

Growth mode analysis of Cu nanoparticles on rutile TiO₂(110)

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The growth mode of Cu nanoparticles deposited on the rutile TiO₂(110) surfaces have been investigated by high-resolution medium energy ion scattering (MEIS). The observed MEIS spectra were well reproduced assuming the hemispherical and two-dimensional islands. The MEIS results indicate that the two-dimensional islands of Cu nanoparticles grow initially up to Cu coverage of 0.5 ML and then three-dimensional islands growth become dominant. Interestingly, the growth mode is almost the same for both reduced TiO₂ and oxygen-rich TiO₂. These results indicate that Cu nanoparticles are formed as both two- and three-dimensional islands on reduced and oxygen-rich TiO₂.

1. Introduction

It is well known that Cu based catalysts are used in reactions such as water gas-shift (WGS: CO + H₂O → CO₂ + H₂), methanol oxidation, methanol synthesis, and others [1, 2]. However, their performance is not fully understood and is highly dependent on the synthesis conditions or the nature of the oxide support. There are three candidates to explain the catalytic activity; [I] changes in the reactive surface area associated with nanoparticle formation, [II] quantum size effect, [III] charge transfer between nanoparticles and substrates. All of these effects certainly contribute to the catalytic activities of Cu nanoparticles; however, it has been shown that the most drastic changes in the catalytic activity can be attributed to changes in the size and shape of Cu nanoparticles. Therefore, it is important to understand distribution of particle size.

In this study, we have measured the areal occupation ratios of two- (2D) and three-dimensional (3D) Cu islands formed on reduced TiO₂ (R-TiO₂) and oxygen-rich TiO₂ (O-TiO₂) by medium energy ion scattering (MEIS).

2. Experimental

The experiment was carried out at beamline 8 connected to a storage ring named AURORA working at SR Center, Ritsumeikan University. 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 ($\Delta E/E = 9 \times 10^{-4}$; ΔE being FWHM), which makes it possible to determine the shape and size of metal nanoparticles [3]. We prepared two types of substrates which have R-TiO₂ and O-TiO₂. Figure 1 illustrates the R- and O-TiO₂(110) surface with a ball and stick model. The O-TiO₂(110) surface was made by exposure of O₂(5N) onto R-TiO₂(110), which were formed by sputtering with 0.75 keV Ar⁺ followed by annealing at 870 K for 10 min in ultra-high vacuum (UHV) of 2×10^{-8} Pa. The O₂ exposure was carried out starting from a temperature of 325 K and down to room

temperature (RT) under O₂ pressure of 4×10^{-4} Pa. Cu was then deposited on the clean surfaces at RT with a Knudsen cell at a rate of 0.08 ML/min under UHV condition. Here, 1 ML means 1.77×10^{15} atoms/cm², corresponding to the areal density of Cu(111). The average size and shape were determined by high-resolution MEIS [3]. Here, the 2D islands were defined by the height of one atomic layer and the shape of 3D islands were approximated by a partial sphere with diameter d and height h . Note that the MEIS analysis was made at RT and all the experiments were performed *in situ* under UHV condition.

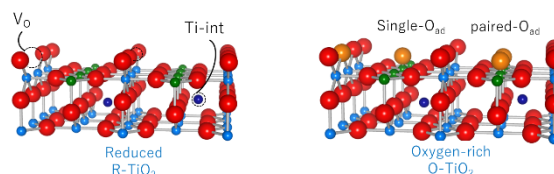


Fig. 1 Ball and stick model for R- (left) and O-TiO₂(110) (right). Red balls represent oxygen and light blue and green balls denote 6-fold Ti and 5-fold Ti, respectively. Orange balls represent O_{ad} atoms and V_O is bridging O vacancy. Dark blue ball denotes interstitial Ti acting as an n-type donor.

3. Results and Discussion

We determined the average size of Cu nanoparticles on R- and O-TiO₂ by high-resolution MEIS. All the MEIS spectra are shown in Fig. 2. With increasing the Cu coverage, the sharp structures of the MEIS spectra observed at $\theta_{\text{out}} = 45^\circ$ become broadened, and the tails of the MEIS spectra observed at $\theta_{\text{out}} = 70^\circ$ extend to the lower energy side. These observations indicate the presence of 3D islands.

