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Infrared reflection absorption spectral study for CO adsorption on Pd/Pt(1 1 1) bimetallic surfaces

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ABSTRACT

Infrared reflection absorption spectroscopy (IRRAS) was used to investigate carbon monoxide (CO) adsorption on 0.15 nm-thick–0.6 nm-thick Pd-deposited Pt(1 1 1) bimetallic surfaces: Pd_x/Pt(1 1 1) (where x is the Pd thickness in nanometers) fabricated using molecular beam epitaxial method at substrate temperatures of 343 K, 473 K, and 673 K. Reflection high-energy electron diffraction (RHEED) measurements for $Pd_{0.15–0.6\ nm}$/Pt(1 1 1) surfaces fabricated at 343 K showed that Pd grows epitaxially on a clean Pt(1 1 1), having an almost identical lattice constant of Pt(1 1 1). The 1.0 L CO exposure to the clean Pt(1 1 1) at room temperature yielded linearly bonded and bridge-bonded CO–Pt bands at 2093 and 1855 cm^{-1}. The CO–Pt band intensities for the CO-exposed Pd_x/Pt(1 1 1) surfaces decreased with increasing Pd thickness. For $Pd_{0.3\ nm}$/Pt(1 1 1) deposited at 343 K, the 1933 cm^{-1} band caused by bridge-bonded CO–Pd enhanced the spectral intensity. The linear-bonded CO–Pt band (2090 cm^{-1}) almost disappeared and the bridge-bonded CO–Pd band dominated the spectra for $Pd_{0.6\ nm}$/Pt(1 1 1). With increasing substrate temperature during the Pd depositions, the relative band intensities of the CO–Pt/CO–Pd increased. For the $Pd_{0.3\ nm}$/Pt(1 1 1) deposited at 673 K, the linear-bonded CO–Pt and bridge-bonded CO–Pd bands are located respectively at 2071 and 1928 cm^{-1}. The temperature-programmed desorption (TPD) spectrum for the 673 K-deposited $Pd_{0.3\ nm}$/Pt(1 1 1) showed that a desorption signal for the adsorbed CO on the Pt sites decreased in intensity and shifted ca. 20 K to a lower temperature than those for the clean Pt(1 1 1). We discuss the CO adsorption behavior on well-defined Pd-deposited Pt(1 1 1) bimetallic surfaces.

1. Introduction

From a catalytic perspective, numerous studies of Pt-based alloys have been undertaken to develop highly efficient and low-noble-metal-content electrode materials for use in fuel cells [1–7]. Although carbon monoxide (CO) poisoning of the platinum electrode surface severely depresses the hydrogen dissociation reaction on the anode electrode, alloying of Pt with Fe, Ni, Co, Pd, Ru, etc., improves the electrodes' CO tolerance [4–10]. However, discussion of the surface poisoning mechanism is not straightforward because of uncertainties in the outermost surface structures, which are expected to influence molecular behavior strongly. The relation between the alloy surface structure and its molecular behavior is a key for improving the catalytic activities of the electrode. Therefore, molecular characterizations of adsorbed CO on well-defined Pt-based alloy surfaces are crucial for elucidating the CO tolerance.

Fabrication of well-defined bimetallic alloy surfaces through vacuum deposition of a metal onto different single-crystal metal substrates has been studied intensively for designing new materials having unique surface properties that are unattainable in a single metal [11–17]. These approaches for constructing specific surface structures are crucial not only for investigating physical, chemical, and electronic properties of bimetallic alloy surfaces, but also for innovating industrial processes, particularly in the fields of heterogeneous catalysis. For example, surface alloying of Pt with Pd has been reported for vacuum-deposited Pd on single-crystal Pt surfaces by low energy electron diffraction (LEED) and Auger electron spectroscopy (AES) [18]. The authors showed that palladium grows on Pt(1 1 1) in a layer-by-layer manner; no evidence for ordered alloy phases was observed. Furthermore, in the field of electrochemistry, the adsorption properties of pseudomorphic Pd films supported on single-crystal Pt surfaces have also received considerable attention [18–20]. Ludwig et al. showed that alloying of Pt with Pd improves electrocatalytic activity for oxygen reduction reaction (ORR) [21].

