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Growth and magnetism of self-organized Co nanoplatelets on Si(111) surface

Ke He, Ming-Hu Pan, Jun-Zhong Wang, Hong Liu, Jin-Feng Jia* and Qi-Kun Xue

State Key Laboratory for Surface Physics, Institute of Physics, The Chinese Academy of Sciences, Beijing 100080, P.R. China

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Magnetic nanodots have great potential for applications in ultrahigh-density information storage, quantum computing and many other fields. In this work, Co nanoplatelets with uniform size, height and shape were fabricated by ultrahigh vacuum metal evaporation on the Si(111)-(7 × 7) surface, using a two-dimensional identical Al cluster array as the template and spacer. The Al clusters reduce Si dangling bonds significantly and prevent the reaction between Si and the ferromagnetic metal Co. Almost all Co nanoplatelets appear as equilateral triangles with a side length of 5.4 nm and a magic thickness of 2 ML, pointing in the [211] direction. *In situ* scanning tunneling microscopy (STM) was used to determine the atomic structure and atomistic formation process of the Co nanoplatelets. Magnetic properties of the Co platelets were measured by SQUID at 5 K. Such quantum dots exhibit unusually high perpendicular magnetic anisotropy. The present study demonstrates a promising pathway to directly integrate magnetic nanostructures with Si-based electronic devices. Copyright © 2006 John Wiley & Sons, Ltd.

KEYWORDS: nanodot; cluster; template; scanning tunneling microscopy; magnetic anisotropy

INTRODUCTION

Nanometer-sized magnetic particles have generated continuous interest since the late 1940s.[1] Scientifically, nanometer-sized magnetic particles could exhibit a wide range of fascinating phenomena, such as surface moment enhancement, superparamagnetism, quantum magnetization effects, etc.[1,2] Technologically, they are good candidates for ultrahigh-density information storage media.[3] Fabrication of magnetic nanoparticles with uniform size, shape and spacing has great significance both in academic studies and industrial applications. However, this mission is a big challenge for current fabrication techniques, because the achievable size has reached the limit of traditional 'top-down' lithography methods.[3] Recently, using periodic surface structures as templates, several groups have obtained uniform[4,5] and even identical[6–8] two-dimensional nanocluster arrays with 'bottom-up' self-assembly methods. These technical advancements open a new way to the fabrication of high-quality nanometer-sized magnetic particles.

Magnetic nanostructures on semiconductor surfaces have attracted much attention in recent years, because this type of materials is the base for the next generation of electronic devices, which utilize the spin degree of freedom of electrons.[9–12] However, the fabrication of magnetic nanoparticles on Si is even more challenging because the strong chemical reactions between Si and ferromagnetic materials can destroy the magnetism of the magnetic nanoparticles. Spacer layers can be deposited first before the growth of magnetic materials to passivate the Si surfaces.[13–15] However, the introduction of passivating layers adds more difficulties in controlling the growth conditions for high-quality magnetic nanoparticles.

In our present work, by using a two-dimensional identical Al cluster array as a passivating layer, we fabricated Co nanoplatelets with a very uniform size and shape on a Si(111)-(7 × 7) surface. The Al clusters suppress the reaction between Co and Si efficiently while keeping the periodicity of Si(111)-(7 × 7), which makes the Co platelets grown on it uniform. A large perpendicular magnetic anisotropy (~0.5 meV/atom) was measured on the Co nanoplatelets.

