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Oxygen induced segregation of aluminum to α-Cu–Al(1 0 0) alloy surfaces studied by low energy ion scattering and X-ray photoelectron spectroscopy

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Abstract

The effect of annealing temperature on the surface composition of α-Cu–Al(1 0 0) alloys for aluminum concentrations of 5, 12 and 17 at% was investigated using X-ray photoelectron spectroscopy (XPS) and low energy ion scattering (LEIS). Two initial states of the sample surfaces were examined: sputter-cleaned and oxidized. The effect of annealing temperature on segregation is different for sputter-cleaned and oxidized samples. Aluminum preferential sputtering and strong oxygen induced aluminum segregation were detected on all examined samples. Whilst for the sputter-cleaned surfaces a small thermal induced segregation was observed, the combination of annealing and oxygen exposure resulted in aluminum enrichment in the 100–300% range relative to the bulk concentration. The segregation rate is proportional to the aluminum concentration for sputter-cleaned surfaces and displays a maximum for the oxidized α-Cu–Al(12 at.%)(1 0 0) surface.

Keywords: Low energy ion scattering (LEIS); Induced segregation; Cu–Al alloy; X-ray photoelectron spectroscopy (XPS); Oxidation

1. Introduction

The possibility of selective enrichment of one alloy constituent at the surface was predicted and established for a large variety of binary alloy systems [1]. This phenomenon, known as surface segregation, has attracted recent interest because of its substantial importance in the areas of metallurgy, heterogeneous catalysis and microelectronics [2,3]. Alloys composed of a simple metal (Al) and a transition metal (Cu) attract scientific interest as model systems in heterogeneous catalysis. α-Cu–Al has long been a prototype for alloy surface studies [1]. Recently there has been renewed interest in segregation of Al in Cu–Al alloys because of its influences on Cu properties (such as low resistance, diffusion, adhesion and corrosion resistance) as a conductor in microelectronic circuits [2,3]. The α-phase of the Cu–Al alloy exists at a composition ranging from 0 to 19.6 at.% Al. X-ray diffraction experiments show that a short range order (SRO) is established for Al concentrations larger than ∼16 at.% Al. For lower concentrations the alloy is considered to be an ideal solid solution [4]. However, more recent measurements of elastic shear coefficient give evidence that the onset of SRO may be as low as 7 at.% Al [5].

The surface composition and reactivity of α-Cu–Al(1 0 0) alloys were studied by AES [6–10], XPS [6,7,9], UPS [11], LEED [6] and LEIS [12–14] for different Al concentrations. It was concluded that weak Al segregation occurs on the clean surfaces [7,13,14], but very strong oxygen induced Al segregation has been observed for these alloys surfaces [8,11,12]. Oxygen bonds to Al during initial exposure, followed by bonding to Cu and Al atoms simultaneously [8,9,12]. Upon heating the oxidized surface to 573 °C, oxygen that was previously bonded to Cu re-bonds to thermally segregated Al atoms and a thin alumina layer is formed [8–13]. However, on clean surface, Al islands do

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not form [9]. Preferential sputtering of Al results in an increase of the Cu surface concentration up to 25% of its nominal bulk value [13,14].

In this study we investigate the surface composition of α-Cu–Al(5, 12, 17 at.%)(1 0 0) alloys as a function of annealing temperature for the sputter-cleaned and oxidized surfaces by low energy ion scattering (LEIS) and X-ray photoelectron spectroscopy (XPS). LEIS is a highly surface sensitive technique for structure and composition studies [15,16]. XPS experiments give chemical information about bonding sites of oxygen at different stages of the experiment. Combining these two techniques allows us to study the variations in surface composition, bonding and segregation process.

2. Experimental procedures

All samples (2 mm thick and 8 mm in diameter) were cut from single crystals grown by the Brigman method and oriented within 1° to the (1 0 0) plane. Prior to insertion into the UHV chamber quite common polishing and cleaning procedures were applied [8]. A differentially pumped ion gun was used for sample sputtering with 5 keV Ar^+ ions at a scattering angle of 135° and chamber pressure of 5×10^{-7} Torr. The base pressure of the UHV chamber was $\sim 1 \times 10^{-9}$ Torr.