Although many investigations for surface structures of Pd-deposited Pt single-crystal surfaces have been conducted, the relation between outermost structures for bimetallic surfaces and their chemical properties has yet to be elucidated. Infrared reflection spectroscopy (IRRAS) is a powerful tool for the study

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of adsorption of simple molecules onto well-defined metal surfaces: its high sensitivity to adsorption sites and metal/molecule interactions supports investigation of the chemical properties of metal and alloy surfaces. Indeed, we have reported IRRAS spectra for CO adsorption on several bimetallic surfaces having periodic atomic structures [17,22–25]. The results indicate clearly that CO is useful as a probe for discussion of surface lattice structures of bimetallic alloys. Therefore, vibrational spectroscopic measurements of CO adsorption on a well-defined bimetallic surface are expected to offer a deeper insight into the specific chemical properties that depend strongly upon the outermost surface of bimetallic alloys.

For this study, we examine CO adsorption on the Pd-deposited Pt(1 1 1) bimetallic surfaces (designated as Pd$_x$/Pt(1 1 1), where x is the Pd thickness in nanometers) fabricated under ultra-high vacuum (UHV) conditions with substrate temperatures of 343 K, 473 K, and 673 K. We conducted IRRAS and temperature-programmed desorption (TPD) measurements for adsorbed CO on the surfaces. The obtained results reveal that the Pd/Pt atomic ratio for the outermost surface of the Pd$_{0.3\ \mathrm{nm}}$/Pt(1 1 1) decreases with increasing the substrate temperature during Pd deposition, thereby modifying CO adsorption behavior on the surfaces.

2. Experimental

Details of the experimental equipment used for this study have been described elsewhere [17,22–25]. Briefly, a Pt(1 1 1) crystal of less than 1° miscut was used as the substrate for Pd deposition. Repeated Ar$^+$ sputtering and annealing at 1250 K under UHV conditions cleaned the Pt(1 1 1) surface. The cleanliness and crystallographic order of the Pt(1 1 1) substrate were verified using Auger electron spectroscopy (AES), reflection high-energy electron diffraction (RHEED), and low-energy electron diffraction (LEED). The Pd was deposited onto the Pt(1 1 1) surface using electron-beam evaporation: the Pd thickness was monitored using a quartz microbalance. The deposition rate was fixed at ca. 0.1 nm/min. The RHEED measurements were carried out using a 10 keV electron beam incident at 2° or less with respect to the surface. The diffraction images were analyzed quantitatively via detection of light emitted from the fluorescent screen using a computer-controlled CCD video camera and a data acquisition system (400; KSA). Exposure of CO to the resultant Pd$_x$/Pt(1 1 1) surfaces was carried out at approximately 7×10^{-10} Torr. The IRRAS spectra of adsorbed CO were recorded at 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 resulting Pd$_x$/Pt(1 1 1) 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 Rico Co. Ltd.). All TPD spectra were recorded with a heating rate of 2 K/s and were background-subtracted.

3. Results and discussion

3.1. RHEED images for Pd$_x$/Pt(1 1 1) fabricated at 343 K

Fig. 1 shows the respective RHEED images of Pd-deposited Pt(1 1 1) surfaces before (a) and after the 0.15 nm-thick (b), 0.3 nm-thick (c), and 0.6 nm-thick Pd (d) depositions. The RHEED image before the Pd depositions shows sharp streaks with the lattice spacing expected for the <1 1 2> direction of Pt(1 1 1) (0.139 nm). As depicted in Fig. 1, separations of the RHEED streaks remained nearly unchanged by the Pd depositions. The difference of lattice constants of Pt (0.392 nm) and Pd (0.389 nm) is only ca. 1%. Furthermore, AES and LEED measurements by Attard et al. yielded no evidence for ordered alloy phases on Pd deposited Pt(1 1 1) surfaces [18]. The authors have concluded that the lattice constant of the ultra thin film of Pd on Pt(1 1 1) scarcely differs from that of Pt(1 1 1). Therefore, the streak separations for the Pd$_{0.15–0.6\ \mathrm{nm}}$/Pt(1 1 1) (Fig. 1) might show that Pd grows on Pt(1 1 1) epitaxially, having almost identical lattice constant.

