Morphologies and Interfacial Structures of Ni Particles on SrTiO₃ Substrates of Different Orientations*

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Ni nanoparticles formed on SrTiO₃ (001) and (110) surfaces are investigated from both horizontal and vertical directions by STM and TEM. Structures and morphologies of the nanoparticles were investigated, and their dependences of morphologies and interfacial structures on surface orientations were found out. Ni nanoparticles mostly possess the modified Wulff construction. While nanoparticles on SrTiO₃ (001) mostly have Ni {001} interfaces, those on SrTiO₃ (110) have either Ni {110} or Ni {111} interfaces. [DOI: 10.1380/ejsnt.2014.391]

Keywords: Scanning Tunneling Microscopy; Transmission electron microscopy; Nickel; Metal-insulator interfaces; Nanoparticles

I. INTRODUCTION

Metal nanoparticles on oxide substrates are widely used in various fields from catalysis, gas-sensing to solid oxide fuels cells [1, 2]. Morphologies as well as interfacial structures are key factors that determine the physical and chemical properties of these particles. Thus not only size but also shape controlled fabrication of nanoparticles is greatly desired to make them fit for practical use. For this purpose, utilization of vicinal, faceted, polar, reconstructed, and strain-controlled growth are being investigated [3-5]. SrTiO₃ (STO) (110) is attracting attention in this context [6, 7]. STO (001) is widely used as substrates for superconducting films and ferroelectric materials, but STO (110) has not been studied a lot so far. In this orientation STO has a repeated stacking of individual SrTiO₄⁺ and O₄⁻ layers along, which makes its termination polar. This makes it a good candidate for a substrate for growing nanoparticles with specific conformations [8]. At the same time, it is scientifically interesting to examine nanoparticle behavior on these less-known surfaces. However, there are only limited numbers of reports of investigation of nanoparticles on these surfaces [9]. In the present study, morphologies of Ni nanoparticles fabricated on both STO (001) and (110) substrates were investigated to understand the differences originated from surface orientations. Ni nanoparticles dispersed over STO (001) and (110) substrates are studied using scanning tunneling microscopy (STM) and transmission electron microscopy (TEM). The microscopes are maintained under ultrahigh vacuum (UHV) and are combined with a UHV sample preparation system, so that formation of nanoparticle/oxide interfaces and consecutive observation and characterization are possible without breaking the vacuum. The morphologies and structures of Ni nanopar-

ticles are investigated from both horizontal and vertical views.

II. EXPERIMENTAL

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 [10]. The samples were prepared from a SrTiO₃ (001) and (110) wafers (La-doped, 5 at.%). They were prepared either as bulk STM samples or as electron transparent TEM samples, and were treated in NH₄-HF buffer solution (buffered HF; BHF, pH -4.5) for 10 min. They were annealed in the cleaning chamber of UTSICS at 1100 K for 30 min. by electron bombardment. Then they were transferred either to TEM or to STM to confirm the cleanliness of the surfaces [11]. Deposition was performed in a deposition chamber of UTSICS by electron beam deposition at RT. The deposition thickness was 0.2 nm to 0.5 nm, and the deposition rate was about 0.01 nm/s. The vacuum during deposition was kept below 5 × 10⁻⁸ Pa. Because the saturated vapor pressure of Ni is negligibly small [12], this deposition condition provides supersaturation. At the same time, it was suggested before that the surface diffusion coefficient of Ni on STO (001) at RT is considerably low [13]. Thus Ni nuclei grow to clusters mainly with directly incident atoms. The samples were again transferred to the microscopes for further observation. TEM images were taken with an accelerating voltage of 200 kV. High-resolution images were acquired with CCD camera (Gatan Orius SC200). STM images were taken in constant current mode with positive sample bias of 1.0 – 2.0 V. Electrochemically etched W tips were used.

