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Self-aligned Co nanoparticle chains supported by single-crystalline Al_2O_3/NiAl(100) template

Wen-Chin Lin
Department of Physics, National Taiwan University, 106 Taipei, Taiwan and Institute of Atomic and Molecular Sciences, Academia Sinica, Taipei, Taiwan

Chien-Cheng Kuo
Department of Physics, National Taiwan University, 106 Taipei, Taiwan and Department of Physics, National Sun Yat-Sen University, Kaohsiung, Taiwan

Meng-Fan Luo
Department of Physics and Nano-Cataylst Research Center, National Central Universtiy, Jhongli City, Taoyuan, Taiwan

Ker-Jar Song
Institute of Atomic and Molecular Sciences, Academia Sinica, Taipei, Taiwan

Minn-Tsong Lin[a)]
Department of Physics, National Taiwan University, 106 Taipei, Taiwan and Institute of Atomic and Molecular Sciences, Academia Sinica, Taipei, Taiwan

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We present Co nanoparticle chains grown by vapor deposition over a single-crystalline Al_2O_3 layers on NiAl(100) with such features as self-limiting size distribution with the average size of ~2.7 nm, well-ordered alignment, and high thermal stability. We attribute these features to peculiar one-dimensional long stripes with ~4 nm interdistance on the surface of the ultrathin Al_2O_3 template. This nanostructure may open the door to numerous applications, such as catalysis and nanostorage, where large area well-ordered nanodots are desired. © *2005 American Institute of Physics*. [DOI: 10.1063/1.1855410]

Nanoparticles or nanodots attract much interest due to their potential applications in electronic and magnetic nanodevices as well as for catalysts in growing further various nanomaterials such as nanotubes or nanowires. However, a realistic application often requires an extremely high achievement in size controlling, size uniformity, and even perfect ordering. In recent decades, a self-organized approach has been realized to be a promising way for growing nanodots with uniform size. Nevertheless, in the area of semiconductor quantum dots, the Stranski–Krastanow growth mode is usually used to describe the presence of the wetting layer at the initial stage as well as the following clustering.[1,2] This reflects the complication of the dot/substrate surface interfacial interaction, increasing the difficulty for controlling nanodot characteristics, such as size uniformity and undesired interdot contact through wetting layers. Very recently, nanodots or nanoclusters without wetting layers have been prepared for the metallic nanoparticles by deposition on insulators or semiconductors.[3–16] For example, Gai *et al.* reported a self-assembly of nanometer-scale Fe dots with narrow size distributions on an insulating substrate (NaCl)[3] due to strain-mediated dot–dot interaction. The particle size in this system, however, is proportional to the deposition amount. On the other hand, another study on $Co/Si_3N_4/Si(111)$[4] shows the self-limiting size distribution which is attributed to a quantum size effect, manifested by local energy minima in the electronic shell structure of Co dot.

Besides the size uniformity, another key issue is to prepare orderly arranged nanoparticles. Ordered alignment determines the spatial symmetry and thus may induce anisotropy in physical and chemical properties. With respect to technological application, well-ordered nanoparticles are also extremely important. For instance, magnetic nanoparticle arrays can be a good candidate for data storage medium. However, the patterning of the nanoparticles is still a challenging work, due to the high cost and resolution limit of conventional lithography as well as the rarity of self-assembled systems. For example, although the 7×7 structure of Si(111) has served as a good template for arranging magic clusters of Ga,[10] In,[11] and Al,[12] due to the formation of silicide, it does not work with magnetic materials like Fe, Co, and Ni.

