Structural and Morphological Study of Ni Clusters Deposited on SrTiO₃ Surfaces Studied by UHV-TEM/STM

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Ni clusters and particles grown on SrTiO₃(001) were investigated with UHV-TEM/STM combined system. Substrate surface was cleaned by chemical etching and subsequent electron beam heating, and confirmed by TEM observation and EELS analysis. Direct observation of Ni clusters deposited on these substrates revealed that they grow epitaxially and coherently. When the cluster size is small, they have almost the same sizes. When they become bigger, their heights and diameters began to show variation. In both cases, their structures were deformed due to lattice strain. Reduction and oxidation process changed their heights and morphology. These results suggest strong interaction at the interface.

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I. INTRODUCTION

Metal clusters grown on oxide surfaces are attracting increasing interests due to their importance in various fields such as insulating films, fuel cells, solar cells, catalysis, and so on [1–3]. One of the key importance of this technology is to control the interface between these surfaces and metal films/particles grown on them. Chemical character including bonding and charge distribution depends strongly on interfacial structure such as epitaxial relationship, coherency, defects, dislocations and so on. Thus model studies under high vacuum are required to control and understand each phenomenon precisely. At the same time, it is of great importance to analyze these systems under “environmental” condition, where ambient atmospheres are tuned to resemble real reaction condition.

SrTiO₃ (STO) single crystals have been investigated numerously due to their applicability as sensors, photocatalysis, gate dielectrics, substrate for high-Tc superconductors and interconnect materials of solid oxide fuel cells [4–6]. STO crystals have simple cubic perovskite structure with ionic charges of Sr²⁺, Ti⁴⁺, and O²⁻. Along [001] direction, the crystals has a repeated stacking of individual TiO₂ and SrO layers. Growth and properties of varieties of metals on STO surfaces have been studied extensively [7]. Ni is one of these metals which are especially well utilized in reactive systems. Previous studies revealed that Ni bonds with outmost surface O to form 2D NiO in very early stages and that work function increases after Ni deposition [8–11]. However, direct observation of first clusters or films as well as their changes in environmental condition has not been performed so far.

In this study, Ni clusters on STO surfaces were observed using UHV- transmission electron microscope (TEM)/scanning tunneling microscope (STM) system. The system enables fabrication and observation of specimens without taking them out of vacuum. Also, reduction and oxidation (redox) were performed in one of the chambers of the system. Direct and consistent observation of Ni clusters in both ideal and semi-actual conditions revealed their morphology and structure as well as properties.

II. EXPERIMENTS

The experiments were performed in Ultrahigh-Vacuum TEM/STM Integrated Characterization System (UTSICS) which is a combination of UHV sample preparation chambers and UHV microscopes (STM: JSPM-4500XT, TEM: JEM-2000VF) with base pressure of ~10⁻⁸ Pa [12].

The substrates were cut from a SrTiO₃(001) wafer (La-doped, 5at.%) to rectangular shapes and prepared as either STM or TEM specimens. Both were treated in NH₄-HF buffer solution (buffered HF:BHF, pH ~4.5) for 10 min. to effectively remove surface SrO planes and achieve TiO₂ termination [13]. After being loaded in UTSICS, they were annealed in the cleaning chamber at about 1100 K for 30 min. by electron bombardment, and were confirmed the cleanness of the surfaces by STM images or TEM profile images.

Deposition was performed in a deposition chamber of UTSICS by electron beam at RT. The deposition rate was about 0.01 nm/s. The samples were transferred to either STM or TEM for further observation.

Redox was performed in the high-vacuum chamber of UTSICS. Some of the samples were repeatedly annealed in oxygen ambient of 3.0 Pa and in vacuum of 1.0×10⁻⁴ Pa with an infrared heater at about 900 K for 30 min.

TEM images were taken with an accelerating voltage of 200 kV. High-resolution images were acquired with CCD camera (Gatan Orius SC200). EELS measurement was performed with Enfina 1000 (Gatan) attached to the UHV-TEM. Ex-situ TEM observation was done with JEM-3000F at 300 kV. The samples were prepared using focused ion beams in this case. STEM images were taken

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III. RESULTS AND DISCUSSION

A. Surface conditions

Controlling the surface condition prior to cluster deposition is crucial to fabricate and observe defined interface. Chemical treatment is effective in obtaining wide and flat surfaces but it leaves undesired carbon related compounds on surfaces. Moreover, ion-milling inevitably cause carbon contamination to TEM samples. Here, simple sample annealing in UHV is adopted for cleaning the substrate surfaces.