Experiments as a function of temperature were performed in the following way: Initially sputter-cleaned samples were measured at room temperature. After heating at a particular temperature for 10 min, the samples were cooled down to room temperature and measured again. This procedure was repeated up to 700 K in 50 K increments without additional sputtering. The sample temperature was measured with an infrared pyrometer (Micron M90Q; temperature resolution of 1 K and accuracy of about 0.5%).

The LEIS spectra were recorded using a primary He^+ energy of 1 keV at room temperature. The full width at half maximum (FWHM) of the incident ion energy was about 2 eV. The chamber pressure during LEIS measurements was kept at 1×10^{-7} Torr of He partial pressure. It is believed [14,17] that during such LEIS experiments less than 1% of a monolayer was removed. XPS experiments were carried out using non-monochromatic Al Kα (1486.6 eV) radiation at normal emission.

All spectroscopic measurements were recorded using a SPECS hemispherical electron analyzer operated at a pass-energy of 97 eV. The positive ion spectra were detected by operating the spectrometer in an inverse polarity mode. Controlled amounts of oxygen (99.999% O_2) were introduced into the UHV chamber via a leak valve.

3. Results

3.1. Surface composition analyzed by LEIS: the effect of annealing the sputter-cleaned surfaces

To determine the compositions of the first layer by He^+ LEIS, suitable scattering geometries should be chosen. The incidence and scattering angles in our experiment were, respectively, 45° and 135°. The ion energy was 1 keV which allows us to assume mostly first layer sensitivity. To reduce the influence of experimental parameters on the data analysis the intensities of all LEIS spectra were normalized to one.

The normalized LEIS spectra measured from the sputter-cleaned α-Cu–Al(1 0 0) surfaces of 5, 12 and 17 at.% Al as a function of annealing temperature are shown in Fig. 1a, b and c, respectively. Peaks due to He^+ ions elastically scattered from Cu, Al and O surface sites can be easily identified and are marked in the spectra. The peak's energy position and intensities are in agreement with previous results and calculations using a simple binary elastic scattering model [13,18].

As can be seen from Fig. 1a–c the Al peak increases with temperature for all samples. Unfortunately, the O peak also somewhat increases during annealing time. This occurs as a result of a small oxygen background in the system and very reactive surfaces. The background oxygen can be estimated by taking into consideration the base pressure of our experiments, the oxygen partial pressure in the system and the time involved in carrying out the annealing and the spectroscopic measurements. We estimate that the oxygen background exposure during an experiment is ∼1 L. Due to adsorption of oxygen and possible shadowing effects it is very difficult to perform quantitative treatment of the LEIS results to derive the Al concentration of the upper surface of the alloys. However, a comparative discussion of the LEIS spectra measured for different alloys is possible. It is usually assumed that the ion survival probability in the scattering event equals one, which actually means that the scattering yield from one atom is not affected by neighboring atoms [13]. Based on this assumption the ratios of Al to Cu and O to Cu peaks are proportional to the concentration ratios of these elements on the surfaces of the alloys. The Al/Cu peaks intensity ratios for the alloys are shown in Fig. 2a as a function of annealing temperature. For all samples, increasing annealing temperature results in the increase of the Al/Cu ratio. A larger nominal concentration of aluminum in the alloy results in a more significant increase in the Al/Cu ratio. The O/Cu peaks intensity ratios are shown in Fig. 2b. As seen from this figure the values measured for the α-Cu–Al(5 at.%)(1 0 0) and α-Cu–Al(12 at.%)(1 0 0) surfaces are proportional to aluminum concentration in the alloys and increase slightly with temperature most likely due to oxygen background adsorption. For the α-Cu–Al(17 at.%)(1 0 0) surface the O/Cu ratio fluctuates within the range of error around the value at room temperature.

3.2. Surface composition analyzed by LEIS: the effect of annealing the oxidized surfaces

LEIS spectra from α-Cu–Al(5, 12, 17 at.%)(1 0 0) alloy surfaces after exposure to 160 L of oxygen as a function of annealing temperature are shown in Fig. 3a–c. The