Figures 3(a) and (b) show the MEIS spectra observed for Cu(0.3 ML)/R-TiO₂(110) at the incident angle of 45° and the emergent angles of 45° and 70° , respectively. The MEIS spectrum observed at $\theta_{\text{out}} = 45^\circ$ is very sensitive to the cluster height, while the

spectrum measured at $\theta_{\text{out}} = 70^\circ$ is dependent upon both height and diameter. The observed MEIS spectra are reproduced well assuming the following fitting parameters: $d = 1.9$ nm, $h = 1.4$ nm, $\sigma_{2D} = 5\%$, $\sigma_{3D} = 6\%$ (σ_{2D} and σ_{3D} are areal occupation ratios of 2D and 3D islands, respectively) and δ (standard deviation in size) = 10 %.

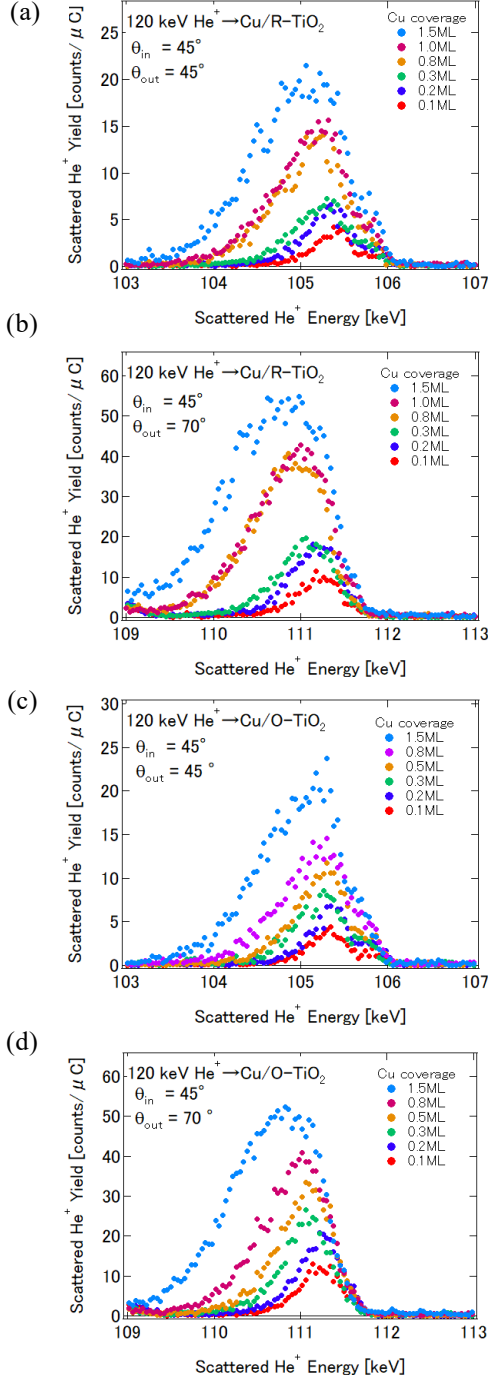


Fig. 2 MEIS spectra observed for 120 keV He⁺ ions scattered from Cu nanoparticles on R- and O-TiO₂(110). The incident and the emergent angles are 45° and 45° [(a), (c)] and 70° [(b), (d)] for R- and O-TiO₂, respectively.

