Carbon Monoxide Adsorption on Ni/Pt(111) Surfaces Investigated by Infrared Reflection Absorption Spectroscopy*

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Infrared reflection absorption spectroscopic (IRRAS) measurements were conducted for carbon monoxide (CO) adsorption on Pt(111) bimetallic surfaces with various thicknesses of deposited Ni, i.e., Nix/Pt(111) (x, Ni thickness in nanometer units), which were fabricated using molecular beam epitaxy at substrate temperatures of 343-473 K. The reflection high-energy electron diffraction (RHEED) patterns for the 343-K-deposited Ni0.1nm−0.6nm/Pt(111) reveal Ni epitaxial growth on Pt(111). The CO exposure to the clean Pt(111) surface at 323 K engenders linearly bonded and bridge-bonded CO−Pt bands at 2093 and 1858 cm⁻¹. The 343-K-deposited Ni0.1nm/Pt(111) gives rise to a new band at 2070 cm⁻¹ in addition to the CO−Pt(111) bands. The new band is most prominent for the Ni0.3nm/Pt(111), on which the bridge-bonded CO on the Ni admetal layer appears at 1874 cm⁻¹. For the Ni0.6nm/Pt(111), the 2070 cm⁻¹ band decreases in intensity and the bridge-bonded CO on the Ni admetal-layer dominates the spectrum, with accompanying weak absorption at 2035 cm⁻¹ caused by linearly adsorbed CO on the Ni layer. The low-energy electron diffraction (LEED) pattern for the 343-K-deposited Ni0.3nm/Pt(111) shows incommensurate higher-order extra spots surrounding integer spots. In contrast, the incommensurate pattern changes to its original six-fold symmetry for the 473-K-deposited Ni0.3nm/Pt(111). In contrast, the RHEED pattern for the 473-K-deposited Ni0.3nm/Pt(111) revealed streaks having slightly wider separations than those for the clean Pt(111). The IRRAS spectrum for the 1.0-L-CO exposed 473-K-deposited Ni0.3nm/Pt(111) reveals single-adsorption at 2074 cm⁻¹. We discuss the CO adsorption behavior of Nix/Pt(111).

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I. INTRODUCTION

From the perspective of heterogeneous catalysis, Pt-Ni alloy is an interesting subject for study. Actually, alloying of Pt with Ni modifies catalytic activities of the individual elements. For example, Chen et al. demonstrated that dehydrogenation and hydrogenation of cyclohexene are unique on a Ni monolayer as compared to those on the clean Pt(111) or on the thick Ni(111) film [1]. Furthermore, 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 [1–10]. The Pt monoxide (CO) tolerance of the anode electrode catalyst for fuel cells is improved by alloying of Pt with Fe, Ni, Co, Pd, Ru, etc., [5]. In addition, Stamenkovic reported that an oxygen reduction reaction (ORR) on the Pt3Ni(111) is ten times more active than that on a pure Pt(111) [8, 9]. These results indicate clearly that the relation between the alloy surface structure and molecular behavior is crucial for elucidating catalysis on Pt-Ni alloy surfaces.

Bimetallic surfaces formed through vacuum deposition of one metal onto a single crystal metal substrate serve as effective templates for discussion of unique surface properties of the alloys. Molecular beam epitaxy (MBE) and ultra-high vacuum (UHV) techniques enable us to create high-quality bimetallic alloy surfaces. Infrared reflection absorption spectroscopy (IRRAS) can provide information not only about surface chemical properties through the vibrational features of adsorbates, but also about surface lattice structures of the alloy [11–16]. The precise characterization of CO adsorption properties of the well-defined Pt-X surface alloys is expected to be linked directly to development of inexpensive electrode materials for use in fuel cells.

We have previously discussed the surface chemistry for the Fex/Pt(111) fabricated by MBE [17, 18]. For this study, we specifically examine CO adsorption on various thicknesses of Ni deposited on Pt(111) (Ni∕Pt(111)) surfaces fabricated by MBE at substrate temperatures of 343-473 K. We conducted IRRAS measurements for adsorbed CO on the Ni∕Pt(111): the results are briefly summarized in this paper.

II. EXPERIMENTAL

Details of the experimental equipment used in this study have been described elsewhere [14–18]. Briefly, a Pt(111) crystal of less than 1° miscut was used as the substrate for Fe deposition. Repeated Ar⁺ sputtering and annealing at 1200 K under UHV conditions cleaned the Pt(111) surface. The cleanliness and crystallographic order of the Pt(111) substrate were verified using Auger electron spectroscopy (AES), reflection high-energy electron diffraction (RHEED), and low-energy electron diffraction (LEED). The Ni was deposited onto the Pt(111) surface using an electron-beam evaporation method: the Ni thickness was monitored using a quartz microbalance; the deposition rate was fixed at ca. 0.1 nm/min. The RHEED measurements were carried out with a 10 keV electron beam incident at nearly 2° or less with respect to the surface. The diffraction images were analyzed quantitatively via detection of light emitted from a fluorescent screen using a computer-controlled
FIG. 1: IRRAS spectra for saturated CO on the Ni₅/Pt(111) fabricated at 343 K. Vertical dotted lines correspond to the peak frequencies of the linearly-bonded (2093 cm⁻¹) and bridge-bonded (1858 cm⁻¹) CO–Pt bands. Right: corresponding RHEED patterns for the clean Pt(111) and as-deposited Ni₅/Pt(111) recorded using electron-beam incidence from the (110) direction.

