



Surface Science Perspectives

Weakly bound buffer layers: A versatile template for metallic nano-clusters growth and film patterning on solid surfaces

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ABSTRACT

Buffer layers composed of weakly bound atoms or molecules on solid surfaces are discussed as a versatile platform for size controlled growth of nano-clusters and for patterning of thin metallic films. Metallic nano-crystals can be prepared and their size and density be controlled by varying the film thickness. Cold metallic or oxide clusters, softly land and deposit on solid substrates via the Buffer Layer Assisted Growth (BLAG) method. Their final structure, therefore, reflects purely the interaction with the substrate with no kinetic constraints that may play a role in direct deposition methods of hot atoms. The nature of the buffer film, being a rare gas or a molecular film, can somewhat affect the shape of clusters as well. Applying laser ablation techniques, these weakly bound films were demonstrated to assist in patterning of metallic films. It operates on practically any cold, flat solid substrate that absorbs the laser light. Parallel stripes at sub-micron width, millimeter long, were obtained experimentally, with line width determined by the ablating laser power. The versatility of these weakly bound films in manipulating the structure of metallic particles and thin films is discussed in its wider potential scope.

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1. Introduction

Metallic clusters at 1–20 nm size range residing on top of oxide solid surfaces are often used as convenient model systems for industrial supported catalysts that could be studied under well defined ultra high vacuum (UHV) conditions [1–5]. Their chemical reactivity as catalysts has been studied over the years and compared to more realistic catalysts often composed of transition metal particles supported on high surface area materials, e.g. silica, alumina, titania or carbon, under high pressure, high temperature conditions [6]. A typical way to grow metallic clusters under model vacuum conditions involves evaporation of hot metallic atoms that upon initial contact with an oxide substrate they diffuse and aggregate. Clusters prepared this way often grow as rather flat, 2D particles with relatively narrow size distribution and maximum density of up to about 5×10^{12} clusters/cm² (as is the case for gold clusters). More sophisticated methods have involved direct deposition of very small clusters (few atoms) that were mass selected before deposition via mass spectrometry time of flight techniques [7,8]. The chemical reactivity of these small metallic clusters could be tested via temperature programmed desorption (TPD) under vacuum conditions. The small size of the metallic clusters enabled quantum calculations of the reactivity pathways of these supported model catalysts [8].

An alternative procedure to grow nanometer size metallic clusters has been introduced by Weaver and co-workers already two decades ago [9–11], employing a layer of rare gas atoms, such as Xe, Kr or Ar, as a buffer for the growth of metallic clusters on top. Subsequent annealing of the sample to room temperature results in buffer material desorption and soft and in particular cold landing of the metal clusters on the substrate via a Buffer Layer Assisted Growth (BLAG) mechanism [9]. It was shown that one can control the clusters size in the range of 1–15 nm (diameter) by varying the buffer layer thickness. Thicker layers lead to the formation of larger clusters, since clusters have longer time to diffuse, aggregate and grow on their way to the substrate, upon buffer evaporation. Recently molecular buffers, such as amorphous solid water (ASW) were shown to be effective as buffers for the growth of inert metals like gold [12]. The practical advantage with molecules like water [13] is that one can cool the sample using LN₂ rather than He cryostat, that is necessary if rare gases are used as buffer materials. More reactive approach, based on buffer layers was also demonstrated. Mg evaporated on a layer of condensed oxygen was shown to form clusters and ramified layers of MgO [14]. Similarly, Ti atoms were deposited on top of a layer of ASW on gold substrate to form TiO₂ clusters upon removal of the ice layer [15]. More recently, Fe atoms evaporated and grown on CCl₄ as buffer layer on FeO(111) substrate revealed very rich reactivity pathways [16].

A different approach, utilizing fast removal of weakly bound buffer layers with metal clusters or thicker films on top using

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pulsed (10 ns) laser ablation techniques [17] has become the basis for a novel laser-patterning technique. It was demonstrated to form parallel metallic stripes at sub-micron widths [13,17–19].

