Low-dimensional structures on carbon-terminated W(110): from metallic nanowires to molecular chains

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Abstract. In recent experiments we have discovered the unique ability of the two-dimensional tungsten surface carbide W(110)/C-R(15×3) to support self-organization of nanostructures with an extreme variety of physical and chemical properties. The goal of the current publication is to provide a comprehensive review of our recent achievements with this system. Using the technique of scanning tunneling microscopy we have observed one-dimensional self-assembly of noble and transition metals. Experiments with fullerene molecules have shown that C60 deposited on the surface carbide self-organizes into clusters with magic numbers and at higher coverage into chains. Angular-resolved photoelectron spectroscopy has provided comprehensive information about the electronic and chemical states in the self-assembled nanostructures.

1. Introduction
The investigation of metallic and molecular nanostructures has been enabled two decades ago by the invention of the scanning tunneling microscope (STM) [1] which opened up the possibility to directly study surfaces at the length scale of individual atoms. So-called self-organized atomic systems represent a particularly exciting example of nanostructures as they may exhibit a perfectly periodic structural arrangement. Once established by STM, such uniform self-organized nanostructures may also be studied by appropriate non-local probes like angle-resolved photoelectron spectroscopy (ARPES) [2, 3] with the aim to uncover their electronic properties and mutual interactions [4].

Self-assembled periodic arrays of nanostructures with reduced dimensionality are typically prepared by decoration of steps [5] or surface reconstructions [6] by the atoms of adsorbed material. However, the method usually works well only for a particular combination of substrate and adsorbate elements. Recently, we begun to study phenomena of self-organization on the two-dimensional surface carbide W(110)/C-R(15×3) and have found that this substrate can be considered as universal template which can support self-assembly of atomic and molecular systems with very contrasting physical and chemical properties.

In the present work we report some of the most fascinating cases of nanostructures self-organized on W(110)/C-R(15×3): Au nanowires, nanostripes of transition metals, and fullerene molecular nanoclusters. Their structural, electronic and chemical properties have been probed by STM and ARPES.
Figure 1. (a) Atomically resolved STM image and (b) LEED pattern of W(110)/C-R(15×3); (c) Generally accepted structural model of this surface carbide.

Figure 2. (a) Atomically resolved STM image and (b) LEED pattern of Au nanowires on W(110)/C-R(15×3); (c) and (d) display anisotropic band dispersions of Au measured with ARPES along and across the wires, respectively.

2. Experimental
Preparation of surface carbide W(110)/C-R(15×3) was done by thermal cracking of hydrocarbons at the surface of clean W(110) followed by a moderate flash to 1600-1800°C [7]. Details on the initial cleaning of W(110) can be found elsewhere [7]. Deposition of metallic materials has been performed by evaporation either from a drop melted on a resistively heated W filament, or from a source heated by electron bombardment. Deposition of C₆₀ was done from a quartz evaporation crucible. Amounts of deposited materials were carefully controlled by microbalance, STM, and photoemission. STM measurements have been performed with an Omicron VT SPM apparatus. We have been using electrochemically etched polycrystalline W tips sputtered and heat treated in situ. Photoemission experiments were done at BESSY using various electron spectrometers and beamlines.

3. Results
Results of the experimental verification of the template W(110)/C-R(15×3) by STM and low-energy electron diffraction (LEED) are reported in Fig. 1(a) and 1(b), respectively. While LEED reveals a rectangular surface lattice rotated by 14° relative to [001] of W, STM supplies more information resolving the inner atomic structure inside the unit cell of the carbon matrix. It turns out as a mesh formed by atomic rows of carbon mutually connected by zigzag chains of carbon atoms. Dimensions of the unit cell are (8Å×13Å). The generally accepted structural model of W(110)/C-R(15×3) is shown in Fig. 1(c) [8, 7]. According to our recent results [7], the carbon nanomesh is embedded into the first atomic layer of W(110). Furthermore, a
Figure 3. STM verification of one-dimensional layer-by-layer growth of Mn on the surface carbide. Images shown correspond to 1.5 ML of Mn as deposited at room temperature (a) and annealed at 500°C (b).

Figure 4. (a), (b) and (c) STM observation of C_{60} molecular clusters with magic numbers and cluster chains; (d) PES verification of chemical state in the clusters; (e) cluster structures obtained theoretically.

one-dimensional periodic bucking of the surface along the direction \( \mathbf{V}_\perp \) appears.