In this letter, we present that Co nanoparticles grown on a single crystalline Al_2O_3 layers on NiAl(100) can satisfy the size uniformity and ordered alignment. Moreover, the Co nanoparticles are thermally stable up to an elevated temperature of 700 K. Such high thermal stability renders this system a good candidate for catalysis application, which many quantum-sized systems induced by electronic structures fail to serve.[4]

The experiment was performed in an ultrahigh vacuum chamber with base pressure $<2\times10^{-10}$ mbar. After cycles of 1.5 keV Ar^+ sputtering and subsequent annealing at 1000 K, the substrate NiAl(100) was exposed to ~1000 L O_2 and then annealed at the same temperature for 1 h. After the oxidation and annealing procedures, the sample was quenched to room temperature for the deposition of Co. The crystalline structure and chemical composition of the sample was char-

a)Author to whom correspondence should be addressed; electronic-mail: mtlin@phys.ntu.edu.tw

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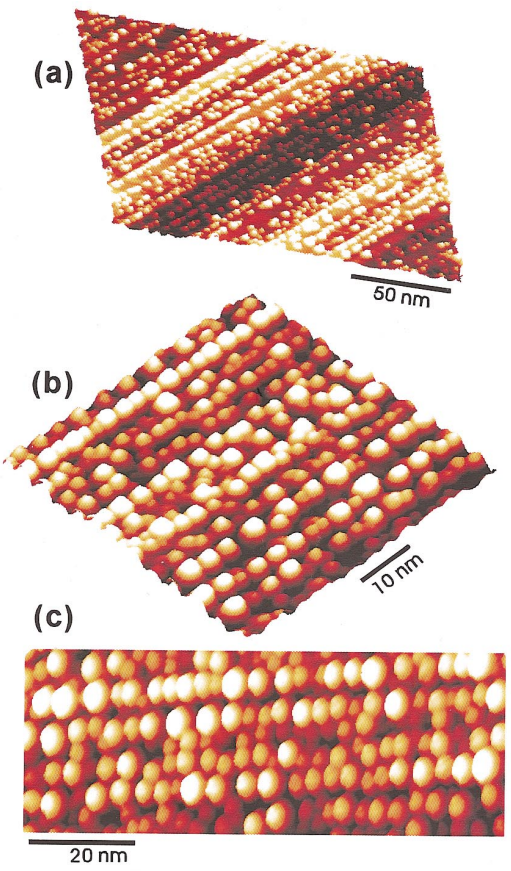

FIG. 1. (Color) STM images of (a) 0.13 ML, (b) 0.73 ML, and (c) 2.2 ML Co deposited on Al_2O_3/NiAl(100). These pictures reveal that cobalt prefers to nucleate nano-sized particles which are aligned by the Al_2O_3/NiAl(100) template with high density and uniform size. Note that the Co particles are well-ordered as one-dimensional chain for all coverages.

acterized and checked by low energy electron diffraction (LEED) and Auger electron spectroscopy, respectively. The morphology of the sample was monitored by scanning tunneling microscopy (STM) using bias voltage of 1.6–2.0 V and tunneling current of 0.8–1 nA.

Figures 1(a)–1(c) present the STM images for 0.13, 0.73, and 2.2 ML Co/Al_2O_3/NiAl(100) in different scales, respectively. [1 ML is the surface atom density of hcp Co(0001) or fcc Co(111) and it means 1.83×10^{15} atoms/cm^2.] Figure 1(a) shows that Co deposition produces uniform-sized nanoparticles which are highly aligned like chains extending more than 200 nm. With more deposition, as shown in Figs. 1(b) and 1(c), both alignment and uniformity are sustained but particle density is highly enhanced. These STM results reveal amazing ordering and size uniformity of the grown particles. Statistical analysis demonstrates the uniformity even further. Figures 2(a) and 2(b) show the height and diameter distribution for 0.43 ML Co/Al_2O_3/NiAl(100), respectively. The average height is 0.9 ± 0.2 nm, and the average diameter is 2.7 ± 0.3 nm. In Fig. 2(b), there seems to be an a-upper boundary in the diameter distribution. Smaller particles are observed (the tail of distribution at 1.5–2.7 nm) and nearly no larger particles can be seen (the clear cut after 3.2 nm). Similar distributions are also found for different amounts of Co deposition, as depicted by Figs. 2(c) and 2(d). Both the average height and diameter of the particles are shown to be almost the same, indicating a self-limiting size distribution. More Co deposition increases the particle density and the average height to ~0.9 nm. However, more Co deposition does not create larger particles >3.5 nm, but only enlarges the existing smaller ones or produce more particles, leading to a good size uniformity as shown in Fig. 1(c).

