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Electron energy loss spectroscopy study of the effect of low-energy Ar^+-ion bombardment on the surface structure and composition of $Pt_{80}Co_{20}$ (1 1 1) alloy

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Abstract

Electron energy loss spectroscopy has been employed for investigation of the effect of 600 eV Ar^+-ion irradiation in the dose range 7×10^{16}–4×10^{17} ions/cm^2 on the atomic structure and surface composition of alloy $Pt_{80}Co_{20}$(1 1 1). A method of the layer-by-layer reconstruction of the lattice interplanar distance changes based on the analysis of the plasmon spectra excitation was proposed. The ion bombardment was shown to result in a non-monotonic variation of the lattice interplanar distance due to formation of the stable defects, with the topmost layer being in the state of compression. Using the ionization energy loss spectra, a layer-by-layer concentration profile of the alloy components was reconstructed for different doses of ion irradiation of the surface. The Ar^+-ion bombardment of the alloy was found to result in the preferential sputtering of Co and in the enrichment of the near-surface region by Pt atoms with formation of an altered layer, which is characterized by a non-monotonic concentration profile dependent on the irradiation dose. The results obtained are discussed in the framework of the models of preferential sputtering and radiation-induced segregation.

Keywords: $Pt_{80}Co_{20}$(1 1 1) alloy; Ion bombardment; EELS; Interplanar distance relaxation; Preferential sputtering; Segregation

1. Introduction

Ion irradiation is widely used as a tool for purposeful modification of the surface layers of alloys. An ion beam interacting with a material inevitably brings about an alteration of different properties of the surface. First of all, the atomic structure is disturbed because of the generation of various types of defects. In particular, at low ion doses, point defects are produced; with increasing ion fluence the damage level increases and a total change of the surface morphology can occur. In the case of alloys the disturbance of the atomic structure is supplemented by a change of the elemental composition in the near-surface region. This effect

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is mostly associated with preferential sputtering of components of the alloy, which can be caused by differences in their sputtering coefficients, atomic mass and surface binding energies. The defects and defect fluxes towards the surface arising under ion bombardment can promote the radiation-induced segregation of one of the components thus resulting in the redistribution of the alloy components in the near-surface layer in addition to the preferential sputtering [1]. A delicate in-depth investigation of such type of segregation requires non-destructive methods of surface analysis to be used [2,3].

For further progress in nanotechnology, microelectronics and catalysis a more detailed study, at the atomic-electronic level, of surface properties of the materials being used is needed. Among these materials are, in particular, the noble-metal-based alloys of the type Pt–Me (where Me: Co, Cu, Ni, Fe) [4,5]. The use of the inert-gas ion bombardment is a promising way of controlled modification of the surface properties of materials.

The aim of the present work was to study, using secondary-electron spectroscopic techniques, the influence of the low-energy Ar^+-ion irradiation on the atomic structure and surface composition of the $Pt_{80}Co_{20}(1\,1\,1)$ alloy.

2. Experimental

A single-crystal sample of the $Pt_{80}Co_{20}(1\,1\,1)$ alloy was investigated in a UHV instrument equipped with electron and ion guns and with a four-grid energy analyser (LEED optics) with an energy resolution of ~0.3% [6]. The atomically clean surface of the sample was produced by several cycles of sputtering by 600 eV Ar^+ ions and annealing at a temperature of $T = 700\,^{\circ}C$ for several hours. The cleanliness and structure of the surface were monitored by Auger electron spectroscopy (AES) and low-energy electron diffraction (LEED). The process of cleaning was terminated when AES showed no traces of carbon, oxygen and sulphur. The distinct diffraction patterns from the (1 1 1) face forming a regular hexahedron indicated a (1×1) bulk structure [7].

The alloy was irradiated along the normal to the surface with a 600 eV Ar^+-ion beam 4 mm in diameter at a current density of $5\,\mu A/cm^2$ produced by an electron-impact ion source for ionization of the working gas (argon of 99.999% purity). The following ion doses were used: $D_1 = 7 \times 10^{16}$, $D_2 = 2 \times 10^{17}$, $D_3 = 3 \times 10^{17}$ and $D_4 = 4 \times 10^{17}$ ions/cm^2. After each dose of irradiation the cleanliness of the surface was checked by AES, and electron energy loss (EEL) spectra were acquired. For each energy of primary electrons, the EEL spectra were recorded in three different points of the sample and their reproducibility was within 5%.

3. Results and discussion

3.1. Ion irradiation and interplanar distance

As the secondary electron emission is sensitive to the state of the surface atomic and electronic structure of materials [2,3], this phenomenon was employed for studying the $Pt_{80}Co_{20}(1\,1\,1)$ surface irradiated by Ar^+ ions with different doses. The EEL spectra measured in the range of energies of primary electrons $E_0 = 200$–600 eV displayed losses caused by excitation of surface and bulk plasmons and by ionization of core levels of platinum ($\Delta E^{Pt}_{O_{2,3}} = 54$ eV) and cobalt ($\Delta E^{Co}_{M_{2,3}} = 62$ eV) [8]. As an example, in Fig. 1 are shown the EEL spectra of bulk plasmons excited by electrons with an energy of 250 eV in the $Pt_{80}Co_{20}(1\,1\,1)$ alloy before and after 600 eV Ar^+-ion bombardment with different doses. It can be seen that ion irradiation results in an essential change of the bulk plasmon energy.

Fig. 2 demonstrates the energy of a bulk plasmon, E^b_{pl}, versus energy of primary electrons, E_0 for the initial surface of the alloy and for the surface after bombardment by different ion doses. The slowly decreasing dependence $E^b_{pl}(E_0)$ for the non-irradiated surface changed after bombardment with a dose of $D_1 = 7 \times 10^{16}$ and a shift of E^b_{pl} towards higher energy and nearly linear growth of E^b_{pl} with increasing E_0 were observed. At higher irradiation doses the bulk plasmon energy increases with energy of primary electrons in a non-monotonic way. For the alloy irradiated