IRRAS and TPD Investigations of Carbon Monoxide Adsorption on MBE grown Fe on Pt(100)*

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Infrared reflection absorption spectroscopy (IRRAS) and temperature programmed desorption (TPD) were used to investigate carbon monoxide (CO) adsorption on 0.25-1.0 monolayer (ML)-thick Fe deposited Pt(100) (Fe₀.25−1ML/Pt(100)). The cleaned Pt(100) surface shows 5×20 reconstruction (Pt(100)-hex). The 1.0-L-CO exposure to the Pt(100)-hex at 300 K yields linearly bonded CO-Pt bands at 2089 and 2081 cm⁻¹. They are ascribable respectively to adsorbed CO on 1×1 and hex domains. Low-energy electron diffraction (LEED) patterns for the 343-K-deposited Feₓ/Pt(100) change from blurred hex (0.25 ML) to 1×1 (≥0.5 ML), indicating that the outermost surface structures changed through Fe thickness. Regarding the Fe₀.25ML/Pt(100), two bands are located at 2082 and 2069 cm⁻¹ for the 1.0-L-CO exposed surface. The Fe₀.5ML/Pt(100), however, reveals a single adsorption band at 2050 cm⁻¹. The CO exposure to the Fe₁.0ML/Pt(100) generates a broad and more red-shifted band at 2027 cm⁻¹. In contrast, the LEED pattern for Fe₀.5ML/Pt(100) fabricated at 873 K shows hex reconstruction. The IRRAS spectrum recorded after 1.0-L-CO exposure for the 873 K deposited Fe₀.5ML/Pt(100) shows an adsorption band at 2073 cm⁻¹ with narrow bandwidth. The CO desorption temperature for the Pt(100)-hex (about 520 K) was shifted to a lower temperature by Fe deposition: the temperatures are about 470 and 430 K for the Fe₀.5ML/Pt(100) fabricated substrate temperatures of 343 and 873 K. Based on IRRAS and TPD results, CO adsorption behavior on the Fex/Pt(100) is discussed.

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I. INTRODUCTION

From catalytic perspectives, numerous studies of Pt-based alloys have been undertaken to develop highly efficient electrode materials for fuel cells. Indeed, alloying of Pt with Fe, Ni, Co, Pd, Ru, etc. improves the CO tolerance of the anode electrode catalyst in fuel cells [1−5]. Stamenevski et al. found a volcano-type relation between the surface electronic structure (the d-band center) and oxygen reduction reaction (ORR) activities for PtₓM, where M = Ni, Co, Fe, Ti, V; PtₓNi is most active for the ORR that proceeds at the cathode electrode [6, 7]. Atomic arrangements and compositions of the outermost alloy surfaces are important issues for improvement of electro-catalytic activities of Pt-bimetallic surfaces. However, discussion of the mechanism is not straightforward because of uncertainties in outermost surface structures that are expected to influence the molecular behaviors on the catalyst surface strongly. The relation between the alloy surface structure and molecular behavior provides clues for elucidating the role of the alloying elements; such a relation is also an important guide for developing inexpensive electrode materials for fuel cells.

Well-defined, ordered alloy surfaces formed through vacuum deposition of a metal on different metal single crystal substrates are typical models for studies of bimetallic epitaxial growth. Furthermore, such bimetallic alloy surfaces serve as an atomic template for examining surface chemical properties, particularly in the field of catalysis [8−14]. Atomic arrangements of the single crystal alloy of Pt₈₀Fe₂₀(111) surface have been studied intensively. Reportedly, an almost pure Pt top layer can be generated by thermal annealing through surface segregation of Pt atoms [15, 16]. Vacuum deposition of a metal onto different single-crystal metal substrate is another experimental approach for constructing well-defined bimetallic alloy surfaces: molecular beam epitaxy (MBE) and ultra-high-vacuum (UHV) techniques make it possible to create bimetallic surface systems. To date, several studies have described surface structures of the vacuum-deposited Fe on single-crystal-Pt surfaces. For example, Hufnagel et al. and He et al. investigated epitaxial growth of Fe on a Pt(100) surface. Jerdev and Koel examined the surface structures of as-deposited and 500-K-annealed Fe/Pt(111) [19]. Furthermore, Lee et al. [20] and Cheng et al. [21] reported surface structures of Fe-deposited Pt(997) vicinal surfaces. Nevertheless, few studies have specifically examined the surface chemistry for well-defined Fe/Pt surfaces, except for high-resolution electron energy loss spectroscopic (HR-EELS) results for CO adsorption on Pt₂₀Fe(111) [22].

