Self-Regulated Ni Cluster Formation on the TiO_2(110) Terrace Studied Using Scanning Tunneling Microscopy

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We have studied the growth mode and morphology of Ni clusters on a TiO_2 (110) surface with a wide terrace using scanning tunneling microscopy (STM) at a low coverage (less than 3 atoms nm^{-2}). The Ni clusters are formed on the terrace at the low coverage of 0.2 atoms nm^{-2}. Their average dimensions are constant in three directions up to 1 atoms nm^{-2}. The Ni clusters have an oval shape with average sizes of 1.8 nm (along [001]) × 1.4 nm (along [$1\bar{1}0$]) × 0.38 nm(in the [110] directions). Above the coverage of 1.0 atoms nm^{-2}, an increase in the cluster height occurs, retaining an almost constant lateral size. It is proposed that the interaction of the Ni cluster and the support surface regulates the Ni cluster size.

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In the supported metal catalysts, metal particle size and morphology dramatically alter the catalytic properties [1,2]. Nickel supported on TiO_2 is a typical catalyst for hydrogenation of CO, and unsaturated hydrocarbon [3]. It is frequently studied in surface science. The electronic and geometric structures of the deposited Ni species have been determined independently by XPS, AES, RHEED, STM and EXAFS [4 - 11]. Previous STM experiments have indicated that three-dimensional particle growth at coverages of 2 and 10 atoms nm^{-2} [8,9]. Interesting features of the Ni metal growth on the TiO_2(110) surface are that the Ni islands are located preferably at step edges and Ni size is controllable by *D* (diffusion coefficient) to *F* (flux rate) ratio (*D*/*F*)[8,9]. Those studies' STM images showed a high step edge density (about 10 lines per 100 nm^2[9] or higher [8]). The Ni adatoms strongly interact with the step edge. Koike et al. reported that the monoatomically dispersed Ni adatoms were adsorbed selectively on the $<1\bar{1}n>$ step edge based on the polarization-dependent total reflection fluorescence EXAFS (PTRF-EXAFS) results [12]. These earlier works have raised us the following questions.

(1) Is it impossible for Ni adatoms to nucleate on the terrace?

(2) If possible what is the structure of Ni cluster growing on the terrace?

These questions have motivated this study. We prepared the TiO_2(110) surface with a low step density (typical density of less than 2 lines per every 100 nm^2) and investigated the growth mode of Ni on the wide terrace of TiO_2(110) using STM.

A rutile TiO_2(110) single crystal (13 × 4 × 0.3 mm^3; Earth Jewelry Co., Japan) was calcined at 1273 K for 2 h in air and then introduced to a STM/AFM UHV chamber(Omicron Nanotechnology GmbH). The base pressure of the chamber was less than 2.0 × 10^{-8} Pa. The sample was cleaned using several cycles of Ar^+ sputtering for 15 min (acceleration energy of 4 keV, ion current of ca. 10 μA) and the annealing at ca. 900 K for 40 min[13-15]. These procedures gave a sharp (1 × 1) LEED pattern. The STM images of the TiO_2(110) were recorded at room temperature with positive sample bias voltages (+1.5 ~ +2.0 V) in a constant current mode(0.2 nA). Nickel was deposited at room temperature using an electron beam evaporator (EFM3; Omicron Nanotechnology GmbH). A typical flux rate was 0.1 atoms nm^{-2} s^{-1} which was monitored in real time by a built-in flux monitor. The absolute amount of Ni deposition was calibrated using a quartz microbalance(ULVAC, CRTM-6000 resolution=0.004 nm in thickness) placed at the sample position. We denoted the surface Ni density in units of atoms nm^{-2}.