Figure 1 shows EELS low-loss spectra acquired from as prepared (a), chemically treated (b), and annealed (c) substrates. Spectrum from as prepared substrates show huge carbon volume plasmon peak at about 24 eV which hides peaks of other elements under cover. When these samples were immersed in BHF for 10 min., the thinnest area of the TEM samples was removed due to etching. It was found from TEM observation that the edges of the samples have either \{110\} or \{100\} planes due to selective etching and that square-shaped openings were formed near them.

Spectrum from these samples show drastic decrease of carbon plasmon intensity as in Fig. 1(b) mainly because the most damaged area by ion beam bombardment was detached. However, there is still small C-peak remained. Small-sized dirt particles were also observed in TEM and transmission electron diffraction (TED).

Annealing these samples at 1100 K in UHV turned the surfaces to be almost carbon-free. Carbon plasmon peak is not recognized in Fig. 1(c). High resolution TEM observation (001 zone axis) revealed flat profile planes formed at the edges of the samples. Figure 2 is a TEM images (Fig. 2(a)) and TED pattern (Fig. 2(b)) obtained from one of these sample. In TEM image, clear (110) edge is observed with surface 1×1 structure. This is also confirmed from the corresponding surface spots in TED pattern (shown by an arrow). The pattern was taken several degrees off zone axis. Although annealing TEM samples has danger of losing the electron- transparent area of the sample, it was effective enough to prepare ideal surface for further deposition.

Annealing samples in UHV produces, however, oxygen vacancies near the surfaces [8, 14, 15]. EELS analysis performed before and after the annealing revealed decrease of O-K peaks. Also, about 5 nm sized clusters are observed on STO surfaces during STM observation after annealing. Formation of small particles on annealed samples has been reported by many research groups [15–19]. The sizes and composition of these particles depend on substrate dopant types and concentrations, and annealing and quenching conditions. While formation of SrO phase is reported on donor doped STO at relatively high temperature [15, 16], TiO phase on STO surfaces was reported at temperature below 1373 K and dopant concentration below 1 at.% [17, 18]. These phenomena can be understood within the framework of point defect chemistry formalism for donor doped STO [20, 21]. The concentration of oxygen vacancies are compensated either by an increase in dopant concentrations or by reducing the electron concentration in the form of Ti desorption. Bigger particles which are likely to be LaTiO are found on that samples as has been reported before [19] which were accidentally annealed at higher temperatures.

B. Ni deposition to controlled surfaces

Ni deposition was performed to UHV-annealed samples. Figure 3(a) shows an STM image of small clusters with the deposition amount of about 0.5 nm. It is seen that the clusters are randomly distributed. From the line profile along the white line (Fig. 3(b)), it shows that the clusters...
FIG. 3: (a) STM image of Ni clusters deposited on a STO (001) surface. 56.8 nm × 56.8 nm. $V_s = 1.0$ V. (b) Line profile along the white line in (a).

![STM image of Ni clusters deposited on a STO (001) surface.](image1)

FIG. 4: TEM images of Ni clusters on (110) edge. (a) Clusters of 1-2 ML in heights (shown by white arrows), and (b) a bigger cluster showing facets. {110} facets are shown by white lines.

![TEM images of Ni clusters on (110) edge.](image2)

are almost uniformly sized. They are typically 2-3 nm in diameters and 0.3 nm in heights.

Figure 4(a) shows TEM micrographs of clusters grown on the (110)STO edge. Ni clusters of almost the same size as those in Fig. 3(a) can be seen. The deposition amount is not known due to the profile configuration of the deposited surface. Again they have typically 2 nm in diameters. Heights of the clusters vary from 1 ML to several MLs. Detailed observation revealed that they grow epitaxially on the surface. They have epitaxial relationship such as (001)$_{\text{STO}}$/[(110)$_{\text{Ni}}$] and [100]$_{\text{STO}}$/[111]$_{\text{Ni}}$, as shown in Fig. 4(b). These clusters are 4-5 ML in heights, and have {110} facets as seen in the figure. In this case the mismatch is 4.2%. Although this mismatch is smaller than that of the clusters observed in Fig. 4(a), the cluster lattice is deformed as can be seen in the figure as bending and curving of the (111) planes. Using the formula of critical film thickness of lattice over layer modeled by van der Merwe on the basis of energy considerations [22], the critical thickness for this epitaxial relationship is roughly calculated to be around 1 nm. The formula is for the case of the film growth, not for islands or particles. However, it does tell the propensity of the clusters here to have large internal energy as well as interfacial energy and to compensate them by forms of structural changes and deformation.

FIG. 5: STM images of Ni particles (a) after oxidation (~3 Pa) and (b) reduction. Both image sizes are 270 nm × 270 nm, $V_s = 1.5$ V.