In this prospective article we shall briefly review the advantage over standard deposition techniques one gains by employing the buffer layer assisted methods for clusters preparation and growth as well as film patterning.

In general, the experimental setup for such studies is typical to surface physics/chemistry under UHV conditions. Surface cleaning and characterization tools in addition to mass spectrometry for TPD analysis, Auger, LEED etc. are used for defining the substrate before buffer material adsorption. TEM samples, mostly thin amorphous carbon (a-C) film on a copper grid, were also used to grow clusters via the BLAG method [10,11]. After removal from vacuum, the samples are analyzed at room temperature by HR-TEM, where exact nano-structure and level of crystallization of the particles can be characterized at the atomic level. Metal deposition techniques often employ hot metallic atoms evaporation using tungsten filament or e-beam heating of the metal to be deposited. The hot atoms dissipate their kinetic energy and cool down immediately upon adsorption on top of the buffer layer, forming small seed clusters. Slow annealing of the system to room temperature leads to desorption of the buffer material and at the same time, the small seed clusters diffuse their way through the evaporated buffer atoms or molecules down to the substrate [9–12]. As the buffer layer becomes thicker, there is more time for the small metallic clusters to reach and attract other clusters, aggregate or coalesce to form larger clusters. It turns out that the actual evaporation time or sublimation rates of the buffer may affect the final size and density of the deposited clusters [11]. This BLAG mechanism results in clusters that are more 3D in nature if compared with clusters grown via direct deposition (DD) process. Buffer layers composed of rare gases, Xe, Kr, Ar were used to grow various metallic clusters such as Ag, Cu, Pd, Co, Ni [9–11] and Au [10–12]. Pure metallic seed clusters on top of the buffer layer result in different final shapes than if the seed clusters interact with adsorbates. This was demonstrated in the case of CO that has modified the final, BLAG deposited Pd clusters [11]. The diffusion mechanism of the clusters on top of and through the subliming buffer films has been modeled by means of Monte-Carlo simulations [10,11]. The model could explain the density and size distribution of clusters, suggesting a competition between clusters diffusivity through the subliming buffer and the time it takes for buffer desorption.

Molecular buffer layers such as amorphous solid water (ASW) were recently introduced [12,20–22], demonstrating its capability to prepare and grow clusters in a similar mechanism to that first demonstrated with rare gases. Very similar growth mechanism was found in both atomic and molecular buffers. Small differences in size distribution obtained using atomic vs. molecular buffer materials were attributed to the significant difference in heat capacity, e.g. comparing Xe to H₂O [12]. This difference is expected to affect mostly the size of the initial seed clusters growing on top of the buffer layer prior to desorption. Yet, compensating factors such as the strength of interaction of the metallic particles with the buffer material and the desorption temperature of the buffer tend to minimize differences caused by the buffer materials [21]. It was recently demonstrated that under certain conditions ASW undergoes de-wetting while desorbing which affects the distribution of sizes and density of metallic particles grown on such films [21].

IR spectroscopy of adsorbed CO molecules was employed as a probe for the fine structure of BLAG prepared gold nano-clusters. Combined with TPD analysis [22], one could find differences between the BLAG and directly deposited (DD) clusters that can be used to explain reported reactivity of the gold DD nano-clusters. FTIR of adsorbed CO on ASW-BLAG prepared Au clusters is shown

in Fig. 1, revealing a single characteristic IR absorption at 2106 cm⁻¹. CO as a marker for gold nano-clusters was found to be sensitive to the size of the clusters: peak intensity increases in the case of small clusters (samples were prepared to maintain similar clusters density), apparently reflecting more sites that support perpendicular adsorbed CO molecules on the small clusters. The frequency, however, is practically insensitive to size.