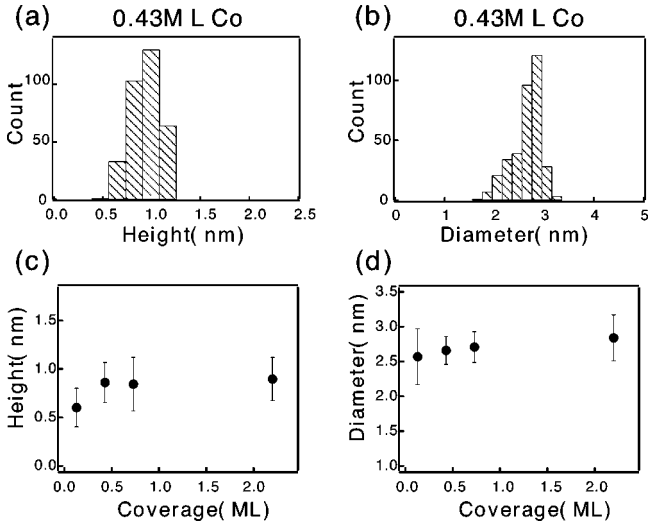

FIG. 2. (a), (b) Height and diameter distribution of 0.43 ML Co/Al_2O_3/NiAl(100). The average height is 0.9 ± 0.2 nm, and the average diameter is 2.7 ± 0.3 nm, which are obtained from Gaussion fitting of the distribution. (c), (d) The average heights and diameters of Co nanoparticles with different coverage.

To investigate the magic alignment of Co nanoparticles, we look into detailed structures of the Al_2O_3 thin film and the early stages of Co nucleation. Figure 3(a) shows the LEED image of Al_2O_3/NiAl(100). The 2×1 superstructure indicates the typical surface structure of single crystal Al_2O_3, and the streaks of the 1×1 spots are corresponding to the formation of domains of Al_2O_3 along the (010) and (001) directions.[17] The splitting of the 2×1 spots, depicted in the inset of Fig. 3(a), is about 1/13 of the interspace between 1×1 spots. Since the lattices constant of NiAl(100) is 2.89 Å,[17] this splitting gives us the average interdistance of

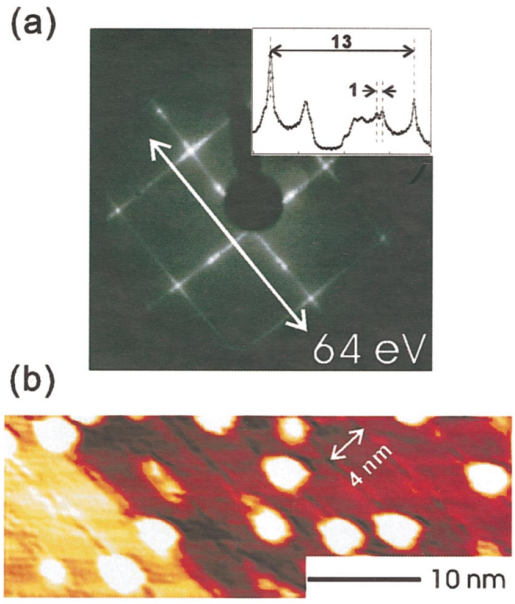

FIG. 3. (Color) (a) LEED pattern of Al_2O_3/NiAl(100). The inset depicts the line profile across the 2×1 superstructure. (b) STM image of 0.05 ML Co/Al_2O_3/NiAl(100).

