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Infrared reflection absorption study of carbon monoxide adsorption on Cu(1 0 0)–*c*(2 × 2)–Pd surfaces formed by palladium vacuum-depositions at various temperatures

T. Wadayama *, H. Osano, K. Hamade, H. Yoshida, T. Maeyama

Department of Materials Science, Graduate School of Engineering Tohoku University, Sendai 980-8579, Japan

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Abstract

Using infrared reflection absorption spectroscopy (IRRAS) and temperature programmed desorption (TPD), we investigated carbon monoxide (CO) adsorption and desorption behaviors on atomic checkerboard structures of Cu and Pd formed by Pd vacuum deposition at various temperatures of Cu(1 0 0). The 0.15-nm-thick Pd deposition onto a clean Cu(1 0 0) surface at room temperature (RT) showed a clear *c*(2 × 2) low-energy electron diffraction (LEED) pattern, i.e. Cu(1 0 0)–*c*(2 × 2)–Pd. The RT-CO exposure to the *c*(2 × 2) surfaces resulted in IRRAS absorption caused by CO adsorbed on the on-top sites of Pd. The LEED patterns of the Pd-deposited Cu(1 0 0) at higher substrate temperatures revealed less-contrasted *c*(2 × 2) patterns. The IRRAS intensities of the linearly bonded CO bands on 373-K-, 473-K-, and 673-K-deposited *c*(2 × 2) surfaces are, respectively, 25%, 22%, and 10% less intense than those on the RT-deposited surface, indicating that Pd coverages at the outermost *c*(2 × 2) surfaces decrease with increasing deposition temperature. In the initial stage of the 90-K-CO exposure to the RT surface, the band attributable to CO bonded to the Pd emerged at 2067 cm^{-1} and shifted to higher frequencies with increasing CO exposure. At saturation coverage, the band was located at 2093 cm^{-1}. In contrast, two distinct bands around 2090 cm^{-1} were apparent on the spectrum of the 473-K-deposited surface: the CO saturation spectrum was dominated by an apparent single absorption at 2090 cm^{-1} for the 673-K-deposited surface. The TPD spectra of the surfaces showed peaks at around 200 and 300 K, which were ascribable respectively to Cu–CO and Pd–CO. Taking into account the TPD and IRRAS results, we discuss the adsorption–desorption behaviors of CO on the ordered checkerboard structures.

Keywords: Palladium; Copper; Infrared absorption spectroscopy; Low energy electron diffraction (LEED); Thermal desorption spectroscopy; Carbon monoxide; Single crystal surfaces

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1. Introduction

Ordered alloy surfaces formed through vacuum deposition of a metal on different metal single crystal substrates are typical surface models for studies of bimetallic epitaxial growth. Furthermore, the ordered bimetallic alloy surfaces serve as an atomic template for examining surface chemical properties, particularly in the field of catalysis [1–5]. Molecular beam epitaxy (MBE) and ultra-high-vacuum (UHV) techniques make it possible to create ordered bimetallic alloy surface systems.

Copper–palladium bimetallic alloys have been particularly subjected to scrutiny because the alloys are useful for reducing automobile-exhaust pollutants [6] and for methanol synthesis [7]. The Cu–Pd alloys have two ordered structures: B2 of Cu–Pd and $L1_2$ of Cu_3Pd [8]. One might expect that low coverage of Pd deposition onto Cu(1 0 0) brings about a surface atomic structure corresponding to the surface orientation of Cu_3Pd. Actually, the top surface of the atomically ordered surface alloy, Cu(1 0 0)–*c*(2 × 2)–Pd, comprises a checkerboard structure of Cu and Pd

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* Corresponding author. Fax: +81 22 795 7319.
E-mail address: wadayamt@material.tohoku.ac.jp (T. Wadayama).

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atoms. The surface is formed by a ca. 0.5 monolayer (ML)-thick Pd deposition on a clean Cu(100) substrate surface at room temperature (RT) [9–15]. To date, several papers have been published for carbon monoxide (CO) adsorption onto the RT-Pd-deposited $c(2\times2)$ surfaces using ultra-violet photoelectron spectroscopy (UPS) and high-resolution electron energy loss (HREELS) spectroscopy [14,16]. Although a consensus holds that the outermost surface of Cu(100)–$c(2\times2)$–Pd comprises $c(2\times2)$ Cu–Pd alloy [9–15], the coverage of Pd on the top surface corresponding to the optimum $c(2\times2)$ alloy surface remains unclear. Furthermore, the deposition temperature of Pd on Cu(100) should affect the Pd coverage on and beneath the top surface of the alloy. Recent low-energy electron microscopic (LEEM) observations conducted by Hannon and co-workers [17] indicate that the $c(2\times2)$ Pd–Cu checkerboard structure is formed in the second Cu layer by depositing Pd at 473 K. A slight change in the atomic composition of alloy surfaces modifies their chemical (catalytic) properties. Therefore, investigations must be made of surface properties of the binary alloys formed at various deposition temperatures. *In-situ* high-resolution molecular vibrational observations might provide important clues to elucidate the catalysis of the ordered Pd–Cu alloy surfaces.

