UDC 539.121.8.04:669.14.046

DISTRIBUTION OF INTERSTITIAL IMPURITIES IN CHROMIUM COATING, OBTAINED BY ION BEAM ASSISTED DEPOSITION

A. Guglya, V. Virich, A. Styervoyedov*, M. Silkin*
National Science Centre "Kharkiv Institute of Physics and Technology",
**V.N. Karazin's Kharkiv National University, (Ukraine)*
Received 19.02.2003

The paper presents the study results of interstitial impurities such as carbon (C), oxygen (O) and nitrogen (N) in Cr coating formed on aluminium substrate at the temperature 300^{0}C under conditions of simultaneous chromium deposition and its bombarding with nitrogen ions of 30 keV energy. It is shown that carbon doesn't penetrate into coating deeper than 1-2 nm. Oxygen is more active and penetrates into coating deeper than (15 nm). Preliminary bombardment of the aluminium substrate by nitrogen ions before coating deposition to doze $1{,}5\cdot10^{17}$ ion/cm^2 leads to considerable saturation by oxygen then by carbon. The oxygen content in aluminium decreases and becomes identical with its distribution in chromium coating after chromium coating deposition. The carbon content in aluminium after coating deposition becomes more increased than the oxygen content

INTRODUCTION

In the present time the beam technologies, such as ion implantation and ion beam assisted deposition are widely used for material properties modification. Under ion implantation process a formation of well-developed dislocate structures and segregations in the material surface layers defining operational characteristics of the product in the future takes place. Under ion beam assisted deposition intensive atom mixing of the condensing material with substrate lattice takes place during simultaneous bombardment by ions with energies of several tens keV.

Under conventional conditions of the present technology realization (the pressure of residual gases in work chamber is $5\cdot10^{-3} – 5\cdot10^{-5}$ Pa) ion-induced physical-chemical interaction processes between residual gases and substrate surface appear. The obtained results of the ion implantation and ion beam assisted deposition (IBAD) showed a visible increase of carbon and oxygen in deposition film, especially in surface layers and mixed area between coating and substrate [1,2]. Such gases being under intensive irradiation will form carbides and oxides, and so will exert uncontrollable influence on the properties of produced films.

Chromium is the perspective material for wear- and corrosion-resistant coatings. On other side, it actively interacts with gas impurities. So, at the designing of chromium-based coatings the study of the accumulating mechanisms of such elements as oxygen, carbon and nitrogen in deposited material during nitrogen ion beam bombarding is an important problem.

The purpose of this research was to study O, C, N admixture distribution of the chromium film obtained by the IBAD method on the aluminium substrate and also its distribution in the chromium-aluminium mixed area with the precut nitrogen irradiation of the substrate.

EXPERIMENTAL PROCEDURE

Experiments have been carried out at the installation of ion beam assisted deposition "Argo-1" [3]. Chromium with the 99.98 purity was evaporated by electron-beam evaporator under conditions of simultaneous bombarding with 30 keV nitrogen ions and ion current density 20 μA/cm^2. The deposition rate was between 0.05-0.1 nm/sec. The substrate temperature was 300 ^{0}C. Aluminium with the 99.995 purity was chosen as a substrate. The substrate surface was smoothed with diamond paste and then elect-ropolished.

To investigate the influence of the precut ion implantation on a component structure of the diffusion layer between coating and substrate some of specimens were irradiated before deposition by nitrogen ions with energy 30 keV at 300^{0}C to the implantation doze $1.5\cdot10^{17}$ ion/cm^2. The working vacuum was $5\cdot10^{-4}$ Pa using oil-free pumping equipment. During the process at turning on ion source vacuum was $4\cdot10^{-3}$ Pa due to the nitrogen expansion in the discharge chamber.

The film structure and component composition was analysed using the secondary ion mass-spectrometry and Auger spectroscopy. The shape of chromium coating was studied with the scanning tunnelling microscopy.