III. RESULTS AND DISCUSSION

Figure 1 depicts the IRRAS spectra for saturated CO on the clean Pt(111) and on the Ni₅₋₀.₆nm/Pt(111) fabricated at 343 K. Corresponding RHEED patterns recorded before CO exposure are shown on the right-hand side. The Ni depositions onto the Pt(111) surface gave rise to new RHEED streaks (indicated by arrows) outside the original streaks. The lattice spacings parallel to the surface atomic rows can be estimated from the separations of the RHEED streaks [19]. In this work, changes in the separation of the streaks were quantitatively estimated by fitting Lorentzian line shapes; the lattice spacing for the (110) direction estimated from the new streaks was about 0.219 nm, the value of which well corresponds to that for Ni(111) surface. Therefore, we deduce that the deposited Ni grows epitaxially on the Pt(111) substrate at the present deposition condition.

The clean Pt(111) (a) shows the linearly bonded and bridge-bonded CO bands at 2093 and 1858 cm⁻¹. On the clean Pt(111), the strong band at 2093 cm⁻¹ which is ascribable to the linearly-bonded CO adsorption dominated the IRRAS spectrum, accompanied with the bridge adsorption band at around 1850 cm⁻¹ [20, 21]. Therefore, the two bands located in the spectrum of (a) can be safely assigned respectively to the linearly bonded and bridge-bonded C–O stretch bands. For the spectrum of the Ni₅₋₁₆nm/Pt(111) surface, the linearly bonded CO–Pt band decreases in intensity and a new absorption band emerges at 2070 cm⁻¹ (denoted by an asterisk). The new band is most prominent for the Ni₅₋₀.₃nm/Pt(111), accompanying the near disappearance of the linearly-bonded CO–Pt band (2093 cm⁻¹) for the uncovered Pt(111) substrate surface. The clean Ni(111) yielded linearly bonded and bridge-bonded CO–C–O stretch bands at around 2030-2060 cm⁻¹ and 1840-1910 cm⁻¹, respectively [22, 23]. Therefore, the broad absorption feature at around 1874 cm⁻¹ (indicated by an arrow) might be assigned to the bridge-bonded CO on the Ni admetal-layer grown on the Pt(111), although contribution of the bridge-bonded CO–Pt (1858 cm⁻¹) cannot be ruled out. The 0.6 nm-thick Ni deposition yields bands at 2035 and 1880 cm⁻¹ in addition to the 2070 cm⁻¹ band (d): the former two bands can be ascribed respectively to adsorbed CO on the on-top and bridge sites of the Ni admetal-layer. It is noteworthy that the Ni depositions give rise to newly emerged bands around 2070 cm⁻¹ (denoted by asterisks). The origin of the 2070 cm⁻¹ band will be discussed later.

Figure 2 shows LEED (left) and RHEED patterns (right) for the Ni₅₋₀.₃nm/Pt(111) fabricated at the Pt(111) substrate temperature of (b) 343 K and (c) 473 K. The patterns for the clean Pt(111) are also depicted in (a). The 0.3-nm-thick Ni deposition at the substrate temperature of 343 K (Fig. 2(b)) brings about extra LEED spots outside the original ones caused by Pt(111) substrate, revealing that incoherent epitaxy of the deposited Ni ad-metal layer on the Pt(111). Similar sub-spots around the original integer beam have been reported for large lattice mismatch systems such as Ni/Pt(111) [24], Co/Pt(111) [25–27], Pt/Ni(111) [28].

In contrast, the 473-K-deposited Ni₅₋₀.₃nm/Pt(111) shows diffuse 1×1 LEED pattern (Fig. 2(c)), indicating structural modification of the outermost surface. The lattice spacing estimated from the RHEED streaks of (c) is 0.239 nm; the value of which is slightly lower than that for the clean Pt(111) (0.244 nm: (a)). The result might reflect inter-diffusion of the deposited Ni with substrate Pt, i.e., surface alloying, because of the high substrate temperature (473 K).

