Vacuum 138 (2017) 139–145

Contents lists available at ScienceDirect

Vacuum

journal homepage: www.elsevier.com/locate/vacuum

Detection by sputtering of deformed areas hidden under a surface

K.A. Tolpin*, K.F. Minnebaev, V.E. Yurasova

Physics Faculty of Moscow State University, Moscow 119991, Russia

ARTICLE INFO

Article history:
Received 14 July 2016
Received in revised form
26 October 2016
Accepted 2 November 2016
Available online 3 November 2016

Keywords:
Sputtering
Binary alloys
Deformation
Molecular-dynamic simulation

ABSTRACT

A sensitive method of visualization by sputtering of deformed areas buried under a surface is developed. The effect of varying the lattice constant and binding-energy of surface atoms of binary disordered alloys on the sputtering of areas deformed by a concentrated load was examined using molecular dynamics. The calculation was carried out for $Cu_{87}Sn_{13}$, $Ni_{97}Fe_3$ and $Fe_{97}Ni_3$ alloys, which are used for manufacturing of coins and items with marking signs. Experimentally and by MD simulations of energy and angular distributions of sputtered particles, we have shown that the best conditions for detection of deformed areas, buried under a surface, occur in the case of irradiation by inert gas ions of sufficiently large mass (Ar^+, Kr^+) with energy of 7–10 keV, when the sputtering yield is close to its maximum value. We suggest using an inclined ion beam, near the maximum of the angular dependence of the sputtering coefficient. This leads to reduction of the time necessary for ion irradiation, and to an increase in clarity of the obtained image due to a cumulative effect in the narrow near-surface layers of the target. Using the recommended parameters of sputtering has allowed us to reveal a destroyed image on a bronze coin and images of completely ground off marking numbers on steel objects.

1. Introduction

Sputtering processes are widely used for analyzing a solid's surface, in particular, to clarify the grain structure of the target [1–3]. This is because atoms located on grain boundaries have smaller binding energy, than those on grain surfaces, and therefore are more easily sputtered. By means of ion irradiation it is also possible to reveal the separate phases of alloys and the areas enriched with any elements if they have different sputtering yields [3].

In Refs. [4,5] it was shown that an area of deformation on a metal surface can be made visible as a result of ion sputtering; for example, an erased image on coins, or, a ground-off brand on various items. The received visible contrast of the previously erased image is connected with increase of sputtering of deformed areas due to reduction of sizes of grains and corresponding increase in quantity of atoms with small binding energy on their boundaries, and also due to radiation-induced diffusion of defects, alloy components and implanted ions into the field of mechanical stresses [6]. A discussion of conditions and reasons for a visible contrast of deformed areas are given in Refs. [6,7].

First experiments on visualization of deformed surfaces were carried out by sputtering the samples in a glow discharge plasma with the voltage between the cathode (the sample) and the anode ranging between 100 and 1000 eV [4]. When ions with such low energy fall at a normal to a surface the sputtering yield is very small. This means that a longer-term irradiation of the sample is required to detect the area of deformation, i.e. up to ten hours for a considerable etching of the original surface with a stamped number. Furthermore, for the incidence of irradiating ions at a normal to the surface, sputtered atoms exit not only from the surface layer of the target, but also from deeper layers, where there may be other areas of deformation, thereby reducing the required image sharpness.

In the present work we have identified, both experimentally, and by a MD simulation, such conditions and parameters of sputtering that would be most favourable for quick and clear detection of areas of buried deformation. We have investigated energy and angular characteristics of the samples before and after the deformation. A change in surface binding energies [8] and a decrease in lattice constants of the samples under deformation have been taken into account. A study of sputtering of poly- and single crystals of binary alloys under deformation is important not only for practical use, but also for deeper understanding how these processes occur.

* Corresponding author.
E-mail address: ktolpin@mail.ru (K.A. Tolpin).

http://dx.doi.org/10.1016/j.vacuum.2016.11.002

2. Research method

As samples we have chosen poly- and single crystals of $Cu_{87}Sn_{13}$, $Ni_{97}Fe_3$ and $Fe_{97}Ni_3$ disordered binary alloys, which are used for manufacturing coins and other objects that have a stamped or marked area of concentrated load deformation. We studied the sputtering process for unchanged composition of crystal faces for $Cu_{87}Sn_{13}$ (fcc lattice), $Ni_{97}Fe_3$ (fcc lattice) and $Fe_{97}Ni_3$ (bcc lattice) with binding energy of surface atoms E_b equal to 3.49, 4.44, and 4.08 eV, respectively [8], and by considering a process of segregation.

We have taken into account such typical properties of binary alloys as surface segregation, disordering and reconstruction, which reflect essential difference between the structure and composition of the surface and the bulk of such alloys [8]. For binary alloys, it has been found out, experimentally and theoretically, that the surface of poly- and single crystals is enriched with heavy components [9–12]. For single crystals, an oscillation of composition in near-surface layers and their reconstruction is observed [12].

2.1. Computer simulation

A molecular dynamics simulation [13,14] of sputtering has been carried out for the case of irradiation of the sample surfaces by Ar^+ and Kr^+ ions with energy E_0 ranging from 0.1 to 10 keV with the angles of ion incidence φ from 0° to 85° (counting from a normal to the surface), and for temperature of sputtered alloy of 20 °C.