THE EXPERIMENTAL RESULTS AND THEIR DISCUSSION

The results of Auger spectroscopic analysis of the aluminium surface area 15 nm wide irradiated by nitrogen ions are shown in Fig.1a. One can see, that if the carbon concentration significantly decreases already on the first 1-2 nm, then oxygen penetrates deeply in big amount. The increase of nitrogen concentration with the depth mainly corresponds to the initial parts of rated curves, describing its distribution in aluminium substrate [4].

It is known that the main processes taking place on the metal surface bombarded by high - energy heavy ions are substrate sputtering, adsorption of gas molecules from remaining atmosphere in vacuum chamber, their dissociation and diffusion into crystal lattice because of its dilatation and radiation-assisted processes [5]. The correlation between quantity of adsorbed molecules of oxygen and carbon is determined mainly by the type of used means of high-vacuum pumping equipment. In our case the use of oil-free pump-down determined low content of carbon. Main sources of oxygen in aluminium are molecules of H_2O, O_2, CO, which have low dissociation energies – 46, 52 and 82 kcal/mole accordingly [6]. The dissociation energy of nitrogen molecules is 205.5 kcal/mole, therefore their penetration into aluminium at the given temperature (300^{0}C) is possible only by ion bombardment.

In the surface area of chromium film deposited onto aluminium with nitrogen ion beam assisting, the oxygen and carbon distribution is quantitatively similar to the shown in Fig.1b. The feature of the doped admixture distribution in deposited chromium is the large content of carbon and low content of oxygen and nitrogen. The explanation of low content of nitrogen is that ion beam assisted deposition takes place while present method of

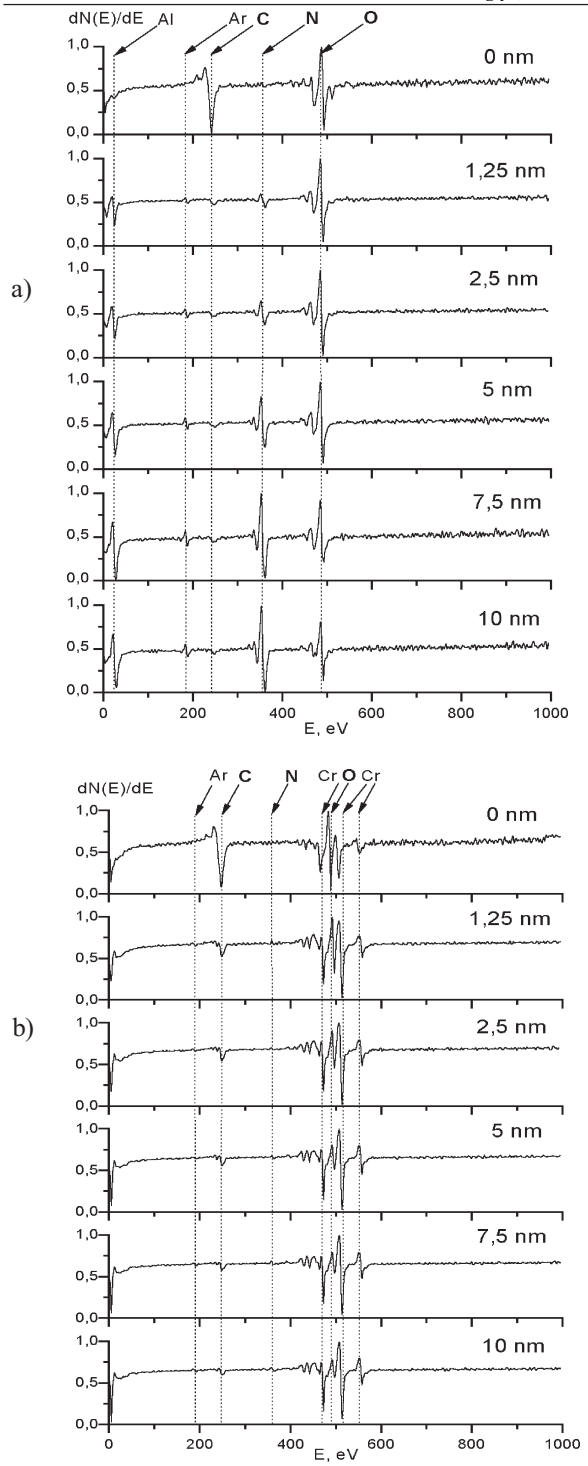

Fig. 1. Auger spectroscopic analysis of interstitial impurities for first 10 nm of the depth. a) Al as irradiated with N^+ ions only, b) deposited Cr film under simultaneous N^+ ion bombardment