When 1–3 ML of Au are deposited onto W(110)/C-R(15×3) and annealed at 550-600°C, a continuous nanowire-like patterned Au film is formed [9, 10]. It can be evidenced by its sharp R(9×1) reconstruction in LEED (Fig. 2(b)). Direct atomically-resolved STM observation of the nanowires produced (Fig. 2(a)) reveals a dramatic non-uniformity of their atomic structure which is induced by the potential profile of the underlying carbidic template. Particularly interesting are electronic properties of this Au nanostructure. ARPES spectra measured for the directions parallel (Fig. 2(c)) and perpendicular (Fig. 2(d)) to the wires demonstrate a remarkable anisotropic dispersion of Au states (they are denoted by dashed lines in Fig. 2). So far, lateral quantization of the \( d \)-band between 4 and 5 eV binding energy had been reported in our earlier work [9]. A particularly novel result is the anisotropy observed in the dispersion of Au peaks located at 0.6-1.0 eV binding energy. These bands appear inside the surface projected band gap of W(110). Their dispersions are parabolic along the wires, while for the perpendicular direction the photoemission peaks of these states nearly vanish. Residual intensity which can still be detected exhibits almost no dispersions. This effect can be explained by electron scattering on the periodic potential of nanowires and corresponding development of new boundary conditions for the electron wave-functions.

Interesting results have been achieved for 3\( d \) transition metals grown on W(110)/C-R(15×3). The STM observation of Mn epitaxy on the surface carbide is reported in Fig. 3. We have
found that nominal coverages of less than 5 ML Mn (Fig. 3(a)) grows layer-by-layer in uniform nanostripes. Moderate annealing of the sample improves somewhat the one dimensional character of Mn nanostructure and reduces the nanostripe width (Fig. 3(b)). In other experiments (not shown here) we have demonstrated the possibility of using the nanowire-like patterned Au film (Fig. 2(a)) itself as supporting template for growth of magnetic nanostructures. In particular, the formation of separated Ni nanostripes aligned to the Au wires was evidenced and characterized in detail by STM [10].

Fascinating effects of self-organization have been observed also for molecular systems. We have performed experiments with \( \text{C}_{60} \) molecules which are the most symmetric representatives of the fullerene class of materials and are famous for their unique low-dimensional electronic, chemical, and magnetic properties. It was revealed in our STM experiment that \( \text{C}_{60} \) deposited on W(110)/C-R(15×3) at room temperature self-organizes into molecular clusters with perfectly uniform shapes and dimensions [11]. Furthermore, the number of molecules in each cluster is "magic" and depends on the total coverage \( \Theta \). The formation of small clusters \( K_1 \) with 4 molecules at \( \Theta=0.2 \) ML (Fig. 4(a)) and \( K_2 \) with 7 molecules at \( \Theta=0.4 \) ML was observed (Fig. 4(b)). At even higher coverage remarkable cluster chains are formed (Fig. 4(c)). Investigation of the chemical state in the system by valence band photoemission (Fig. 4(d)) does not reveal any effects of charge transfer in the electronic structure of molecular orbitals HOMO-\( n \) exactly as in the case of \( \text{C}_{60} \) adsorbed on graphite [12]. This result identifies van der Waals interactions as dominating between the molecules and the substrate and allows for a theoretical simulation of the cluster growth on the surface carbide in the framework of the Girifalco approach [13]. In such a way, adsorbed \( \text{C}_{60} \) can be considered as two-dimensional molecular gas weakly bound to the substrate by polarization forces. Cluster structures obtained by simple static modeling (Fig. 4(e)) were found to be in perfect agreement with experiment [11].

4. Summary

In summary, we have investigated aspects of self-organization generated by the two-dimensional tungsten surface carbide W(110)/C-R(15×3). This template, due to its chemical passivity and complicated potential profile on an appropriate length scale, has the potential to become an extremely important substrate for self-assembled nanostructures. In particular, self organization of Au nanowires, magnetic nanostructures, and molecular clusters of fullerenes \( \text{C}_{60} \) was demonstrated. Metallic nanowires have additionally been characterized by photoelectron spectroscopy. Intriguing quantum-size effects due to reduced dimensionality of the nanostructures were revealed.

5. References

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