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Nano-donuts on metal surfaces

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ABSTRACT

Nano-structures comprising of a pit surrounded by a circular ridge that resemble nano-donuts have been observed on flat terraces of both Au(1 1 1) and Al(1 0 0) surfaces after low energy (1.5–2 keV) rare gas (*rg*) ion implantation. From time lapse scanning tunneling microscopy, we demonstrate that these donuts originate from the *rg* bubbles that migrate out from the sub-surface region. The circular shape of the donuts is observed for both Ar and Ne bubbles. The donuts and the related nano-structures represent different stages of large time scale co-operative relaxation of Au atoms by long range elastic interaction after the *rg* bubbles leave the metal.

1. Introduction

Embedded nanosystems in the sub-surface region are of current research interest because of their wide range of intriguing properties [1,2]. Rare gas (*rg*) bubbles in metals is a special class of embedded nanosystem that is of technological significance in nuclear reactors [3] and also displays interesting physical phenomena [4–10]. For example, *rg* bubbles formed by high energy (≈10–150 keV) ion implantation exist in solid state even at room temperature (RT) and are over-pressurized by the lattice [4,5]. Solid to fluid transition in Xe bubbles was demonstrated by transmission electron microscopy [6]. *rg* bubbles in the sub-surface region of metals are formed by implantation of low energy (≈1–5 keV) ions [11–16]. The earliest evidence of such bubbles was reported in Pt(1 1 1) using scanning tunneling microscopy (STM) [11]: protrusions of subatomic to one atomic layer height resulting from the presence of *rg* bubbles in the subsurface region were observed. In a subsequent STM study, Schmid et al. demonstrated presence of interference features that originate from quantum well states formed by confinement of the electron wave function between the Al(1 1 1) surface and the Ar bubbles implanted in the sub-surface region [12].

X-ray photoelectron spectroscopy (XPS) established the influence of dynamical final state screening by Al conduction electrons on the binding energy and shape of Ar core-level peaks [13]. A bimodal size distribution of Ne bubbles in Al was reported, the smaller (bigger) bubbles being in solid (fluid) state [14]. In a later study, it was shown that surface, bulk and multiple plasmons of Al are excited by photoemission from the *rg* bubbles [15].

In this work, using STM and XPS, we establish that rare gas bubbles in Au(1 1 1) and Al(1 0 0) erupt through the surface leaving an imprint comprising of a pit surrounded by a circular ridge that resembles a nano-donut. Prior to this, the bubbles form protrusions on the surface that are less than an atomic step height due to elastic lattice deformation. The different nano-structures reported here represent different stages of large time scale co-operative relaxation of Au atoms by long range elastic interaction after the *rg* bubbles come out through the surface. The novelty of the present study is that here the surface is perturbed from inside, which is fundamentally different from perturbing the surface from outside, for example, by adlayer deposition.

2. Experimental

The STM experiments were carried out in a VT-AFM system from Omicron GmbH, Germany at a base pressure of 4×10^{-11} mbar. The tungsten tip was biased and the crystals were at ground potential. The details of the image analysis is discussed elsewhere [17]. The STM images were recorded at RT after about 180 min of stopping the annealing at higher temperatures for avoiding temperature induced drift. Atomically clean Au(1 1 1) and Al(1 0 0) single crystal surfaces were obtained by sputtering by 1–1.5 keV Ar ions and annealing cycles (675 K). Low energy electron-diffraction shows sharp spots of expected symmetry and XPS shows absence of any implanted rare gas and oxygen or carbon impurity. Rare gas ions were then implanted at an angle of 65° with respect to the surface normal with different implantation energies (E_i) using IQE 11/35 sputtering source from Specs GmbH, Germany. A fluence

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of 1 monolayer (ML) is attained when the number of Ar ions that impinge is equal to the number of substrate atoms on the surface per unit area. As in our earlier studies [13,18], fluence is determined using the formula

$$F = \frac{Q \times t}{A \times n_A} \quad (1)$$

where, Q is the total charge flowing through the sample per unit time measured by the sample current and t is the time for which the ion beam is incident on the sample, and A is the area of the sample exposed to the ion beam, and n_A is the surface atom density. To determine the total charge, we have applied a positive bias for each E_i to account for the overestimation of the current though the sample due to electron emission. T_A represents the temperature during implantation i.e. simultaneous annealing, whereas T_{Ap} represents the temperature for subsequent or post annealing. In case of Au, smooth surface could be obtained by simultaneous annealing at about T_A = 500–525 K. On the other hand, to obtain such a smooth Au surface by post annealing, a much higher temperature (T_{Ap} = 675 K) is required where no *rg* bubbles are observed. So, simultaneous annealing is used for Au. The annealing time in all cases was 20 min. The XPS measurements were carried out using AlKα X-ray source and Phoibos 100 electron energy analyzer from Specs GmbH, Germany.