the surface modification as compared with ion implantation. Under ion beam assisted deposition the capture of oxygen (and carbon) is possible only in a short time interval as long as the film deposits to thickness 2-3 nm. While the border of coating moves to the front of ion beam the entry of interstitial impurities from the residual atmosphere stops and its redistribution due to radiation-enhanced diffusion takes place.

Secondary ion mass-spectrometry was carried out on the aluminium specimens with precut nitrogen ion implantation to doze $1.5 \cdot 10^{17}$ ion/cm^2 and without it and with the following chromium ion beam assisted deposition. The coating was sputtered by argon ions with energy of 5 keV. All thickness of chromium coating (100 nm) and aluminium substrate subjected to nitrogen ion beam bombardment was investigated. The distribution of oxygen and carbon is shown in the Fig.2a (without preliminary nitrogen ion processing) and Fig.2b (with preliminary processing).

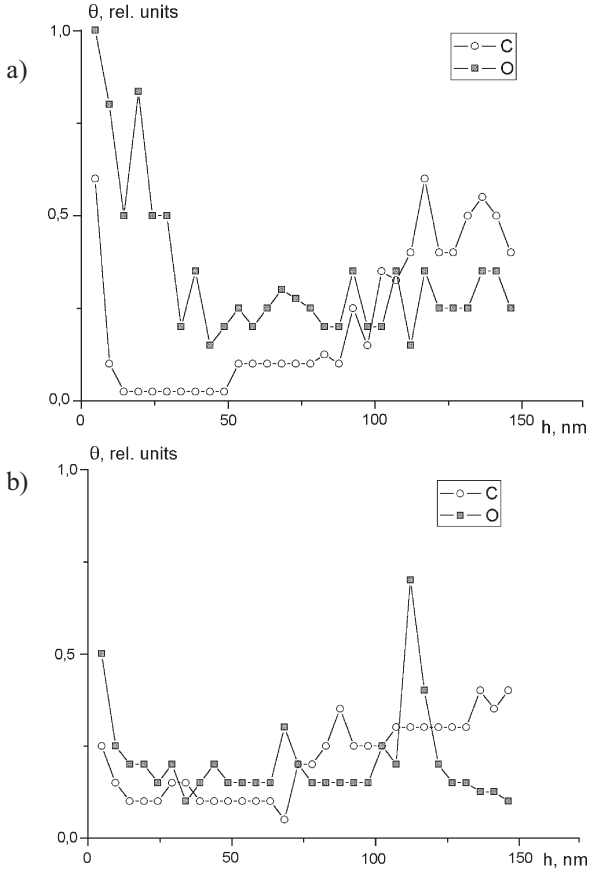

Fig. 2.The oxygen and carbon distribution a) without preliminary ion processing; b) with preliminary ion processing

One can see that O, C distribution in the surface layer is similarto the results of Auger spectroscopy. However, it is seen that the carbon content increases in transition zone coating-substrate. As a result, unlike data shown in the Fig.1 in aluminium substrate there dominates carbon but not oxygen. Oxygen content in all zone coating-substrate is approximately the same.

Now, we don't have enough convincing explanation of this effect. It is necessary to make additional investigations. In our case the carbon perhaps hits the aluminium surface during the chromium deposition and diffuses deep into substrate as a result of assisted irradiation.

Also, it was interesting to investigate a degree of the surface roughness obtained under ion beam assisted deposition. The difference between this method and many plasma technologies is the absence of the drop component in the condensed material flow. TThe typical relief of chromium coating deposited on the aluminium by IBAD technology and obtained with the use of AFM/STM for UHV applications from Omicron Company is shown on Fig.3. Measurements carried out on 10 parts of different specimens showed that averaged value of roughness is 5 nm. This result is typical for the IBAD coatings [9].

