

## Growth of Co Nanoclusters on Si<sub>3</sub>N<sub>4</sub> Surface Formed on Si(111) \*

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We have grown high density Co clusters with a narrow-sized distribution on the Si<sub>3</sub>N<sub>4</sub>(0001)-(8 × 8) surface. In the submonolayer regime, Co clusters tend to keep a certain size (~1.45 nm in diameter) irrespective of coverage. With increasing coverage above 0.92 ML, two new clusters with certain but larger sizes are formed. This novel growth behaviour can be explained by the quantum size effect [Phys. Rev. Lett. 90 (2003) 185506]. It is found that the Co cluster size distribution can be improved by post annealing. Even at high temperature (700 °C), no reaction of Co with Si<sub>3</sub>N<sub>4</sub> is observed, indicating that Si<sub>3</sub>N<sub>4</sub>(0001)-(8 × 8) is a promising substrate for growth of magnetic nanostructures.

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In the past decade, nanoclusters have attracted considerable attention due to their novel electronic, optical and magnetic properties, which do not exist in the corresponding bulk materials.<sup>[1]</sup> They also provided potential possibilities for innovative technological applications, such as nanocatalysis,<sup>[2,3]</sup> optical and electronic devices<sup>[4-6]</sup> and ultrahigh-density magnetic recording.<sup>[7-9]</sup> Great efforts have been made to achieve nanocluster arrays with good size uniformity and spatial distribution.<sup>[10-15]</sup> Recently, we have successfully grown a series of metal cluster arrays on Si(111)-(7 × 7) substrates.<sup>[13-15]</sup> Both the size uniformity and the spatial distribution of the clusters are perfectly well. However, magnetic transition metal (TM) arrays have remained a challenge because of the strong reaction of TM atoms with silicon. Silicide reactions occur spontaneously once TM atoms are deposited on the Si surface, and in most cases, the magnetism vanishes.<sup>[16]</sup> Growth of magnetic layers and nanostructures on the Si substrate is attractive in terms of a great potential integration of magnetic recording to the well-developed Si technology.

In this Letter, we report on the growth of Co on Si<sub>3</sub>N<sub>4</sub> surface, which is formed through thermal nitridation of the Si(111)-(7 × 7) surface by NH<sub>3</sub>. We choose Si<sub>3</sub>N<sub>4</sub> as a substrate for TM growth for two reasons. First, Si<sub>3</sub>N<sub>4</sub> is a dielectric film and can effectively prevent TM from reacting with the Si substrate. Second, the Si<sub>3</sub>N<sub>4</sub> surface is (8 × 8) reconstructed and has a structure similar to Si(111)-(7 × 7) that may serve as an ideal template for growth of perfect ordered Co cluster array.

The experiments were carried out in an Omicron VT scanning tunnelling microscopy (STM) system with a base pressure of  $5 \times 10^{-11}$  Torr. Once loaded into the system, the Si(111) sample was first degassed