Unlike standard deposition methods where the size and density of growing clusters are strongly coupled, it was shown that recycling the BLAG procedure can result in a simple and useful decoupling of size from density of the clusters [20,22]. Moreover, this multiple BLAG procedure can be used to co-deposit more than one metallic element, as was demonstrated for co-deposition of Pd and Au [22]. High resolution TEM inspection of the clusters formed via BLAG reveals that upon annealing to room temperature nano-crystals are formed, stabilized mostly along the closed packed fcc(111) orientation (in the case of gold and palladium). A low density sample of co-deposited Au and Pd prepared via BLAG over 10ML of ASW is shown in Fig. 2.

Sublimation rates do affect the final size and density of grown metallic particles via BLAG, as mentioned above [11]. A question has arisen, therefore, how efficient will be extremely rapid heating (10⁻⁸ s time scale) and removal of buffer films, tens to hundreds of monolayers thick, when compared with slow annealing as a potential pathway for film patterning. The first experimental demonstration used pulsed Nd:YAG laser in order to ablate a uniform layer of Xe covered by one monolayer of potassium [17]. In situ second harmonic generation (SHG) detection from the top potassium film revealed that a single laser pulse, 10 ns long, can remove the entire Xe layer with the K atoms on top, above a certain laser power. This observation was further developed into laser-patterning of a gold film when a single laser pulse was split into two identical beams that recombine on the surface to interfere, heat the surface at the constructive interfering stripes and lead to selective buffer layer ablation from these stripes [13,17–19]. In Fig. 3 such gold stripes are shown, demonstrating that the width of the patterned metallic stripes can be controlled by the laser power. In a lift-off mode of operation one initially forms buffer (Xe in Fig. 3) “grating” from the weakly bound buffer, then deposit thin metal film on top. A second, uniform and higher power laser pulse then removes the remaining Xe with the metal film on top. Metallic stripes that were directly deposited on the substrate and cannot be removed by the second laser pulse since it is bound significantly stronger to the substrate are left behind, patterned on the substrate [13].

The metallic clusters and the laser-patterning procedure were combined in order to form coverage modulation in a grating-like

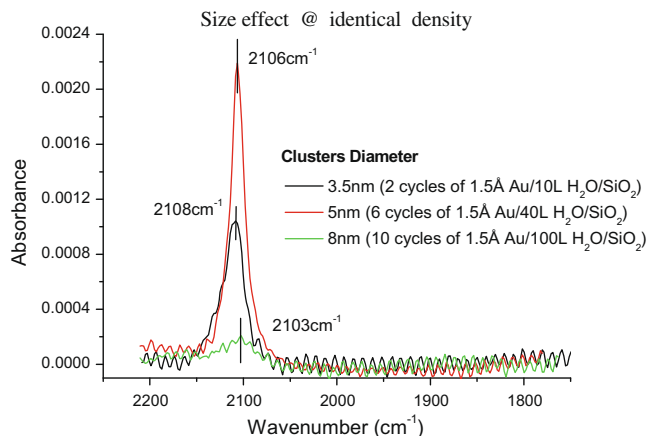


Fig. 1. FTIR of CO adsorbed at 110 K on Au nano-clusters prepared via multiple-cycle ASW-BLAG procedure.

form [23]. This procedure enables one to diffract coherent light (He–Ne laser) from such grating and thus enable direct measure-

ment of clusters diffusion in real time, as a function of clusters size and type of substrate, as schematically demonstrated in Fig. 4. It was shown that, as expected, small clusters diffuse faster than larger ones on top of clean Ru(001) substrate. On oxygen covered ruthenium, however, only minor size dependence was found. The great sensitivity of the gold clusters, 3–10 nm in size, to a relatively small difference in the nature of the substrate was explained by the better commensurability of the (111) oriented gold clusters to the clean Ru(001). This result in a stronger “friction” between the gold clusters and the clean ruthenium that increases with the cluster size, therefore stronger dependence on the cluster size was expected and actually reported [23]. Larger mismatch of the structure of Au(111) clusters with the O/Ru(001) in its (2×2) overlayer structure leads to “skating” of the clusters as a result of the smaller friction.