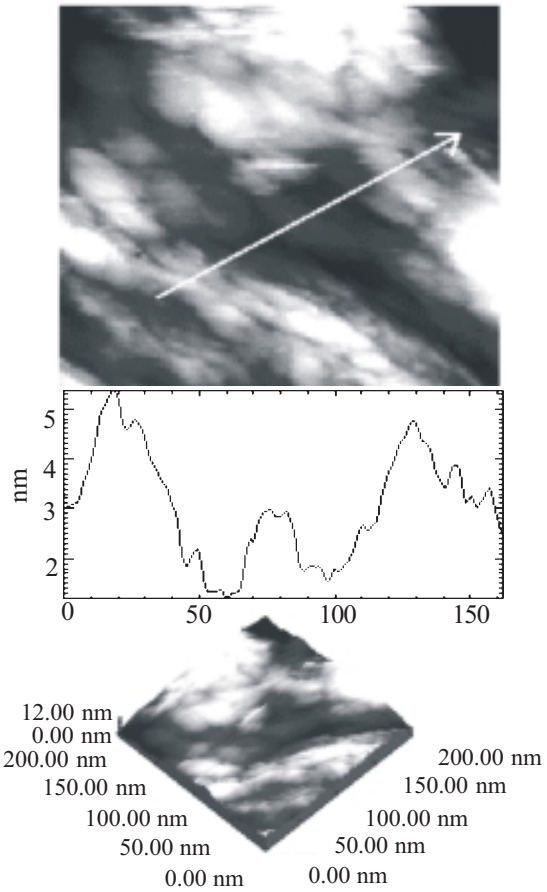

Fig.3. (Cr-N)-Al composite relief obtained with tunnelling microscope.

CONCLUSION

Our experimental results showed that deposition of chromium coating on aluminium under conditions of simultaneous irradiation by nitrogen ions of 30 keV energy doesn't to visible coating contamination by interstitial impurities - O, C. These elements are located in narrow region of 5-10 nm near the condensate surface. Preliminary nitrogen ion bombardment of the substrate before coating deposition disorders the aluminium surface and leads to more considerable contamination of surface by oxygen. However, after deposition of coating its content in surface layer lowers and becomes less than the content of carbon.

ACKNOWLEDGEMENTS

One of the authors (A. Styervoyedov) acknowledges L. Euler grant (DAAD), project-nr: A02/02846, which allowed him to perform the AES and STM measurements at the Institute of Physics and Physical Technologies of Clausthal Technical University. He also thanks to Prof. Dr. V. Kempter, Prof. Dr. N.T. Gladkikh and the members of their groups for their assistance with the measurements and for stimulating discussions.

The part of this work was supported by STCU grant № 2050.

REFERENCE

1. Weiyi Y., Guangyuan L., Yawen S. A microstructural investigation of 52100 steel by N^+ implantation and recoil implantation // Nucl. Instr. & Meth. In Phys. Res. -1989. -B39. -P. 563-566.
2. Belyi A.V. Structural changes in titanium nitride coating, processed by ion bombardment//SURFACE. Physics, chemistry, mechanics. –1989. – № 10. –C. 128-133. (in Russian)
3. Guglya A., Marchenko Y., Perun N.. Technology and equipment of high energy ion beam assisted processing of materials // Metallurgical Science and Thermal Processing of Metal -1996. - №3. C. 29-30. (in Russian)
4. Guglya A., Malykhin D., Marchenko I., Nekludov I. Methodical aspects of formation of two-component materials with use of ion beam assisted technology // Metal Science and the Newest Technologies -2002. -T. 24. №9. –C. 1295-1304. (in Russian)
5. Farkas D., Singer I., Rangaswamy M. Modeling of high fluence Ti ion implantation and vacuum carburization in steel // J. Appl. Phys. -1985. -57(4), -15, -P. 1114-1120.
6. Kogan V., Semenenko Y., Seriugin A. Internal stresses in the chromium condensates obtained in various vacuum conditions. // Physics and Chemistry of Materials Processing.–1980. – №4. -C. 81-85. (in Russian)
7. Kirsanov V., Gann V., Yudin O. Structure of space distribution calculation of vacancy clusters in metals irradiated with a stream of accelerated ions // Questions of a Nuclear Science and Technics. Physics of radiation damages and radiation materiology. -1981. -№1/15. -C.28-30. (in Russian)
8. Guglya A., Marchenko I., Malykhin D., Nekludov I.. Production of Cr-N films by the ion beam-assisted deposition technology: experiment and computer simulation // Surface and Coating Technology. –2003, –№164-165. –P. 286-292.
9. Ma C.H., Huang J.H., Chen H. A study of preferred orientation of vanadium nitride and zirconium nitride coatings on silicon prepared by ion beam assisted deposition // Surface and Coating Technology.–2000. –№ 133-134. – P. 289-294.