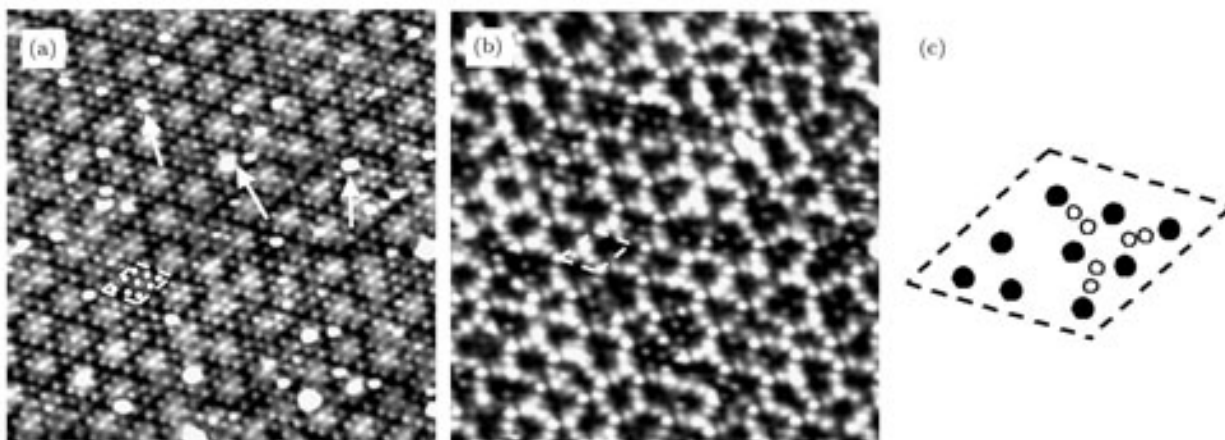
at about 500 °C for several hours. Then the sample was flashed to 1250 °C to remove the silicon oxide and other contaminants while the vacuum is kept within  $1 \times 10^{-9}$  Torr. Clean Si(111)-(7 × 7) surfaces can be routinely obtained by this treatment. The Si<sub>3</sub>N<sub>4</sub>(0001)-(8 × 8) surface was obtained by exposing the clean Si(111) surface to NH<sub>3</sub> with a partial pressure of  $\sim 10^{-7}$  Torr at a substrate temperature of 850 °C.<sup>[17,18]</sup> In order to improve the quality of the Si<sub>3</sub>N<sub>4</sub>(0001)-(8 × 8) surface, the samples were usually annealed at the same temperature for several minutes after NH<sub>3</sub> exposure. An infrared pyrometer was used to monitor the sample temperature. Co was deposited through direct current heating of a tantalum boat at a rate of  $\sim 0.5$  ML/min (1 ML correspond to  $7.8 \times 10^{14}$  atoms cm<sup>-2</sup>, the site density of the unreconstructed Si(111)-(1 × 1) surface). The Co flux was calibrated by a prior experiment of Co deposition on the Si(111)-(7 × 7) surface. Chemical-etched tungsten tips were used as the STM probe. All the STM images were acquired in constant-current mode at room temperature (RT).

Figure 1(a) shows a filled-state STM image of the Si<sub>3</sub>N<sub>4</sub>(0001)-(8 × 8) surface. A unit cell is outlined by the diamond in the image, which has the side length of 3.07 nm ( $8a_0$ ,  $a_0 = 0.384$  nm, the lattice constant of the Si(111) plane), i.e., the surface is (8 × 8) reconstructed.<sup>[17-19]</sup> The bright dots denoted by the arrows in the image are impurities that originate mainly from the complex thermal nitridation process. These impurities can be greatly decreased by post-annealing for a long time, which is shown in Fig. 1(b). The unit cell contains nine bright dots, as indicated by the nine white solid circles. According to the structure model by Ahn *et al.*, these spots correspond to nine nitrogen atoms on the outermost layer.