EXPERIMENTAL

The experiments were performed with an OMICRON variable temperature scanning tunneling microscope (STM) operated in an ultrahigh vacuum ($\leq 8 \times 10^{-11}$ mbar), equipped with a low energy electron diffraction (LEED)/Auger spectrometer. Our sample was a P-doped Si(111) wafer with a resistivity of 3–5 Ω cm. Clean Si(111) substrates are prepared by well-established annealing and flashing procedures. A boron nitride crucible was used to produce Al (purity 99.9999%) atomic beams. During deposition, the Al cell temperature was 900 °C, corresponding to a deposition rate of 0.067 monolayer (ML)/min (1 ML = 7.8×10^{14} atoms/cm^2). Co was deposited by the direct-current heating of a tungsten wire coated with a Co film. The Co deposition rate was about 0.1 ML/min. The magnetic properties of the samples were investigated by an *ex situ* commercial SQUID magnetometer. A chemically

*Correspondence to: Jin-Feng Jia, State Key Laboratory for Surface Physics, Institute of Physics, The Chinese Academy of Sciences, Beijing 100080, P.R. China. E-mail: jfjia@aphy.iphy.ac.cn
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etched tungsten tip was used as the STM probe. All STM images reported here were recorded at room temperature with a tunneling current of 20 to 50 pA.

RESULTS AND DISCUSSION

The fabrication of a 2D Al artificial nanocluster crystal on Si(111)-(7 × 7) has been reported by us previously.[6–8] STM images of the Al artificial nanocluster crystal are shown in Fig. 1(a) and (b). The atomic structure of the Al cluster has been determined by STM combined with first-principles total energy calculations, and is shown in Fig. 1(c). According to this model, Al clusters remove 12 dangling bonds from each 7 × 7 unit cell, leaving only 7 dangling bonds. This decreases the reactivity of the Si(111)-(7 × 7) surface greatly. The high stability and periodicity make the novel surface of the 2D Al artificial crystal an innovative template for the growth of other nanostructures.

After depositing 0.06 ML of Co at room temperature on the Al nanocluster artificial crystal (Fig. 2(a)), we can see that many Al clusters become larger and brighter (indicated by an arrow in Fig. 2(a)). These clusters must be where the Co atoms nucleate. Interestingly, the nucleation takes place preferentially at Al clusters on faulted half unit cells (FHUCs) of Si(111)-(7 × 7). Some metals, for example, Pd,[16] Ag,[17] Pb,[18] and In,[6–8] have also been reported to absorb preferentially on FHUCs of Si. This effect results from the different bonding energies of FHUCs and unfaulted half unit cells (UFHUCs).[6–8] Although in our experiments, the Al clusters occupy both halves of the unit cell equally,[6–8] the structural difference of the two halves still persists, which contributes to the different nucleation possibilities of Co atoms. Subsequently deposited Co atoms at room temperature grow into many small clusters. However, both the size and the shape of the clusters look very random (Fig. 2(b)).

At a higher substrate temperature of about 70–80 °C, initially deposited Co atoms still mostly nucleate at Al clusters on FHUC (Fig. 2(c)). Interestingly, for higher coverage, the Co nucleus grows into nanoplatelets with regular equilateral triangular shapes (Fig. 2(d)). We can see that the area not covered by Co platelets keeps the Al nanocluster array. Since Co atoms react strongly with Si and can destroy the 7 × 7 reconstruction completely even at submonolayer coverage,[19] this observation suggests that the reaction has been reduced greatly. Moreover, we found that an increase in the substrate temperature will reduce the Co platelet density. It also suggests that the Co platelet formation is not dominated by the reaction between Co atoms and the substrate, but by the nucleation of Co atoms.[19]

The STM images for different bias voltages are shown in Fig. 3. There is little change on the Co platelets. However, a dark region around every Co platelet can be observed with a bias voltage between +1.5 V and +2.5 V. The area of the dark region increases with the bias voltage. This is due to a reduced density of state above the Fermi level. A possible mechanism is due to charge transfer between the Co platelets and the Si substrate beneath the platelets. This result also confirms that there is no reaction between Co and Si.

