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The surface structure of reconstructed Pt(211)-(2 x 1) determined using surface x-ray diffraction

Masashi Nakamura, Nagahiro Hoshi, Kazushi Sumitani* and Osami Sakata*
Department of Applied Chemistry and Biotechnology, Graduate School of Engineering, Chiba University, Yayoi-cho 1-33, Inage-ku, Chiba 263-8522, Japan
Fax: 81-43-290-3382, e-mail: mnakamura@faculty.chiba-u.jp (M. Nakamura)
Fax: 81-43-290-3384, e-mail: hoshi@faculty.chiba-u.jp (N. Hoshi)
*Materials Science Division, Japan Synchrotron Radiation Research Institute / SPring-8, Kouto 1-1-1, Sayo, Sayo-gun, Hyogo 679-5198, Japan
Fax: 81-791-58-0830, e-mail: o-sakata@spring8.or.jp (O. Sakata)

The surface structure of reconstructed Pt(211) has been studied using surface x-ray diffraction (SXD). Pt(211) reconstructs to (2 x 1) structure after annealing to 1400 K, whereas the surface has (1 x 1) structure after annealing at T < 1200 K. Crystallographic analysis of the x-ray diffraction from the reconstructed surface shows a 2-missing-row structure. The space between the 1st and 2nd layers is contracted by 16 % compared with that of bulk-terminated Pt(211). The multilayer relaxation occurs between the topmost and the 5th layer. The optimized structure of the (2 x 1)-reconstructed surface is different from the structure predicted by DFT calculations.
Key words: Platinum, Reconstruction, Surface x-ray diffraction, High-index surface

1. INTRODUCTION

The structures of stepped and kinked surfaces have been the subject of numerous theoretical and experimental studies because of the development of many technologically important phenomena such as catalysis and crystal growth.[1,2] Step and kink atoms affect the electronic structure, catalytic reactivity, nucleation, and impurity trapping on surfaces. Studies on kinked and stepped structures are not only of fundamental interest but also of technological importance. Numerous experimental investigations of surface structure on high-index planes have been carried out using low-energy electron diffraction (LEED),[3,4] scanning tunneling microscopy (STM),[1,5] and surface x-ray diffraction (SXD).[6,7] These studies have indicated that the surface structure of high-index planes often gives rise to the reconstruction or relaxation from bulk-terminated to complicated structure because atoms in deeper layers are exposed on the surface.

Theoretical and experimental studies have revealed that Pt(311) = 2(100)-(111) reconstructs into a (2 x 1) structure reminiscent of the classical missing-row reconstruction such as that of Pt(110) and Au(110).[5,8] The driving force for this missing-row reconstruction is thought to minimize the surface energy by expansion of the closed-packed (111) facet. Therefore, Pt(210) = 2(100)-(110) does not cause the surface reconstruction.[4] Since the Pt(211) surface consists of (111) terraces and (100) steps as shown in Fig. 1(a), the missing-row reconstruction of Pt(211) expands the (111) facet. There are two possible models for Pt(211)-(2 x 1). Figures 1(b) and (c) show 1-missing-row and 2-missing-row, respectively. However, it is controversial whether Pt(211) reconstructs or not. Theoretical calculations have predicted that Pt(211) surface favors the (1 x 1) structure.[8] In contrast, field ion microscopy (FIM) has suggested the (2 x 1) reconstruction.[9]

We report herein the surface structure of Pt(211) using surface x-ray diffraction. The structure of the reconstructed Pt(211) surface was determined in atomic scale by the measurement of the crystal truncation rod (CTR) and the fractional order rod. The structural relaxation of the inner layer is also discussed.