We have discussed the outermost structure for Fe/Pt(111) bimetallic surfaces fabricated by MBE using infrared reflection absorption spectroscopy (IRRAS) [23, 24]. The outermost Pt layer (Pt skin) generated by the 0.5 monolayer (ML)-thick Fe deposition on the Pt(111) at 473 K yielded a very sharp single adsorption band of linearly bonded CO-Pt bonds at 2060 cm⁻¹; the band is 30 cm⁻¹ lower than that obtained on a clean Pt(111) [24]. For the present study, IRRAS and temperature programmed desorption (TPD) investigations were

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conducted for CO adsorption on 0.25-1.0-ML-thick-Fe deposited Pt(100) (Fe$_x$/Pt(100))

II. EXPERIMENTAL

The experimental equipment and methods used in this work have been described elsewhere [12-14, 23, 24]. The Pt(100) (<1° miscut) crystal surface was cleaned by repeated Ar$^+$ sputtering and annealing at 1000 K under ultra-high vacuum (UHV) conditions. Surface cleanliness and crystallographic order were verified with low-energy electron diffraction (LEED) and Auger electron spectroscopy (AES). The LEED pattern for the resulting Pt(100) surface revealed 5×20 surface reconstruction (Pt(100)-hex). Iron of 99.999% purity was deposited onto the Pt(100)-hex using a Knudsen cell. The Fe thickness in ML units was estimated based on the deposition time and the Pt(100)-hex using a Knudsen cell. Iron of 99.999% purity was deposited onto Pt(100) surface revealed 5×20 reconstruction (so-called “Pt(100)-hex”) [25], as presented in Fig. 1(a). Figure 1(b) shows that the 0.25-ML-thick-Fe deposition results in a very blurred hex pattern. In contrast, a rather clear 1×1 pattern is apparent for the 0.5-ML-thick Fe deposited Pt(100) (c): the Fe deposition of 1.0-ML-thickness reveals a less-contrast 1×1 pattern (d).

Figure 2 shows IRRAS spectra for the Pt(100)-hex and those of various thicknesses of Fe deposited Pt(100)-hex after 1.0-L-CO exposure recorded at ca. 300 K. The CO adsorption behavior on the Pt(100)-hex surface [26, 27] is rather complicated: adsorbed CO onto the surface induces phase transition from the hex to 1×1. Bradshaw et al. [26] showed that linear-bonded CO IRRAS bands for the 1×1 and hex domains of Pt(100) are positioned at around 2090 and 2085 cm$^{-1}$ during CO exposures at 300 K and that the frequencies are sensitive to both CO ambient pressures and substrate temperatures. Independently, King et al. [27] reported IRRAS peak frequencies for adsorbed CO bands on the 1×1 and hex domains at ca. 2080 and 2070 cm$^{-1}$. Based on the published results described above, two bands at 2089 and 2080 cm$^{-1}$ on the spectrum for the 1.0-L-CO exposed Pt(100)-hex at 300 K might be assigned respectively to CO adsorption on 0.25-ML/Pt(100) and those of various thicknesses of Fe deposited Pt(100)-hex after 1.0-L-CO exposure recorded at ca. 300 K. The CO adsorption behavior on the Pt(100)-hex surface [26, 27] is rather complicated: adsorbed CO onto the surface induces phase transition from the hex to 1×1. Bradshaw et al. [26] showed that linear-bonded CO IRRAS bands for the 1×1 and hex domains of Pt(100) are positioned at around 2090 and 2085 cm$^{-1}$ during CO exposures at 300 K and that the frequencies are sensitive to both CO ambient pressures and substrate temperatures. Independently, King et al. [27] reported IRRAS peak frequencies for adsorbed CO bands on the 1×1 and hex domains at ca. 2080 and 2070 cm$^{-1}$. Based on the published results described above, two bands at 2089 and 2080 cm$^{-1}$ on the spectrum for the 1.0-L-CO exposed Pt(100)-hex at 300 K might be assigned respectively to CO adsorption on the 1×1 and hex domains.

The Fe$_{0.25}ML$/Pt(100), whose LEED pattern shows a blurred hex structure, yields two bands at 2082 and 2069 cm$^{-1}$, the frequencies are 7-12 cm$^{-1}$ lower than those for the Pt(100)-hex. On the other hand, the 0.5-ML-thick Fe deposition engenders a single absorption at 2050 cm$^{-1}$: the 1.0-L-CO exposure to the Fe$_{1.0ML}$/Pt(100) generates a broad absorption band at 2027 cm$^{-1}$. The

Figure 1 portrays LEED patterns of the Pt(100) surfaces recorded before (a), and after 0.25-ML- (b), 0.5-ML- (c), and 1.0-ML-thick (d) Fe deposition at 343 K. After the cleaning procedure in UHV, the Pt(100) substrate surface shows 5×20 reconstruction (so-called “Pt(100)-hex”) [25], as presented in Fig. 1(a). Figure 1(b) shows that the 0.25-ML-thick-Fe deposition results in a very blurred hex pattern. In contrast, a rather clear 1×1 pattern is apparent for the 0.5-ML-thick Fe deposited Pt(100) (c): the Fe deposition of 1.0-ML-thickness reveals a less-contrast 1×1 pattern (d).

