Carbon monoxide adsorption on Pd-deposited Cu(1 1 0) surface: Infrared reflection absorption and temperature programmed desorption studies

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ABSTRACT

We investigated carbon monoxide (CO) adsorption and desorption behaviors on 0.1-nm-, 0.15-nm-, and 0.3-nm-thick-Pd-deposited Cu(1 1 0) surfaces using infrared reflection absorption (IRRAS) and temperature-programmed desorption (TPD) spectroscopic methods. CO was exposed to the 0.1-nm-thick-Pd/Cu(1 1 0) surface at the substrate temperature of 90 K. The IR band attributable to CO bonded to Cu atoms emerged at 2092 cm^{-1}: the band was located at 2100 cm^{-1} at saturation coverage, with a shoulder at 2110 cm^{-1}. In addition to these bands, weak absorptions attributable to the Pd–CO bonds appeared at 2050 and 1960 cm^{-1}. With increasing Pd thickness, the Pd related-bands became increasingly prominent. Particularly at the early stage of exposure, the band at 2115 cm^{-1} became visible. The band at 2117 cm^{-1} dominated the spectra all through the exposures for the 0.3-nm-thick-Pd surface. The TPD spectra of the surfaces showed two remarkable features at around 220–250 and 320–390 K, ascribable ,respectively, to Cu–CO and Pd–CO. The desorption peaks shifted to higher temperatures with increasing Pd thickness. Based on the TPD and IRRAS results, we discuss the adsorption–desorption behaviors of CO on the Pd/Cu(1 1 0) surfaces.

1. Introduction

An interesting and intensively studied bimetallic system is that of Cu–Pd. In fact, Cu and Pd form binary alloys with two ordered structures: B2 of Cu–Pd and L1$_2$ of Cu$_3$Pd [1]. The Cu–Pd alloys are a practical catalyst for alkene oxidation [2], ethanol decomposition [3], water gas shift reaction [4], reducing automobile-exhaust pollutants [5], and for methanol synthesis [6]. Great interest has arisen in the bimetallic surface that is formed through vacuum deposition of one metal on the single crystal substrate of another metal because such a surface is an attractive template for studying not only surface alloy structures but also catalytic activities, which differ from those of individual surfaces [7–11]. Two types of ordered surface structures are known to be formed on a Cu(1 0 0) substrate by vacuum deposition of Pd: a half-monolayer (ML)-thick and a one-monolayer-thick Pd deposition, respectively, generate Cu(1 0 0)-$c(2 \times 2)$-Pd [12–21] and Cu(1 0 0)-(2×2)p4g-Pd [13–17,22,23]. Related to Pd depositions on Cu(1 1 1), several reports have been published [18–20,24]; recent reflection by high-energy electron

diffraction (RHEED) investigation [25,26] reveals that Pd grows initially with in-plane Cu(1 1 1) lattice parameter and the parameter reaches the value of clean Pd(1 1 1) with increasing coverage. Regarding Cu(1 1 0), alloying behaviors of the deposited Pd and substrate Cu atoms have been reported using a scanning tunneling microprobe (STM), X-ray photoelectron spectroscopy (XPS), low-energy electron diffraction (LEED), and temperature programmed desorption (TPD) [27–29]. The dynamic behavior of probe molecules, e.g. carbon monoxide (CO) at the Pd/Cu(1 1 0) surface, would cast some light not only on its surface chemistry but also on the atomic structure of the outermost surface because Pd and Cu atoms at the top surface of Pd/Cu(1 1 0) should have different properties for adsorption and desorption of the probe molecule.

