Electronically patterning through one-dimensional nanostripes with high density of states on single-crystalline Al_2O_3 domain

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Self-assembled one-dimensional nanostripes on the single-crystalline Al_2O_3 domains are found to be the nucleation sites of nanoparticles through an enhanced density of states observed by the scanning tunneling microscopy and spectroscopy. Bias-dependent topographic images and the conductivity spectra indicate that these nanostripes have both enhanced occupied and unoccupied states within the oxide bandgap. These more metallic nanostripes have stronger electronically trapping ability than the oxide domain, which can be used as a one-dimensional electronically self-patterned template for the guided growth of nanostructures. © 2008 American Institute of Physics. [DOI: 10.1063/1.2996578]

Nanostructures have become more and more important due to the potential application in nanoelectronic devices, magnetic nanostorage, heterogeneous catalysis, sensor development, etc. And in the past years, large amount of approaches have been developed into growth of different kinds of nanostructures. For example, the chemical synthetic works of semiconductor nanocrystals and silver nanowire¹⁻³ and ordered array of nanostructures were fabricated by using the technique of electron beam lithography.⁴⁻⁶ Recently, deposition of metals on semiconductor⁷⁻¹² or insulating oxide surface¹³⁻²⁰ was also used to grow nanoparticles or nanodots with great size uniformity.

However, besides different approaches of growing nanostructures, how to construct a template with functionality of the guided growth of nanostructures is also a crucial issue in the technological application as well as fundamental research. Ordered array of nanostructures provide possibility of mass customization for realistic application in nanotechnology and such spatial symmetry of nanostructures may create anisotropy to have influence on the physical or chemical properties. In particular, self-patterned and guided growth of nanostructures systems deserve many efforts to develop due to the high cost and resolution limit of electron beam lithography technique. Therefore, in this letter, an electronically patterning approach is proposed and used to have a guided growth of Co nanoparticles.²¹

Self-assembled one-dimensional nanostripes grown on the single-crystalline Al_2O_3 domain with high density of states were used as the electronically patterning template to grow well-ordered Co nanoparticles. In application of the technique of the scanning tunneling spectroscopy, the electronic properties of these nanostripes were investigated. From the tunneling spectra, these nanostripes demonstrate an enhanced density of states in both the occupied and unoccupied regions within the oxide bandgap. Such more metallic property of nanostripes exhibited a strong trapping ability,

providing the primary nucleation site of deposited metals.

The experiment was carried out in an UHV chamber with a base pressure $<2 \times 10^{-10}$ mbar. The NiAl(100) substrate was sputtered by cycles of 2 KeV Ar^+ and subsequently annealed to 1000 K whereas the temperature was monitored by thermocouple directly contacted on the NiAl(100) crystal. After annealing at 1000 K for 1 h, the substrate NiAl(100) was exposed to the oxygen gas at 1000 K and this procedure leads to formation of single-crystalline Al_2O_3 domain due to the segregation of aluminum on the surface of the NiAl(100) at high temperature.^{22,23} Further, by controlling the amount of oxygen dosage, 10 L, for example, the substrate surface of NiAl(100) can have partially single-crystalline Al_2O_3 domain growth. On the other hand, if we increase the oxygen dosage to 1000 L, the substrate surface of NiAl(100) can have fully single-crystalline Al_2O_3 domain covered. In the large scale scanning tunneling microscopy (STM) image shown in Fig. 1(a), the surface is covered by fully crystalline oxide thin film with nanostripes self-organized grown on it, indicated by the bright protrusive lines with the line profile in the inset. Besides, the crystalline structure and chemical composition of sample was checked by low energy electron diffraction (LEED) and Auger elec-

FIG. 1. (Color online) (a) Large scale STM image of surface covered by full crystalline Al_2O_3 domain. Inset is the line profile of protrusive nanostripes self-organized grown on Al_2O_3 domain. (image sizes $200 \times 200 \text{ nm}^2$, $U = +2.4 \text{ V}$, $I = 0.4 \text{ nA}$). (b) LEED pattern of full crystalline Al_2O_3 domain; there is the 2×1 superstructure of typical single crystal Al_2O_3 and the splitting of the 2×1 are indicated by the white arrow.

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FIG. 2. (Color online) [(a) and (b)] STM images of a single long Al_2O_3 domain with two nanostripes at the bias voltage of +3.0 V (concave) and -0.5 V (protrusive), respectively (image size $17.4 \times 29.2 \text{ nm}^2$). (c) Extended bias voltage dependence of apparent heights. The color mapping indicates the topographic relative height contrast reverse.

tron spectroscopy, respectively. As shown in the LEED pattern in Fig. 1(b), 2×1 superstructure indicates the presence of single crystalline Al_2O_3 film, and the splitting of the 2×1 spots comes from the periodic nanostripe formation due to the lattice mismatch between the oxide film and the $\text{NiAl}(100)$ substrate. This also supports the finding observed by STM. The deposition rates are calibrated from the epitaxial growth on $\text{Cu}(100)$,^{24,25} the 1 ML defined in this letter is the surface atom density on $\text{Cu}(100)$, i.e., $1.54 \times 10^{15} \text{ atoms/cm}^2$.