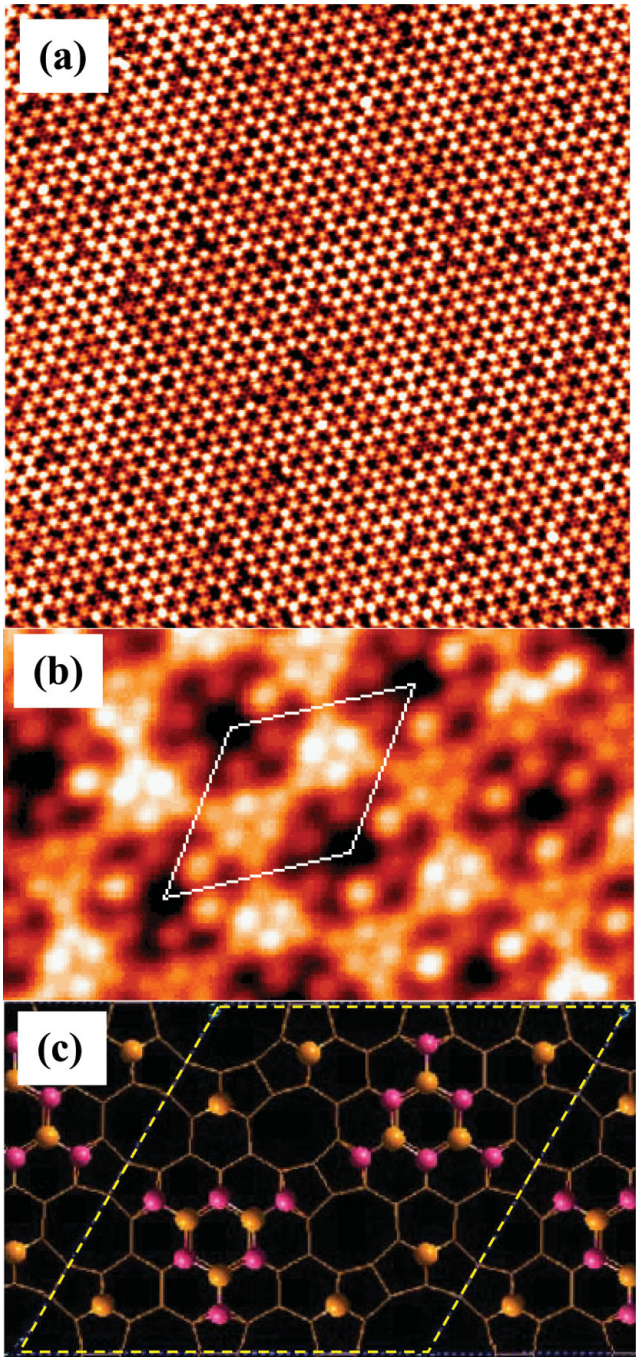

Figure 1. (a) STM image of identical Al nanocluster arrays. The image was obtained at +2.0 V. The image size is 75 nm × 75 nm. (b) Close-up view of the Al nanocluster array in (a). The image size is 7.5 nm × 7.5 nm. A unit cell is labeled. (c) Top view of the atomic structure model established for the Al cluster. The purple balls represent Al atoms and the orange ones represent Si atoms.

The Al nanocluster array plays a key role in reducing the reaction between Co and Si. It was reported that the cobalt silicide reaction on Si(111) surface is preceded by Co atoms occupying interstitial sites under the adatoms,[20] and the preferentially occupied sites are those under the centered adatoms. Al nanoclusters just locate on the positions of centered adatoms, which increase the occupation energy of the underlying interstitial sites or the kinetic energy barrier

