



Full Length Article

Investigation of the structural anisotropy in a self-assembling glycinate layer on Cu(100) by scanning tunneling microscopy and density functional theory calculations



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ABSTRACT

Self-assembling organic molecule-metal interfaces exhibiting free-electron like (FEL) states offers an attractive bottom-up approach to fabricating materials for molecular electronics. Accomplishing this, however, requires detailed understanding of the fundamental driving mechanisms behind the self-assembly process. For instance, it is still unresolved as to why the adsorption of glycine ($[\text{NH}_2(\text{CH}_2)\text{COOH}]$) on isotropic Cu(100) single crystal surface leads, via deprotonation and self-assembly, to a glycinate ($[\text{NH}_2(\text{CH}_2)\text{COO}^-]$) layer that exhibits anisotropic FEL behavior. Here, we report on bias-dependent scanning tunneling microscopy (STM) experiments and density functional theory (DFT) calculations for glycine adsorption on Cu(100) single crystal surface. We find that after physical vapor deposition (PVD) of glycine on Cu(100), glycinate self-assembles into an overlayer exhibiting $c(2 \times 4)$ and $p(2 \times 4)$ symmetries with non-identical adsorption sites. Our findings underscore the intricacy of electrical conductivity in nanomolecular organic overlayers and the critical role the structural anisotropy at molecule-metal interface plays in the fabrication of materials for molecular electronics.

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1. Introduction

The self-assembly of organic molecules on metal surfaces has attracted increasing interest [1] since a bottom-up approach to building nanostructures offers several benefits over the top-down approach. In the field of molecular electronics, a great deal of attention has been recently paid to free-electron-like (FEL) states discovered at self-assembling molecule-metal interfaces. The FEL states in molecularly conducting systems typically exhibit an electron effective mass that is sensitive to the composition and structure of the adlayer. The electron effective mass, in turn, correlates with carrier mobility. By understanding how the metal substrate influences the conformation, reactivity, and bonding of organic layer, the carrier mobility in such systems could be tailored for specific purposes simply by modifying the substrate structure and composition.

Whereas clean metal surfaces, in general, do not exhibit FEL behavior [2], well-ordered molecular layers on metal surfaces may display FEL properties, thus making them conducive to fabrication of molecular electronics. For instance, adsorption of perylene-3,4,9,10-tetracarboxylic-3,4,9,10-dianhydride (PTCDA) on Ag(111) surface leads to the formation of a confined *isotropic* 2D interface state via hybridization of the lowest unoccupied molecular state of PTCDA and the well-known Ag(111) surface state [2–6]. Even more interestingly, an *anisotropic* FEL state can be induced in molecular layers on electronically *isotropic* substrates. In particular, upon adsorption at room temperature glycine ($[\text{NH}_2(\text{CH}_2)\text{COOH}]$), the simplest of amino acids, undergoes a deprotonation reaction on Cu(100) and forms a well-ordered $p(2 \times 4)$ phase of glycinate ($[\text{NH}_2(\text{CH}_2)\text{COO}^-]$) molecules [7–18].

In their recent scanning tunneling microscopy and spectroscopy (STM/STS) experiments Kanazawa et al. reported strong *anisotropic* FEL dispersion relations for the $p(2 \times 4)$ phase, with the effective masses being different by one order of magnitude in $[1\ 1\ 0]$ and $[-1\ 1\ 0]$ directions [17]. The prospect of one being able to exert control over the degree of anisotropy in total or local electrical conductance by modifying the structure of molecular layers is an attractive

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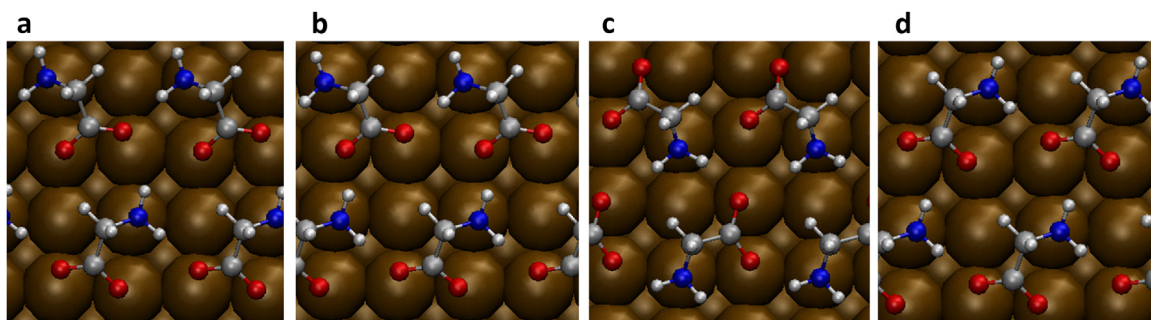


Fig. 1. Earlier proposed molecular configuration for glycinate on Cu(100) [17]. Proposed alternatives are shown for $p(2 \times 4)$, Str-d (a), Str-h (b) and Str-3 (c) and $c(2 \times 4)$ (d) phases. For details see the text. Ochre, gray, blue, red and white spheres represent Cu, C, N, O and H respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

one. To accomplish this goal does, however, require molecular level knowledge of the driving mechanisms behind the self-assembly process, details of molecular bonding and electronic structure.

