Self-assembled supported Co nanocrystals: The adhesion energy of face-centered-cubic Co on $SrTiO_3(001)$-(2×2)

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We have investigated the structure and morphology of self-assembled cobalt nanocrystals supported on a $SrTiO_3(001)$-(2×2) substrate using scanning tunneling microscopy. Nanocrystals with a truncated pyramid shape were imaged, allowing crystallographic identification of the cluster facets. These nanocrystals result from the epitaxial growth of fcc Co on $SrTiO_3(001)$. The dimension of the nanocrystal facets at equilibrium and an energy minimization calculation result in $\gamma_{adh}=(3.96\pm0.37)\mathrm{J/m^2}$ for the adhesion energy of face-centered-cubic $Co/SrTiO_3(001)$-(2×2).
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Morphology is a key factor that determines the physical and chemical properties of nanocrystals. Their magnetic properties in particular can be significantly influenced by their shape. With regard to applications, one ultimate objective is to create organized arrays of self-assembled magnetic nanocrystals of similar sizes and shapes for use in superhigh density recording media. An initial step toward this goal is to gain a deeper understanding of the processing conditions required for self-assembled magnetic nanocrystal growth.

In this letter, we report on the epitaxial growth of Co nanocrystals on a $SrTiO_3(001)$ substrate. Co particles are model experimental systems for studying magnetoresistance[1] and magnetic anisotropy.[2–4] The understanding of the Co particle properties requires a precise description of their atomic structure, because Co can adopt different crystallographic structures. The Co natural bulk structure is hexagonal close packed,[5–8] but Co can grow epitaxially in the form of metastable body-centered-cubic (bcc),[9,10] face-centered-cubic (fcc),[6–8,11–13] or face-cenetred-tetragonal[14] thin films. The crystal structure can affect the properties of the clusters.[15]

Interest in the $SrTiO_3$ surface has emerged from its electronic properties[16] and its use as a substrate for supported nanocrystal growth.[17] The $SrTiO_3(001)$ surface presents a multitude of different reconstructions[18,19] depending on sample preparation, which can be used for the growth of regular nanocrystals over macroscopic length scales. $SrTiO_3$ crystallizes into the cubic perovskite structure with a 3.905 Å lattice parameter. In its pure form it has a 3.2 eV band gap which would make it unsuitable for imaging in the scanning tunneling microscope (STM). To overcome this problem, we use crystals doped with 0.5% (weight) Nb. The crystals were epipolished (001) and supplied by PI-KEM, UK. We deposited Co from an electron-beam evaporator (Oxford Applied Research EGN4) using 99.95% pure Co rods supplied by Goodfellow, UK. Our STM is manufactured by JEOL (JSTM 4500s) and operates in an ultrahigh vacuum (UHV) (10^{-8} Pa). We used etched W tips for imaging the samples at room temperature with a bias voltage applied to the sample. A $SrTiO_3(001)$-(2×2) reconstructed surface was obtained after Ar^+ bombardment and annealing in UHV at 800 °C for 5 h.

Figure 1 shows the atomic structure of the $SrTiO_3(001)$-(2×2) surface used for cobalt deposition. The periodicities along the ⟨100⟩ crystallographic axes are 7.7 Å, which is close to the double periodicity of $SrTiO_3(001)$ (3.905Å). The (2×2) reconstruction was also verified by low-energy electron diffraction.

Figure 2 shows the topography of the $SrTiO_3(001)$-(2×2) surface following deposition of 3 monolayers (MLs) of Co on a substrate heated to 320 °C followed by a subsequent 45 min anneal at 320 °C. The large-scale STM image [Fig. 2(a)] shows that Co has self-assembled into similarly sized nanocrystals. The Co nanocrystals have a square top surface and a square base. Only this shape of nanocrystal was observed. At higher magnification [Fig. 2(b)], around 80 Co nanocrystals can be seen in the $60\times60\ \mathrm{nm^2}$ image, the nanocrystals have the shape of a truncated pyramid. The predominant cluster height was measured at 15.8Å. Nanocrystal heights are quantized into steps of 1.8Å [Fig. 2(c)]. The side facets of the nanocrystals were measured at an angle of $54.3°\pm3.4°$ with respect to the substrate. These investigations of the shapes show that Co is cubic packed and the nanocrystals have a (001) top facet and four (111) side facets. If re-entrant (111) facets were present on the nanocrystals then (001) side facets would also exist giving rise to an

