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RAPID COMMUNICATION

Orientational and translational ordering of sub-monolayer films of passivated multiply-twinned gold clusters

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Abstract. The influence of the substrate on the translational and orientational ordering in sub-monolayer films of passivated multiply-twinned gold clusters has been investigated using high resolution and dark field transmission electron microscopy. Although clear differences were observed in the degree of translational ordering on amorphous carbon and etched silicon substrates, there was no corresponding variation in the crystallographic orientation of the nanocrystal cores. The results demonstrate that the orientation of passivated clusters with multiply-twinned cores is effectively random with respect to both the superlattice and the substrate.

The novel properties of nanometre-scale metal and semiconductor particles have stimulated intensive studies of size-selected atomic clusters [1, 2] with the aim of creating materials with unique electronic and optical traits [3]. However, these novel properties are expected to depend not only on the cluster size but also on other parameters, such as surface passivation of the cluster and, in the case of deposited clusters, the arrangement of the nanoparticles on the substrate. Thus, the phenomenon of self-assembly of surfactant-stabilized metal clusters on surfaces has received considerable attention recently [4–15].

Since ordered arrays have been observed with transmission electron microscopy [4, 5], the influence of the particle size [6, 7], size distribution [7] and solvent [8, 9] on the self-assembly has been investigated. Also the ordered arrays have been imaged and manipulated with the tip of a scanning tunnelling microscope [10, 11]. These investigations have generally employed graphite or amorphous carbon as the substrate, and they have concentrated on translational ordering. Preferred crystallographic orientations of the metal core with respect to the cluster superlattice, which were predicted using molecular dynamics calculations [12], have been reported by only one group [13, 14] who employed clusters dominated by the truncated octahedral shape. Harfenist *et al* [15] have investigated multiply-twinned clusters on amorphous carbon substrates and suggested that multiply-twinned clusters behave like spherical particles with respect to the self-assembled superlattice.

Since these investigations have been carried out mainly on amorphous carbon substrates, little is known about the influence of the substrate on both translational and orientational ordering. In particular, possible applications of passivated clusters will most likely require a silicon substrate. Here we compare the degree of translational and orientational ordering of passivated multiply-twinned gold clusters on amorphous carbon and silicon surfaces.

The passivated gold clusters used here were produced using the inverse micelle method [16] and consist of a charge-neutral gold core (3–7 nm in diameter) surrounded by $C_{12}H_{25}S$ ligands (roughly 1.8 nm in length). The clusters were dissolved in a toluene solution which was diluted to an appropriate level to produce sub-monolayer films after drop deposition onto substrates, which had been pre-prepared as specimens for TEM. The silicon substrates were produced by cutting 3 mm discs from a (001) single crystal wafer of silicon before chemical polishing to perforation using a rotating beaker apparatus with a mixture of 11% HF in

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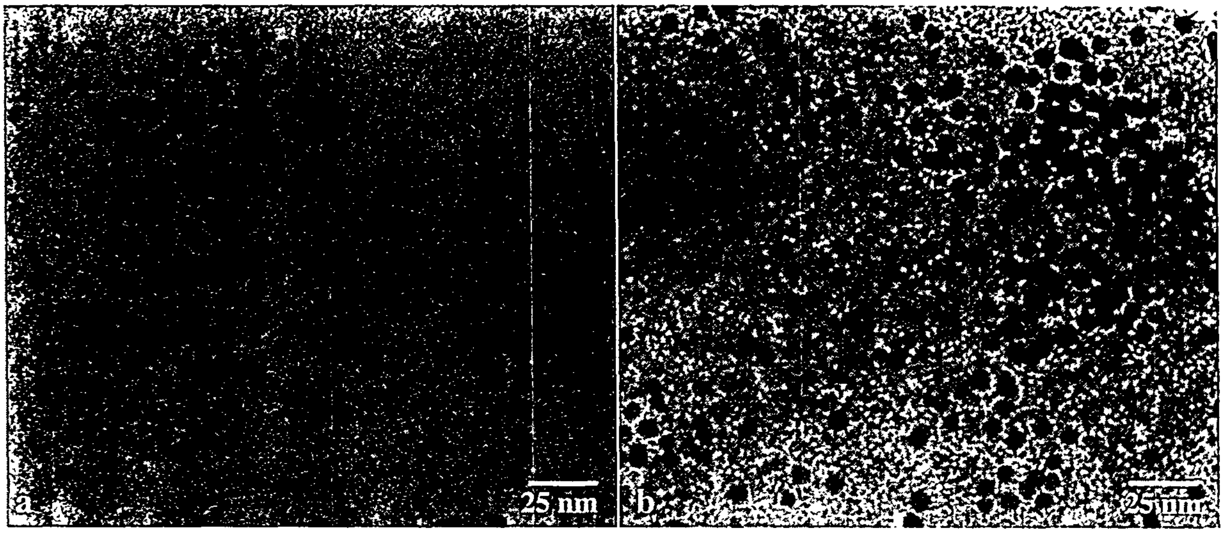