Figure 3 shows IRRAS spectral changes for CO-saturated Ni₅₋₀.₃nm/Pt(111) surfaces fabricated at 343-473 K. As might be readily apparent from the figure, the bands caused not only by the linearly bonded CO–Pt(111) (2090 cm⁻¹) but also by the bridge-bonded CO–Ni admetal layer (1880 cm⁻¹) disappear for the Ni₅₋₀.₃nm/Pt(111) fabricated at higher deposition temperatures. In contrast, the 2070 cm⁻¹ band is enhanced with increasing deposition temperature. Although the width of the 2070 cm⁻¹ band for the 473-K-deposited Ni₅₋₂₀nm/Pt(111) (full width at half maximum: FWHM ca. 9 cm⁻¹) is slightly greater than that for the clean Pt(111) (FWHM of 7 cm⁻¹), the band intensity is almost equal to that for the clean Pt(111). The result indicates that the electrical as well as structural properties for the outermost surface are rather homogeneous. The spectral changes with increasing deposition temperatures probably reflect thermal activation of inter-diffusion.
FIG. 2: LEED and RHEED patterns before and after Ni depositions of 0.3 nm thickness on clean Pt(111) at 343 K and 473 K: (a) clean Pt(111), (b) 343-K-deposited Ni0.3nm/Pt(111), and (c) 473K-deposited Ni0.3nm/Pt(111). The LEED patterns are collected from the ⟨110⟩ direction using electron-beam incidence of 10 keV.

of the deposited Ni with the substrate Pt. Actually, as presented in Fig. 2(c), the lattice spacing estimated from the distance between the RHEED streaks for the 473-K-deposited Ni0.3nm/Pt(111) is 0.005 nm narrower that for the clean Pt(111). The nearest neighbor distance for Ni (0.249 nm) is lower than that of Pt (0.277 nm). Therefore, incorporation of the deposited Ni atoms into the Pt lattice is expected to decrease in lattice distance. Therefore, the narrower lattice distance might result from alloying of the deposited Ni with substrate Pt at the substrate temperature of 473 K.

We recently investigated CO adsorption behavior on the Fe3/1/Pt(111) using IRRAS, TPD and RHEED [18]: a 0.5-ML-thick-Fe deposition onto the 473-K-Pt(111) surface generated a homogeneous Pt outermost layer (Pt skin) that formed through the surface segregation of substrate Pt atoms. The adsorbed CO on the Pt skin gave rise to a sharp absorption band at 2060 cm⁻¹. Similar surface segregation of the substrate Pt atoms is expected to take place for the Ni depositions onto the Pt(111). The arriving Ni atoms eject substrate Pt to form a cluster at the outermost growing surface. The clusters diffuse at the surface through the thermal energy of the sample and are finally trapped at the step edge of the original surface to generate the outermost Pt layer. Indeed, as for the Pt5Ni1−x(111), a compositional oscillation of the deposited Ni and substrate Pt atoms across the three outermost layers was reported by Gauthier et al. [29]. Moreover, slow-energy ion scattering results for the annealed Pt3Ni(111), (110), and (110) surfaces [9] explicitly indicate that the surface atomic layer of all three Pt3Ni crystals is pure Pt. Therefore, taking into account the previous results, the 2070 cm⁻¹ band might be assigned to CO adsorption on the outermost Pt layer (Pt skin) generated through the Ni deposition process, although a much smaller amount of Ni atoms at the outermost surface cannot be ruled out.

As portrayed in Fig. 3, the linearly bonded CO band dominates the CO adsorbed onto the Pt skin; no band attributable to the bridge-bonded CO is located on the spectrum for the 473-K-deposited Ni0.3nm/Pt(111), as opposed to the clean Pt(111), at which both linearly bonded and bridge-bonded CO–Pt bands appear (bottom). Similar less-intense bridge-bonded CO bands were reported for the Pt alloy electrode in electrochemical systems [5] and for the Pt80Fe20(111) [30]. Disappearance of the bridge-bonded CO–Pt band for the 473-K-deposited Ni0.3nm/Pt(111) surface might also correspond to modification in the electronic structure of the Pt skin layer.

IV. CONCLUSIONS

In this study, IRRAS measurements were conducted for CO adsorption on Ni5(x=0.1−0.6nm)/Pt(111) fabricated using Ni vacuum deposition on clean Pt(111) substrates at 343 K and 473 K. The CO–Pt band intensities were decreased steeply by the Ni depositions of 0.1-
0.3 nm at 343 K, accompanied by a new absorption at ca. 2070 cm$^{-1}$. For the Ni$_{0.6}$nm/Pt(111), the bridge-bonded (1880 cm$^{-1}$) and linearly bonded CO–Ni bands (2035 cm$^{-1}$) dominated the spectra. The new band is most enhanced in intensity with FWHM of ca. 9 cm$^{-1}$ for the 473K-deposited Ni$_{0.3}$nm/Pt(111). The results suggest that the 0.3-nm-thick Ni deposition at 473 K onto the Pt(111) creates the Pt skin that was generated through surface segregation of the substrate Pt atoms. The Pt skin on the deposited Ni atoms gives rise to the 20 cm$^{-1}$ red-shifted linear-bonded C–O stretch band in comparison to that for the clean Pt(111) because the Pt skin is expected to have an electronic property and atomic structure that are quite distinct from those of Pt(111).

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