III. RESULTS AND DISCUSSIONS

Figure 1 displays STM images of STO substrates after annealing. It is seen that both STO (001) (Fig. 1a) and STO (110) (Fig. 1b) substrates are cleaned almost

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FIG. 1. STM images of STO substrates after annealing at 1100 K for 30 min. a) An STO (001) substrate ($V_{\text{sample}} = +1.0$ V, $I = 0.2$ nA, $54 \text{ nm} \times 54 \text{ nm}$), and b) an STO (110) substrate ($V_{\text{sample}} = +1.2$ V, $I = 0.5$ nA, $26 \text{ nm} \times 26 \text{ nm}$).

entirely and have flat terraces. Certain areas on them have surface phases, which is especially obvious in Fig. 1b where rectangular-arranged surface atom arrays appear. There are several medium to big sized holes in both images. These come from either by BHF treatment or electron beam annealing. BHF treatment is reported to effectively remove surface SrO planes and achieve flat TiO_2 -terminated terraces [14]. If there are surface defects, these locations act as etching centers resulting in formation of bigger holes. Besides these holes, there observed smaller surface defects scattered over the entire surfaces. These could be oxygen defect complexes formed during annealing [15].

Figure 2 displays TEM profile images of the same two types of substrates after annealing. Figure 2a shows a STO (100) surface, which is perpendicular to the previous (001) surface, looking from [001] direction, and Fig. 1b shows a STO (110) surface looking from [110] direction. Both surfaces are atomically flat and are with surface defects (missing atomic rows) in places. Surface reconstructions are not observed on both surfaces. Thus the surface structures of the STM samples and the TEM samples considerably resemble each other.

FIG. 2. TEM profile-view images of STO substrates after annealing. a) An STO (100) substrate, the profile surface is STO (100). b) An STO (110) substrate, the profile surface is STO (110).

Deposited Ni particles on these surfaces were also observed with both STM and TEM. Their STM images are shown in figure 3. The particle morphologies were dependent on surface orientations. Particles on the STO (001) surface (Fig. 3a) have similar sizes of about 1 – 3 nm and square morphologies. This fact agrees with the previous results of their growth in cube-on-cube mode on STO (001) substrates [13, 16]. Cube-on-cube growth is a growth with an epitaxial relationship such as

$$\text{STO}_{(001)} // \text{Metal}_{(001)}, \text{STO}_{[100]} // \text{Metal}_{[100]}. \quad (\text{I})$$

In this growth manner, the particles most likely to grow with 4-fold symmetry as truncated pyramids. It is a shape cut from the Winterbottom (modified Wulff) construction [17] with {001} planes making the topmost surface and the interface. Square shaped appearances of the particles in the figure match with this shape. The sides of the squares are mostly aligned along either [110] or $[1\bar{1}0]$. This is also consistent with the truncated pyramid shape. Epitaxial relationship (I) has a large lattice mismatch f of -9.8% , which inevitably generates large strain in nanoparticles. Generally speaking, cube-on-cube growth is favored for metals with small value of f by its low interface energy due to a high density of near coincident sites for *fcc* metal atoms on an O sub-lattice. As mentioned above, this does not apply for Ni growth due to large value of f , and particles tend to grow three dimensionally. This explains the reason why the Ni particles

FIG. 3. STM images of STO substrates after deposition of Ni (0.2 nm). a) Ni particles on an STO (001) surface ($V_{\text{sample}} = +1.0$ V, $I = 0.3$ nA, $62 \text{ nm} \times 62 \text{ nm}$), and b) Ni particles on an STO (110) substrate ($V_{\text{sample}} = +1.2$ V, $I = 0.5$ nA, $95 \text{ nm} \times 95 \text{ nm}$).

have similar sizes; beyond these sizes the internal strain due to lattice mismatch becomes too large to form a particle.

In the meanwhile, Ni particles on STO (110) surface have varying sizes and morphologies (Fig. 3b). Their sizes range from 1 nm to 8 nm. Some of them have square or rectangular shapes while others have hexagonal or truncated triangular shapes. It is simply inferred that square and rectangular particles have the same kind of epitaxial relationship as cube-on-cube, in this case, rectangle-on-rectangle, such as

$$\text{STO}_{(110)} // \text{Ni}_{(110)}, \text{STO}_{[001]} // \text{Ni}_{[001]}. \quad (\text{II})$$

