Nanoscale Pits as Templates for Building a Molecular Device**

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Template-based assembly is a promising approach to the construction of functional nanostructures at surfaces with atomic-scale precision. By using surface structures to steer the growth of adsorbates, a higher level of control can be attained in comparison with self-organization alone.[1–3] In this Communication, we demonstrate a template-based method for producing gold nanoparticles with a tunable nanometer-scale spacing on a KBr(001) surface. The gaps between the nanoparticles are bridged with 3,4,9,10-perylenetetracarboxylic dianhydride (PTCDA) molecules by trapping the molecules in the same template structures. This approach provides a foundation for constructing a molecular device on an insulator in ultrahigh vacuum. To study the importance of metal–molecule interactions during growth, we also investigate the sequential growth of PTCDA, as well as C60, with various metals.

There are many examples in the literature of templated growth on surfaces, including the growth of metals on vicinal metal surfaces,[4] the growth of molecules on nanostructured metal surfaces,[5] and the growth of molecules on supramolecular assemblies.[6] However, for applications in molecular electronics,[7–9] an insulating substrate is critically important since it permits the use of a planar geometry without leakage currents. To date there are few examples of templated growth on insulating surfaces.[3] The decoration of steps by metal adsorbates has been used to infer the structure of insulating surfaces since the late 1950s.[10] More recently, magnetic nanowire and nanocluster arrays have been created on faceted NaCl(110) and (111) surfaces, respectively.[11] In addition, radiation-induced rectangular pits have been shown to be capable of trapping SubPc[12] and PTCDA molecules[13,14] on a KBr(001) surface. The size and shape of the resulting molecular nanostructures is controlled by the dimensions of the pits.

Here, we demonstrate the use of monolayer-deep rectangular nanopits for templating the growth of gold and PTCDA on a KBr surface. Through a judicious choice of metal coverage, most of the pit corners are decorated with gold nanoparticles. The PTCDA molecules are positioned between the metal nanoparticles by trapping the molecules inside the pits. The role of metal–molecule interactions will also be discussed.

Figure 1 shows a pit-templated surface after gold deposition. Because metals are preferentially nucleated at steps on alkali halide surfaces,[10] the nanoparticle nucleation occurs primarily around the pit edges. In the case of gold on KBr, this occurs on the top side of the steps. Moreover, the vast majority of the particles are at the pit corners. The gold coverage (0.005 nm at a rate of 0.008 nm/min) was chosen such that there are only a few nanoparticles per pit. The pit size is controlled by the dose of charge,[15] therefore, the distances between the nanoparticles can be tuned. The nearest neighbor distance between the nanoparticles shown in Figure 1 is about 8 nm.

PTCDA molecules were placed in close proximity to the metal nanoparticles by trapping the molecules inside the pits. Figure 2a shows an example where the sample was pre-
pared by depositing gold and then PTCDA onto a nanostructured KBr(001) surface. As seen in previous studies of PTCDA on pitted KBr surfaces, some of the pits are filled with PTCDA molecules, with most of the islands having a height of 3 layers.[14] The fact that the gold does not interfere with the PTCDA growth suggests that the gold and PTCDA interact weakly. The importance of the metal–molecule interaction in terms of growth and the properties of a molecular device will be discussed later.

In terms of building a molecular device, the metal nanoparticles may serve as nanoscopic contact pads for the molecular crystallites. The concept is illustrated in Figure 2b. A technique such as shadow-mask evaporation[16–19] could be used to connect the contact pads to larger-scale electrodes in ultrahigh vacuum, although alignment between the sample features and the mask remains a great challenge. This can potentially be addressed by using a dynamic stencil mask.[20] Furthermore, to facilitate the contacting process, the nanoparticles can be made larger by depositing more metal, making the problem of interfacing with the system a matter of contacting a 20–50-nm structure rather than a 1–10-nm structure. The spacing of the nanoparticles, and the number of molecules trapped between them, is controlled by the pit size, which can be readily varied.[15]

