

Electronic State Changes of Cu₃Pt(111) Surfaces

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It is well known that Cu-Pt alloys exhibit high catalytic activity in oxidation of CO to CO₂. However, the reaction mechanism has not been completely understood. The stoichiometric Cu₃Pt alloy undergoes a bulk-ordered-disordered phase transition at about 850 K [1]. Changes in the surface structure due to alloying have a large effect on catalytic activity, so it is important to understand the electronic state of the alloy surface. In this study, we report changes in the electronic state of the ordered and disordered Cu₃Pt (111) surface.

The experiment was performed at beamline 8 named SORIS system at SR Center, Ritsumeikan University [2]. The sample was cleaned with a cycle of Ar⁺ ion sputtering and annealing. The two different surface phases are obtained; an ordered surface with a (2 × 2) structure annealed at 973 K and a disordered surface with a (1 × 1) structure annealed at 673 K. Since the ordered surface is a Cu-rich surface and the disordered surface is a Pt-rich surface, the composition ratio of Cu and Pt on each surface is different [3]. Each surface was identified by reflection high-energy electron diffraction (RHEED). The photoelectron spectroscopy (PES) measurements were also performed at room temperature under ultrahigh vacuum of ~5 × 10⁻⁸ Pa.

Figure 1 shows the core-level spectra of Cu 3*p* and Pt 4*f* on the two different surface phases by SR light of 130 eV. The feature around 70.8 eV is attributed to Pt 4*f*_{7/2} state, around 74.2 eV to Pt 4*f*_{5/2} state, around 74.5 eV to Cu 3*p*_{3/2} state, and around 76.9 eV to Cu 3*p*_{1/2} state. The intensity of Cu 3*p* on the disordered surface [Fig. 1(b)] is weaker than that on the ordered surface [Fig. 1(a)], which is consistent with the Pt-rich disordered surface. In order to evaluate the surface composition, we have fitted the PES spectra since the Pt 4*f*_{5/2} and Cu 3*p*_{3/2} core levels overlap (Fig. 1). Assuming that the PES intensity ratio of Cu 3*p* to Pt 4*f* corresponds to the composition ratio for the ordered surface [Cu₃Pt(111)], the composition for the disordered surface is estimated to be Cu_{1.1}Pt₁ from the PES intensity ratio. Previous study has revealed that the preferential sputtering causes Pt enriched surface of Cu₆₈Pt₃₂ [3]. This composition difference for the disordered surface suggests that the Ar⁺ ion sputtering condition (and moderate annealing) can control the surface Pt ordering. Indeed, in this experimental Ar⁺ ion sputtering (and annealing) condition, Pt(111) surface states may be formed since the Pt 4*f* core-level width becomes broaden [4] for the disordered surface.

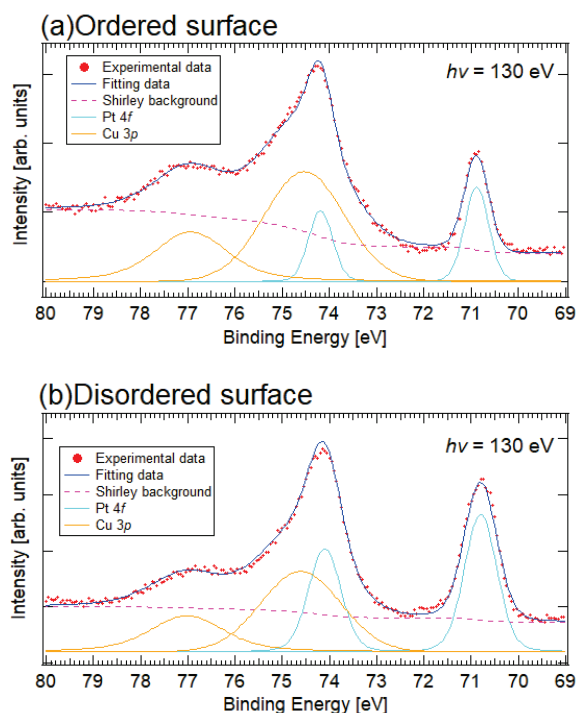


Fig. 1 Cu 3*p* and Pt 4*f* spectra on the ordered (a) and the disordered (b) Cu₃Pt(111) surfaces. The fitting results are also shown.

References

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