

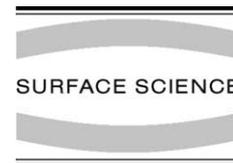


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Surface Science Perspectives

## Playing Tetris at the nanoscale

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The ability to fabricate arrays of functional nanostructures with controlled size, shape and stability, precisely positioned on a substrate of choice, is an ongoing challenge in nanotechnology [1,2]. In this context, the bottom-up approach is emerging as a promising method for the growth and processing of nanostructured materials. This approach is based on the concepts of (organic) self-assembly [3] or (inorganic) self-organization [4] of nanostructures on a suitable substrate [5]. Surface nanotemplates [6], i.e. substrates that are artificially or naturally patterned at the nanoscale, are frequently used to control self-assembly or self-organization processes. Such templates are often able to provide surface cues that may guide the formation of ordered structures, including e.g. tissue regeneration [7]. The 6H-SiC(0001) nanomesh is a particularly interesting template in that it expresses a periodic array of nanopores whose size and spacing can be tailored in the 2–3 nm range [8]. Chen et al. had previously identified this SiC nanomesh as a chemically inert nanoscale template which directs the nucleation and controls the growth of Co clusters during metal vapor deposition, so that a 2D array of Co nanoparticles with relatively uniform spacing and a very narrow size distribution results [8,9]. On page 176 of a recent issue, Chen et al. [10] report the first thorough structural characterization of this 6H-SiC(0001) nanomesh template using complementary surface sensitive techniques.

Other recent examples of templates include long-range (e.g. mesoscale) reconstructions [11,12] and step bunching [13], host–guest inclusions formed by metal–organic coordinated networks [14,15] and other types of ‘nanomeshes’ [16]. Despite the widespread use of patterned substrates, the structure and properties of such templates are often poorly understood.

Silicon carbide (SiC) is a wide band-gap ( $\sim 2.35$  eV) semiconductor which has been extensively investigated both for its fundamental interest and for possible applications. This extraordinary IV–IV compound

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is refractory, chemically inert, stable at high temperatures, extremely hard and resistant to radiation damage [17,18]. Thanks to these uncommon characteristics, it is a particularly suitable material for device applications in harsh environments, as well as where there is a requisite for high power, high temperature, high voltage (including e.g. heterobipolar transistors) and high speed electronic devices and sensors [19]. Moreover it is an implantable bio- and hemo-compatible material [20,21]. In the silicon–carbon phase diagram, SiC is the only thermodynamically stable compound [22]. However, surface effects allow segregation and may lead to Si- or C-rich surfaces [25], exhibiting marked differences in morphology and reactivity. In the present case, the surface's carbon termination renders it chemically inert. This type of segregation is similar to the case of certain metal alloys [23,24] for which a stoichiometry that is not possible in the bulk may occur at the surface, thus conferring special properties.

In a recent issue, Chen et al. [10] provide a detailed description of the surface structure of the 6H-SiC(0001) nanomesh template for self-assembly by powerfully combining Scanning Tunneling Microscopy (STM), Low Energy Electron Diffraction (LEED), X-ray Photoemission Spectroscopy (XPS) and Angle Resolved Photo Electron Spectroscopy (ARPES) from a synchrotron source with Density Functional Theory (DFT) calculations. They provide a new understanding of the atomic scale structure of the SiC nanomesh, addressing and even solving various controversies previously reported in the literature. This represents a new and significant step towards controlled bottom-up growth of nanostructures on nanotemplates.

The structure of the 6H-SiC(0001) surface is resolved by combining structural information from LEED patterns and STM (filled-state) imaging in real space at two different annealing temperatures [10]. The surface is shown to evolve towards the pure carbon nanomesh phase via an intermediate state characterized by shorter periodicity and lower order. High-resolution STM imaging reveals the honeycomb organization of the nanomesh obtained after annealing the 6H-SiC(0001) surface. Remarkably, the size of the honeycomb pores can be tailored to some extent (enlarged by  $\sim 20\%$  from 2 to 2.5 nm) by means of a longer thermal treatment whereas further prolonged annealing results in a distortion of the honeycomb. This demonstrates that the features of the nanomesh can be controlled with nanometer precision by varying the annealing time and temperature. As shown in Fig. 1(a) and (b), this surface can be thought of as a *dynamic* template with tunable lattice parameter and pore diameter.

Chen et al. earlier found that cobalt deposition from the vapor phase onto this template yields three-dimensional Co nanoclusters of nearly fixed size whose number density increases linearly with coverage [8,9], as suggested in Fig. 1(c) and (d). They also observed that upon thermal treatment the nanoclusters resisted agglomeration and remained stable, which is clear evidence of suppressed Co diffusion on the nanomesh. This ability to control, confine and maintain the size of magnetic nanoclusters may have interesting applications in data storage and computing. The new analysis by Chen et al. [10] provides an improved understanding of how nanoclusters assemble on the nanomesh. There are still, however, some open questions about this template and its ability to drive self-organization. In particular, the Co island density they reported [9] is not consistent with full coverage (i.e., every pore filled with a Co cluster) as claimed by the authors, and in fact the average island spacing is more consistent with a situation in which only every other pore (the next-nearest neighbor) are filled with a cluster.