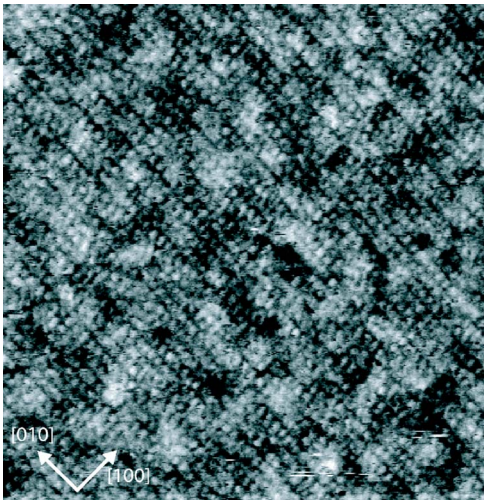

FIG. 1. (Color online) STM image of the $SrTiO_3(001)$-(2×2) reconstructed surface ($39\times40\ \mathrm{nm^2}$; $V_s=+1.0$ V, $I_t=50$ pA).

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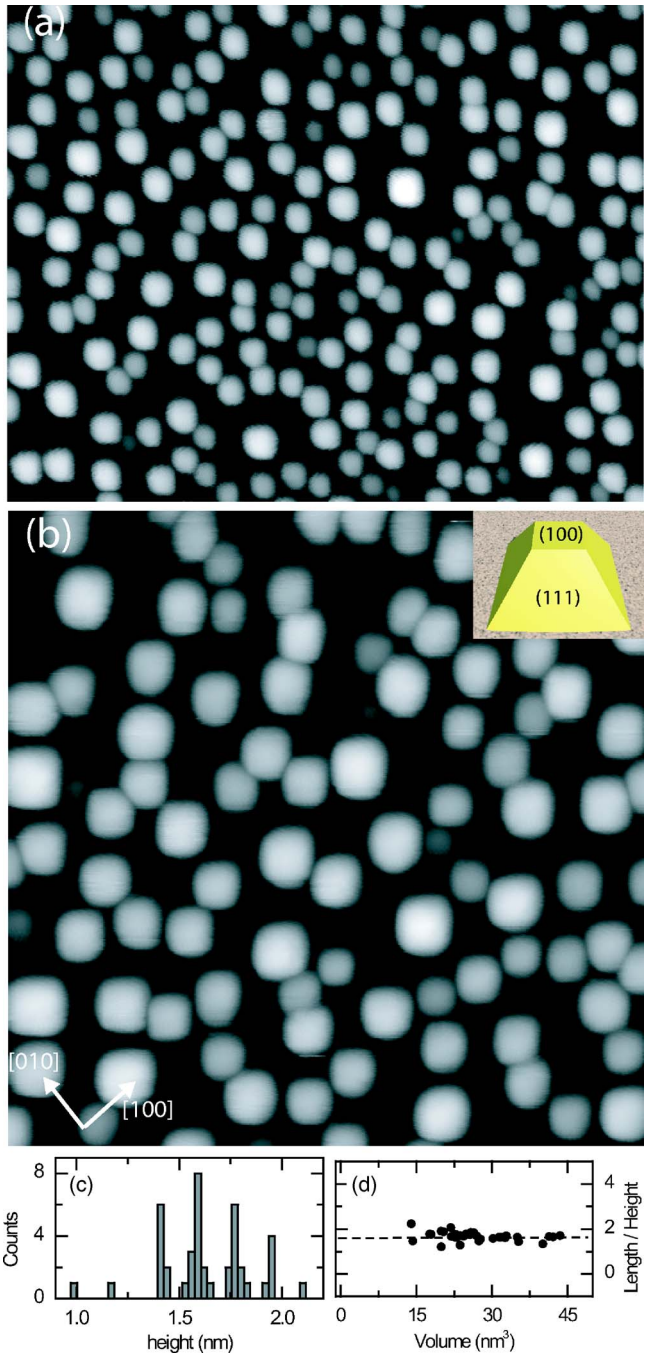