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~3.8 nm for one-dimensional stripes (the domain boundaries), as indicated by the STM image in Fig. 3(b) for 0.05 ML $Co/Al_2O_3/NiAl(100)$. The background of Fig. 3(b) was composed of long Al_2O_3 domain. Such domains are separated by the one-dimensional stripes (island boundaries or fine structure) and have average width ~4.0 nm, consistent with the result extracted from the LEED pattern. The gray and dark backgrounds correspond to two different terraces, respectively. The step height in Fig. 3(b) is ~3.0 nm.[17] These observed features of $Al_2O_3/NiAl(100)$ are consistent with the results of previous studies.[17,18]

The bright dots in Fig. 3(b) are Co nanoparticles. We note that the nanoparticles always straddle the one-dimensional strips between long Al_2O_3 domains. The results imply that the stripes are more favorable nucleation sites and consequently nanoparticles grow along the stripes and form a nearly perfect one-dimensional chains, as shown in Figs. 1(a)–1(c). Moreover, due to the short distance in between the boundaries, nucleation occurs almost exclusively along these narrow lines and thus the spectacular alignment of the nanoparticles formed. That is, the alignment is predetermined by the structure of the oxide, and does not have much to do with the mutual interactions among the nanoparticles. This also provides a natural explanation why several different metals (Fe, Cu, Ag) we tried all show the same kind of spectacular alignment. We are inspired that this template has great advantages for self-organized one-dimensional nanopatterning, particularly for nanoparticles.

It is interesting to compare our results to those from $Al_2O_3/NiAl(110)$,[19,20] where one did not observe the stripes. In the study of Pd and Rh on $Al_2O_3/NiAl(110)$ by Bäumer *et al.*,[21] although steps and film domain boundaries are favored nucleation centers, it is difficult to create high density of one-dimensionally aligned nanoparticles because the domain boundaries is irregular and the interdistance is large. As $Co/Al_2O_3/NiAl(110)$[21] is concerned, the nucleation is primarily at point defects randomly distributed on $Al_2O_3/NiAl(110)$. As a result, its ordering is even worse. In contrast, deposited Co atoms on $Al_2O_3/NiAl(100)$ nucleate along the one-dimensional stripes as well as steps, as shown in Fig. 2(b), while we note the steps have no priority. Additionally, the interdistance of the one-dimensional stripes is only around 4 nm. Therefore, the grown Co nanoparticles are so well aligned by the stripes even at very high density. Very similar features are also found for other materials, such as Fe, Cu, and Ag on $Al_2O_3/NiAl(100)$, indicating its superiority as a template for growing one-dimensionally well-ordered nanoparticles.

We also examined the thermal stability of Co nanoparticles supported by $Al_2O_3/NiAl(100)$. The sample was annealed to a selection of temperatures and as shown in Fig. 4, the main feature of $Co/Al_2O_3/NiAl(100)$ can be sustained at much higher annealing temperature up to 700 K, as compared to that of $Co/Si_3N_4/Si(111)$ (400 K).[4] Annealing to 800 K results in sintering of particles and the appearance of larger particles due to thermal diffusion. Similar behavior of the thermal stability was also found in metal particles on $Al_2O_3/NiAl(110)$.[22] Thermal stability of the system typically depends on the deposit-template interfacial interaction and nucleation energy of the particles. To achieve detailed understanding of the thermal stability requires further investigation.

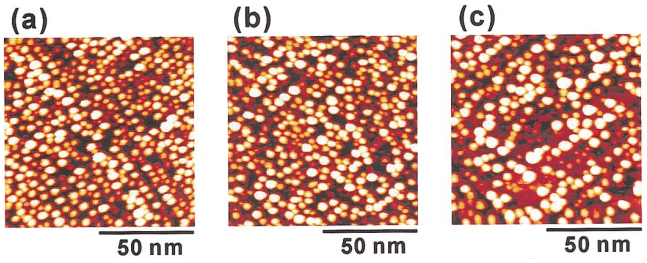

FIG. 4. (Color) (a)–(c) STM images of 2.2 ML $Co/Al_2O_3/NiAl(100)$ after annealing at 700, 750, and 800 K, respectively, for 10 min.

In summary, high temperature oxidation of NiAl(100) provided a single crystalline Al_2O_3 layer as a template for self-organized nanopatterning. Co nanoparticles show a self-limiting size distribution, and are directed by domain boundaries or linear stripes on the single crystalline Al_2O_3 surface, forming regular one-dimensional particle chains. The well-ordered Co nanoparticles were stable up to an elevated temperature of ~700 K, providing a promising application in catalysis for various purposes, such as growing patterned nanomaterials.

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