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Controlling island size distributions: a comparison of nickel and copper growth on TiO$_2$(110)

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Abstract

Scanning tunneling microscopy studies of Ni islands deposited on TiO$_2$(110) show that the islands grow three-dimensionally at room temperature with an average height of approximately 6.5 Å and diameter of 30 Å. The broadness of the island size distributions can be controlled by the diffusion ($D$) to deposition flux ($F$) ratio, with the narrowest distribution corresponding to the smallest $D/F$ ratio. Decreasing the flux or increasing the diffusion rate by increasing the deposition temperature results in a lower island density, larger islands and a broader size distribution. Although the Ni–TiO$_2$ interfacial energy should be greater than that of Cu–TiO$_2$, the Ni islands do not grow flatter on the surface compared to Cu. The higher surface free energy for Ni relative to Cu apparently dominates over the greater interfacial energy for Ni, resulting in Cu and Ni islands with the same aspect ratios. The island densities, average sizes and spatial distributions are roughly the same for both Cu and Ni growth, and we find no evidence that Ni diffusion is slower on TiO$_2$ compared to Cu diffusion. A major difference between Ni and Cu growth is in island sintering at elevated temperatures. Large Cu islands (67 Å diameter, 22 Å height) are produced after deposition at room temperature and annealing to 800 K, whereas the Ni islands undergo much slower growth under the same conditions (34 Å diameter, 6.6 Å height). This effect is explained by the stronger metal–metal bond strength for Ni compared to Cu since adatom detachment is the rate limiting step in island sintering.

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For oxide-supported metal particles, recent studies in the catalysis literature have shown that particle size can have a strong influence on the surface chemistry of the particles [1–3]. It has been proposed that these particle size effects may be due to different electronic properties of the nanoparticles compared to those of the bulk materials, as in the case of Au [4] and Pt [5] on titania. Another possibility is that the different surface structures of various sized particles give rise to different active surface sites, as in the case of CO oxidation on Pd [6,7]. Metal nanoparticles deposited on single-crystal oxide surfaces in ultrahigh vacuum serve as simple model systems that can be used to better understand the more complex commercial catalysts. In order to investigate potential particle size effects, it is crucial to be able to prepare metal
particles of various sizes with uniform size distributions.

In this study, we have grown Ni islands on a single-crystal rutile TiO$_2$(1 1 0)-(1 × 1) surface and have characterized their sizes and size distributions using scanning tunneling microscopy (STM). Titania is an ideal surface for these studies since it can be made sufficiently conductive for STM experiments by heating in ultrahigh vacuum to remove oxygen from the bulk resulting in a n-type semiconductor. Furthermore, the (1 1 0) surface of titania is relatively stable up to moderate temperatures (<1100 K) which allows for a clean surface to be prepared by sputtering and annealing. We have found that Ni islands grow three-dimensionally at room temperature with size distributions that can be controlled by the diffusion ($D$) to flux ($F$) ratio during deposition. For room temperature deposition at a flux of 0.16 ML/min, the diffusion of Ni on titania is sufficiently fast compared to flux in order to produce islands with a relatively narrow size distribution. The growth of Ni on TiO$_2$ is nearly identical to that of Cu under the same deposition conditions. However, the sintering of Ni islands requires much higher temperatures compared to Cu.

Experiments were carried out in an ultrahigh vacuum chamber with a base pressure of $\lesssim 7 \times 10^{-11}$ Torr. This chamber is equipped with an Omicron variable-temperature STM (VT-STM 25), X-ray photoelectron spectroscopy system (EA125), low energy electron diffraction optics (SPEC3), and ion sputter gun (ISE10) [8]. The rutile TiO$_2$(1 1 0) crystal (Commercial Crystal Laboratories) was mounted on a standard Omicron sample plate and heated by electron bombardment; the details of the sample holder design have been described elsewhere [9]. A separate TiO$_2$ crystal mounted in the Omicron variable-temperature holder [9] was used for experiments involving deposition at high temperature. The titania crystal was cleaned by Ar$^+$ ion sputtering (1 keV, 3–4 $\mu$A current to the sample) and annealed at 1050 K for 4 min. The resulting surface was free of contamination, as confirmed by X-ray photoelectron spectroscopy, and exhibited a sharp (1 × 1) LEED pattern. STM images of this surface showed terraces 100–150 Å wide separated by steps of 3.2 Å, as expected for a well ordered TiO$_2$(1 1 0) surface, and the atomic Ti rows spaced by 6.5 Å were visible in higher resolution images. Cu was deposited from a commercial electron beam evaporator (Omicron EF3) consisting of a heated molybdenum crucible containing pure Cu (Alfa Aesar, 99.9999%) pellets. Ni evaporation was achieved using a home-built metal doser which consisted of 0.2 mm diameter Ni wire (Aldrich 99.995%) and tungsten wire wrapped around a Mo rod [10]. Coverages and deposition fluxes were calculated from the average size and density of the metal islands.

