

# Photoemission study of glycine adsorption on Cu/Au(111) interfaces

Xueying Zhao, José Rodríguez \*

*Chemistry Department, Brookhaven National Laboratory, Upton, NY 11973, USA*

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## Abstract

The adsorption of glycine on Au(111) pre-deposited with different amounts of Cu was investigated with both conventional X-ray photoelectron spectroscopy (XPS) and synchrotron-based photoemission. In the Cu submonolayer range, glycine physically adsorbs on the Cu/Au(111) surfaces in its zwitterionic form ( $\text{NH}_3^+\text{CH}_2\text{COO}^-$ ) and completely desorbs at 350 K. The C 1s, O 1s and N 1s core level binding energies monotonically increase with Cu coverage. This indicates that, in the Cu submonolayer range, the admetal is alloyed with Au rather than forming overlayers on the Au(111) substrate, consistent with our recent experimental and theoretical results [X. Zhao, P. Liu, J. Hrbek, J.A. Rodríguez, M. Pérez, Surf. Sci. 592 (2005) 25]. Upon increasing the amount of deposited Cu over 1 ML, part of the glycine overlayer transforms from the zwitterionic form to the anionic form ( $\text{NH}_2\text{CH}_2\text{COO}^-$ ) and adsorbs chemically on the Cu/Au(111) surface with the N 1s binding energy shifted by  $-2.3$  eV. When the amount of deposited Cu is at 3.0 or 6.0 ML, the intensity of the N 1s chemisorption peak increases with aging time at 300 K. It indicates that glycine adsorption induces Cu segregation from the subsurface region onto the top layer of the substrate. Judging from the initial N 1s peak intensities, it is concluded that 64% and 36% of the top layer are still occupied by Au atoms before glycine adsorption even when the amounts of deposited Cu are 3.0 and 6.0 ML, respectively. On the Au(111) surface pre-dosed with 6.0 ML of Cu, part of the chemisorbed glycine will desorb and part will decompose upon heating to 450–500 K. In addition, about 20% of the glycine exists in the neutral form when the glycine overlayer was dosed on Cu/Au(111) held at 100 K.

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## 1. Introduction

Amino acids are the typical building blocks of biological molecules, and its adsorption on various solid surfaces has attracted great attention in recent decades. They can be used as model molecules for adsorption of proteins and peptides on various surfaces. The adsorption of glycine, the simplest amino acid, has been extensively studied on various solid substrates. Many studies have been done on noble metals, such as Cu [1–8], Ag [2,9], Au [2,10–12], and Pt [13,14]. The adsorption configuration of glycine depends on the chemical properties of a given substrate. It has been demonstrated that on Cu surfaces, glycine chem-

ically adsorbs in the anion form:  $\text{NH}_2\text{CH}_2\text{COO}^-$  [2,6], while on Au and Ag surfaces, glycine physically exists in the zwitterionic form:  $\text{NH}_3^+\text{CH}_2\text{COO}^-$  [2,9–11]. Very few researches have been done on binary metal surfaces, except one on NiAl(110) [15] and one on Ag/Cu(001) and (111) [16]. On the NiAl(110) surface, glycine preferentially attacks the aluminum sites upon adsorption. In the Ag/Cu(001) and (111) cases, due to the inability for Ag and Cu to form an alloy, a spillover phenomenon was observed on the Ag partially covered Cu(001) and (111) surfaces. Glycine adsorbates first deprotonate in the anionic form on the Cu areas and then diffuse to the Ag areas to chemically adsorb [16].

The phase diagram for the Cu–Au binary system indicates that they can form solid solutions (i.e., alloys) such as AuCu or AuCu<sub>3</sub> [17]. Thus, if Cu is deposited on Au surfaces, alloy formation can be expected. In the

\* Corresponding author. Fax: +1 631 344 5815.  
E-mail address: [rodriguez@bnl.gov](mailto:rodriguez@bnl.gov) (J. Rodríguez).

