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Fabrication of Mo pyramidal-shape single atom tips covered by a noble metal

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ABSTRACT

The effect of annealing temperature on the faceting phenomena has been studied for pure molybdenum (Mo) and Mo tips covered with palladium (Pd), platinum (Pt), rhodium (Rh), or iridium (Ir) by field ion microscopy (FIM). For these Mo samples, three {2 1 1} facets were found to expand to {1 1 1} facets and form pyramidal structures after annealing at the temperature of 1100–1300 K. The pyramidal single atom tips (SATs) were formed on Pd-, Pt- and Rh-covered Mo tips. Two types of pyramidal structure, stacked by either 1, 3, 10 or 1, 6, 15 atoms for the top three layers were found. However, no SATs were found on pure Mo and Ir-covered tips. This indicates that noble metal adsorption, which can increase the difference of surface-free-energy anisotropy, indeed benefits the formation of SATs on Mo systems. Additionally, an SAT cannot be obtained for the Ir-covered Mo systems, because Ir is easily alloyed with Mo.

1. Introduction

A super-sharp tip is one of the most important elements in nano-science and nano-technology. The sharpest tip is the single atom tip (SAT), which has only one atom, with a diameter of about 10^{-10} m. The SAT has attracted much research effort due to its unique properties and potentially wide range of applications. First, it is an optimal point electron and ion source. Its advantages include high brightness, stability and long time maintainability. Second, it is an ion beam with good focus [1–4] of the smaller half angle from a local enhanced electric field, which can resolve the problem of chromatic aberration. Third, its electron beam has high coherence, so the wave properties of the spatially well-defined electron source can be used in many applications, including high-resolution transmission electron microscope and shadowing electron microscope with holographic capability [5]. Fourth, it can also be applied in scanning probe microscopes to achieve the best spatial resolution.

In the 1990s, Madey et al. found that ultrathin noble metal films grown on a tungsten W (1 1 1) surface can undergo massive reconstruction upon annealing to form three-sided pyramids with {2 1 1} facets [6–9]. The driving force of the facet formation was attributed to an increase in surface-free-energy anisotropy, as later confirmed by theoretical calculations [10,11]. Inspired by this adsorbate-induced faceting process, the SAT can simply be completed via thermodynamic equilibrium in an ultra-high vacuum (UHV). The W (1 1 1) faceting to a single atom tip is induced by heating 1–2 ML noble metals, including Pd, Pt, Rh, and Ir to 1000 K after adsorption [2,12]. Further, Madey presented the oxygen-induced faceting of Ir (2 1 0) [13], which allowed a single-atom tip of Ir to be produced [14]. Because faceting is a thermodynamic process, the tip can be regenerated by simple annealing even if it is destroyed [4,15], which ensures a very long lifetime for this type of SAT.

In most cases, the metals can easily form oxides with oxygen. Thus if a metal has oxides that can be removed easily, this would contribute to an SAT application. Molybdenum (Mo) and W have the same body-centered cubic structure as well as similar lattice constant, physical and chemical properties [16,17]. However, the oxygen desorption temperature of Mo is about ∼1600 K [18,19], lower than that of W, which is about ∼1800 K [20]. Importantly, removing oxides and cleaning the Mo surface is easier than for W. In addition, according to the Zhang et al's simulation, which was calculated by using the second nearest-neighbor modified embedded atom method, the surface free energy $E_{(2\,1\,1)} = 3277\ \mathrm{ergs/cm^2}$ is lower than the $E_{(1\,1\,1)} = 3429\ \mathrm{ergs/cm^2}$ for Mo surfaces [21]. Therefore, the area of {2 1 1} facets will increase relative to (1 1 1). SAT might be formed if {2 1 1} facets replaced (1 1 1) completely after reconstruction.

Using first principle calculations, Che et al. that found faceting agents such as Pd and Pt induce significant anisotropy in the surface energy when ultra-thin layers of noble metals are grown on a Mo (1 1 1) substrate [11,22–24]. For these elements, to lower the

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surface formation energy is a substantial task. The surface-free-energy anisotropy of the noble metal covered surfaces is much larger than that of the clean surfaces. Therefore, the three {2 1 1} facets will increase in area to form a triangular pyramidal structure on (1 1 1) facets. On the other hand, both Madey and Dańko et al. used field emission microscopy (FEM) [25], low-energy electron diffraction (LEED) [16,26], X-ray photoelectron spectroscopy (XPS) [27] and scanning tunneling microscope [28] to observe and found that the adsorption of more than one physical layer of Pd will induce Mo (1 1 1) to rearrange to form three symmetric pyramidal structure by {2 1 1} facets after heating to 1100 K. Therefore, we believe it is possible to produce Mo ultra-sharp tips and further SATs.

