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Surface alloying of immiscible metals: Mo on Au(1 1 1) studied by STM

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Abstract

Alloy formation and growth of regular arrays of Mo nanostructures were discovered during studies of Mo growth on Au(1 1 1) surfaces. The behavior of Mo deposited via physical vapor deposition was studied as a function of temperature using scanning tunneling microscopy (STM) and Auger electron spectroscopy (AES). Between 300 K and 450 K, regular arrays of Mo clusters form by preferential nucleation of Mo at elbow sites of the herringbone reconstruction. The Mo clusters are 1 or 2 atomic layers high, and are stable upon annealing up to at least 600 K. For deposition temperatures at or above 525 K, substitutional surface alloying competes with nucleation on terrace sites. The formation of a surface alloy is inferred from the evolution of a serrated step-edge morphology caused by attachment of ejected Au atoms, and a decrease of the Mo surface coverage, as well as the appearance of vacancy islands in the Au surface after chemically-driven de-alloying of Mo. The formation of a Mo–Au surface alloy is quite remarkable as Mo and Au are bulk immiscible. Even surface alloying would not be expected from the viewpoint of stress relaxation.
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Keywords: Scanning tunneling microscopy; Auger electron spectroscopy; Surface chemical reaction; Gold; Molybdenum; Molybdenum oxides

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1. Introduction

Recently, the formation of two-dimensional surface alloys has attracted considerable interest due to its technological relevance in various fields such as heterogeneous catalysis, corrosion, surface

hardening, and bonding [1–21]. Surface alloying is a promising means to modify the characteristics of a surface and, thus, to design surfaces with unique electronic, catalytic and mechanical properties. The formation of surface alloys is not limited to metal combinations which are miscible in the bulk, but is also observed for a variety of immiscible metal combinations, such as noble metals (Cu, Ag, Au) on refractory metals (Mo, W) and vice versa [1,3,4,7,10,11,15].

Although bulk alloying is well understood, the driving forces for the formation of surface alloys are still a matter of investigation, in particular in the case of immiscible systems. Various models have been proposed in the literature. For example, Tersoff [5] attributed the formation of surface alloys between immiscible elements with an atomic size mismatch, such as Au on Ni, to a reduced strain energy of the misfitting atoms at the surface relative to the bulk. In case of the Cu/W(100) system, the formation of a substitutional surface alloy has been explained in terms of a $c(2 \times 2)/W(100)$ vacancy structure, stabilized by Cu [4]. More recently, first principles calculations revealed that surface alloying of noble metals (Cu, Ag, Au) with W(001) and Mo(001) surfaces is caused by the difference in electronegativity [7].

Recently, we investigated the deposition of Mo on Au(111) from a $Mo(CO)_6$ precursor. The chemical vapor deposition (CVD) approach leads to preferential nucleation of Mo clusters at step edges. Although Mo/Au is a bulk immiscible system, there is evidence for alloying/intermixing based on the observation of holes that develop in the Au substrate after Mo deposition [22,23]. Further evidence for the intermixing of Mo and Au is that the deposited Mo clusters exhibit a reduced reactivity towards dissociation of O_2 or CO compared to bulk Mo [1]. The results discussed above are also consistent with recent DFT calculations which predict that Mo on Au(111) prefers to be embedded in the Au surface rather than being adsorbed on the surface [1,24]. However, Mo–Au intermixing should further increase the tensile stress of the Au(111) surface (atomic size mismatch of ~5%) and therefore make surface alloying unfavorable [5,25].

The combination of its inertness and its regular dislocation pattern (known as herringbone reconstruction) makes the Au(111) surface an ideal template for self-organized growth of nanostructures. The reconstruction mechanism has been described in more detail elsewhere [26,27]. Briefly, the Au(111) surface is uniaxially contracted (4.2%) along the close-packed [1–10] directions leading to fcc and hcp stacking regions that are separated by dislocation lines. In addition, a regular alternation of uniaxially contracted domains allows a more isotropic contraction of the surface layer. This leads to the well known zigzag (chevron or herringbone) pattern, where the bending points (elbows) form a periodic network of dislocations. Indeed, previous studies of the physical vapor deposition (PVD) of Fe [28], Co [29], Mo [30] and Ni [31] on the Au(111) herringbone have demonstrated that preferential nucleation of these metals occurs at the elbows.

In the present paper, we describe the formation of a substitutional Mo–Au surface alloy via PVD of Mo on Au(111) as a function of the deposition temperature. The Mo induced changes of the surface morphology and surface composition are characterized by scanning tunneling microscopy (STM) and Auger electron spectroscopy (AES). Our results shed new light on the reduced reactivity of Mo clusters on Au(111) surfaces.

2. Experimental

All experiments were performed in a commercial ultrahigh vacuum (UHV) system with a base pressure of 5×10^{-11} mbar. The system has separate compartments for sample preparation, e.g. Mo evaporation, and sample characterization. The latter is equipped with commercial instrumentation for scanning probe microscopy (SPM) (Omicron), Auger electron spectroscopy (AES) and low energy electron diffraction (LEED). The Au(111) sample was cleaned by cycles of Ar^+ sputtering at room temperature (60 min/1000 eV/ 4 μA) and annealing (10 min at 900 K followed by 1 h at 700 K). This procedure was repeated until no contaminants were detected by means of AES. The sample was radiatively heated, and the temperature was calibrated using a Cr–Al thermocouple attached to the sample holder.