In conclusion, utilization of weakly bound buffer layers has been demonstrated as a powerful template for the growth and manipulation of metallic nano-clusters. This concept enables independent control over size and density of the clusters and the growth of bi-metallic layers. BLAG clusters are deposited as cold particles on any type of substrate. This paves the way to study the effect of substrate on various properties of the clusters, e.g. adsorption, chemical reactivity etc., because the substrate is not significantly affecting the growth process. Such chemical reactivity studies are currently performed, looking for, e.g. benzene formation from acetylene on top of pure Pd clusters on SiO₂ substrate. The reactivity of pure Pd has been compared to that of Pd–Au alloy

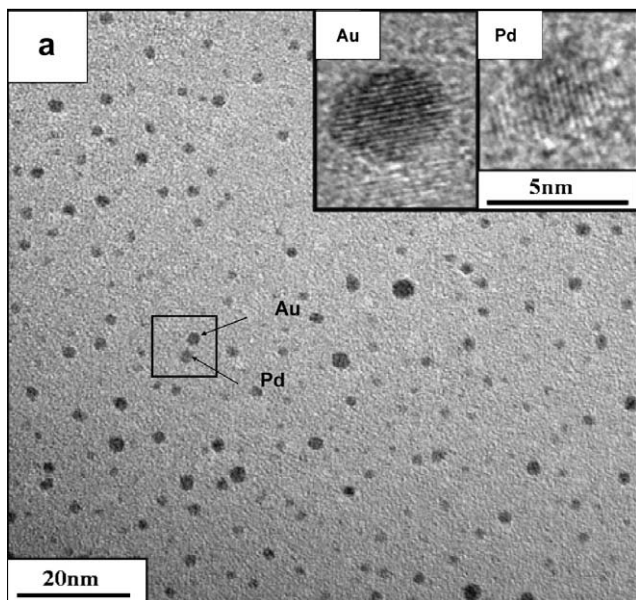


Fig. 2. Gold and palladium clusters co-deposited via multiple ASW-BLAG procedure. HR-TEM inspection of the clusters clearly shows the formation of (111) oriented nano-crystals of both fcc elements.