In the present paper, we report the FIM (field ion microscopy) research on Mo SAT growth. The possible growth conditions including annealing temperature and various noble metals are discussed.

2. Experimental procedure

Experiments were carried out using FIM (background pressure of 2×10^{-8} Pa) equipped with a micro-channel plate (MCP) image intensifier. The images were obtained using helium (or neon) as image gas under the pressure of 2×10^{-3} Pa, and recorded with either a video or a digital camera. Tips were prepared from Mo 0.125 mm wires of 99.99% purity by means of direct-current electro-polishing in a KOH (aq.), and spot-welded on a 0.1 mm W loop with two 0.1 mm Pt potential leads. The sharply pointed tips, fabricated by the above-mentioned procedures, were subsequently shaped to an atomically smooth end-form by field evaporation in an ultra-high vacuum chamber. Mo tips covered with noble metal were prepared by evaporating deposition. Pd (Pt, Rh, Ir) was thermally deposited from a well-degassed Pd (Pt, Rh, Ir) wire coil. Finally, different results were observed and recorded after

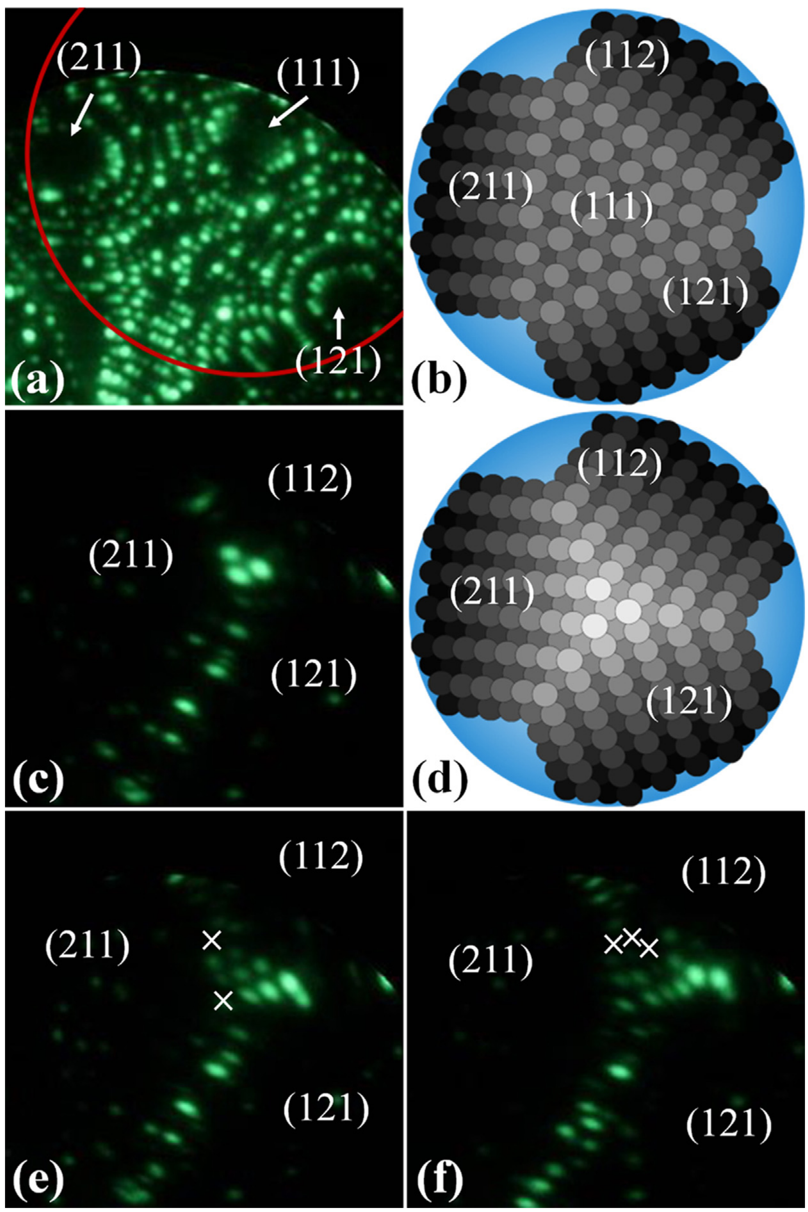

Fig. 1. FIM image showing the pyramid formed on pure Mo (1 1 1) after annealing at 1300 K for 10 min. (a) Mo clean surface obtained by field evaporation. (b) Atomistic model shows the (1 1 1) and three {2 1 1} facets structure of tip before heating. (c) The top layer ends with 3 atoms after annealing. (d) Top view model of the tip with 3-10-21 stacking sequence. (e) The second layer consists of 10 atoms. (f) The third layer consists of 21 atoms. Where it is possible that the pyramidal structure was destroyed by continuous field evaporation we use "×" to mark missing atoms.