![STM images of Ni particles after oxidation and reduction.](image3)

clusters grow epitaxially and coherently even with this large mismatch indicates that there is a strong interaction, mostly a chemical reaction between the Ni clusters and the substrate. The ratio of numbers of atoms on and inside the particles is more than 50% for those clusters, so it is expected that surface energy plays dominant role in determining the cluster morphology.

When the deposited amount is increased, the clusters becomes bigger and some of them have other epitaxial relationship such as (001)$_{\text{STO}}$/[(110)$_{\text{Ni}}$] and [100]$_{\text{STO}}$/[111]$_{\text{Ni}}$, as shown in Fig. 4(b). These clusters are 4-5 ML in heights, and have {110} facets as seen in the figure. In this case the mismatch is 4.2%. Although this mismatch is smaller than that of the clusters observed in Fig. 4(a), the cluster lattice is deformed as can be seen in the figure as bending and curving of the (111) planes. Using the formula of critical film thickness of lattice over layer modeled by van der Merwe on the basis of energy considerations [22], the critical thickness for this epitaxial relationship is roughly calculated to be around 1 nm. The formula is for the case of the film growth, not for islands or particles. However, it does tell the propensity of the clusters here to have large internal energy as well as interfacial energy and to compensate them by forms of structural changes and deformation.

Previous results suggest the formation of a two-dimensional NiO layer at the interface [9, 11]. Although it is not known from the present study whether such layer exists or not, it can be said that the interfacial Ni atoms interact with the substrate surface strongly and that the interaction is the prime factor to restrict the cluster structure and morphology. When Ni clusters become bigger and rather are called as particles, their diameters and heights show diverse variation.

C. Redox reaction

The samples were transferred to the high vacuum chamber and went through redox process. Ni clusters agglomerated into bigger particles at the first annealing, but after that they just changed their morphology and structure repeatedly and reversibly. Figure 5 shows STM images of the particles during the redox. The images are somewhat noisy because compensation of oxygen deficiency caused the loss of conductivity of the substrate surface. The par-
particles after the first oxidation (Fig. 5(a)) and after the successive reduction (Fig. 5(b)) have almost the same diameters of 20 nm. However, their heights are about 5-6 nm and 2-3 nm for Figs. 5(a) and 5(b), respectively. Also, their I-V characters obtained by tunneling spectroscopy were semiconducting with energy gap of about 3.2 eV and semi-metallic, respectively. These results suggest that the particles are changing from NiO to Ni by expanding up to the vertical direction and vice versa during redox processes.

Ex-situ cross-sectional TEM observation of these particles revealed their structures as NiO with NaCl structure \((a = 0.417 \text{ nm})\) and Ni, respectively. Both grow epitaxially but not coherently on the substrate. So the particles are relaxed compared to previous Ni clusters. Now that the ratio of numbers of atoms on and inside the particles is less than 10\%, the constraint factor is volume energy than surface energy [23].

Because lattice parameter difference between Ni and NiO is significant \((-1.19)\), the volume of Ni particles increases approximately 66\% when they are oxidized into NiO particles. The influence of thermal strain due to mismatch of thermal expansion coefficient is negligible in the present case of nano-sized particles \((11.1\times10^{-6}, 13.3\times10^{-6}, 15.0\times10^{-6}/K, \text{for STO, Ni, and NiO, respectively})\). Thus, it is rather volume increase which might affect the stability of the particles. Ni desorption is not likely to happen at the present temperature range [11]. However, the clusters do not conspicuously change their morphologies and diameters even after 4 times repetition of redox. It is suggested that the clusters rather grow vertically during the processes.

IV. CONCLUSION

Ni clusters and particles grown on SrTiO\(_3\) (001) were investigated with UHV-TEM/STM combined system. Substrate surface cleaning was done by BHF etching and subsequent electron beam heating at 1100 K. EELS analysis suggested the disappearance of surface contamination. TEM and TED observation show clean 1×1 surface structures. However, STM observation revealed some nano-sized particles which might be related to annealing.

Ni clusters showed epitaxial relationship such as \((001)_{\text{STO}}//([\overline{1}12]_{\text{Ni}})\) and \([\overline{1}10]_{\text{STO}}//[110]_{\text{Ni}}\) and \((001)_{\text{STO}}//[110]_{\text{Ni}}\) and \([100]_{\text{STO}}//[111]_{\text{Ni}}\). They grow epitaxially and coherently. When the deposited amount is about 0.5 nm, they are almost uniformly sized both in vertical and in horizontal. When the deposited amount is increased, their heights and diameters began to show variation. Their structure was deformed due to lattice strain. The clusters aggregated after annealing. Reduction and oxidation processes change their morphology. While their heights change drastically, their vertical sizes were almost unchanged. These results suggest strong interaction at the interface.

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