Infrared spectroscopy is useful to provide information not only about surface chemical properties through the vibrational features of adsorbates, but also about surface lattice structures of the alloy [18–24]. We investigated CO adsorption on a Cu(100)–(2×2)p4g–Pd surface that was formed by 0.3-nm-thick RT deposition of Pd and discussed the atomic structure of the p4g surface [25] using infrared reflection absorption spectroscopy (IRRAS). In this study, we specifically examine the chemical properties of the MBE-grown Cu(100)–$c(2\times2)$–Pd bimetallic surfaces fabricated using 0.15-nm-thick Pd depositions on Cu(100) at various deposition temperatures. Behaviors of CO adsorption and desorption from RT-deposited to 673-K-deposited $c(2\times2)$ structures are discussed in this paper based on IRRAS, low-energy electron diffraction (LEED), and temperature-programmed desorption (TPD) results.

2. Experimental

The experimental equipment and methods used in the present work have been described elsewhere [26–29]. Briefly, Cu(100) (<1° miscut) was used as a substrate for Pd deposition. Each surface was cleaned by repeated Ar^+ sputtering and annealing under ultra-high vacuum (UHV) conditions. The cleanliness and crystallographic order were verified using Auger electron spectroscopy (AES), reflection high-energy electron diffraction (RHEED), and LEED. Then, Pd of 99.99% purity was deposited by electron-beam evaporation onto the Cu(100) substrate surface held at RT, 373 K, 473 K, and 673 K. The base pressure of our UHV chamber was 4×10^{-11} Torr and the pressure during Pd deposition was ca. 1×10^{-10} Torr. The palladium film thicknesses were monitored using a quartz crystal micro-balance and the deposition rate was fixed at about 0.1 nm/min. Exposures of CO to the resultant substrate surfaces were conducted at approximately 7×10^{-10} Torr. The surface structures after deposition and during CO exposures were observed using LEED. The IRRAS spectra were recorded during exposure using an FT-IR spectrophotometer (RS-2; Mattson Instruments) equipped with a liquid-N_2-cooled HgCdTe detector: 2 cm^{-1} resolution at an average of 300 scans was adopted. Each spectrum is presented here as a ratio with the spectrum recorded before CO exposure. The TPD spectra of CO on the surfaces were recorded using a quadrupole mass spectrometer (RGA100; SRS). Heating of the sample was performed using thermal radiation emitted from an infrared heating system (GVH198; Thermo Riko Co. Ltd.). For TPD measurements, the sample was oriented to face an aperture (3-mm-diameter) in a stainless steel tube surrounding the ionization space of the mass spectrometer. All TPD spectra were recorded with a heating rate of 2.5 K/s and were background-subtracted.

3. Results and discussion

3.1. LEED patterns of the Cu(100)–$c(2\times2)$–Pd fabricated at various deposition temperatures

Fig. 1 shows the LEED patterns of the Cu(100) surfaces recorded (a) before, (b) after 0.15-nm-thick Pd deposition at RT, (c) at 473 K, and (d) at 673 K. Fig. 1b shows that RT-Pd deposition onto a clean Cu(100) surface at RT brings about a clear $c(2\times2)$ LEED pattern, indicating that the top surface comprises the Cu–Pd checkerboard

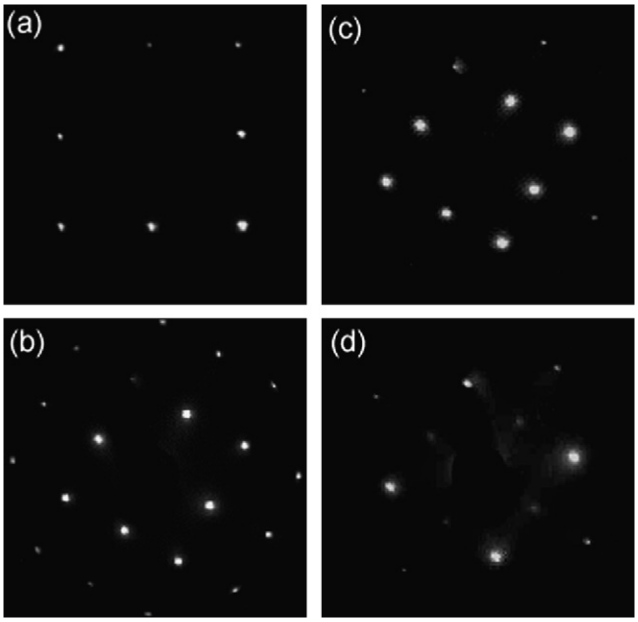

Fig. 1. LEED patterns of the 0.15-nm-thick Pd on Cu(100) surfaces: (a) "clean" Cu(100) at 125 eV, (b) RT-deposition at 117 eV, (c) 473-K-deposition at 117 eV, and (d) 673-K-deposition at 117 eV.