The truncated triangular particles could have several interface structures. Most commonly observed ones in general are hexagon, which means interface and topmost planes are $\{111\}$ [18]. Other low index interfaces are also possible. STO has a perovskite structure with $a = 0.3905$ nm and Ni has a fcc structure with $a = 0.3524$ nm. So most matching planes are STO $\{002\}$ ($d = 0.195$ nm) and Ni $\{111\}$ ($d = 0.203$ nm) planes. If this orientation

FIG. 4. TEM profile-view images of STO substrates after Ni deposition. a) Ni particles on an STO (100) profile surface, and b) Ni particles on an STO (110) profile surface.

relationship occurs, the interface should naturally be either $\{110\}$ or $\{112\}$. Because the present system has not reached equilibrium, both cases are possible.

To make these assumptions clearer, Ni deposition with the same conditions as the STM samples was performed on TEM samples. Figure 4 displays the resultant profile view images of both orientations. Ni particles formed on profile surfaces are observed in both cases. Nanoparticles looking from STO $[001]$ are shown in Fig. 4a. The nanoparticle on the left side shows lattice fringes as illustrated in the figure. Their distances are about 0.18 nm which corresponds to Ni $\{002\}$ ($d = 0.176$ nm) in both vertical and horizontal directions. This implies that this nanoparticle actually has an epitaxial orientation relationship (I) with the interface. Though faintly imaged, its side surfaces makes about 45 degrees angle with the interface. Thus these correspond to “truncated” parts of the pyramid, namely $\langle 110 \rangle$ ridge lines.

Figure 4b shows a nanoparticle sitting on STO $(1\bar{1}0)$ surface step edge. Its topmost surface, whose normal vector is shown by a white arrow, is Ni $\{110\}$, and side surfaces, shown by black arrows, are Ni $\{111\}$. Hence this nanoparticle has an orientation relationship (II). Most of the nanoparticles are identified to have either this relationship or Ni $\{111\}$ interface, although there are other nanoparticles which do not show any fringes nor have clear shapes. Thus it can be said that the square or rectangular nanoparticles found in Fig. 3b should have $\{110\}$ interfaces and that the hexagonal ones have $\{111\}$ interfaces.

Orientation relationship (II) tends to be found in smaller nanoparticles as in the case of cube-on-cube growth (I), because it also has the same large misfit of -9.8% , and hence a large strain which prohibits larger particle growth. On the contrary, nanoparticles with $\{111\}$ interface grow completely incommensurately in a relaxed mode, so they could grow larger. This is evident in Fig. 3b, where bigger particles appeared to have hexagonal or truncated triangular shapes. Still, it is characteristic that some nanoparticles prefer to have $\{001\}$ or $\{110\}$ interfaces than the lowest energy $\{111\}$ interfaces. When there are only a few to a few tens of atoms exist in one cluster, they are easily to be influenced by the substrate atomic potentials and sometimes forms interfaces reflecting the atomic arrangements of the substrate surfaces, and/or show metal-on-top stabilization mechanism in which metal atoms directly interact with the substrate surface [19, 20]. Also, Ni clusters /particles are known to be highly reactive, and its catalysts show strong metal-support interactions [21, 22]. Vlachos et al. reported Ni–O loss peak in EEL spectrum after RT deposition of Ni onto STO (001) surface [23], which implies the occurrence of Ni–O interfacial reaction. Thus Ni atoms are likely to form nuclei on positions where they are deposited, probably being chemisorbed to the substrate, and hence forming the interface reflecting the substrate cubic or rectangle surface structure.

IV. CONCLUSIONS

In conclusion, Ni nanoparticles formed on both STO (001) and (110) surfaces are studied by both STM and TEM. The structures and morphologies of Ni nanoparticles were investigated from horizontal and vertical views. The morphologies of Ni nanoparticles vary depending on surface orientations. The nanoparticles had the Winterbottom construction or truncated version of this construction. Epitaxial relationships for both cases are also obtained. They were mostly STO (001) // Ni (001), STO [100] // Ni [100] and STO (110) // Ni (110), STO [001] // Ni [001], but some particles on STO (110) have $\{111\}$ interfaces, too. The preference of some Ni nanoparticles to form higher energy interfaces is found out.

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