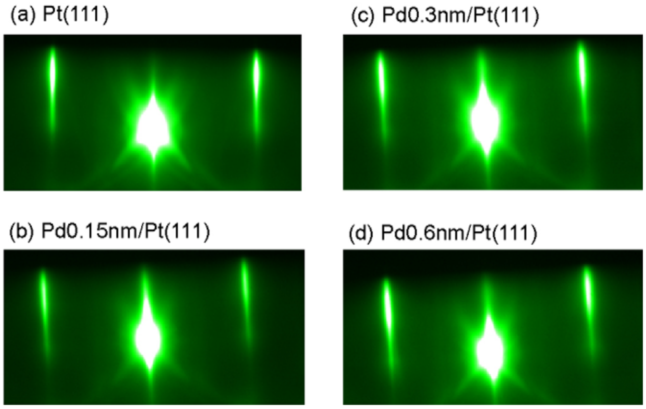

Fig. 1. RHEED images for clean Pt(1 1 1) (a), 0.15-nm-thick (b), 0.3-nm-thick (c), and 0.6-nm-thick (d) Pd deposited Pt(1 1 1) at a substrate temperature of 343 K. The direction of electron-beam incidence is <1 1 2>.

3.2. IRRAS spectra for CO adsorbed onto 343 K fabricated Pd$_x$/Pt(1 1 1)

Fig. 2 depicts IRRAS spectra for CO adsorbed onto the clean Pt(1 1 1) and on the Pd$_{0.15–0.6\ \mathrm{nm}}$/Pt(1 1 1) fabricated at 343 K as a function of CO exposure. On the clean Pt(1 1 1), the strong band at 2093 cm^{-1}, which is ascribable to the linear-bonded CO adsorption, dominated the IRRAS spectra, with an accompanying bridge adsorption band at around 1850 cm^{-1} [26,27]. Therefore, the two bands located in the spectra of (a) can be safely assigned respectively as linearly bonded and bridge-bonded C–O stretch bands.

The IRRAS spectra for the 0.15 nm-Pd-deposited surface (b) show bands at 2082 cm^{-1} and 1850 cm^{-1} at 0.12 L CO exposure. The band at 2082 cm^{-1} shifts to higher frequency, accompanied by

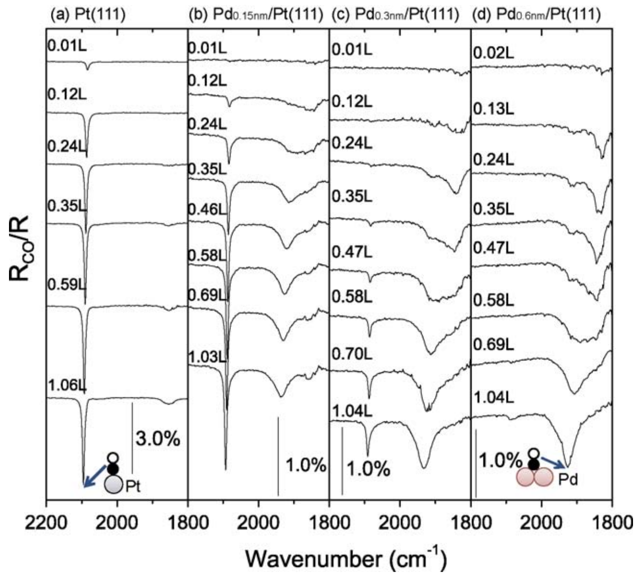

Fig. 2. IRRAS spectra for adsorbed CO on Pd$_x$/Pt(1 1 1) fabricated as a function of CO exposure; clean Pt (a), Pd thickness is 0.15 nm (b), 0.3 nm (c), and 0.6 nm (d).