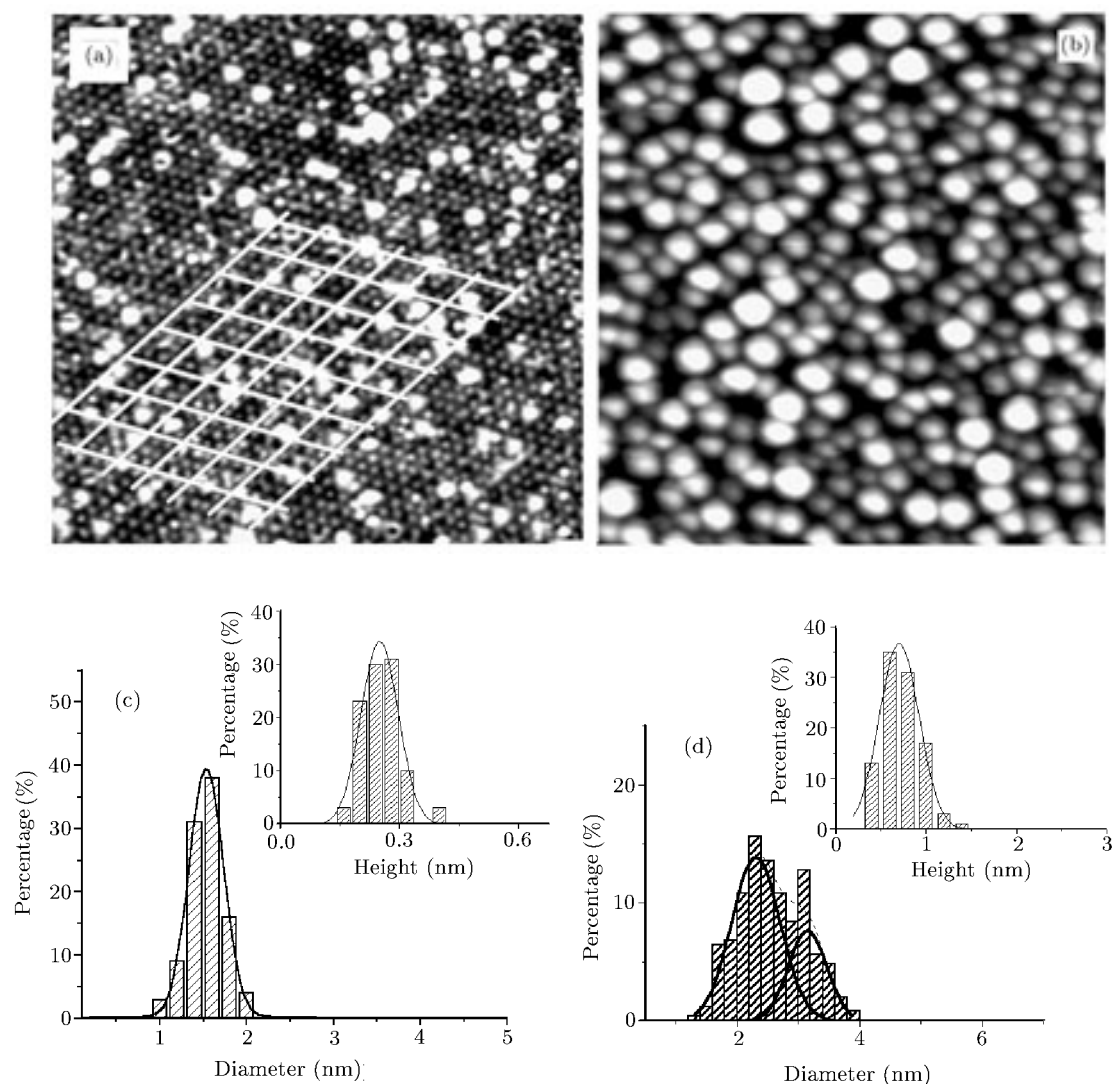
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**Fig. 1.** STM images of  $\text{Si}_3\text{N}_4(0001)-(8 \times 8)$ . (a) Filled-state STM image (taken at  $V_S = -3$  V,  $40 \text{ nm} \times 40 \text{ nm}$ ). A unit cell is outlined with solid-line diamond. Nine white solid circles denote the nine nitrogen adatoms in the unit cell. (b) Empty state STM image (taken at  $V_S = 3$  V,  $40 \text{ nm} \times 40 \text{ nm}$ ). A unit cell is outlined with dashed-line diamond. (c) Partial-charge-density distribution of the atomic model of  $\text{Si}_3\text{N}_4(0001)-(8 \times 8)$  from Ref. [19].