Figure 2(a) and 2(b) demonstrate the STM images of low oxygen exposure growth of a single long Al_2O_3 domain with two nanostripes at the bias voltages of +3.0 and -0.5 V. Topographically, these two nanostripes appear as the dark (concave) and the bright (protrusive) lines at +3.0 and -0.5 V, respectively. From the line profiles at the bottom of

FIG. 3. (Color online) (a) STM topographic image of the nanostripes (image size $20 \times 20 \text{ nm}^2$, $U = +2.0 \text{ V}$, $I = 0.4 \text{ nA}$). (b) Current mapping image at -1.8 V. (c) I - V curves of the oxide domain and the nanostripe. The dI/dV curves are obtained in the inset and indicate the enhanced density of states induced by the nanostripes. (d) A series of conductance spectra in the log scale taken from A to B [see (b)] and the gap states induced by the nanostripes are indicated by the two white arrows.

Figs. 2(a) and 2(b), the apparent height of Al_2O_3 domain decreases about 1.5 Å from ~ 3.0 to $\sim 1.5 \text{ Å}$ as the bias voltage is reduced from +3.0 to -0.5 V. Moreover, there is a relative height contrast reverse between the nanostripes and the domain at about +1.5 V and, as shown in the Fig. 2(c), the extended series of line profiles with the color mapping also clearly indicates such relative height contrast reverse. According to the previous study,¹⁵ the nanostripes in the topography are not concave but protrusive. But, from our above experimental results, we can see that these topographically protrusive nanostripes reported in the previous study¹⁵ are actually due to the different scanning bias voltages. And such relative height contrast reverse reflects that the electronic properties of nanostripes are different from the oxide domain.

In order to have further understanding of the electronic properties about these nanostripes,²⁶ we did the measurement of the $I(V)$ characteristics by the tunneling spectroscopy. In the spectroscopy mode, the current is recorded as a function of bias voltages while the feedback loop is off at each pixel of the STM image. The morphology of a single long Al_2O_3 domain with two nanostripes as well as the current mapping image taken at -1.8 V are depicted in Figs. 3(a) and 3(b), respectively. In Fig. 3(b), as marked by the solid circle, the two nanostripes are presented by different color levels as compared to the Al_2O_3 domain (open circle) and this means the current value of nanostripes is different from Al_2O_3 domain at -1.8 V. The corresponding $I(V)$ curves plotted in Fig. 3(c) indicate smaller bandgap for the nanostripes as compared to the Al_2O_3 domain. The conductivity spectra shown in the inset of Fig. 3(c) directly elucidate that the nanostripe has higher density of states than the oxide domain in both the occupied and unoccupied regions. These conductivity spectra also explain the phenomenon of relative height contrast reverse described in the above bias-dependent ap-

FIG. 4. (Color online) (a) STM image of the single Al_2O_3 domain with two nanostripes (image size $50 \times 70 \text{ nm}^2$, $U = +3.0 \text{ V}$, $I = 0.4 \text{ nA}$). (b) *In situ* image after depositing of 0.25 ML Co/ Al_2O_3 /NiAl(100) (image size $50 \times 70 \text{ nm}^2$, $U = +2.0 \text{ V}$, $I = 0.4 \text{ nA}$); the nanostripes demonstrate the strong trapping ability and turn the Co nanoparticles into the one-dimensional nanoparticle chains. (c) Random growth of 0.15 ML Co nanoparticles on the Al_2O_3 domain in the absence of nanostripes (image size $100 \times 100 \text{ nm}^2$, $U = +2.0 \text{ V}$, $I = 0.4 \text{ nA}$). (d) 0.15 ML Co deposited on full Al_2O_3 domain on NiAl(100) at room temperature (image size $100 \times 100 \text{ nm}^2$, $U = +2.0 \text{ V}$, $I = 1.2 \text{ nA}$). This image reveals that the well-ordered cobalt nanoparticles can be grown through such one-dimensional electronically self-patterned template.

parent height measurements. A series of log conductance spectra taken from A to B [see Fig. 3(b)] demonstrates the enhanced density of states of nanostripes within the energy range of the oxide bandgap, as indicated by the two white arrows in the Fig. 3(d). This shows that these nanostripes are electronically more metallic than the oxide domain.

Figures 4(a) and 4(b) display the *in situ* images before and after deposition of 0.25 ML Co on the same single long Al_2O_3 domain with two one-dimensional nanostripes. After 0.25 ML Co deposition, the Co atoms nucleate along the nanostripes and form the highly aligned nanoparticle chains. Moreover, for comparison, a single long Al_2O_3 domain without nanostripes was prepared at low oxygen gas dosage condition. On such domain, in contrast to that with nanostripes, only disordered Co nanoparticles were grown in a way without any electronic preference, as shown in Fig. 4(c).

As mentioned above, if we increase the amount of oxygen dosage to 1000 L, a surface fully covered Al_2O_3 domain with nanostripes can be grown. The morphology of self-aligned 0.15 ML Co nanoparticles grown on such template are shown in Fig. 4(d). These more metallic nanostripes demonstrate the strong electronically trapping ability of supported nanoparticles. In application of this functionality, well-ordered nanostructures or chemical molecules can also be grown on this electronically self-patterned template.

According to the simple band-orbital mixing model,^{27,28} the oxide with smaller bandgap has more density of states to hybridize with the molecule orbitals easily, leading to stron-

ger adsorption energy. This model could be also used to explain the finding of the well-ordered Co nanoparticles nucleated at the one-dimensional nanostripes, where the enhanced density of states within the energy range of the oxide bandgap may increase the adsorption energy, and in turn the nucleation probability of Co particles at nanostripes.

In summary, from the conductivity spectra, the nanostripes on the Al_2O_3 domain have both enhanced occupied and unoccupied states within the oxide bandgap. Such more metallic nanostripes can easily hybridize with orbitals of adsorbates as compared to the Al_2O_3 domain. An electronically self-patterned template can be formed in this way for a guided growth of nanomaterials or chemical molecules with well ordering.

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