Figure 1 shows a wide range of STM image (150 × 150 nm^2) for the Ni on the TiO_2 (110) with the coverage of 1 atoms nm^{-2}. This picture depicts only two steps. The average step density was 1.5 lines per 100 nm^2. We observed that many flat and small Ni islands on the terrace and Ni clusters were not predominantly located at the step edges though previous studies had found [8,9] that islands were formed selectively on the step edges. The size was apparently uniform. The Ni clusters were oval with the long axis along the [001] direction, as shown in Fig.2, which corresponds

to a narrow scanned image. The Ni cluster was influenced by the TiO_2(110) anisotropic structure [4]. Figure 3 shows the cluster size distribution for the sample with 1 atoms nm^{-2}. The lengths along the [001] and $[1\bar{1}0]$ directions were measured using full width at half maximum (FWHM) of cluster images. Size distributions in both directions were sharp; they approximated a Gaussian distribution. The standard deviations in both directions were 0.3 nm. The average lengths along the [001] direction and the $[1\bar{1}0]$ direction were 1.8 nm and 1.4 nm, respectively. It is noteworthy that the STM often overestimates the particle size because of the tip convolution effect [16]. These values are the maximum estimation of the cluster size. The cluster was rather flat. The average height was 0.38 nm, as measured from the Ti rows. Judging from the Ni atomic diameter (ca. 0.25 nm), the height corresponded to one or two atomic layers. Tanner et al. claimed that spherical Ni islands grew at the step edges [8]. They did not give particle size explicitly, but judging from the Fig.1 in reference [8], the particle diameter was 1.2 - 3.0 nm. Zhou et al. reported that Ni islands grew three-dimensionally with average height of 0.62 nm and diameter of 3.0 nm [9]. Therefore, we infer that the Ni cluster grown on the terrace site was smaller than those reported previously. We sometimes found Ni clusters at the step edges. The clusters were as small as those found on the terrace. The difference from the previous works was smaller D/F in addition to the step density. Our flux rate(F) was roughly equivalent to those of Tanner's experiments[8], but about one-order faster than the flux rate used by Zhou[9]. The deposition temperature in the previous work was

equal or higher than ours which may increase the diffusion constant(D). Different particles sizes determined here and in previous reports are attributed to different D/F and step densities discussed later.

Figure 4 shows STM images of the Ni deposited on the TiO_2(110) with various Ni coverages. The cluster size seemed to be unrelated to the coverage. The shape was oval for all coverages. We observed a cluster at the coverage of 0.2 atoms nm^{-2}. Xu et al. reported that Pd dimers and tetramers were observed on TiO_2(110) terrace at the coverage of 0.3 atoms nm^{-2}[17]. They suggested that the dimer was the most stable cluster. We observed no such small clusters as dimers or tetramers. This means the dimers and tetramers were not stable clusters in the case of Ni at room temperature. Figure 5 shows the coverage dependence of average sizes along the [001] and the $[1\bar{1}0]$ directions together with the cluster height. The lateral size and height of the cluster were almost constant upto 1 atoms nm^{-2}. The cluster density increased with the coverage. Above 1 atoms nm^{-2}, the height started to increase with a gradual growth in the lateral directions while the cluster density increase was slow. The 1 atoms nm^{-2} seemed to be a critical point from the flat two-dimensional nucleation to the three-dimensional cluster growth. Growth rate in the lateral direction is slower than that in the vertical direction because the number of the newly coming Ni atoms is larger on the Ni cluster terrace than the number of Ni atoms growing at the peripheral regions.

The following list summarizes our salient findings in this work.

1. Ni clusters *can grow on terrace regions* on the TiO_2(110) surface with sufficiently low step density and at the low D/F growth conditions.
2. The Ni clusters are formed at the very low coverage of 0.2 atoms nm^{-2}.
3. The Ni cluster is oval. Dimensions of the cluster with coverage less than 1 atoms nm^{-2} are distributed sharply around 1.8 nm along the [001] and around 1.4 nm along the $[1\bar{1}0]$ directions in average. The cluster is flat with height of 0.38 nm.
4. Additional deposition of Ni increases the cluster height; the cluster density increase rate lessens.

Taking all previous and present experimental data into account, we propose the following growth mechanism of Ni clusters on the TiO_2(110) surface. The Ni adatom can reach the step edges where the Ni adatom can stably adsorb [12] and can be a nucleation site to grow Ni islands [8,9] if the density of Ni adatoms is low and their diffusion rate is high. On the other hand, when the Ni adatom density becomes larger, the Ni adatom finds the other Ni atom to form a dimer before reaching the step edges. The dimer is less mobile and stays longer on the terrace. The dimer captures another migrating adatom to grow clusters. These dimer and clusters decay by losing the Ni atom. In this sense, the dimer and clusters are called as subcritical clusters where the decay

process is faster than the growth process [18]. The Ni adatoms migrating on the terrace are caught by the step edges if the step density is high. Consequently, the Ni adatoms on the terrace became fewer. The dimer and the subcritical clusters on the terrace decrease accordingly and finally vanish. For this reason, the cluster was little observed on the terrace site in the previous literature [8,9].