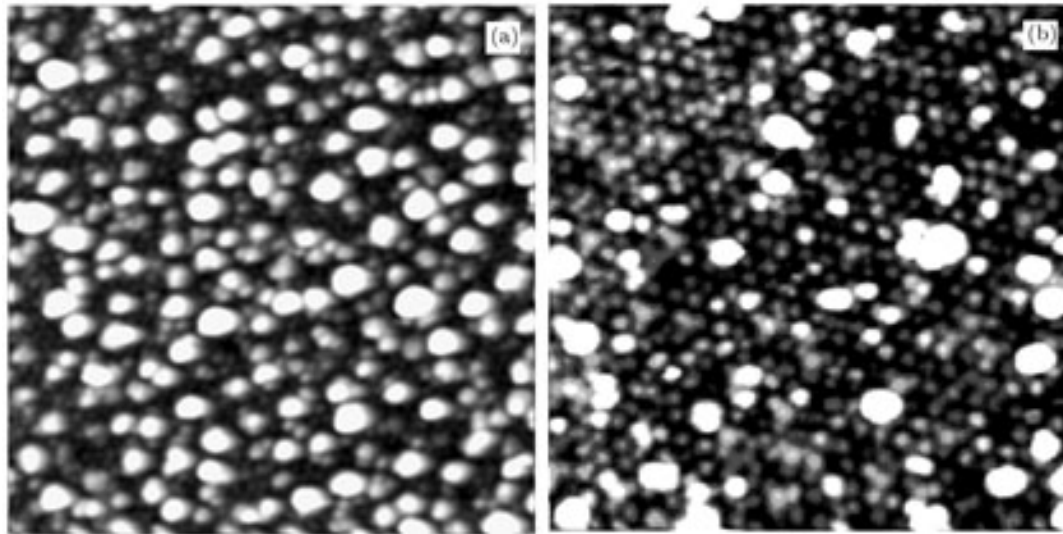


**Fig. 2.** STM images of Co on  $\text{Si}_3\text{N}_4$  taken at (a) low coverage of  $\sim 0.1$  ML ( $50 \text{ nm} \times 50 \text{ nm}$ ); (b) high coverage of  $1.5$  ML ( $50 \text{ nm} \times 50 \text{ nm}$ ). The diameter and height distributions of the Co clusters and the corresponding Gaussian fits. (c) For  $0.1$  ML and (d) for  $1.5$  ML. All the images were taken at  $V_S = -3$  V.

The nine atoms are bonded to the rest atoms in the rest layer in different configurations, which results in an asymmetry on the left and right half of the unit cell.<sup>[19]</sup> Fig. 1(c) shows the partial-charge-density (PCD) distribution of the model by Ahn *et al.*, in which the bright dots represent the charge density contributed from the nitrogen adatoms and the grey dots the atoms in the rest layer.<sup>[19]</sup> The filled-state image [Fig. 1(a)] is in good agreement with the PCD distribution of the model.

When deposited at RT, Co atoms immediately form three-dimensional clusters on the  $\text{Si}_3\text{N}_4$  surface. Figure 2(a) shows an STM image of submonolayer Co (0.1 ML) covered ( $8 \times 8$ ) surface. The Co clusters appear a circular shape, with a size of 1.38 nm–1.58 nm,

and height of 0.2 nm–0.4 nm, corresponding to one to two Co layers, respectively. In general, magnetic materials have relatively high surface energies (2.7 J/m<sup>2</sup> for Co),<sup>[20]</sup> compared with  $\text{Si}_3\text{N}_4$  ( $< 1.0 \text{ J/m}^2$ ).<sup>[21]</sup> Taken account of such a large surface energy difference, it is unsurprising that the growth proceeds in a 3D growth mode. Unlike metal clusters on Si(111)-( $7 \times 7$ )<sup>[13–15]</sup> and Co on Au(111),<sup>[22,23]</sup> no preferred Co nucleation site is observed on the  $\text{Si}_3\text{N}_4(0001)$ -( $8 \times 8$ ) surface. As we can see from Fig. 2(a), the Co clusters are randomly located either within the unit cell, or at the edge or at the corner of the unit cell. In addition, no preference for nucleation at defect sites is observed either.



**Fig. 3.** STM images of Co with the coverage of 1.5 ML on  $\text{Si}_3\text{N}_4$  (a) after annealing at 250°C for 5 min (50 nm $\times$ 50 nm) and (b) after annealing at 700°C for 5 min (30 nm $\times$ 30 nm). All the images were taken at  $V_S = -3 \text{ V}$ .

It is found that there is a very narrow size distribution of the Co clusters at low coverage. Figure 2(c) shows the lateral size and height distributions of the Co clusters at 0.1 ML along with the Gaussian fits. The peaks of the Gaussian fits of the lateral size  $d$  and height of the clusters are 1.45 nm and 0.24 nm, respectively. The dispersion of the lateral size  $d$ ,  $\Delta d = (\langle d^2 \rangle - \langle d \rangle^2)^{1/2}$ , is only 0.21 nm. With the increasing Co coverage, the cluster size remains to be stable at such a value (around 1.45 nm), and the cluster density increases monotonically in the submonolayer regime as reported by Gwo *et al.* very recently.<sup>[24]</sup> This situation will not change until the clusters cover the entire surface with the maximum number density of  $\sim 3.0 \times 10^{13} \text{ cm}^{-2}$ , which corresponds to a Co coverage of 0.92 ML.