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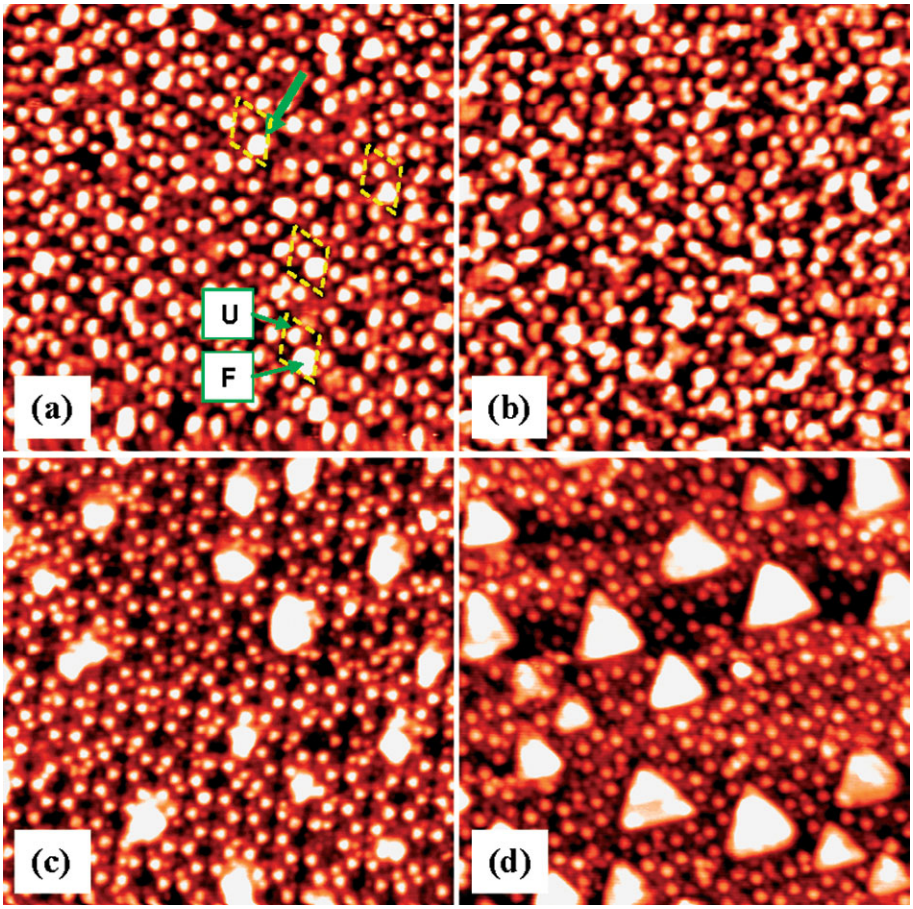

Figure 2. (a) STM image of 0.06 ML Co deposited on Al nanocluster array at room temperature with $V_s = -1.8$V. The image size is 30 nm × 30 nm. 'U' is for the unfaulted half and 'F' is for faulted half. One of the initial nucleation sites of Co is indicated by an arrow. (b) STM image of 0.5 ML Co deposited on Al nanocluster array at room temperature with $V_s = -1.5$V. The image size is 30 nm × 30 nm. (c) STM image of 0.1 ML Co deposited on Al nanocluster array at about 70–80 °C at $V_s = -2.0$ V. The image size is 33 nm × 33 nm. (d) STM image of 0.4 ML Co deposited on Al nanocluster array at about 70–80 °C at $V_s = -1.5$ V. The image size is 35 nm × 35 nm.

of entering these sites. So the silicidation is largely reduced by only 0.25 ML of Al.

Optimizing the deposition condition, we obtained uniform Co platelets in a large area (Fig. 4(a)). Nearly all Co platelets have the same equilateral triangular shape pointing to [211] direction, i.e. same as the shape of UFHUCs. From the size distribution of Co platelets (inset of Fig. 4(a)), we find that about 80% of Co platelets have an edge length of 5.4 nm, which is two times the unit cell size of Si(111)-(7 × 7). The heights of the platelets are mostly 3.2 Å (2 ML). From an STM image with a higher resolution (Fig. 4(b)), we found that the edges of Co platelets are basically along the borders of unit cells of (7 × 7). At higher Co coverages (Fig. 4(c)), the edge length of Co platelets is always an integral multiple of the unit cell size of Si(111)-(7 × 7) and the platelet heights are still mostly two layers.