FIG. 2. (Color online) Co deposition onto a 320 °C $SrTiO_3(001)$-(2×2) substrate followed by a 320 °C anneal gives rise to truncated pyramid-shaped nanocrystals as shown in the STM image (a) (100×80 nm^2) and (b) (60×60 nm^2); ($V_s=+1.0$ V, $I_t=0.3$ nA). Inset: Truncated pyramid shape, the {111} and {001} faces are indicated. The island height histogram is shown in (c), and the constant height-to-length ratio is shown in (d).

imaged octahedral nanocrystal base, which was never observed. The interface is a (001) plane and the interface crystallography is $(001)_{Co}\|(001)_{SrTiO_3}$, $[100]_{Co}\|[100]_{SrTiO_3}$. As a guide to the eye, we have shown in Fig. 2(b) (inset) a schematic illustration of a truncated pyramid. The ratio of the length (l) of the top square to the height (h) of the truncated pyramids as a function of volume is shown in Fig. 2(d). In order to reduce the effect of tip convolution, the top flat surface dimension (l) is taken until the beginning curvature, which indicates the position of the edge. The constant ratio of $l/h=1.68\pm0.19$ implies that these pyramidal nanocrystals have reached their equilibrium shape. The error in the ratio denotes the standard deviation of the measurements.

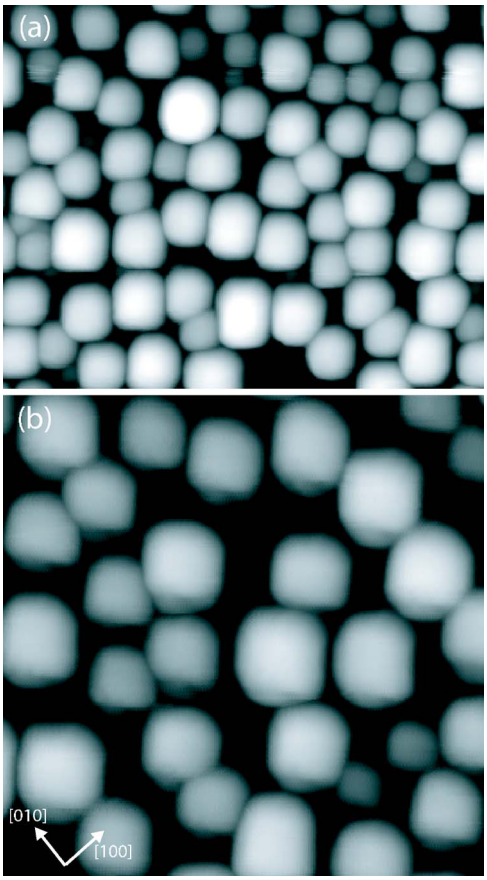

FIG. 3. (Color online) Co deposition onto a 385 °C $SrTiO_3(001)$-(2×2) substrate followed by a 385 °C anneal gives rise to truncated pyramid-shaped nanocrystals as shown in the STM image (a) (100×80 nm^2) and (b) (60×60 nm^2); ($V_s=+1.0$ V, $I_t=0.3$ nA).

