum (Mo) (228.4 eV binding energy) and a lower contribution of molybdenum in oxide forms  $\text{MoO}_x$  ( $x \approx 2$ , at 229.5 eV) are present in graphite. The proportions of Mo and  $\text{MoO}_x$  are estimated as 60% and 40% in the modified

Table 3

Data of chemical analysis of a sample, prepared by Mo deposition and irradiation with 15 keV  $\text{Mo}^+$  ions

Depth (nm)	Content of sample (at.%)			
	C	O	Mo	Si
0.0	79.9	14.9	0.7	4.5
2.5	88.3	7.0	1.6	3.1
12.5	85.5	7.3	4.2	3.0
42.5	86.9	6.7	3.4 <sup>†</sup>	3.0

layer of graphite. Observation of spectra in the O 1s and W 4f regions allows us to consider that almost all oxygen atoms are in chemical connection with tungsten atoms in the W/C system.

#### 4. Conclusions

CIBAD of Cu, Co, Mo, W on graphite leads to deep penetration of metals into a target, showing that, in addition to known models of IBM, atomic transport in the Me/C system depends on the damage energy deposited in the atomic collision cascade. Our experiments were conducted in conditions of overlapping subcascades and they satisfy the conditions of a “global” spike model, developed in Ref. [11]. Therefore under these circumstances chemical forces such as the heat of mixing, cohesive energy and probably other reasons may play an important role as was noted in our earlier studies of (Cr, Ni, Cu, W)/Ti, Cu/Al, Pd/Fe systems constructed by means of IBM and IBAD [12,13] and in other studies of different systems [14,15].

It follows from the data provided by RBS and XPS techniques that there are no additional admixtures in modification by means of CIBAD graphite. Oxygen and silicon may be eliminated by an ultrahigh vacuum system as in Ref. [16].

XPS analysis shows that in the Mo/C system nearly 60% of metallic molybdenum and 40% of oxide  $\text{MoO}_x$  ( $x \approx 2$ ) are formed while in the W/C system almost every atom of tungsten is oxidized.

Copper is a metal which is less associated with oxygen within the investigated systems.

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