In the following, we will discuss the mechanism that dominates the formation of regular, uniform Co islands. Growth within HUCs of Si(111)-(7 × 7) is easier than that across the boundaries, because in the latter case, less atom rearrangement and bond-breaking are required owing to the locally 'flat' nature of HUCs and the geometric constraint from the unit cell boundaries of Si(111)-7 × 7.[21] So the Co platelets would cover integrated HUCs. The triangular shape with the same orientation, instead of hexagonal shapes, suggests that the two sets of edges, opposite to each other, are nonequivalent. From the structure schemes in Fig. 4(b) and (c), we can see that the Co platelets are bordered only by FHUCs of Al/Si substrate. So we argue that because of the structural difference between the FHUC and UFHUC, the atomic or/and electronic structures of the lateral borders between Co platelets and Al/Si substrate are different for the two kinds of HUCs. The platelet edges bordering FHUCs have lower border energies than those bordering UFHUCs, which results in the domination of the former.[22]

Another interesting character of the Co platelets is their 'magic' thickness of two atomic layers. The formation of quantum well states due to the confinement of electrons in metal islands could lead to larger stability of the islands with special thicknesses.[23,24] This effect has also been observed in ferromagnetic metals.[25] So, quantum well states may also dominate the 'magic' thickness of the two layers here.

These Co nanoplatelets show interesting magnetic properties. A 3-nm thick Au layer was deposited on the sample before transportation to avoid oxidation. Figure 5(a) shows an M–H loop of a typical sample that mainly contains Co

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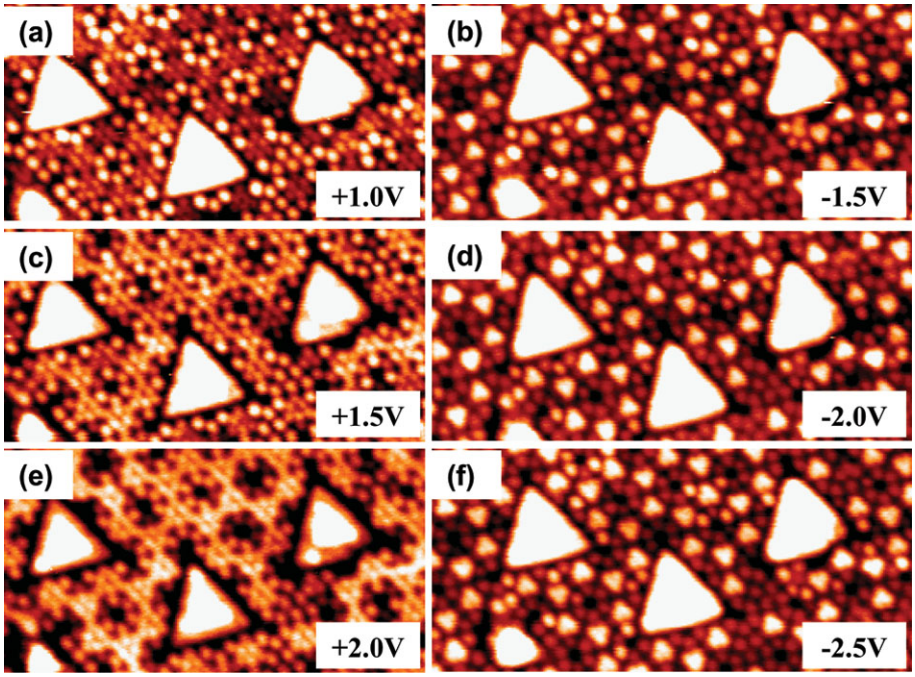

Figure 3. STM images of Co platelets at various bias voltages. The image size is 30 nm × 15 nm. The bias voltages in (a)–(f) are +1.0 V, −1.5 V, +1.5 V, −2.0 V, +2.0 V and −2.5 V, respectively.