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prominent absorption features located at around 2082 (Fe$_{0.25}$ML/Pt(100))-2027 (Fe$_{0.6}$ML/Pt(100)) cm$^{-1}$ might be ascribed to CO adsorbed on the surface Pt atoms that affected by neighboring Fe atoms [24], revealing that CO adsorb on the surface Pt atoms rather than on Fe atoms. These peak frequency changes correspond well to changes in the LEED patterns (Fig. 1), probably reflecting the amount of deposited Fe.

The IRRAS spectra for the 623-K-deposited Fe$_x$/Pt(100) surfaces showed single absorption bands at 2080 (0.25-ML-thick-Fe), 2045 (0.5 ML), and 2033 cm$^{-1}$ (1.0 ML), respectively, after CO exposure of 1.0 L (not shown here). Figure 3 portrays IRRAS and TPD spectra for the Pt(100)-hex and Fe$_{0.5}$ML/Pt(100) substrates fabricated at temperatures of 343 and 873 K. As the figure shows, the 873-K-Fe-deposited Fe$_{0.5}$ML/Pt(100) reveals a C–O stretch band at 2073 cm$^{-1}$ with full-width at half maximum (FWHM) of 16 cm$^{-1}$; the band is 23 cm$^{-1}$ narrower in frequency and 18 cm$^{-1}$ in band width than those for the 343-K-Fe-deposited surface. Furthermore, the LEED pattern for the 873-K-Fe-deposited surface shows “hex”-like reconstruction. He et al. investigated structural and magnetic properties of ultrathin Fe films deposited on Pt(100) [18]. They showed that, in comparison to the STM image for the as-deposited Fe$_{0.6}$ML/Pt(100), the STM for the 600-K-annealed Fe$_{0.6}$ML/Pt(100) exhibited more ordered islands having characteristic row-like reconstruction of the Pt(100). Our previous IRRAS results for the Fe$_x$/Pt(111) [24] showed that the 0.5-ML-thick Fe deposition on the 473-K-Pt(111) generated the most intense C–O stretch band at 2060 cm$^{-1}$ with FWHM of 9 cm$^{-1}$. We infer that the 2060 cm$^{-1}$ band can be ascribed to adsorbed CO on the outermost Pt layer (Pt skin) on the incoming Fe atoms formed through segregation of substrate Pt atoms. This phenomenon might reflect the difference in surface energy of the deposited and substrate metals, i.e., the deposited Fe showing higher surface energy tends to inter-diffuse into the Pt lattice to reduce the surface energy. Indeed, Hufnagel et al. [28] investigated epitaxial Fe/Pt(100) multilayers using X-ray diffraction. Results showed that the thin fcc-Fe layer (<1.2 nm) is actually an intermixed fcc Fe-Pt interfacial layer. Therefore, the 2073 cm$^{-1}$ band emerged for the 873-K-Fe-deposited Fe$_{0.5}$ML/Pt(100) is ascribable to CO adsorption on the hex-reconstructed Pt outermost layer generated through the surface segregation of the substrate Pt atoms.

The CO desorption temperature for the 2.0-L-CO exposed Pt(100)-hex is about 520 K (Fig. 3); that temperature well corresponds to values reported in the literature [29–31]. The desorption peak shift to lower temperature by Fe deposition and the peaks are located respectively at about 470 and 430 K for the 1.0-L-CO exposed Fe$_{0.5}$ML/Pt(100) fabricated substrate temperatures of 343 and 873 K. The results suggest that the Fe depositions weaken the CO-metal bond strength for the Fe/Pt(100) surfaces, which might be related to low CO-poisoning of the Pt-Fe alloy electrode in the fuel cell [2].

**IV. CONCLUSION**

The CO adsorption behavior on Fe$_{x}$((x=0.25–1.0)ML)/Pt(100) surfaces fabricated using Fe vacuum deposition onto the Pt(100)-hex was investigated. The LEED patterns for the 343-K-deposited Fe$_x$/Pt(100) change from blurred hex (0.25 ML) to 1\times1 (>0.5 ML), reflecting that the outermost surface
structures changed as a result of Fe deposition. Regarding the Fe_{0.25ML}/Pt(100), the two bands are located at 2082 and 2069 cm\(^{-1}\) after 1.0-L-CO exposure. The Fe_{0.5ML}/Pt(100) reveals a single absorption band at 2050 cm\(^{-1}\). The CO exposure to the Fe_{1.0ML}/Pt(100) surface generates a rather broad and more red-shifted band at 2027 cm\(^{-1}\). The LEED pattern for Fe_{0.5ML}/Pt(100) fabricated at 873 K shows hex reconstruction. The 1.0-L-CO exposure to the Fe_{0.5ML}/Pt(100) creates an IRRAS absorption band at 2073 cm\(^{-1}\).