Figure 1. TEM bright field images of passivated gold clusters: (a) islands of self-assembled clusters on an amorphous carbon substrate; (b) single clusters and irregularly-shaped islands of clusters on silicon.

HNO_3. This method ensures minimal mechanical damage of the substrate and produces large electron transparent areas. The Si discs were then cleaned by repeated rinsing in acetone and methanol. We note that since the preparation was carried out in air there is expected to be a thin native oxide layer on the samples. The amorphous carbon substrates were produced by evaporating a thin film of carbon onto a glass slide, which is floated off in water and transferred onto a copper support grid. To ensure that the drying conditions and cluster concentration on the two substrate types were directly comparable, all of the observations presented in this paper were obtained from a single TEM specimen produced by transfer of electron-transparent fragments of a silicon substrate to an area of a copper grid from which the carbon film had been removed. The samples were examined in a top-entry JEOL 200 CX TEM ($C_s = 1.1$ mm) operating at 200 kV.

On the amorphous carbon substrate the passivated Au clusters were found to form well-defined islands, mainly of monolayer coverage, in which the clusters showed hexagonal ordering, as observed previously [17]. A typical example of such islands is shown in figure 1 (a). The hexagonal arrangement in the islands is well developed, but various defects are also evident, presumably due to the relatively large size distribution of the clusters (3–7 nm, average diameter 5.4 nm). On the silicon substrate the arrangement of the passivated clusters differed noticeably from that on carbon, showing a mixture of isolated clusters and islands of various thickness (i.e. including multilayer structures) in a given region. A typical area is shown in figure 1(b), where smaller islands of irregular shape, and sometimes two or more layers in thickness are evident. We note that in our experiments the extent of self-assembly on the silicon substrate appeared to vary across the sample, presumably because of variation in the surface termination, but in general the translational ordering on silicon was certainly less pronounced than on carbon.

In order to observe directly the orientation of the cluster cores, high resolution lattice images were also obtained. However, it has been shown recently [18], that fringes observed in such small particles are not necessarily related to lattice planes, due to interference effects between diffracted beams. To overcome this problem, dark field images were obtained at the same magnification as the lattice images, using a relatively large objective aperture to include a large segment (roughly a quarter) of the gold (111) diffraction ring. Figures 2 (a) and (b) show, respectively, axial bright field and dark field images of a typical self-assembled island on an amorphous carbon substrate. The dark field image, figure 2 (b), shows clearly that some of the clusters exhibit twinned structures. An example of this is the particle shown in figures 2 (c) and (d) (also marked with a white box in figures 2 (a) and (b), respectively), which exhibits the five-fold twinning characteristic of decahedral particles [19, 20]. Particles with a single twin boundary, icosahedral particles and more complicated twinned particles were also observed. The position of the objective aperture used to form figures 2 (b) and (d) is indicated in figure 2 (e), which shows a selected area diffraction pattern (SADP) of the sample.

There is no clear evidence of orientational order from any of our TEM observations of clusters on amorphous carbon substrates. The proportion of the clusters which showed lattice fringes in high resolution images, such as figure 2 (a), was 53% and the proportion of the clusters which gave rise to well observable contrast in dark field images, such as figure 2 (b), was determined to be 35–38%. It should be pointed out that both numbers are not directly comparable since only a part of the diffraction ring is used for dark field imaging. Finally, in selected area diffraction patterns, such as figure 2 (e), which were obtained from the islands, there is no evidence of an enhanced intensity in parts of the diffraction rings as would be expected for arrays of orientationally ordered clusters.