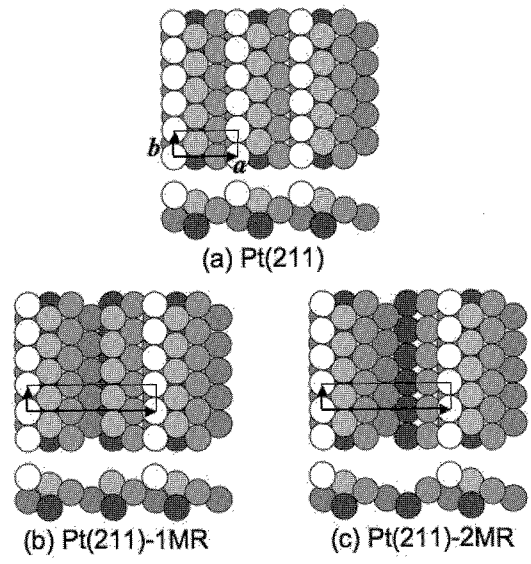

Fig. 1. Schematic models of (a) ideal bulk terminated surface, (b) 1-missing-row, and (c) 2-missing-row reconstruction of Pt(211).

2. EXPERIMENTAL

Pt(211) sample (Surface Preparation Laboratory, The Netherlands) with a diameter of 10 mm was oriented within 0.1°. Sample cleaning was achieved by Ar^+ sputtering at 600 V for 30 min. The sample was then heated at 800 K in 3 x 10^{-5} Pa oxygen for 5 min in order to remove carbon and sulfur contaminations. The sample was annealed in vacuum at 1400 K for 2 min, and then cooled to 25 K. The sample temperature was measured using an Alumel-Chromel thermocouple (< 1550 K). Surface x-ray diffraction measurements were performed with a UHV chamber (base pressure 1 x 10^{-8} Pa) mounted on a (2 + 2)-circle diffractometer at BL13XU for surface and interface structure determination in SPring-8.[10] The incident x-ray energy was 20 keV. The incident angle was fixed at 0.7° (α fixed mode). The detector was a scintillation counter, and Soller slits with an angular resolution of 0.4° were used. The slits in front of the detector were fully opened. Integrated intensities were measured by rocking scans around the axis of the surface normal. The intensities reported herein are corrected for Lorentz and polarization factors. A rectangular surface coordinate system was used for the Pt(211) crystal in which the reciprocal wave vector was $Q = Ha^* + Kb^* + Lc^*$, where $a^* = 2\pi/a$, $b^* = 2\pi/b$, $c^* = 2\pi/c$, $a = 0.6797$, $b = 0.2775$, $c = 0.9613$ nm, and L is along the surface normal direction. The structural analysis were performed using ANA-ROD.[11]

3. RESULTS AND DISCUSSION

Figure 2 shows the LEED pattern of clean Pt(211) after annealing to 1400 K. The appearance of a half-order spot along the a^* axis indicates (2 x 1) reconstruction. The half-order spot was observed at annealing temperatures above 1200 K, whereas the surface obtained after annealing below 1200 K has a (1 x 1) structure. The sharp (2 x 1) pattern was obtained by annealing above 1400 K.

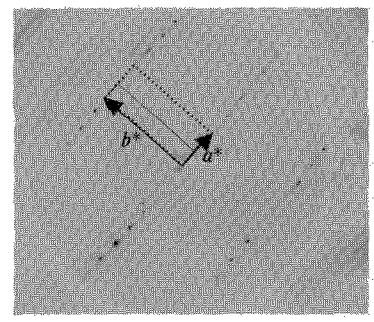

Fig. 2. (2 x 1) LEED pattern of Pt(211) with an incident electron energy of 90 eV. The solid and dotted lines indicate (2 x 1) and (1 x 1) unit cells, respectively.