It does not require much of an extrapolation from here to imagine future investigations in which building blocks with different sizes and shapes (reminiscent of the computer game “Tetris”) and with special self-assembling properties are made to land on the template as determined by its structure and then assemble with one or more neighbors, as suggested in Fig. 1(e) and (f). The variable pore size and chemical inertness of this template make it extremely appealing for controlled growth of organic molecules with varying size and shape. “Tetris-like” deposition of organic molecules on a suitable nanomesh may lead for instance to the construction of nanostructures with predefined features, particularly attractive for future electronics.

In principle, this flexible template should allow to control the spacing between the deposited nanostructures (e.g. quantum dots, magnetic dots and catalysts for growing carbon nanotubes), which is a very

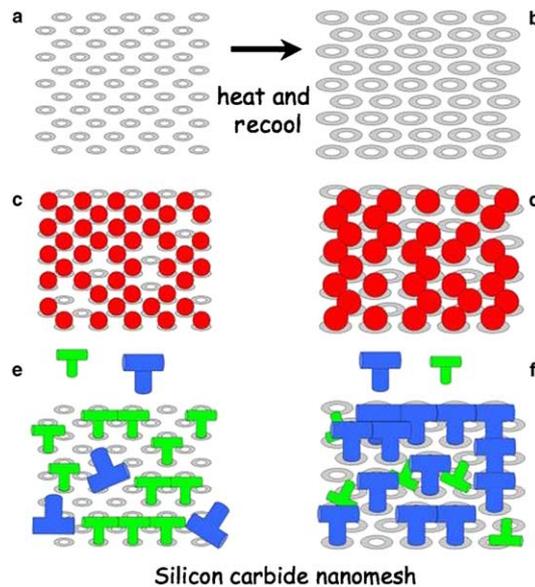


Fig. 1. Playing Tetris at the nanoscale. As shown by Chen et al. [10], different metastable phases of the 6H-SiC(0001) surface are accessible via thermal treatment. Fig. 1(a) shows honeycomb network with pore dimensions of 2 nm. After thermal treatment the pore size increases by 20%, as shown in Fig. 1(b). In this way, the surface acts as a dynamic template which can accommodate building blocks of different sizes, as shown in Fig. 1(c) and (d) (the spherical adsorbates are reminiscent of the Co clusters previously deposited by Chen et al. [9] on the same template). In future studies, we expect that the nanomesh will also be able to accommodate building blocks of different shape, similarly to the computer game “Tetris” (Fig. 1(e) and (f)). Neighboring building blocks may assemble, forming ordered structures with confined size and controlled spacing, as dictated by this tunable template and by their mutual interactions.

important issue for device applications. The control of size, shape and spacing allows to imagine various methods to take advantage of two-dimensional arrays of functional nanostructures. Finally, the biocompatibility of the SiC nanomesh renders it a candidate template for biomolecular assembly, opening many unexplored and stimulating possibilities for fundamental and applied studies. As a consequence the sophisticated tools available to surface scientists can shed new light onto nanoscale aspects of biocompatibility [7], which are related mainly to surface and interface properties, thus guiding the exploration of novel potential biomaterials.

Another crucial point for a thorough understanding of the 6H-SiC(0001) template was the determination of the chemical nature of the carbonaceous species at the surface. Chen et al. [10] performed an elegant in situ XPS experiment to elucidate how surface chemistry changes as a result of thermal treatment. Following the shift of the C 1s core level spectrum at five different annealing temperatures, they demonstrate that surface graphitization occurs at a temperature higher than that required for formation of the carbon nanomesh template. This spectroscopic information was combined with ARPES from a synchrotron source, used to estimate the thickness of the carbonaceous layer at the surface. The results are consistent with the proposed theoretical model, according to which the carbon nanomesh lies above an incomplete carbon layer, where only the center of the nanomesh contains C. This result is particularly important since it clearly explains the previously reported [8,9] chemical inertness of the surface towards silicide formation and indicates a possible reason for the biocompatibility of the SiC surface.

Although some SiC-based devices are actually available today, the main problems in SiC technology are the high cost of wafer production and the high density of defects, which degrades the electronic proper-

ties. However, Nakamura and co-workers [26,27] have recently demonstrated a novel method of growing ultrahigh-quality silicon carbide single crystals, which may soon lead to new opportunities for this material and may assist in preparing surface templates with a reduced defect density. Thus the impact of the work by Chen et al. [10] is further enhanced by this recent breakthrough in SiC crystal growth.

The article by Chen et al. is an excellent reminder that the real power of Surface Science lies in combining complementary techniques that reveal the interplay between electronic structure, chemistry and surface morphology [28]. In addition it opens up exciting possibilities in the area of template-assisted growth at the nanoscale. Thanks to the dynamic tunability of the nanomesh, this Tetris approach may be used to modulate the spacing between inorganic nanostructures, as well as to drive and control the ordered self-assembly of more complex building blocks such as organic and biological molecules.

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