STM images of a 1.0 ML coverage of Ni deposited at room temperature and at 500 K are shown in Fig. 1. In all cases, the Ni islands grow

Fig. 1. Scanning tunneling microscopy images for a 1.0 ML coverage of Ni deposited on TiO$_2$(1 1 0) under the following conditions: (a) 0.16 ML/min at 295 K; (b) 0.02 ML/min at 295 K; and (c) 0.02 ML/min at 500 K. All images are 1000 Å × 1000 Å and were collected with a tunneling current of 0.2 nA and sample bias of +1.7 V. Average island diameters, heights and island densities were 28.6 ± 4.8, 6.2 ± 1.5 Å, and $7 \times 10^{12}$ cm$^{-2}$ for (a); 33.1 ± 5.5, 6.5 ± 2.0 Å, and $5 \times 10^{12}$ cm$^{-2}$ for (b); and 63.0 ± 12.0, 13.7 ± 3.8 Å, and $0.9 \times 10^{12}$ cm$^{-2}$ for (c), respectively.
three-dimensionally and are preferentially located at the step edges, which represent the highest coordination site; these characteristics have also been observed in a previous study of Ni on TiO$_2$(1 1 0) [11]. A comparison of the Ni islands deposited at room temperature at a flux of 0.16 and 0.02 ML/min indicates that lower flux results in larger islands with lower island densities. When Ni is deposited at 500 K and 0.02 ML/min in order to increase the rate of diffusion, much larger islands with smaller island densities are produced. Island dimensions and densities are reported in the caption for Fig. 1. In general, the $D/F$ ratio appears to control island sizes and densities. For small $D/F$ ratios, the rate of adatom diffusion is relatively slow compared to the rate of deposition. In this case, it is more likely that an adatom will encounter another adatom and form a new island before it can diffuse on the surface and join an existing island. Notably, this same behavior was observed for the growth of Cu islands on TiO$_2$(1 1 0)-(1 × 2) [9].

Fig. 2 demonstrates that the island size distributions are also controlled by the $D/F$ ratio, with smaller values of $D/F$ producing the narrowest size distributions. Deposition at room temperature at 0.16 ML/min corresponds to the smallest $D/F$ ratio and yields the most uniform size distribution. For room temperature deposition at lower flux, the distribution begins to broaden. Deposition at 500 K causes extensive broadening of the size distribution. Very large islands (86 Å diameter, 21 Å height) as well as very small islands (31 Å diameter, 6 Å height) are formed upon low flux deposition at 500 K. Since the rate of diffusion has an exponential dependence on temperature, it is not surprising that increasing the temperature by roughly 70% has a greater effect on the distribution than increasing the flux by a factor of 10. Previous studies of Cu on TiO$_2$(1 1 0)-(1 × 2) have also showed that small $D/F$ ratios during growth generate narrow size distributions [9].

If we consider the case in which there is no Ni adatom diffusion, the density of Ni atoms on the surface at any given time should be same for all regions since the Ni deposition itself is uniform over the surface. If rate of diffusion is slow compared to the deposition flux, the density of Ni atoms on the surface is still roughly the same over all regions of the surface, and therefore the islands grow to approximately the same size. In contrast, if the diffusion is fast compared to flux, the Ni adatoms can diffuse on the surface until they encounter existing islands. Consequently, some islands will grow larger than others since the Ni atom density is no longer uniform over the surface.

The growth of Ni on TiO$_2$(1 1 0) is similar to that of Cu. The STM images in Fig. 3 show that a 1 ML coverage deposited at 0.02 ML/min produces Ni and Cu islands with the roughly the same island sizes, densities and spatial distributions. The average island dimensions for the Cu islands were