The general consensus is that glycinate bonds with the Cu(100) surface in a tridentate configuration with the N atom of the amino group and both O atoms of the carboxylate group bound to the metal substrate. The first structural model by Zhao et al. (called Str-d hereafter) was proposed for the $p(2 \times 4)$ phase on the basis of low-energy electron diffraction (LEED) and scanning tunneling microscopy (STM) [8]. The adsorption geometry is schematically illustrated in Fig. 1a. Although free glycinate does not exhibit chirality, two enantiomeric isomers are possible for glycinate adsorbed on Cu(100). Utilizing photoelectron diffraction (PhD) and reflection-absorption infrared spectroscopy, a slightly modified $p(2 \times 4)$ structure (Str-h, see Fig. 1b) was proposed by Kang et al. and Efstathiou and Woodruff [13,15]. In this structure the adsorption site of the molecules is identical to the adsorption site in the model of Fig. 1a. Density functional theory (DFT) based calculations performed by Mae and Morikawa argued for the structural model Str-d rather than the Str-h [14]. More recently, in an exhaustive DFT based computational study Zhi-Xin Hu et al. [18] concluded that the most likely structure of the $p(2 \times 4)$ phase is the arrangement shown in Fig. 1c (Str-3), where the O–O line in the glycine molecule is oriented roughly parallel to the longer edge of the $p(2 \times 4)$ unit cell. In this model, all molecules occupy identical surface sites and display the same conformation. However, some earlier experimental results hint of a more complicated scenario: there are two non-equivalent glycinate-related protrusions in STM images of the $p(2 \times 4)$ structure (e.g. see Fig. 2e in Ref. [16] and Fig. 4 in Ref. [18]). It can be clearly seen in Fig. 1a–c that heterochirality of glycinate in the earlier $p(2 \times 4)$ models cannot account for this STM observation, because of the mirror symmetry of the two adsorption configurations of the molecule. Therefore, the heterochirality cannot reconcile the earlier structural models with the experimental STM results. Moreover, simulated STM images for the earlier models give rise to the identical STM protrusions. This discrepancy is a serious obstacle to understanding the $p(2 \times 4)$ structure. Thus, in spite of considerable experimental and theoretical studies, the exact molecular arrangement of the $p(2 \times 4)$ glycinate phase so far remains under debate.

In this study we revisit the glycine's adsorption on Cu(100) by conducting *bias-dependent* STM measurements and DFT calculations. Our experimental findings show that the analysis of earlier STM results have missed evidence for two non-identical adsorption sites, which, in line with DFT calculations, suggest a novel asymmetrical $p(2 \times 4)$ model for glycine/Cu(100). In particular, two non-equivalent protrusions were observed in the $p(2 \times 4)$ structure, which were previously ascribed to STM tip effects or the heterochirality of the glycine molecules sitting at equivalent sites. However,

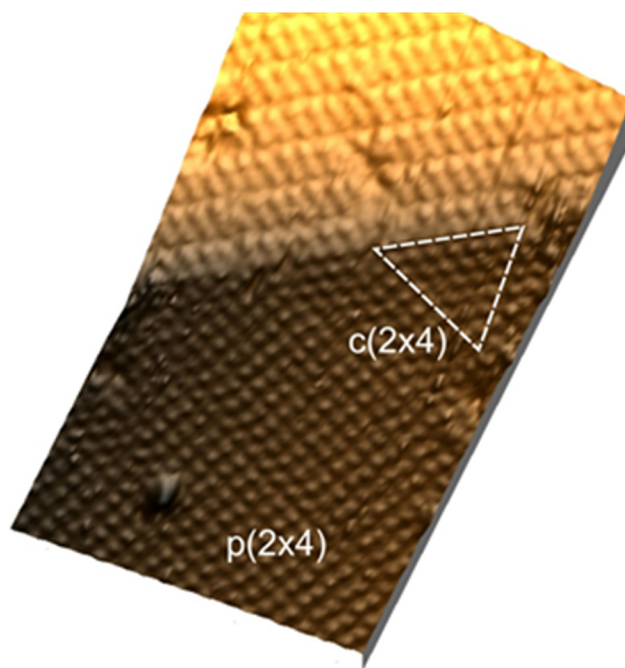


Fig. 2. 3D filled-state STM image of the glycinate/Cu(100) surface at 0.60 ML coverage. One of domains of the $c(2 \times 4)$ structure is outlined. The sample bias voltage is -1.1 V and the tunneling current is 0.2 nA. The area is 18.8 nm \times 11 nm.

our results indicated that the glycine molecules adsorbed on two non-identical sites of Cu(100) in the $p(2 \times 4)$ phase, which also leads to non-equivalent protrusions. Our results are consistent with the earlier STM, LEED, and PhD results in terms of molecular geometry. The non-identical adsorption sites thus offer a plausible explanation to the anisotropy of the surface and also suggest that glycine may have more than one $p(2 \times 4)$ phase on the surface.

2. Materials and methods

All experiments were performed in situ in an ultrahigh vacuum (UHV) system with a base pressure of $<1 \times 10^{-10}$ mbar, equipped with a scanning tunneling microscope (UHV 300 Series VT-STM, RHK Technology Inc.) and an x-ray photoelectron spectrometer (ESCA3000 XPS, VG Microtech Inc.). The UHV system is described in more detail elsewhere [19]. A Cu(100) sample of 6n purity, cut to $\pm 0.5^\circ$ tolerance, was used. The Cu(100) surface was cleaned by repeated cycles of 10 min Ar^+ ion bombardment (2.0 kV, $15 \mu\text{A}$) and 10 min electron beam annealing at 700 K. The sample temperature was monitored using *n*-type thermocouple attached in contact with the sample. The surface cleanliness was verified by X-ray

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