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[1] F. Maillard, G.-Q. Lu, A. Wieckowski, and U. Stimming, J. Phys. Chem. B 109, 16290 (2005) and references therein.
[2] H. Igarashi, T. Fujino, Y. Zhu, H. Uchida, and M. Watanabe, Phys. Chem. Chem. Phys. 3, 306 (2001).
[3] T. Toda, H. Igarashi, H. Uchida, and M. Watanabe, J. Electrochem. Soc. 146, 3750 (1999).
[4] C. Pedroso, T. Waku, and E. Iglesias, J. Catal. 233, 242 (2005).
[5] M. J. Ball, C. A. Lucas, N. M. Marković, V. Stamenković, and P. N. Ross, Surf. Sci. 540, 295 (2003).
[6] V. R. Stamenković, B. S. Mun, M. Arenz, K. J. Mayrhofer, C. A. Lucas, G. Wang, P. N. Ross, and N. M. Marković, Nature Materials 6, 241 (2007).
[7] V. R. Stamenković, B. Fowler, B. S. Mun, G. Wang, P. N. Ross, C. A. Lucas, and N. M. Marković, Science 315, 493 (2007).
[8] H. Shimizu, K. Christmann, and G. Ertl, J. Catal. 61, 412 (1980).
[9] F. M. Hoffmann and J. J. Paul, J. Chem. Phys. 86, 2990 (1987).
[10] B. E. Hayden, K. Kretzschmar, and A. M. Bradshaw, Surf. Sci. 155, 553 (1985).
[11] F. M. Hoffmann, Surf. Sci. Rep. 3, 107 (1983).
[12] T. Wadayama, K. Kubo, T. Yamashita, T. Tanabe, and A. Hatta, J. Phys. Chem. B 107, 3708 (2003).
[13] T. Wadayama, Y. Sasaki, K. Shionitou, and A. Hatta, Surf. Sci. 592, 72 (2005).
[14] T. Wadayama, H. Osano, K. Hamade, H. Yoshida, and T. Maejima, Surf. Sci. 601, 2214 (2007).
[15] P. Beccat, Y. Gauthier, R. Baudoin-Savois, and J. C. Bertolini, Surf. Sci. 238, 105 (1990).
[16] C. Creemers and P. Deurinck, Surf. Interface Anal. 25, 177 (1997).
[17] T. C. Hufnagel, M. C. Kautzky, B. J. Daniels, and B. M. Clemens, J. Appl. Phys. 85, 2609 (1999).
[18] K. He, L. J. Zhang, X. C. Ma, J. F. Jia, Q. K. Xue, and Z. Q. Qiu, Phys. Rev. B 72, 155432 (2005).
[19] D. I. Jerdev and B. E. Koel, Surf. Sci. 513, L391 (2002).
[20] T. Y. Lee, S. Sarbach, K. Kuhnke, and K. Kern, Surf. Sci. 600, 3266 (2006).
[21] R. Cheng, K. Y. Guslienko, F. Y. Faradin, J. E. Pearson, H. F. Ding, D. Li, and S. D. Bader, Phys. Rev. B 72, 014409 (2005).
[22] A. Ath, M. Abon, P. Beccat, J. C. Bertolini, and B. Tardy, Surf. Sci. 302, 121 (1994).
[23] T. Wadayama, H. Osano, K. Murakami, T. Maejima, and H. Yoshida, J. Phys.: Conf. Series 100, 012007 (2008).
[24] T. Wadayama, H. Osano, T. Maeyama, H. Yoshida, K. Murakami, N. Todoroki, and S. Oda, J. Phys. Chem. C 112, 8944 (2008).
[25] P. Heilmann, K. Heinz, and K. Muller, Surf. Sci. 83, 487 (1979).
[26] R. Martin, P. Gardner, and A. M. Bradshaw, Surf. Sci. 342, 69 (1995).
[27] M. Kim, W. S. Sim, and D. A. King, J. Chem. Soc., Faraday Trans. 92, 4781 (1996).
[28] T. C. Hufnagel, M. C. Kautzky, B. J. Daniels, and B. M. Clemens, J. Appl. Phys. 85, 2609 (1999).
[29] R. W. McBee and L. D. Schmidt, Surf. Sci. 66, 101 (1977).
[30] S. R. Kelemen, T. E. Fisher, and J. A. Schwarz, Surf. Sci. 81, 440 (1979).
[31] A. Crossley and D. A. King, Surf. Sci. 95, 131 (1980).