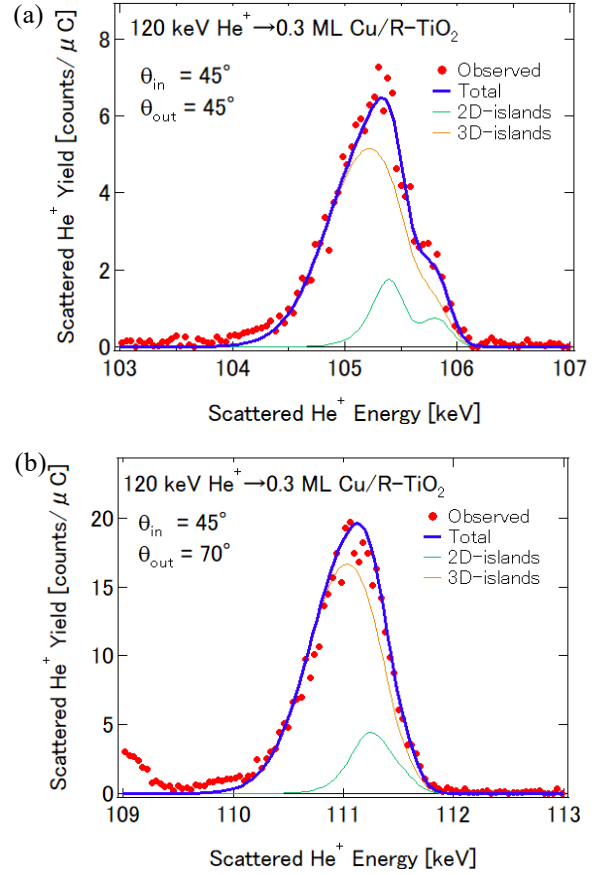


Fig. 3 (a) MEIS spectra observed for 120 keV He⁺ ions scattered from Cu(0.3 ML)/ R-TiO₂(110) at $\theta_{\text{in}} = 45^\circ$ and $\theta_{\text{out}} = 45^\circ$. The blue curve corresponds to the best-fit spectrum obtained assuming $d = 1.9$ nm, $h = 1.4$ nm, $\sigma_{2D} = 5\%$, $\sigma_{3D} = 6\%$ and $\delta = 10\%$. The green and yellow curves denote scattering component from 2D and 3D islands, respectively. (b) MEIS spectra observed at $\theta_{\text{in}} = 45^\circ$ and $\theta_{\text{out}} = 70^\circ$. The used symbols are the same as those in (a).

Figure 4 shows the diameter and the height for 3D islands on R- and O-TiO₂ as a function of Cu coverage. Both d and h increase almost linearly with increasing Cu coverage. Interestingly, the ratio of h/d decreases at high Cu coverage (0.5 for hemisphere) and growth mode of Cu nanoparticles is almost the same for both surfaces.

Figure 5 shows the areal occupation ratio of Cu nanoparticle on R- and O-TiO₂ as a function of Cu coverage. Starting from 2D islands formation, all 2D islands change into 3D islands with above 0.8 ML of Cu coverage. Also in this case, growth mode is almost the same for both surfaces. Such a growth mode is quite different from Au/TiO₂(110), where it is different in growth mode depending on the surface condition [3]. According to DFT calculations [4, 5], deposited Au grows on steps and defects of TiO₂(110) because the Au cluster is weakly bound

and essentially can move freely on the oxide surface. The presence of V_O on $TiO_2(110)$ drastically increases the adsorption energy of Au. On the other hand, the Cu atom was preferentially adsorbed on two O_{br} with a bonding energy of - 1.76 eV and Cu/ TiO_2 interactions are much stronger than Au/ TiO_2 interactions. Furthermore, Au prefers to bind to V_O but this is not the case for Cu. Thus, Cu is quite different from Au in metal/oxide interactions, which affect the size, dispersion, and surface position of the metal particles.

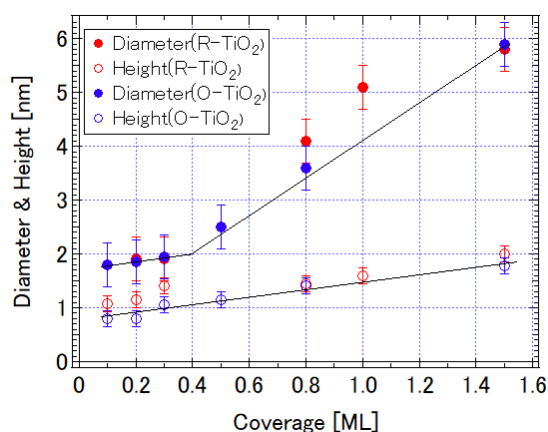


Fig. 4 Average d (closed circles) and h (open circles) determined by MEIS for 3D islands as a function of Cu coverage.

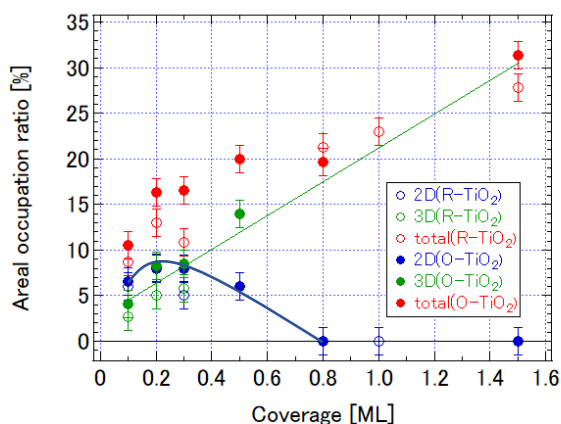


Fig. 5 Areal occupation ratios for 2D (blue circles) and 3D (green circles) islands as a function of Cu coverage. Red circles denote areal occupation ratios of 2D plus 3D islands.

4. Conclusions

In this study, we have studied the particle size of Cu nanoparticles deposited on the rutile $TiO_2(110)$ surfaces by MEIS. The MEIS analysis reveals that the 2D islands grow initially up to Cu coverage of 0.5 ML and then 3D islands growth become dominant for both surfaces. Such a growth mode is different from Au/ $TiO_2(110)$. This difference is caused by the difference in adsorption energy of Au

and Cu for TiO_2 surfaces.

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References

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