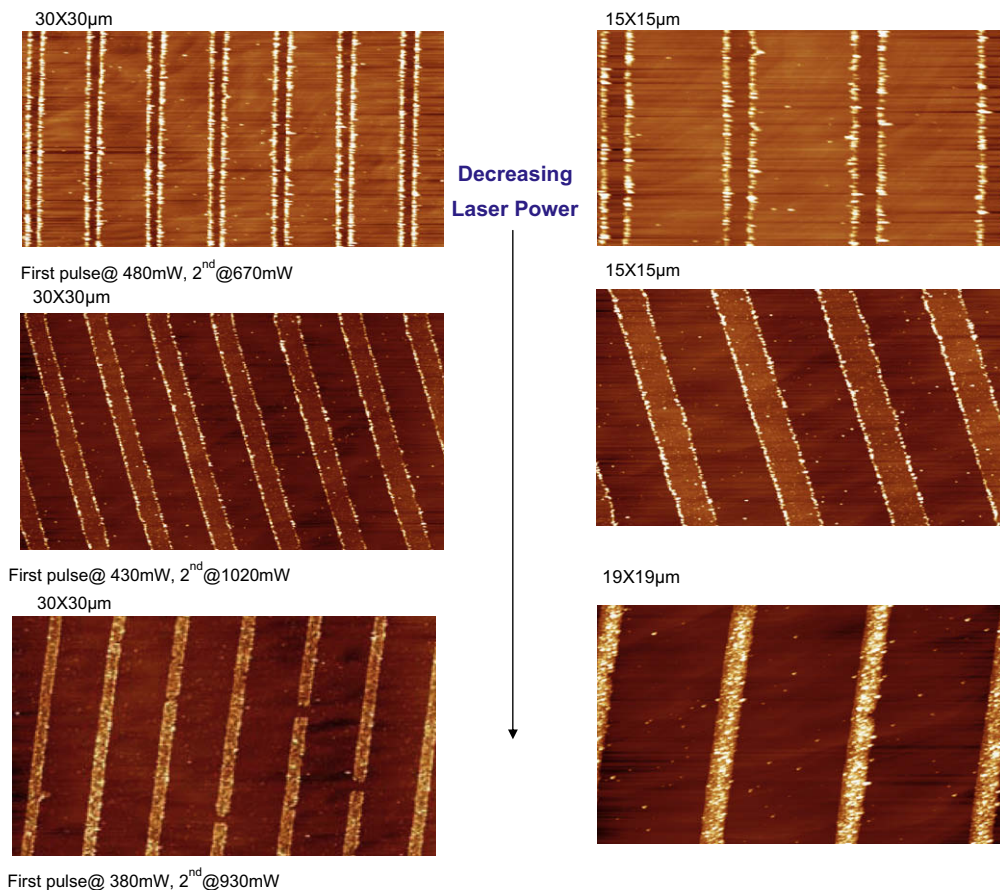


Fig. 3. AFM images of the result of Buffer Layer Assisted Laser-Patterning technique employing a lift-off procedure. The buffer was a 60ML Xe with subsequent deposition of gold film, 8 nm thick, employing Nd:YAG laser at its fundamental wavelength of 1064 nm. Reducing the first (interfering) pulse intensity results in narrower gold (bright stripes in the figure above) lines on the surface. The substrate was a Ru(001) single crystal surface and the entire patterning was performed under ultra high vacuum conditions.

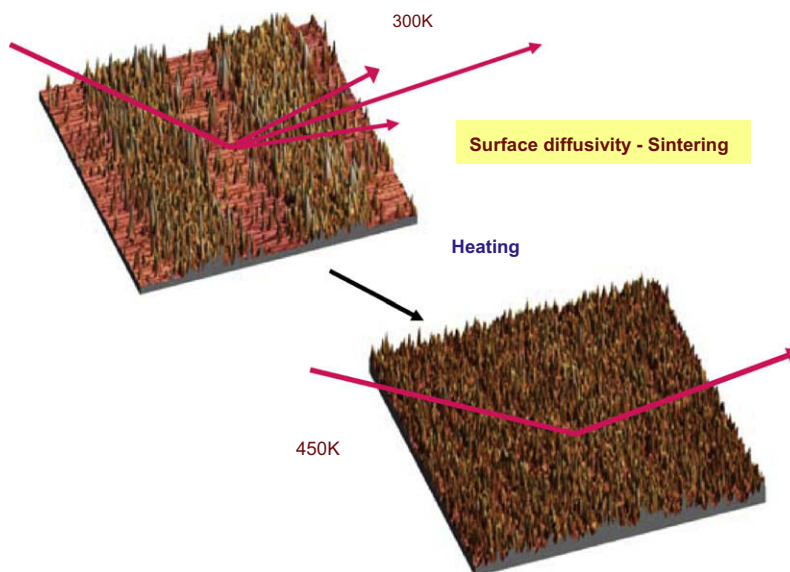


Fig. 4. AFM imaging of gold clusters coverage grating formed via weakly bound buffer layer (Xe) laser-patterning, before onset of surface mobility (300 K) and after annealing to 450 K.

clusters grown via BLAG. Preliminary results suggest that the alloy clusters are significantly more reactive than pure Pd.

The weakly bound buffer layer template was further developed into a laser-patterning procedure. In this application thin metallic films were shown to form controllable stripes in a grating-like shape. Sub-micron wide, millimeters long set of conducting wires can be obtained using a single laser pulse. The cold stripes deposited on a pre-organized substrate can be of great advantage for the design of delicate, non-damaging contacts over molecular and nano-wire based “molecular electronics” setup. Buffer layer assisted patterning can potentially be developed into a particularly clean and friendly conducting layer structural design as an alternative for photo-lithography.

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