3. Results and discussion

3.1. Scanning tunneling microscopy on Ar implanted Au(1 1 1) and Al(1 0 0) surfaces

The STM image of Au(1 1 1) (Fig. 1(a)) after Ar ion implantation at T_A = 545 K shows four exposed layers with flat terraces that exhibit the well known herringbone reconstruction [19]. This is in agreement with earlier reports that *rg* ion bombardment with T_A>500 K causes layer by layer removal in Au(1 1 1), rather than pit formation that is observed below 500 K [20–22]. Curiously, features resembling dots are observed in the image, as shown by the vertical arrows. An expanded image (Fig. 1(c)) of the area within a white square containing one such dot shows that its shape is nearly circular. The height profile (Fig. 1(d)) along the dashed horizontal line in Fig. 1(c) shows that it is actually a protrusion of nearly Gaussian shape, with a height (h_p) of 0.23 nm and a diameter (d_p) of 3.7 nm, given by the full width at half maximum. Interestingly, for all the protrusions observed, h_p is always smaller than an atomic step height (0.24 nm) and varies from 0.02 nm to 0.23 nm. This establishes that the protrusions are not Au adatom islands, since their heights are always less than an atomic step height. Moreover, we have shown in Ref. [22] that adatom islands of such small size (<370 nm^2 in area) disappear by adatom detachment without leaving any imprint, unlike the protrusions observed here, as discussed in the next paragraph. The size of the protrusions indicates that the strain is spread over many lattice sites on the Au(1 1 1) surface. Such protrusions or bumps of sub-atomic height have been observed on Pt(1 1 1) [11]. Their origin has been explained as follows [11]: a dislocation loop that is a disc of interstitial atoms is punched out by an overpressurized bubble and thus its volume increases. The punched out dislocation loop might glide to the surface if it becomes glissile and become an adatom island. However, protrusions less than the step height could be formed due to elastic lattice deformation due to the bubble or the punched out loop below the surface [11,23].

While protrusions have been reported in literature [11], we find evidence of a completely different type of nano-structure on the Au(1 1 1) surface that resembles a donut of nearly regular circular shape (horizontal arrows, Fig. 1(e)). A zoomed image (Fig. 1(f)) and its height profile (Fig. 1(g)) show that the nano-donut comprises of a pit surrounded by a circular ridge with outer diameter d_d. The other

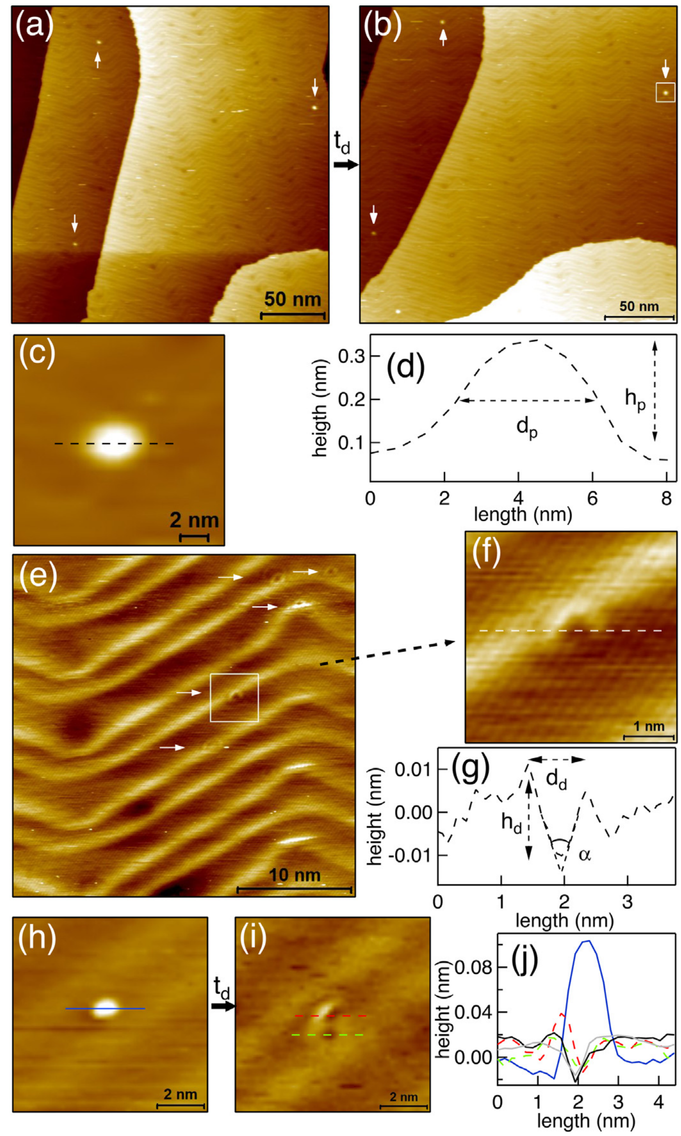

Fig. 1. (a) Constant current (I_T = 1 nA, U_T = 1 V) STM topography images showing protrusions of sub-atomic heights (vertical arrows) on Au(1 1 1) surface after implantation with 2 keV Ar ions and 5 ML fluence at annealing temperature T_A = 545 K, white arrows indicate the protrusions. (b) STM image of the same area after a time delay of t_d = 400 s. The defects such as islands, pits and clusters are annealed out because of implantation at high T_A (= 545 K) [22]. The region denoted by the white square is expanded to show (c) a protrusion and the corresponding (d) height profile. (e) Donut shaped pit structures (horizontal arrows), where the area marked by white rectangle shows (f) a donut in an expanded scale and (g) its height profile. In order to account for the gradient of the surface due to the herringbone reconstruction of Au(1 1 1) surface, a second order polynomial background has been subtracted in (g). Time delay (t_d = 500 s) images on the same area show that a (h) protrusion transforms into (i) two donut-like pit structures. The height profiles along the dashed lines in (h) and (i) are shown in (j).

parameters that define the shape of the donuts are the depth (h_d) of the pit in the center of the circular ridge and its opening angle (α). An important clue about the origin of the donuts is obtained from the two sequential images on the same area with a time delay (t_d) of about 500 s: the protrusion in Fig. 1(h) transforms to a double donut-like structure with two pits (green and red line profiles in Fig. 1(i) and (j)). This indicates that the donuts form because the Ar bubbles present below the protrusions erupt out of the surface. This event that occurs naturally is rare and could be observed by chance in Fig. 1(h) and (i), since in most cases, the protrusions remain unaffected by scanning (see for example Fig. 1(a) and (b)). Moreover, in Fig. 1, only one protrusion converted into donut, while the others