Infrared reflection absorption spectroscopy (IRRAS) is useful for the study of vibrational states of the adsorbate. The frequency and the width of bands caused by adsorbate are quite sensitive to the surface properties, giving us information related not only to the surface chemistry of adsorbates, but also that related to the surface atomic structure of the binary metal surface. It has been demonstrated [30–35] that carbon monoxide (CO) is useful to probe surface lattice structures of the metal. Surface lattice structures can be evaluated using LEED, RHEED, and/or STM, whereas IRRAS spectra

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for a simple probe-molecule like CO can give us a clue for discussing a relation between local atomic structures and molecular behavior of the surface. We have investigated Pd–Cu bimetallic surfaces fabricated by vacuum deposition of Pd on Cu(1 0 0) (Cu(1 0 0)-$c(2 \times 2)$-Pd [21], Cu(1 0 0)-(2×2)p4g-Pd [23]), and Cu(1 1 1) [26] single crystal surfaces.

For this study, we conducted IRRAS measurements for CO adsorbed Pd/Cu(1 1 0) bimetallic surfaces, combined with TPD. Based on the results, IR assignments for adsorbed CO bands on the surfaces are discussed.

2. Experimental

The experimental equipment and methods used in the present work have been described elsewhere [21,23,26,36–40]. The Cu(1 1 0) ($<1°$ miscut) crystal surface was cleaned by repeated Ar^+ sputtering and annealing under ultra-high vacuum (UHV) conditions. Surface cleanliness and crystallographic order were verified with low energy electron diffraction (LEED) and Auger electron spectroscopy (AES). Then, Pd of 99.99% purity was deposited by electron-beam evaporation onto the Cu substrate at room temperature. The base pressure of the UHV chamber was 4×10^{-11} Torr and the pressure during deposition was ca. 1×10^{-10} Torr. The mass thickness of Pd was monitored using a quartz micro-balance and the deposition rate was fixed at about 0.1 nm/min. Exposures of CO (99.9% in purity; Takachiho Kagaku Co.) to the resultant surfaces were conducted at approximately 7×10^{-10} Torr. The IRRAS spectra were recorded with 2 cm^{-1} resolution as an average of 300 scans using an FT-IR spectrophotometer (RS-2; Mattson Instruments) equipped with a liquid-N$_2$-cooled HgCdTe detector. 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. IRRAS spectra of CO adsorbed on Pd/Cu(1 1 0) surfaces at 90 K

Several authors have reported Pd growth on a Cu(1 1 0) surface, in which 0.7–1.2-ML-thick Pd depositions generated p(2×1) LEED pattern [27–29]. However, the contrast of (1×1) LEED pattern for the clean Cu(1 1 0) merely decreased with increasing Pd thickness of 0.1–0.3 nm, suggesting a poor long-range order of p(2×1) in the present deposition condition. Our previous investigations for the Cu(1 0 0)-$c(2 \times 2)$-Pd surface conducted in the same MBE system showed that 0.15-nm-thick-Pd deposition onto the clean Cu(1 0 0) surface gave rise to the clearest $c(2 \times 2)$ LEED pattern [21]. Therefore, the 0.15-nm-thick-Pd deposition on the Cu(1 1 0) might correspond to Pd coverage of approximately 0.5 ML. The more open surface structure of Cu(1 1 0) seems to correlate with the poor surface ordering of the Pd/Cu(1 1 0).

Fig. 1 shows IRRAS spectra of CO adsorbed on a clean surface and those of various thicknesses of Pd deposited on Cu(1 1 0) at 90 K as a function of CO exposure. For comparison, IRRAS spectra for CO adsorption on the clean Cu(1 1 0) are also presented. In view of surface alloying, we must consider CO adsorption on both Pd and Cu atoms. As portrayed in Fig. 1(a), a single intense band around 2091 cm^{-1} dominates the spectra. The band is safely assigned to
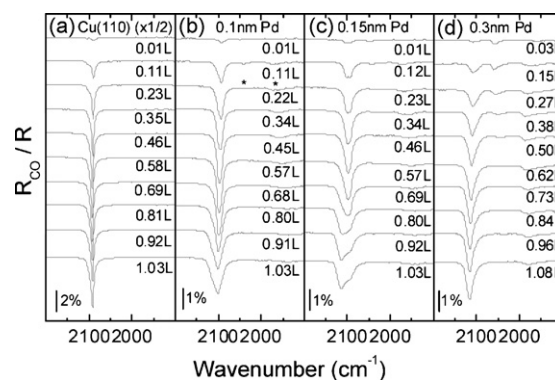
Fig. 1. IRRAS spectra of CO adsorbed at 90 K on surfaces as a function of increasing CO exposure: (a) clean Cu(1 1 0), (b) 0.1-nm-thick-, (c) 0.15-nm-thick-, and (d) 0.3-nm-thick-Pd-deposited Cu(1 1 0).

