Rapid-temperature-rising induced reduction of NiO film grown on Ni(111) surface

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To clarify the potential of Ni surfaces as an alternative catalyst of Pt for exhaust gases of automobiles, the oxidation and reduction reaction kinetics on Ni(111) surfaces were investigated by X-ray photoelectron spectroscopy using synchrotron radiation ($h\nu$ = 1100 eV) at BL23SU, SPring-8. By annealing at 700℃ under H_2 atmosphere at $P_{H2} = 9 \times 10^{-4}$ Pa for 600 s, there were no traces of carbon, oxygen, sulfur, and chlorine contaminants within the detection limit.

For the clean Ni(111) surface, the Ni $2p_{3/2}$ photoelectron spectrum is fitted well with an asymmetric Voigt function (Peak A) with 6-eV satellite as demonstrated in Fig. 1(a). [1]. After oxidizing the Ni(111) surface, four symmetric Voigt functions with different widths are necessary for obtaining a good accordance with the measured spectrum in addition to Peak A as separated in Fig 1(b). Peak B, C, and D is ascribed to charge transfer satellites from O 2p to Ni 3d states, $\underline{c}3d^9\underline{L}$, nonlocal $\underline{c}3d^9\underline{L}$, and $\underline{c}3d^{10}\underline{L}^2$, respectively, where $\underline{c}$ and $\underline{L}$ denote a hole in Ni 2p and O 2p, respectively. Peak E is a component with no charge transfer, $\underline{c}3d^8$. The thickness of the NiO film, d_{NiO}, were obtained from the photoelectron intensity ratio of the sum of the $\underline{c}3d^9\underline{L}$, nonlocal $\underline{c}3d^9\underline{L}$, $\underline{c}3d^{10}\underline{L}^2$, and $\underline{c}3d^8$ components to Ni metal component as shown in Fig, 2. The d_{NiO} shows a parabolic dependence on time, indicating that the NiO growth is governed by O diffusion through the NiO layer. When raising the temperature from 350 to 700℃ at the same time of stopping O_2 supply, a steep decrease of d_{NiO} is caused only during the rapid temperature rising and then d_{NiO} shows no significant decrease during the isothermal annealing at 700 ℃. The observed rapid-temperature-rising induced reduction of the NiO film is considered in terms of the difference of thermal expansion coefficient between Ni and NiO, surface NiO component and O_2 desorption from the NiO surface, which were examined by changing the surface sensitive (θ = 0° and 70°).

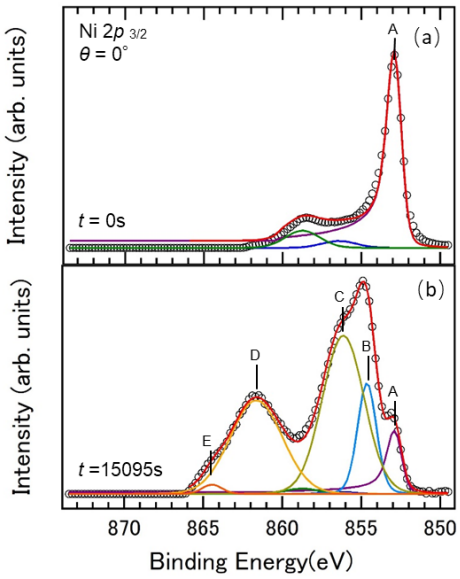

Fig. 1. Ni $2p_{3/2}$ XPS spectra (a) before and (b) after oxidizing Ni(111) surface.

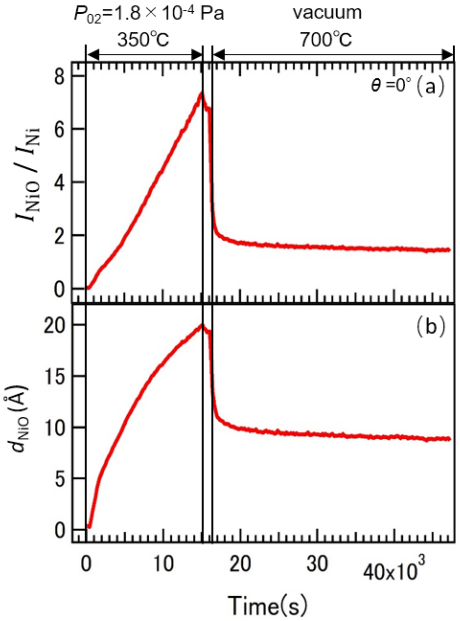

Fig. 2. Time evolutions of (a) I_{NiO}/I_{Ni} and (b) d_{NiO}.

[1] I. Preda et al., Phys. Rev. B 77, 075411 (2008).