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Fig. 2. Island size distributions for a 1.0 ML coverage of Ni deposited on TiO$_2$(1 1 0) under the following conditions: (a) 0.16 ML/min at 295 K; (b) 0.02 ML/min at 295 K; and (c) 0.02 ML/min at 500 K. The scale for the x-axis (0–15,000 Å$^3$) is the same for (a) and (b) but is much larger for (c) (0–65,000 Å$^3$). Distributions are based on measurement of at least 120 islands, and island sizes are represented by their volumes, assuming a paraboloid island shape.
32.3 ± 5.2 Å in diameter and 6.8 ± 1.8 Å in height in comparison to 33.1 ± 5.5 and 6.5 ± 2.0 Å, respectively for Ni. Although both Cu and Ni islands tend to decorate the step edges, a higher fraction of Ni islands are located at the step edges compared to Cu. Based on thermodynamics, three-dimensional island growth should occur if $\gamma_{\text{TiO}_2} < \gamma_m + \gamma_{m/\text{TiO}_2}$ where $\gamma_{\text{TiO}_2}$ and $\gamma_m$ are the surface free energies of the titania and metal, respectively, and $\gamma_{m/\text{TiO}_2}$ is the interfacial energy between the metal and titania. The surface free energy of Ni ($\sim$1.7 J/m$^2$) [12,13] is higher than that of Cu ($\sim$1.3 J/m$^2$) [12–14]. Since the surface free energy of titania ($\sim$0.7 J/m$^2$) [15] is lower than that of both metals, the islands should grow three-dimensionally unless a strong metal–oxide interface is formed. For Cu, metal–TiO$_2$ interaction is known to be relatively weak [16,17], and therefore three-dimensional island growth is observed. Although the Ni–TiO$_2$ adhesion energy is not known, it is expected that the Ni–TiO$_2$ interaction should be stronger than that of Cu–TiO$_2$. Adhesion energies for Cu and Ni on other oxide surfaces such as Al$_2$O$_3$ and SiO$_2$ have been reported in the literature, and in both cases, the adhesion energy is stronger for Ni compared to Cu ($\sim$1.3 vs. 0.49 J/m$^2$ on Al$_2$O$_3$ and $\sim$0.87 vs. 0.47 J/m$^2$ on SiO$_2$) [12–14,18]. Furthermore, the strength of the metal–oxide interaction generally scales with the admetal–oxygen bond strength [12,19], and the Ni–O bond (392 kJ/mol) is stronger than Cu–O (273 kJ/mol), based on data for gas phase diatomics [20]. It might be expected that the Ni islands should grow flatter on the surface compared with Cu islands; this is provided that the stronger Ni–TiO$_2$ interactions, which favor two-dimensional growth, can offset the higher surface free energy of Ni, which favors three-dimensional growth. These STM experiments show that the Ni and Cu islands have approximately the same aspect ratios, and the Ni islands are not flatter than the Cu islands; thus, the higher surface free energy for Ni is the factor that controls the growth of the Ni islands. As a result of the strong Ni–TiO$_2$ interaction, it is also possible that the diffusion of Ni on TiO$_2$ might be slower than Cu on TiO$_2$. Slower diffusion would produce smaller Ni islands with a higher island density, which is not observed in Fig. 3. The STM data for Cu and Ni growth under similar conditions of flux and coverage show no evidence for slower Ni adatom diffusion compared to Cu. In fact, the higher fraction of Ni islands located at step edges suggests that perhaps the diffusion of Ni atoms is slightly higher.

Although the growth of Cu and Ni are similar at room temperature, annealing results in significant Cu island growth whereas Ni island growth is much slower. Fig. 4 shows STM images of 1.5 ML of Ni and Cu deposited at room temperature. Both the Cu and Ni islands have average diameters of 30–33 Å and heights of 6.5–7.5 Å. After annealing to 800 K for 1 min, the average size of the Cu islands increased to 67 Å in diameter and 22 Å in height. In contrast, only a minor change in the average Ni island size occurred upon annealing to the same temperature (34 Å diameter, 6.6 Å height).
There are two steps involved in the growth of an island upon annealing: detachment of an adatom from an existing island, and diffusion of the adatom to a new island. In order to understand which of these steps controls the kinetics of island growth, deposition at elevated temperatures was compared with deposition at room temperature followed by annealing (Fig. 5). The following experiments were carried out using a titania crystal mounted in the variable-temperature (VT) sample holder; by using the same power settings for the pyrolytic boron nitride heater in the VT holder, the same sample temperatures could be achieved. For the Cu and Ni islands deposited at room temperature and annealed for an hour at an estimated temperature of 400–450 K, the islands had average dimensions (4.0–5.7 Å height, 25–35 Å diameter), which were only slightly larger than the unannealed islands. However, islands deposited at 400–450 K were substantially bigger, with average sizes for both Cu and Ni islands ranging from 8 to 10 Å in height and roughly 40 Å in diameter. This experiment demonstrates that adatom detachment, not diffusion, is the rate limiting step in island sintering for Cu and Ni. At elevated temperatures, the adatoms have sufficient energy to diffuse on the surface, but the energy barrier for adatom detachment prevents substantial island growth. Since the Ni–Ni bond strength is greater than the Cu–Cu bond strength (203 vs. 177 kJ/mol based on gas phase diatomics [20]), the barrier for Ni adatom detachment should be higher than for Cu. Therefore, the slower growth of Ni islands after annealing can be explained by a greater energy barrier for adatom detachment.

In conclusion, we have shown that the island size distributions for Ni islands grown on TiO$_2$-(1 1 0)-(1 × 1) become narrower when the $D/F$ ratio during deposition is decreased. Despite the stronger metal–oxide interactions for Ni compared to Cu, the growth of Ni and Cu at room temperature are nearly identical in terms of island sizes, densities and spatial distributions. The diffusion of Ni
does not appear to be slower than that of Cu, and Ni islands have the same aspect ratio as Cu islands. The slower sintering of Ni islands at 800 K is attributed to a stronger metal–metal bond that increases the energy required for adatom detachment in the sintering process.

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