CO adsorbed on the on-top site of the clean Cu(1 1 0) [41]. For CO exposure of 0.01 L to the 0.1-nm-thick-Pd surface (Fig. 1(b)), a band appears at 2092 cm^{-1}. With increasing CO exposure, the band increases in intensity. At saturation coverage (1.03 L), the band locates at 2100 cm^{-1} accompanied by a shoulder at the higher frequency side (ca. 2110 cm^{-1}). Aside from these bands, very weak absorptions (indicated by asterisks) appear at 2060 and 1960 cm^{-1} at exposures greater than 0.11-L-CO. For the 0.15-nm-thick-Pd surface (Fig. 1(c)), four bands are located at 2100, 2094, 2041, and 1971 cm^{-1} in the spectrum of 0.12 L. The latter two bands seem to disappear above 0.34 L, but the former two bands increase in intensity with increasing CO exposure. The bands become an apparent single absorption peak (2098 cm^{-1}) at 0.46 L. At CO exposures greater than 0.69 L, the band at 2115 cm^{-1} dominates the spectra. The spectral change for the 0.3-nm-thick-Pd surface (Fig. 1(d)) reveals almost the same band behaviors except for the 2100 cm^{-1} band, which seems to disappear, even at 0.27 L. At 1.08-L-CO exposure, a strong IRRAS band is positioned at 2117 cm^{-1}, accompanied by weak absorption at 1980 cm^{-1}.

The C–O stretch frequencies for different adsorption sites of Pd, Cu, and Pd/Cu bimetallic surfaces investigated earlier and in the present work are presented in Table 1. Referring to the results in Table 1, all bands in Fig. 1 are located in regions of the linear and bridge adsorptions of CO on the Pd and Cu atoms. Lu et al. investigated CO adsorption on Cu(1 0 0)-$c(2 \times 2)$-Pd surface alloys

Table 1
Vibrational frequencies of adsorbed CO on Pd and Cu surfaces

Surface	Adsorption site and frequency (cm^{-1})		
	On-top	Bridge	Three-fold hollow
Cu(1 0 0) [42]	2079–2088		
Cu(1 1 1) [34,43]	2070–2080		
Cu(1 1 0) [41]	2088–2104		
Cu cluster [31,32,44]	2104–2133		
Pd(1 0 0) [45,46]	2096	1895–1997	
Pd(1 1 1) [45]	2095	1948	1813–1836
Pd(2 1 0) [45]		1878–1996	
Pd(particles)/SiO$_2$/Mo(1 1 2) [47]	2073–2110	1909–1999	1805–1886
Cu(1 0 0)-$c(2 \times 2)$-Pd [17]	2088 (Cu)		
	2056 (Pd)		
Cu(1 0 0)-$c(2 \times 2)$-Pd [21]	2093 (Cu)		
	2045–2064 (Pd)		
	2110 (Cu clusters)		
Pd in Cu(1 0 0)-p4g-Pd [26]			
Room temperature	2060–2070	1907–1927	1819–1826
90 K	2067–2078	1931–1961	1850–1880
	2093		
Pd/Cu(1 1 0) (Present work)	(90 K)	2041–2117	1990–1990