When coverage is above 1 ML, we found that the Co clusters begin to increase in size, while the density decreases. Figure 2(b) shows an STM image

at the coverage of 1.5 ML. At this coverage, the Co clusters almost cover the entire surface, and the density of clusters has decreased from  $3.0 \times 10^{13} \text{ cm}^{-2}$  to  $1.51 \times 10^{13} \text{ cm}^{-2}$ . These clusters have sizes of 2.0 nm–3.0 nm, suggesting that island coalescence has occurred. Figure 2(d) shows the lateral size and height distributions of the Co clusters at 1.5 ML. The mean cluster size and height are 2.59 nm and 0.60 nm, respectively. The dispersion of the lateral size broadens to 0.60 nm. Two typical sizes of Co clusters are observed at this coverage, one is at 2.3–2.4 nm, and the other at 3.1–3.3 nm. Thus, we carried out the multi-peaks Gaussian fitting as shown in Fig. 2(d). The result shows that the optimized sizes are 2.35 nm and 3.16 nm, respectively. The existence of these two typical clusters is the main reason of the observed broadening of the size distribution, while the size dispersion of each kind of clusters is small.

The size distribution of the clusters can be

improved by the post-annealing. Figure 3(a) shows an STM image obtained by annealing a 1.5 ML Co-covered sample at 250°C for 5 min. From the image, we observed that many small Co clusters shown in Fig. 2(b) disappeared, and there is a large change in the cluster density (from  $1.51 \times 10^{13} \text{ cm}^{-2}$  to  $0.77 \times 10^{13} \text{ cm}^{-2}$  after annealing). In contrast, the size and number of the bigger clusters change very little, and this kind of clusters is very stable even at the elevated temperature. The conventional Ostwald Ripening cannot explain this result, because the big clusters do not grow large at the expense of the small ones.<sup>[25]</sup> Because of disappearance of the small clusters, the clusters become much more uniform. Moreover, we found that the  $\text{Si}_3\text{N}_4$  layer is very stable even after heating to higher temperature. Figure 3(b) shows an STM image of one of the samples annealed at 750°C for 5 min. At this temperature, most Co clusters were desorbed from the surface, but the  $\text{Si}_3\text{N}_4(0001)-(8 \times 8)$  surface is preserved. Thus, no reaction of Co with  $\text{Si}_3\text{N}_4$  is observed.

In most cases, growth of metal on an inert substrate is dominated by nucleation on defect sites.<sup>[26]</sup> However, this is not consistent with the present case, in which the density of the Co islands increases linearly with the coverage in the submonolayer regime, and the average cluster size remains nearly a constant.<sup>[24]</sup> Gwo *et al.* attributed it to the quantum-size effect (QSE) in the ultrasmall size regime (the number of atoms  $N < 100$ ).<sup>[24]</sup> According to their model, Co clusters containing atoms of magic numbers, such as 6, 11, and 18, have relatively high stability. Thus Co atoms can nucleate metastable clusters with sizes smaller than the critical cluster size. We also estimated the atom number  $N$  in each Co clusters using  $N = \rho V$ , where  $\rho$  is the atomic density of bulk Co ( $\rho_{\text{Co}} = 9.10 \times 10^{22} \text{ atoms/cm}^3$ ) and  $V$  is the volume of the cluster. The volume is related to the cluster size  $d$  and height  $h$  via,<sup>[24]</sup>

$$V = \frac{\pi}{8}d^2h + \frac{\pi}{6}h^3.$$

As a result, the average number of atoms per cluster at the coverage of 0.1 ML is 18, which exactly matches one of these magic numbers. The experimental abundance spectrum also shows some peaks at certain numbers. For the two kinds of clusters that occur frequently at coverage of 1.5 ML, the small one consists of 114 atoms and the big one 236. The former agrees with the magic number predicted by Gwo *et al.*<sup>[24]</sup> There have not been any data for the big clusters to be compared with. Since the big clusters do not grow at the expense of the clusters containing 114 atoms, and remain unchanged after the annealing at 250°C, the big ones must be remarkably stable and the stability is probably also related to the QSE.

In summary, we have grown nanometre-sized Co clusters with narrow size distribution on the

$\text{Si}_3\text{N}_4(111)-(8 \times 8)$  surface. The novel growth behaviour of Co on  $\text{Si}_3\text{N}_4$  can be explained by QSE proposed by Gwo *et al.* Due to this effect, the uniformity of the clusters can be greatly improved by a dedicate annealing process. High temperature annealing (at 700°C) leads to desorption of Co atoms from the surface, whereas the clean  $\text{Si}_3\text{N}_4$  surface could be recovered, indicating  $\text{Si}_3\text{N}_4(0001)-(8 \times 8)$  to be a suitable substrate to grow magnetic nanostructures.

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