We now show results for a similar experiment to the one just described but at an increased temperature. Figure 3 shows the topography of the $SrTiO_3(001)$-(2×2) surface following 385 °C deposition of 4 ML of Co and a subsequent 45 min anneal at 385 °C. Around 30 Co nanocrystals can be seen in the 60×60 nm^2 image. The increase in temperature affects the mobility of the Co on the surface. At higher temperatures, the nucleation rate decreases and less clusters are formed but they are larger. Nevertheless the nanocrystal shapes stay the same, i.e., the same length to height ratio is maintained as for the smaller crystals. We did not observe any shape transitions with volume or temperature as observed in the case of $Pd/SrTiO_3(001)$,[17] or in strained Ge on Si growth.[20,21]

The STM images show that cobalt adopts cubic packing on $SrTiO_3(001)$ to form truncated pyramid nanocrystals. Cubic packed Co thin films can exist in the bcc (lattice constant $a_{bcc}=2.82$ Å) and fcc structure (lattice constant $a_{fcc}=3.545$ Å). The interplanar periodicity along the [001] direction is one-half of the unit-cell dimension for both lattices (1.44Å for bcc, 1.77Å for fcc). The height quantization of 1.8Å of the nanocrystals, as shown in Fig. 2(c), indicates that in our experiments Co is fcc packed. When considering the lattice matching of the cobalt to the $SrTiO_3(001)$ substrate, we find that for the Co bcc structure there is a 27.8% lattice mismatch, whereas for the fcc structure the mismatch is only 9.2%.

The equilibrium shape of a cobalt nanocrystal on a $SrTiO_3(001)$ substrate is determined by the surface energies of the Co crystal facets (γ_{hkl}), the interface energy between the Co crystal and the substrate (γ_i), and the surface energy of the substrate (γ_{STO}). In our case, only {111} and {001} facets are seen on the nanocrystals and therefore the change in surface and interface energy between a bare substrate and one supporting a crystal is:

$$E = \gamma_{001}A_{001} + \gamma_{111}A_{111} + \gamma_i A_i - \gamma_{STO}A_i,$$
$$= \gamma_{001}A_{001} + \gamma_{111}A_{111} + \gamma^* A_i, \quad (1)$$

where A_{001} and A_{111} are the Co facet areas, A_i is the interface area, and γ^* is defined as $\gamma_i - \gamma_{STO}$.[22] For a supported crystal of a given volume to find its equilibrium shape, E will be at a minimum. Straightforward analysis via the modified Wulff construction,[22] or by minimizing E analytically, results in the following equation for γ^* for the truncated pyramid shape as a function of γ_{001}, γ_{111}, and the length-to-height ratio.

$$\gamma^* = \frac{h}{l}\sqrt{2}(\sqrt{3}\gamma_{111} - \gamma_{001}) - \gamma_{001}. \quad (2)$$

In this equation, we can substitute the l/h ratio from our experimentally determined value, and use the theoretically calculated fcc Co surface energies of Alden *et al.*[23] ($\gamma_{001} = 2.78\ J/m^2$, $\gamma_{111} = 2.70\ J/m^2$). We estimate a $\pm 0.10\ J/m^2$ error associated with the Co surface energies. This results in $\gamma^* = (-1.18 \pm 0.30) J/m^2$. The adhesion energy γ_{adh} is defined by

$$\gamma_{adh} = \gamma_{001} - \gamma_i + \gamma_{STO} = \gamma_{001} - \gamma^*. \quad (3)$$

This results in $\gamma_{adh} = (3.96 \pm 0.37) J/m^2$.

In summary, we have investigated Co nanocrystal self-assembly on a $SrTiO_3(001)$-(2×2) support. Our results show that cobalt crystallizes into a fcc structure, which results in truncated pyramid nanocrystal formation. A volume/shape analysis of these crystals shows that they have attained an equilibrium shape. Quantitative information on the effective surface energy has been derived from a detailed comparison between the observed shape of the nanocrystals and that resulting from a Wulff construction based on calculated surface energies. For fcc Co on $SrTiO_3(001)$-(2×2), we have obtained a value of the adhesion energy $\gamma_{adh} = (3.96 \pm 0.37) J/m^2$. This system is a model template to study the size dependent magnetic properties of self-assembled pyramidal Co nanocrystals.

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