Figures 3 (a) and (b) are, respectively, axial bright field and dark field images obtained from clusters on a silicon substrate. Although some particles showed clear lattice fringes, it was not possible to obtain a measure of the proportion of the clusters which did so because of the presence of other effects, including moiré fringes and the tendency of the clusters to form multilayers. In dark field images, such as figure 3 (b), obtained with the silicon

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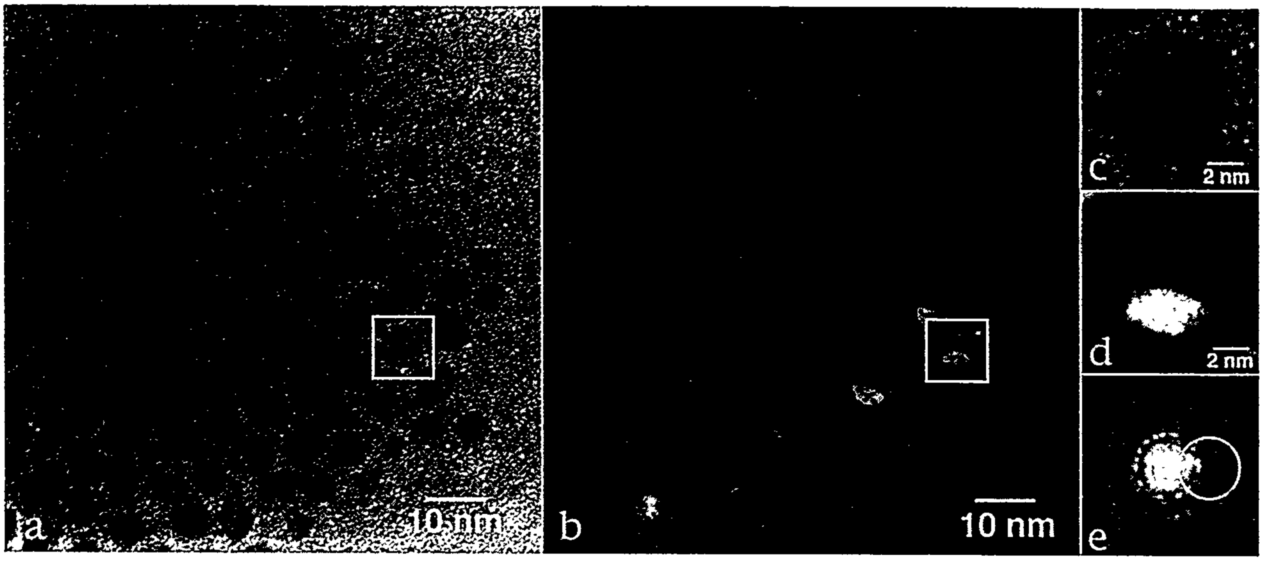

Figure 2. TEM data obtained from an island of self-assembled passivated gold clusters on an amorphous carbon film: (a) many-beam bright field image; (b) dark field image from the same area as in (a); (c) high resolution image of the particle marked in (a); (d) magnified dark field image of the particle marked in (b); (e) SADP with the objective aperture position used for (b) and (d) indicated.

