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Morphological and Structural Observation of Ni and Fe Clusters on $SrTiO_3$ (001) and (110) surfaces

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Abstract

Ni and Fe clusters formed on $SrTiO_3$ (001) and (110) surfaces were analyzed using UHV-TEM and UHV-STM. Cluster morphologies as well as interface structures were investigated depending on substrate surface orientations. The results are applicable to cluster engineering.

1. Introduction

Metal layers or clusters on oxide surfaces are used in various fields such as insulating films, magnetic storage, fuel cells, solar cells, catalysis, and play essential roles [1, 2]. Controlling of cluster sizes, locations and orientations is greatly required to achieve or improve their specific characters. Thus surface engineering methodology is being investigated intensively [3, 4]

$SrTiO_3$ (STO) (001) is one of the basic oxide materials being used diversely and suited for surface engineering [5, 6], and now new attempts are being carried out to utilize other orientations of this material for the same purpose [7, 8]. Especially used ones are STO (110) and (111) whose terminations are polar. For this reason these surfaces are less stable but at the same time there are chances of surface manipulation in a desired way by controlling polarity and redistribution of the charge. They could be used as a platform of anisotropic growth of clusters and particles, or modified layers. Thus further investigation of these surfaces is worth further investigation. In this study, Ni and Fe clusters and nano-particles on clean $SrTiO_3$ (STO) substrates of two kinds of orientations were analyzed using UHV-TEM /STM combined system.

2. Experiments

The experiments were performed in a 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 $\sim 10^{-8}$Pa [9].

The specimens were prepared from $SrTiO_3$ (001) and (110) wafers (La-doped, 5at.%). The samples were treated in NH_4-HF buffer solution (buffered HF :BHF, pH ~4.5) to effectively remove surface SrO planes and achieve flat TiO_2-terminated terraces [10]. They were annealed in UHV at 1100K for 30 min. before metal deposition at room temperature (RT). They were transferred to either TEM or STM for further observations. The clusters were observed by both plan-view and profile-view imaging.

3. Results and Discussions

Surface conditions

Annealing in UHV environment was effective in removing surface contamination from samples of both orientations. Carbon peaks became undetectable in EEL spectra after annealing [11]. This was also confirmed by the disappearance of carbon related spots from diffraction patterns. The patterns of STO (001) did not show any specific surface reconstruction spots, which indicated that the most part of the surfaces are composed of simple 1x1 structure. This structure is observed by others under reducing conditions [12], which is also the case of the present study.

STO (110) patterns showed extra spots which are likely to come from surface superstructure. They could imply (1x2) reconstruction [13] which is associated with TiO_2-termination accompanied by microfaceting. However, our high-resolution (HR) TEM imaging and atomic image simulations using Multi-slice code [14] support simple TiO_2 terminated surface model with some O-vacancies. It is possible that the entire surface may have other surface terminations simultaneously as suggested by the diffraction pattern. HR-TEM also showed atomically flat surfaces on both substrates.

Ni deposition

Deposited Ni clusters were typically 2-5 nm in sizes and 2-3nm in heights for both orientations. STM observation revealed that they are randomly and separately distributed and that they are outlined either by square or truncated triangle. TEM profile-view imaging revealed that Ni clusters have modified Wulff (Winterbottom) shapes [15] with their Wulff points almost on the surface planes (partial wetting) as shown in Fig. 1. Ni clusters on STO (001) tend to show truncated pyramid shape, while those on STO (110) have hut or hexagonal shapes. Their epitaxial relationships mostly have either cube-on-cube [16]

(100)STO // (100)Ni and [010]STO // [010]Ni

or rectangle-on-rectangle relationships

(110)STO // (110)Ni and [001]STO // [001]Ni.

The lattice mismatch f of these configurations correspond to -9.8% in both cases so the clusters prefer to grow in a

non-stoichiometric mode. Using the surface energies and the interface energy, the adhesion energy of a cluster can be written as

$$E_{ad} = \gamma_{Ni} + \gamma_{STO} - \gamma_{int} \qquad (1)$$

From positions of the Wulff points, the adhesion energy of clusters on both surfaces was roughly estimated as about 2 J/m^2 [17]. Ni nanoparticles on STO (001) substrates are known to be catalytically active for synthesis of carbon nanotubes (CNT) [6]. Present results suggest that clusters on both surfaces have strong adhesion energy and that they would be suitable for a base growth of CNT.

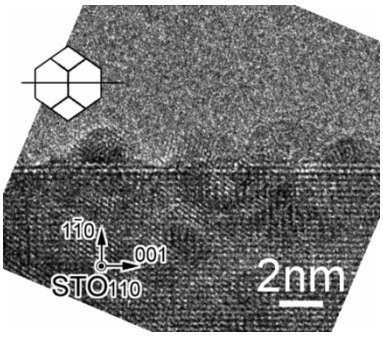

Fig.1 TEM profile-view image of Ni clusters on STO (110) surface.

Fe depositions

Deposited Fe clusters were also 2-5 nm in sizes, but 1-2nm in heights with more flattened morphologies. Their Wulff points do not lie within the equilibrium shapes. Their epitaxial relationship was

(110)STO // (010)Fe and [001]STO // [001]Fe.

The misfit of this configuration is about +3.6% in [110] direction. The fact they grow flattened with this mismatch suggests that interface free energy is relatively small compared with Ni cluster case.

3. Conclusions

Ni and Fe clusters grown on $SrTiO_3$ (001) and (110) substrates were studied with UHV-TEM/STM. Before cluster deposition, both surfaces were cleaned effectively by BHF treatment followed by electron beam annealing and showed atomic level flatness.

Both clusters grow about 2-5 nm in sizes but Ni clusters were higher than Fe clusters. Their interfacial structures and morphologies depend on substrate surface orientations. In both cases, most of the clusters have the Winterbottom constructions. On STO (001) this appears as truncated pyramids. On (110) they are either huts or hexagons. Those clusters are under the condition of partial wetting.

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