When the step density and/or D/F are sufficiently low, Ni adatoms can persist longer on the terrace. Larger adatom density on the terrace increases the probability for adatoms to reach dimers and subcritical clusters; subsequently the average size of subcritical clusters increases. Some subcritical clusters grow a critical cluster size and catch one more adatom to be a stable cluster [19-21]. The stable cluster has a low decay probability and the clusters are found on the terrace. Depending on the step edges and the D/F value, the nucleation site switched from the step edge to the terrace. Similar interaction of the step edges in the layer growth has been reported on the Si on Si single crystal surface[22 -25].

These coverages up to 1 atoms nm^{-2} might be classified into a so-called pure nucleation region in the diffusion-mediated island formation theory [19]. However, the Ni cluster growth on the TiO_2(110) is different from nucleation and growth process on metal. In the islands on metal surfaces, the smallest clusters are dimers[20]. The stable cluster size on the TiO_2 (110) terrace is composed of more than 10 atoms, maybe of around 40 atoms. The other difference is that the

vertical growth is preferably observed when the coverage is greater than 1 atoms nm^{-2}. Vertical growth occurs not because of the direct impingement, but the surface migration, because the cluster occupies only about 5% of the total area (cluster density 0.02 nm^{-2}; cluster area per cluster = 1.4 × 1.8 nm^2 = 2.5 nm^2; consequently, the total surface area of Ni clusters = 2.5 nm^2 × 0.02 nm^{-2}=0.05). Similar cluster growth phenomenon was reported on Cu on TiO_2 (110) [16]. Small Cu islands of a certain size were created and their density increased linearly up to the saturation coverage where the density increase ceased and the height increase began. Such a growth mode is known as self-limiting. However, because the cluster's lateral size is regulated to a certain value in this work, we call such a growth mode 'self-regulated'. The size regulation of the Ni cluster on the TiO_2(110) terrace indicates that the cluster having the specified size has a maximum stabilization energy caused by the structural matching of the Ni cluster with the TiO_2(110) lattice. Single Ni adatoms have too little interaction with TiO_2(110) surface to be stabilized on the terrace site [12]. In this sense, the interaction between the Ni cluster and the TiO_2 (110) is the "collective interaction" through multipoint bond formation. Addition of Ni atoms to the stable cluster occurs in the vertical direction more readily than in the lateral direction because the Ni-Ni bond formation in the vertical direction may gain more stabilization energy than the Ni-TiO_2 interaction at the peripheral region of the cluster.

We found that size-regulated Ni clusters form on the terrace site at the coverage of 0.2 atoms

nm^{-2} and that the lateral size and height are kept constant up to 1 atoms nm^{-2} with a linear increase of the cluster density.

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Figure captions

Fig. 1 STM images of Ni clusters on TiO_2(110) at the coverage of 1 atoms nm^{-2} . a) A wider range image. The area depicted is 150 × 150 nm^2. Sample bias was 2.5 V and current was 0.1 nA.

Fig. 2 A narrow scan STM image. The depicted is 7.2 x 6.4 nm^2 . The Sample bias was 2.5 V and current was 0.2 nA.

Fig. 3 Cluster size distribution curves of the Ni clusters on the TiO_2(110) surface for 1.0 atoms nm^{-2}. (a) parallel to [001], (b) parallel to $[1\bar{1}0]$, and (c) parallel to [110] (height). Solid line is a Gaussian approximated curve.

Fig. 4 STM image of Ni deposited on the TiO_2(110) clean surface at room temperature: (a) 0.2 atoms nm^{-2}, (b)1.0 atoms nm^{-2}, and (c) 1.7 atoms nm^{-2}, 30 nm × 30 nm with bias voltage=+2.5 V, and tunneling current=0.2 nA.

Fig. 5 Dependence of average sizes, height and density of the Ni clusters on the coverage: (a) parallel to [001] direction on TiO_2(110); (b) parallel to $[1\bar{1}0]$ direction on TiO_2(110); (c) average height (parallel to [110]); and (d) cluster density.