РОЗПОДІЛ ДОМІШОК ВПРОВАДЖУВАННЯ У ХРОМОВОМУ ПОКРИТТІ, ЩО ОТРИМУЄТЬСЯ З ВИКОРИСТАННЯМ ІМПЛАНТАЦІЙНО-СТИМУЛЬОВАНОГО ОСАДЖЕННЯ

О.Г. Гугля, В.Д. Вірич, А.М. Стєрвоєдов, М.Ю. Сілкін

Представлено результати досліджень розподілу домішок впровадження в плівках хрому отриманих методом іонно-стимульованого осадження. Хром, чистотою 99,98 осаджувався на алюмінієву підкладку до товщини 100÷150нм, при швидкості осадження 0.05-0.1 нм/сек, енергії пучка асистуючих N^+ іонів E = 30 кеВ, щільності току j = 20 мка/см^2, температурі підкладки T = 200 ^{0}C. Плівки напилювалися на чисту Al підкладку (Al чистотою 99.995) і попередньо оброблену N^+ іонами до дози 1,5·10^{17} іон/см^2. Показано, що вуглець не поширюється всередину покриття далі, ніж на 1-2 нм. Кисень більш активний і проникає в покриття глибше 15 нм. Попередня імплантація N^+ у Al підкладку до дози 1,5·10^{17} іон/см^2 приводить до значного насичення його киснем і, у меншому ступені, вуглецем. Після нанесення хрому кількість кисню в Al знижується і стає однаковим з його розподілом у хромовому покритті. Кількість вуглецю в Al після нанесення покриття навпаки стає більшим, ніж кількість кисню.

РАСПРЕДЕЛЕНИЕ ПРИМЕСЕЙ ВНЕДРЕНИЯ В ХРОМОВОМ ПОКРЫТИИ, ПОЛУЧАЕМОМ С ИСПОЛЬЗОВАНИЕМ ИМПЛАНТАЦИОННО-СТИМУЛИРОВАННОГО ОСАЖДЕНИЯ

А.Г. Гугля, В.Д. Вирич, А.Н. Стервоедов, М.Ю. Силкин

Представлены результаты исследований распределения примесей внедрения в пленках хрома, полученных методом ионно-стимулированного осаждения. Хром, чистотой 99,98, осаждался на алюминиевую подложку до толщины 100÷150 нм, при скорости осаждения 0.05-0.1 нм/сек, энергии пучка ассистирующих N^+ ионов E = 30 кэВ, плотности тока j = 20 мкА/см^2 и температуре подложки T = 300^o C. Пленки напылялись на чистую Al подложку (Al чистотой 99.995) и предварительно обработанную N^+ ионами до дозы 1,5·10^{17} ион/см^2. Показано, что углерод не распространяется вглубь покрытия дальше, чем на 1-2 нм. Кислород более активен и проникает в покрытие глубже 15 нм. Предварительная имплантация N^+ в Al подложку до дозы 1,5·10^{17} ион/см^2 приводит к значительному насыщению его кислородом и, в меньшей степени, углеродом. После нанесения хрома содержание кислорода в Al снижается и становится одинаковым с его распределением в хромовом покрытии. Содержание углерода в Al после нанесения покрытия наоборот становится большим, чем содержание кислорода.