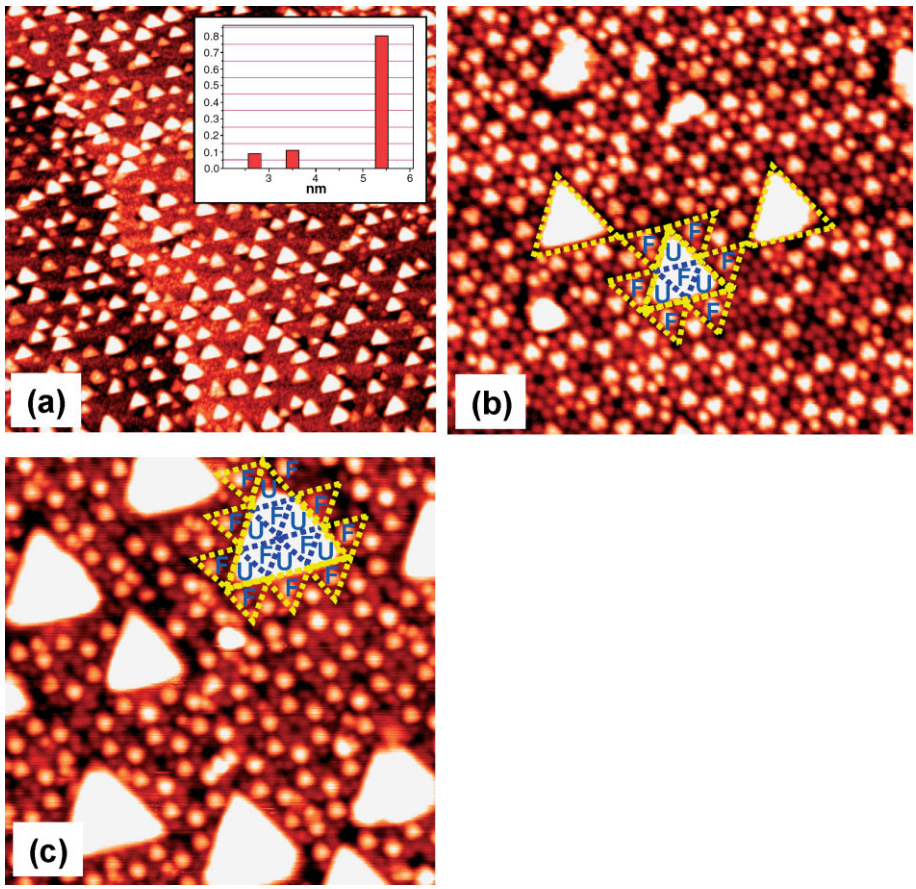

Figure 4. (a) A 150 nm × 150 nm STM image of uniformly distributed Co platelets (0.4 ML). The image was obtained at −2.0 V. The inset shows the size distribution. (b) A 25 nm × 25 nm STM image of Co platelets (0.4 ML). 'U' is for the unfaulted half and 'F' is for the faulted half. Yellow dashed lines sketch the HUCs of (7 × 7). (c) A 25 nm × 25 nm STM image of Co platelets, 0.6 ML. 'U' is for the unfaulted half and 'F' is for the faulted half. Yellow dashed lines sketch the HUCs of (7 × 7).

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platelets with edge lengths two times the size of a (7×7) unit cell. The loop was taken at 5 K in a perpendicular external magnetic field. The diamagnetic background of the Si substrate has been subtracted from the original data. From this loop, we can observe an obvious hysteresis. The M–H loop in the in-plane magnetic field at the same temperature was also measured (not shown here), which showed no hysteresis. Therefore, the easy magnetization axes of the Co nanoplatelets are perpendicular to the sample plane.

The dependence of magnetic moments of the sample on temperatures between 4.5 K and 150 K was measured while applying a 200 G field perpendicular to the sample surface, as shown in Fig. 5(b). The curve reveals a typical superparamagnetic (SP) behavior with a blocking temperature $T_B \sim 40$ K.

The magnetic anisotropy energy of the Co platelets can be estimated from the measured blocking temperature with the relationship $E_A = kT_B \ln(\tau/\tau_0)$,[1] where τ_0 is the order of 10^{-9} s and τ is the measurement time with the order of 10^2 s. So we can obtain an E_A of about 90 meV per platelet for this sample, which corresponds to a magnetic anisotropic energy of 0.5 meV per Co atom. It is about ten times larger than the uniaxial magnetocrystalline anisotropy of bulk hcp Co (0.045 meV/atom).