To study the structure–function relationship in such a device, the position and orientation of the molecules can be measured by noncontact atomic force microscopy (NC-AFM). Figure 2c shows the herringbone arrangement of the PTCDA molecules in a templated rectangular crystallite. To date, it has not been possible to use NC-AFM to measure the atomic structure of the metal nanoparticles. As suggested in recent experimental and theoretical work, this may be due to an inherently weak corrugation and the prevalence of instabilities that occur at the small tip–sample separations required for atomic-scale resolution.[20] Nevertheless, the crystallographic structure of the particles can be measured ex situ by transmission electron microscopy (TEM). Figure 2d shows an example of a fivefold symmetric multiply twinned gold nanoparticle. A well-defined system structure is desirable for stringent comparisons with modeling, which show that the detailed structure of a molecular device, and in particular the molecule–electrode interface, is of primary importance.[21–23]

In an effort to clarify the role of the metal–molecule interactions during growth, the sequential growth of several metal–molecule pairs on an untemplated KBr(001) surface was considered. These measurements show that the strength of the metal–molecule interaction and the order of deposition are of utmost importance.

Deposition of the metal prior to the molecule provided a means of gauging the relative strengths of the metal–molecule interactions: weakly interacting pairs (e.g., Au–PTCDA) grew nearly independently (Figure 3a), and strongly interacting pairs (e.g., Au–C60, Pd–C60, Ta–C60) showed nucleation of the molecules around the metals (Figure 3b). In the case of strong metal–molecule interactions, molecular islands were formed with metal nanoparticles at the center (Figure 3c). Because of the high density of nucleation sites, the island sizes were quite uniform.

Deposition in the opposite order, that is, molecule then metal, resulted in the diffusion of the metal under or into the molecular film. Figure 3d shows an example where C60...
was deposited prior to gold. At the periphery of the C60 islands, the gold interacts with the C60 and nucleates along the island edges. In addition, many protrusions are seen in the molecular islands. High-resolution measurements show that the protrusions are made up of C60 molecules that are 0.26 ± 0.03-nm taller than the surrounding molecules. This height corresponds reasonably well with the height of a single atomic layer of gold; for example, for the (111) plane, the height is 0.235 nm. Therefore, it is likely that the gold that impinges on the C60 islands diffuses through the C60 lattice, probably through the interstices, and forms flat islands underneath or between the C60 layers. Similar disruptions were seen in a PTCDA film after the deposition of tantalum (not shown). This type of templated assembly is promising for constructing a planar molecular device with a well-defined system structure on an insulator in ultrahigh vacuum. The realization of such a device would open up the possibility of probing the structure by NC-AFM, thereby providing much needed information about the relationship between structure and function, and allowing for stringent comparisons with theoretical modeling.

Experimental Section

The samples were prepared and characterized under ultrahigh vacuum (base pressure < 4 × 10-9 Pa) in a JEOL JSPM 4500 A system. After cleaving a KBr crystal (Korth Kristalle, Germany) in situ along the (001) plane and heating the sample to 150 °C for one hour to remove residual charge, nanopits with a mean side length of 8 nm were created on the surface. The method of pit creation is described in detail elsewhere. An Oxford Applied Research EGN4 electron-beam evaporator, fitted with a charge-retarding grid, was used to deposit the metals (Au, Pd, Ta), and a Kentax thermal evaporator was used to deposit...
the molecules (PTCDA, C60). The surface topography of the samples was measured by NC-AFM\cite{24,25} at room temperature. A Nanosurf easy PLL was employed for the frequency detection and constant amplitude control. Cantilevers (Nanosensors) with a typical spring constant and resonance frequency of 40–50 N m\(^{-1}\) and 170 kHz, respectively, were used with an oscillation amplitude of 5 nm. Samples were prepared for TEM observation by following the procedure from Bassett, in which the surface structures are embedded in a thin carbon film that is floated onto a TEM grid.\cite{10} A JEOL JEM-2010 TEM was used with an acceleration voltage of 200 kV.

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