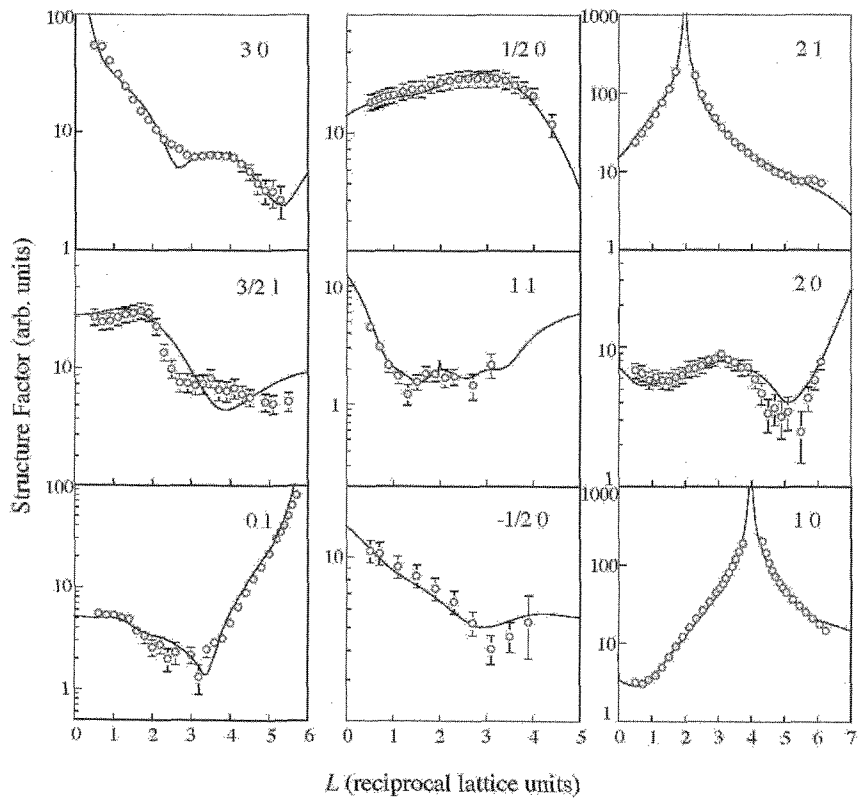

Fig. 3. Structure factor along the CTRs and non-integer rods. The circles and solid lines are observed and calculated structure factors from the optimized model, respectively.

We measured -1 0, -1/2 1, -1/2 -1, -1/2 0, 0 1, 0 -1, 1/2 0, 1/2 1, 1/2 -1, 1 0, 1 1, 1 -1, 3/2 0, 3/2 1, 3/2 -1, 2 0, 2 1, 2 -1, and 3 0 diffraction rods from the Pt(211)-(2 x 1) surface. Data consisting of 160 reflections along 9 fraction order rods, and 245 reflections along 10 CTRs were measured for the structure determination. The structure factors were averaged assuming pm symmetry to yield 287 nonequivalent reflections with a reproducibility of 10 %. We optimized structural parameters, the scale factor, the surface fraction factor, the occupancy factor, and the roughness factor. The isotropic Deby-Waller factor of Pt atoms in the first layer were refined, whereas those below the 2nd layer were fixed at the bulk value of 0.07 $Å^2$.[12] All parameters were refined simultaneously using data sets for both crystal truncation rods (CTRs) and fraction order rods. Structural factors calculated on the basis of the 2-missing-row model are in good agreement with experimental data with χ^2 value of 2.0 as compared to 3.1 for the 1-missing-row model. Figure 3 shows the structure factors of CTRs and fractional order rods. The circles and solid lines in Fig. 3 show the observed and calculated structure factors, respectively.

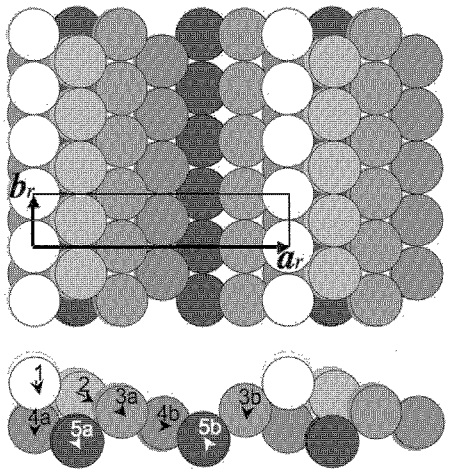

Fig. 4. Top and side views of the optimized model of Pt(211). Dashed circles indicate the bulk position of each atom. Arrows indicate the direction of atomic shift from the bulk position.

