Size change of Cu nanoparticles on rutile TiO_2(110) by oxygen exposure

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It is well known that Cu based catalysts are used in the reactions such as water gas-shift, methanol oxidation, CO oxidation, and so on. In spite of many efforts, however, the mechanism leading to strong catalytic activities of Cu nanoparticles is still a debatable issue. In the previous study [1], we have found the growth mode of Cu nanoparticles deposited on the rutile TiO_2(110) surfaces by medium energy ion scattering (MEIS). As a result, the two- (2D) dimensional islands grow initially up to Cu coverage of 0.5 ML and then the three- (3D) islands growth become dominant. In this work, we have measured the particle size of oxygen-exposed Cu nanoparticles by MEIS.

The experiments were performed at beamline 8 named SORIS set up at Ritsumeikan SR center. In the present MEIS analysis, we used 120 keV He^+ ions and scattered He^+ ions were energy-analyzed by a toroidal electrostatic analyzer (ESA) with an excellent energy resolution ($\Delta E/E = 9 \times 10^{-4}$; FWHM). We prepared the oxygen-rich surfaces (O-TiO_2) by exposure of O_2 onto the reduced TiO_2 surfaces, which were formed by sputtering with 0.75 keV Ar^+ followed by annealing at 870 K for 10 min in UHV. Cu was deposited on the clean surfaces at RT with a Kundsen cell under UHV condition.

Fig. 1 (a) and (b) indicate the MEIS spectra observed for Cu(0.7 ML)/O-TiO_2(110) at an incident angle of 45° and emergent angle of 45° and 70°, respectively. The observed MEIS spectra are reproduced well assuming the following fitting parameters: d (diameter) = 3.1 nm, h (height) = 1.0 nm and δ (standard deviation in size) = 10 %. Interestingly, the average size of Cu nanoparticles has decreased and standard deviation has increased (d = 2.5 nm, h = 0.95 nm, δ = 32 %) after O_2 exposure of 100 L (Fig. 2). Such size changes have also observed by J. Zhou *et. al.* [2]. The decrease in size of this Cu nanoparticles is probably come from that the adsorption of oxygen appears to weaken the Cu-Cu bond.

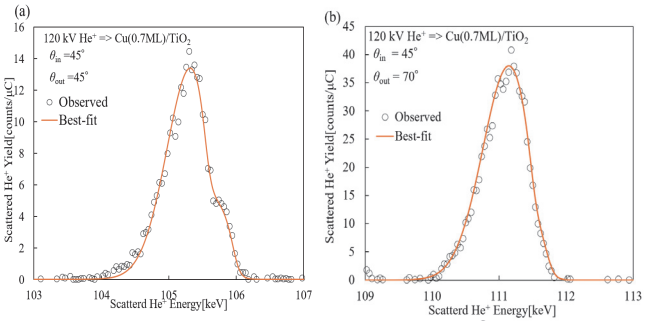

Fig. 1 MEIS spectra observed for 120 keV He^+ ions scattered from Cu(0.7 ML)/O-TiO_2(110) at an incident angle of 45° and emergent angle of 45° (a) and 70° (b), respectively.

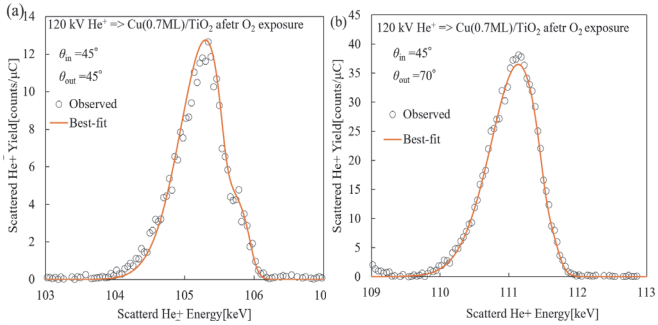

Fig. 2 MEIS spectra observed for 120 keV He^+ ions scattered from Cu(0.7 ML)/O-TiO_2(110) after O_2 exposure of 100 L at an incident angle of 45° and emergent angle of 45° (a) and 70° (b), respectively.

References

[1] T. Aoki, K. Mitsuhara, and M. Takizawa, *e-J. Surf. Sci,* **2018**, *16, 225*.
[2] J. Zhou, Y. C. Kang, and D. A. Chen, *J. Phys. Chem. B* **2003**, *107, 6664-6667*.