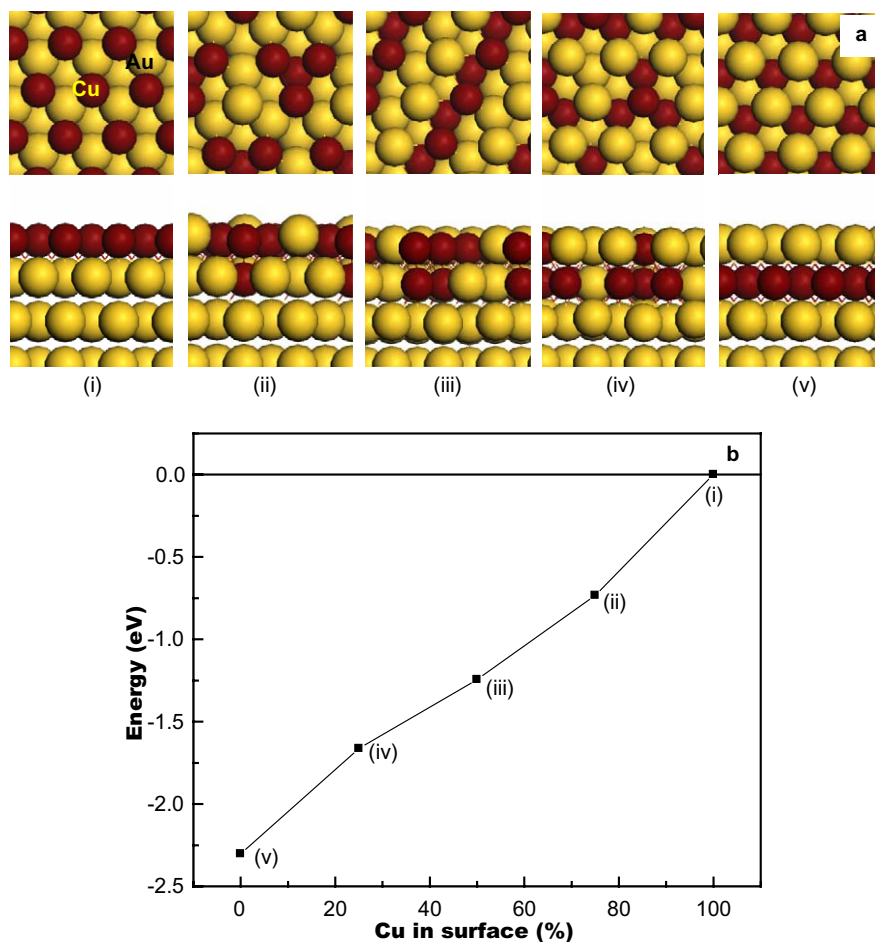


Fig. 1. (a) Various optimized configurations for depositing one monolayer of Cu in a Au(111) surface [23]. For each configuration, the upper and the lower drawings display the top and side view, respectively. “i” to “v” corresponds to different configurations with a Cu concentration ( $\theta_{Cu}$ ) in the surface of 100%, 75%, 50%, 25% and 0%, respectively. (b) Calculated surface stability of Cu/Au(111) as a function of  $\theta_{Cu}$  [23]. Here the stability is expressed in reference to the case of a Cu overlayer on Au(111) with a Cu concentration in the surface of 100% as shown in (i) of (a).

electrochemical deposition of Cu on Au(111) electrodes, no intermixing between Cu and Au was reported [18–21]. Under UHV conditions, it was reported that Cu adsorbed pseudomorphically on Au(111) at submonolayer coverages [22]. Intermixing happened above one monolayer coverage. This result was obtained by RHEED. But in submonolayer coverages, whether Cu really forms a pseudomorphic layer is questionable, because RHEED allows a structural analysis but not an element content analysis. Recent ISS experiments [23] clearly demonstrated that Cu intermixes with the Au(111) substrate at 300 K or higher temperature, but a substantial fraction of the Cu atoms stays on the Au(111) surface when the deposition is done at 100 K. DFT calculations for Cu/Au(111) further show that Cu atoms are more stable when penetrating into the substrate rather than sitting on the surface, as shown in Fig. 1 [23]. An adsorbate like atomic O breaks the Cu–Au alloys to form  $CuO_x$ , while the  $SO_2$  molecule interacts weakly with the Cu/Au(111) interfaces [23].

In this study, we investigated the behavior of glycine on Au(111) pre-covered with different amounts of Cu. Since Au and Cu are very miscible and glycine has quite different

adsorption forms on these metals, ensemble *affects* and surface segregation may play an important role for determining the chemical interactions in the glycine/Cu/Au(111) system.

## 2. Experimental

This study was conducted in a UHV chamber located at the end station of the U7A beamline in the National synchrotron light source (NSLS) at Brookhaven National Laboratory. Both conventional XPS and synchrotron-based photoemission ( $h\nu = 500$  eV) were used in this experiment. The UHV chamber, with a base pressure less than  $4 \times 10^{-10}$  Torr, is fitted with a hemispherical electron energy analyzer that has multi-channel detection, a quadrupole mass spectrometer (SRS-RGA), and a twin anode (Mg and Al) X-ray source. The combined energy resolution in the photoemission experiments was 0.3–0.4 eV. The binding energy values were determined with respect to the Fermi level. The Au(111) single crystal was held by two Ta heating legs of a manipulator [24]. The sample could be cooled down to 100 K by thermal contact with

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