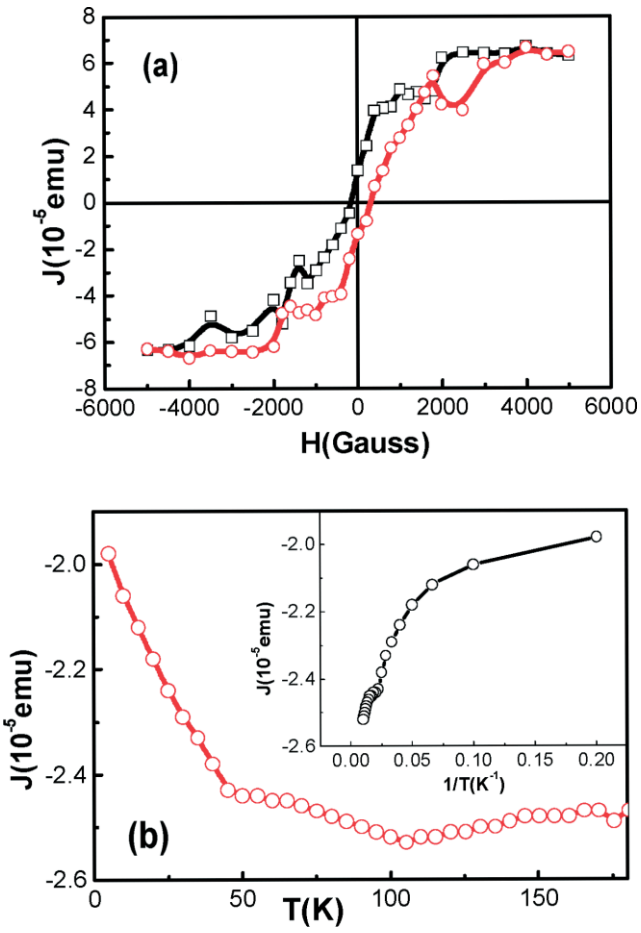

Figure 5. (a) M–H hysteresis loop of Co platelets with edge length two times the size of Si(111)-(7×7) at 5 K after background subtraction. The external magnetic field is applied perpendicular to the sample surface. (b) The dependence of magnetic moments on temperature from 4.5 K to 175 K while applying 200 G field perpendicular to the sample surface (The inverse of the magnetization *versus* T is shown in the inset of Fig. 5 (b)).

The unusually high magnetic anisotropy of Co platelets possibly comes from their extremely thin and planar geometry. When the dimension of a magnet is reduced in one direction to several atomic layers, the broken symmetry will lead to an additional anisotropy, usually in the same direction as that of dimension reduction, which is called surface anisotropy. The surface anisotropy of a material can be one order larger than its bulk magnetic crystalline anisotropy.[2] In this experiment, the thickness of the Co platelets is only two atomic layers while the lateral size is as large as 5.4 nm. So the surface anisotropy may lead to a strong perpendicular magnetic anisotropy.

SUMMARY

Using two-dimensional identical Al clusters as passivating layers and templates, we fabricated Co quantum platelet assemblies on Si(111)-(7×7) surfaces. The Co platelets are of uniform size and height and have a regular equilateral triangular shape with the same orientation. The Al nanocluster array efficiently reduces the strong interaction between Co and Si substrates. The energy barrier of platelet growth across the boundaries of HUCs makes the Co platelet sizes uniform. The different energies of the edges bordering FHUCs and those bordering UFHUCs make Co platelets to have the same orientation. The favored height of the bilayer is attributed to the quantum size effect. The Co nanoplatelets show a perpendicular anisotropy ten times larger than that of bulk Co, which makes them good candidates for in-chip, high-density magnetic storage.

Acknowledgements

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