Table I: Atomic coordinates for the optimum geometry of reconstructed Pt(211). The coordinate system of reconstructed surface is the rectangular. a_r = 1.359, b_r = 0.2775, and c_r = 0.9613 nm.

	coordinates		
	x	*y*	*z*
Pt1	0.0046(15)	0.0000	0.9693(12)
Pt2	0.1894(10)	0.5000	0.8991(8)
Pt3a	0.3482(15)	0.0000	0.8197(11)
Pt3b	0.8327(15)	0.0000	0.8419(12)
Pt4a	-0.0002(12)	0.5000	0.7367(9)
Pt4b	0.5089(12)	0.5000	0.7569(11)
Pt5a	0.1771(7)	0.0000	0.6561(8)
Pt5b	0.6695(8)	0.0000	0.6698(9)

The optimized structure for reconstructed Pt(211)-(2 x 1) is shown in Fig. 4. The roughness factor was estimated to be β = 0.23(1) using the approximate β-model. The surface fraction and occupancy factor of 1st layer were 1.0(1) and 0.78(1), respectively. The atomic positions of the refined structure are listed in Table I. The Pt(211)-(2 x 1) surface has a hill-and valley structure that consists of 5 atomic rows (111) facet and 3 atomic rows (100) facet. The most pronounced feature regarding to the refinement model is that the atoms between the 1st and 3rd layers are remarkably shifted downward. The vertical positions of atoms 1, 2, and 3a are shifted by 0.0295(11), 0.0169(7), and 0.0131(11) nm, respectively, compared with the ideal bulk-terminated position. In consequence, the interlayer spacing of the 1st (1st – 2nd layer spacing) and 2nd (2nd -3rd layer spacing, the 3rd layer is the average value) layers are contracted by 16 and 18 %, respectively. This large atomic displacement diminishes the difference in height between the top-layer rows and the in-between row. A similar contraction is reported on the other various stepped surface.[3,6,7] The 2-missing-row structure exposes the deeper atoms, on the surface, which gives rise to the multilayer relaxation. The reduced coordination number of atoms exposed on the surface allows them to strongly bind to subsurface atoms. The subsurface below the sixth layer does not displace from the bulk-phase position. It is known that the surface layer of stepped-surface induces a large relaxation in order to decrease the surface free energy.[13,14]

The lifting of the 2 x 1 reconstruction did not occur after annealing to the maximum measurable temperature at 1550 K. The irreversible reconstruction from (1 x 1) to (2 x 1) is associated with a thermally activated process because a number of surface atoms migrate for the 2-missing-row reconstruction. FIM supports (2 x 1) reconstruction at temperatures above 400 K.[9] On the other hand, DFT calculations have indicated that the reconstructed surface of Pt(211) is unstable rather than the (1 x 1) surface.[8] We cannot fully explain the difference between the theoretical and experimental results. However, the structural model optimized by SXD is different from that predicted by DFT calculations. The calculated 2-missing-row model shows no contraction of the 2nd interlayer spacing.

4. CONCLUSIONS

The surface structure of reconstructed Pt(211)-(2 x 1) was determined using surface x-ray diffraction. It was found that Pt(211) reconstructs into the two-missing row structure above 1200 K. The interlayer spacing shows 16 and 18 % contraction in the 1st and 2nd spacing, respectively. Multilayer relaxation is induced by the large corrugation result from the 2-missing-row reconstruction.

5. ACKNOWLEDGMENT

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