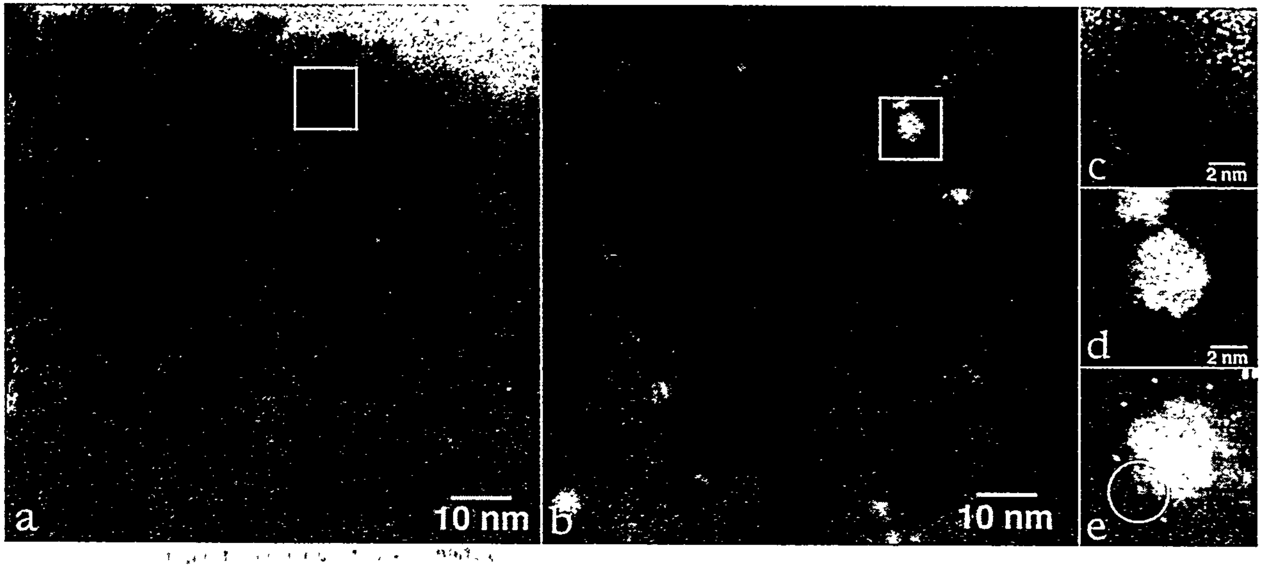

Figure 3. TEM data obtained from a region containing passivated gold clusters on a silicon substrate: (a) many-beam bright field image; (b) dark field image from the same area as in (a); (c) magnified high resolution image of the particle marked in (a)—the fringes correspond to moiré fringes; (d) magnified dark field image of the particle marked in (b); (e) SADP with the objective aperture position used for (b) and (d) indicated.

substrate tilted slightly off the [001] axis such effects were less pronounced (since the silicon diffraction spot is weak). It was found that about 33–42% of the clusters gave rise to contrast. Figures 3 (c) and (d) are magnified views of the particle marked with a white box in figures 3 (a) and (b), respectively, which shows not lattice but strong moiré fringes. Figure 3 (e) is a selected area diffraction pattern in which the position of the objective aperture used to form figures 3 (b) and (d) is indicated. It should be noted that the gold diffraction rings are too weak to be visible against the silicon spots.

The difference in translational ordering between the two substrates is marked. Although extended self-assembled islands were always observed on amorphous carbon, on silicon this was much less apparent and also varied in degree across the sample. Self-assembly of passivated clusters has been observed on a SiO_x substrate [13], and it has been shown [8, 9] that the wetting by the solvent has a major influence on the self-assembly process. The wetting depends on the silicon surface termination which can vary across the specimen because of the etching and cleaning process. The differences in translational ordering on amorphous carbon and crystalline silicon can therefore be attributed to different wetting of the substrate by the solvent as well as different energetic barriers for lateral diffusion of the clusters across the two substrates.

Despite the difference in translational ordering on the two substrates there was no significant change in orientational ordering. Orientational ordering of passivated truncated octahedral particles, including a relationship between nanocrystal core facets and the cluster superlattice arrangement, has been predicted by Luedtke and Landman [12] and reported experimentally by Harfenist *et al* [14]. Luedtke and Landman [12] have also predicted a dependence of the orientation of individual passivated clusters on the strength of the interaction between the chains and the substrate, again for truncated octahedral particles. The passivated clusters employed in the present work, however, show no preferred orientational ordering. This can be attributed to the fact that many of the particles are multiply-twinned. Harfenist *et al* have reported in a further study [15] an analysis of 300 passivated multiply-twinned nanocrystals with a narrow size distribution in a self-assembled array on amorphous carbon. They concluded from high resolution bright field imaging that 170 of these (57%) showed lattice fringes. This figure is remarkably close to the number of clusters in the present work which showed lattice fringes on amorphous carbon (53%), although in our case the self-assembled arrays are smaller and show defects due to a broader cluster size distribution. Our observations therefore suggest that the orientation of passivated multiply-twinned particles is independent of the degree of translational ordering due to a weak cluster–cluster interaction. Furthermore, despite the differences in the solvent–surface and cluster–surface interaction on amorphous carbon and silicon substrates the number of clusters visible (and therefore oriented) in dark field imaging is very similar. Therefore, it can be concluded that the orientation of multiply-twinned particles is independent of the interaction with the substrate.

In conclusion, the degree of lateral ordering within the cluster layer varies significantly between the amorphous carbon and silicon substrates which we have investigated. This behaviour can be attributed to differences in the wetting of the substrate by the solvent (toluene) and in the cluster diffusion barriers for the two substrates. Our work shows that passivated multiply-twinned clusters, despite being faceted, behave like spherical particles with respect to their orientational ordering on the substrate. Their orientation is therefore effectively random, independent of both the ordering within the cluster superlattice and the character of the substrate.

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