

A Surface Structure of Ni Species at a very low Coverage on a TiO₂(110) Surface by Polarization-Dependent Total Reflection Fluorescence EXAFS (PTRF-EXAFS)

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Introduction

Metal-oxide interaction has been widely studied because it is one of the important issues in many fields such as catalysts, sensors, and electronic devices. Development in SPM (Scanning probe microscopy) and surface X-ray technique have provided the registry, morphology and texture of the deposited metal. However, the problem about the bond structure between the metal and metal oxide is still under debate. We have found Ni on Al₂O₃(0001) preferably interacted with surface oxygen atoms to adsorb atomically on the 3 fold hollow site at the initial stage of deposition.[1] However Ni on TiO₂(110) easily aggregates to a Ni cluster at the same coverage where atomically dispersed Ni was observed on Al₂O₃(001) surface, indicating the number of stable adsorption sites for Ni on TiO₂(110) surface is less than that on Al₂O₃(001). We therefore carried out the 3 dimensional EXAFS analysis on a much smaller amount of Ni species ($1 \times 10^{13} / \text{cm}^2$) in order to reveal the first interaction between Ni and the TiO₂(110) surface.

Experimental

A TiO₂(110) surface was cleaned by Ar⁺-sputtering and 873 K-annealing cycles which gave a clean (1x1) LEED pattern. The Ni was evaporated from a tungsten filament which was wrapped with a Ni wire. Polarization dependent XAFS was measured at BL9A beam line in a total reflection fluorescence mode. The sample was kept under 10^{-8} Pa. The fluorescence X-ray was detected by a Canberra 19-element SSD.

Results and Discussion

Figure 1 shows the PTRF-XAFS oscillations for the Ni species with $1 \times 10^{13} \text{ cm}^{-2}$. The EXAFS oscillation shows the quick sinusoidal damping indicating the presence of Ni-O bonding and atomically dispersed Ni species. We could have the atomically dispersed Ni species. We carried out the simulation analysis using FEFF. We could not reproduce the observed EXAFS oscillations based on the various terrace adsorption sites. We then think about the defect sites and found that the Ni species adsorbed on the [11b1] step edge as shown in Fig.2 could well reproduce the observed data. The number of

[11b1] was about the order of 10^{13} cm^{-2} estimated from STM. This may be the reason why we could have atomically dispersed Ni species only at a very low coverage. Note that the Ni adsorption site was corresponding to a virtual Ti site if the second layer TiO₂ grew. This is because Ni-O bond was rather covalent and the Ni should adsorb the virtual cation site.

The virtual cation site on the terrace was atop site of oxygen. However, the Ni on an atop site must be unstable because of the single Ni-O bond and thus migrates until the collision with the other Ni atoms or with the step edges. We could thus conclude that the interaction between Ni and the surface oxygen was covalent bond and the adsorption site was the virtual cation site. This conclusion is in good agreement with our previous conclusion.

[1] K. Ijima, Y. Koike, W.-J. Chun, Y. Satio, Y. Tanizawa, T. Shido, Y. Iwasawa, M. Nomura, and K. Asakura, *Chem,Phys.Lett.* **384**, 134-138 (2004).

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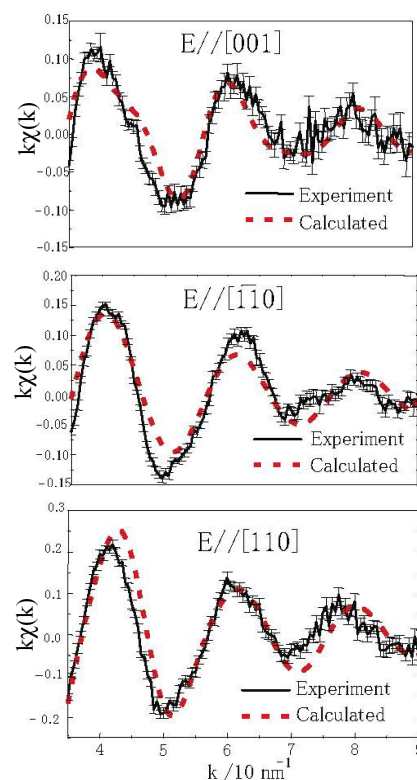


Figure 1 PTRF-XAFS oscillations for the Ni species with $1 \times 10^{13} \text{ cm}^{-2}$ with different polarization directions.

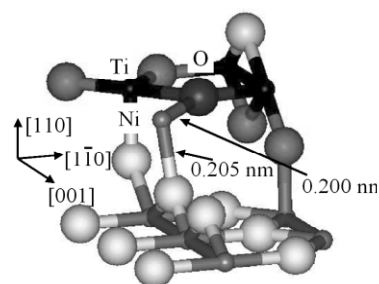


Figure 2 A model structure of Ni adsorbed on the step edge.