A MD model, developed in Ref. [15], with a movable single crystal block consisting of 250 atoms has been used (see also [16]). For calculating the polycrystal sputtering yield, the block is turned by arbitrary angles for each incident ion. Equations of motion are integrated according to the Euler predictor-corrector method which is stable [17,18]. Inelastic losses are calculated by means of the Firsov formula [19]. Thermal oscillations are assumed to be uncorrelated. The interaction potential is as follows:

$$U(r) = A_{bm}\cdot\exp(-r/a_{bm}) + (A_b/r)\cdot\exp(-2r/a_{bm})$$

with constants $A_{bm} = 52\ (Z_1Z_2)^{3/4}$ [20], $a_{bm} = 0.0219$ nm, $A_b = (Z_1Z_2\cdot e^2)$, where Z_1 and Z_2 are atomic numbers of the incident ion and of the target atom, and r is the radius-vector.

We have calculated for the components of the alloys a change in the lattice constant Δa and a change in the binding energy of surface atoms ΔE_b under a pressure of 10 GPa (per area of 3 mm^2), which is used for industrial marking of coins and products. For the alloys in question we used the following parameters, which are close to data given in Ref. [21] for iron: $\Delta a = 5\%$ and $\Delta E_b = 11\%$ for $Cu_{87}Sn_{13}$; $\Delta a = 5\%$ and $\Delta E_b = 16\%$ for $Ni_{97}Fe_3$; $\Delta a = 5\%$ and $\Delta E_b = 19\%$ for $Fe_{97}Ni_3$.

2.2. Experiment

The composition and structure of the samples with the latent deformation area under the surface at various depths were investigated at several stages of surface treatment, including the sputtering by Ar^+ and Kr^+ ions with the energy E_0 from 7 to 10 keV. Irradiation of coins and objects with marks, was carried out in the system shown schematically in Fig. 1.

The improved von Ardenne ion source allowed well-focused beams of argon ions with a current density of 1 mA/cm^2 at the energy $E_0 = 10$ keV to be obtained. The ion beam, after acceleration and focusing by a single electrostatic lens, passed through a hole in a quartz screen and bombarded the sample. A glass collector, on which the sputtered particles were collected, was placed parallel to the studied surface in front of the sample. Sputtered particles produced by normal ($\varphi = 0°$) or inclined incidence of the ion beam were deposited on this collector. The collector was used to determine the orientation of single crystal samples using the sputtered spot patterns. To obtain sufficiently clear and contrast images of buried deformation areas under the surface, the time of sputtering and the ion current density were chosen experimentally.

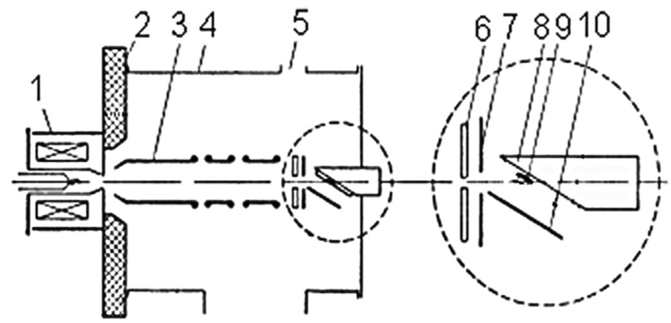

Fig. 1. Schematic diagram of sputtering system 1 – ion source, 2 – insulator, 3 – electrostatic lens, 4 – container, 5 – window, 6 – quartz screen, 7 and 10 – glass collectors, 8 – holder, 9 – specimen.

The topography of the surface has been studied using a scanning LEO-1455 (Carl Zeiss) electron microscope.

3. Results and discussion

3.1. Energy dependencies of sputtering under crystal deformation and without it

3.1.1. Tin bronze $Cu_{87}Sn_{13}$

By MD simulation we investigated the energy dependence of sputtering yield $Y(E_0)$ for polycrystal and single crystal disordered tin bronze $Cu_{87}Sn_{13}$ alloy before and after deformation. The results are shown in Fig. 2a. For comparison, the same data is shown for the (001) face of a single crystal, Fig. 2b.

For non-deformed polycrystals of $Cu_{87}Sn_{13}$ alloy and for the (001) face the dependences of $Y(E_0)$ are similar to those observed for copper samples [3], in terms of both the shape of curves and values of sputtering coefficients. For samples after deformation the shape of $Y_c(E_0)$ dependences remains the same, but the sputtering yield increases because of the increase in the bulk density of the sample.

The sputtering yield of the polycrystal sample increases greatly under deformation. At $E_0 = 7$ keV, the changes of sputtering yield after deformation are: ΔY ~25% for $Cu_{87}Sn_{13}$, ~22% for Cu and about 3% for Sn. This smaller influence of deformation when sputtering Sn is defined by the low content and a chaotic arrangement of atoms of tin in the disordered $Cu_{87}Sn_{13}$ alloy. For the (001) face the values ΔY ~ 15% for $Cu_{87}Sn_{13}$, 13% for Cu and 2% for Sn.

Taking into account segregation of tin bronze leads to a small reduction of sputtering coefficient $Y(E_0)$ both before and after crystal deformation. This is explained by the smaller value of sputtering yield of tin (which forms the top layer under segregation), than that of copper.

Fig. 3 shows the difference (ΔY) of energy dependence between sputtering yield before and after deformation for a tin-bronze polycrystal.

It is seen that for energies of 7 ÷ 10 keV the value of ΔY practically does not differ from its maximum value. The same results were obtained when irradiating by Kr^+ ions. Therefore, these energies of ions need to be used when probing the buried layers by sputtering.

It should be noted that the deposited energy-depth distribution