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Study of two types of Ir or Rh covered single atom pyramidal W tips

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Abstract

The growth of a single-atom sharp pyramid tips on a tungsten substrate by depositing noble metals of the Pt family was investigated by field ion microscopy earlier. The Pd or Pt covered single-atom W pyramidal tips have been successfully prepared and established by our group. They are thermally and chemically stable and can easily be regenerated. In this study, we report the establishing and structural analysis of Rh and Ir covered single-atom W pyramidal tips. Two types of stable structures with bcc {211} facets are found for both metals. One is stacked by 1, 3, 10 atoms, and the other is stacked by 1, 6, 15 atoms for the top three layers and so on in series from the top to the deeper layers. The single atom tip is destroyed layer by layer after field evaporation to observe the structures of the different layers. However, the tip can be regenerated after it is annealed again and the two types of structures appear systematically depending on the annealing temperature. The regeneration process is investigated and the growth parameters of the two different types of Rh or Ir covered W tip are determined. The differences in the activation barrier and binding energy of these two types are calculated to be 0.08 eV and 0.064 eV for Rh covered single atom tips, and 0.03 eV and 0.14 eV for Ir covered single atom tips, respectively. Possible mechanisms and the relevance for application are discussed.

Keywords: Field ion microscopy; Single atom tip; Surface thermodynamics; Rhodium; Iridium; Tungsten

1. Introduction

Well-defined single-atom tips as field emission (FE) or focus ion beam (FIB) source are of great interest for producing coherent and bright electron and bright ion beams [1,2]. They can strongly improve the resolution in electron or ion microscopy and further reduce the size of nanostructures in micro-machining or lithography. Single-atom tips are also highly desirable for scanning tunneling microscopes (STM) [3], since they can achieve the optimum lateral resolution and also provide well-defined tips for measurements of the electronic structure of surfaces. Several groups [4–6] have proposed different approaches to create single-atom tips, and the most reliable and easiest methods have been reported by us recently [7–9]. The Pt family metal covered single-atom tips are thermodynamically and chemically stable, so the structure remains even after an extended period of field emission. Furthermore, they can not only be regenerated, but also be taken out of the ultra-high vacuum (UHV) chamber without change. The application of such single-atom tips becomes very attractive and practical.

The driving force of the formation of these tips are attributed to the increase of the surface energy anisotropy as the metal films are adsorbed on the W (111) surface, which has been confirmed by theoretical calculations by Chen [10] and reconstruction experiments by Madey et al. [11]. However, the faceting process of different metals may have differences in detail. The 1-3-10 atom stacking, which always appears in the top three layers of Pd covered single-atom tips, does not fit the stacking rule of the regular BCC structure as expected for W as the substrate. Naturally, this leads to the question, why the expected 1-6-15 atom stacking is not observed. Obtaining the same stacking

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after regeneration is a desirable property for further theoretical investigation and application purposes. Therefore, we must understand more about the stacking energy.

In this study, vacuum evaporation and electroplating are used to produce Rh and Ir covered single-crystal (or poly-crystal) W (1 1 1) tips. Simply by annealing the Rh or Ir-coated W (1 1 1) tip in a vacuum chamber, single-atom tips are initially prepared and regenerated. However, two kinds of atomically perfect stacking appear alternately. The atomic stacking is examined with field ion microscopy (FIM) [12], and the differences of activation barrier and binding energy of these two types are determined according to their temperature dependent occurrence in the regeneration process.

2. Experiment

A tungsten tip is prepared from a ⟨1 1 1⟩ orientated single-crystal wire of 0.35 mm in diameter or a poly-crystal wire of 0.1 mm in diameter by electrochemical etching [12]. To prepare a clean and defect-free surface for the electro-deposition, the tip is immersed into the base electrolyte (0.1 M HCl) and held at −0.6 V vs. SCE for 3 min to reduce the surface oxide layer [13], then a small drop (15 µl) of Ir or Rh plating electrolyte is introduced into the base electrolyte. Instantly, the cathodic current increases drastically to manifest that the electroplating is taking place on the tip apex. In case of UHV vapor deposition, the tungsten tip is sent into the UHV chamber (base pressure less than 10^{-9} torr) and heated at 1000 K for several minutes. For tip coating, well-degassed Ir and Rh wire coils (0.1 mm diameter) are used as evaporators.

All investigations are made with a home-built UHV-FIM chamber, which has already been described in detail elsewhere [12]. For the operation of the FIM, neon gas of 2×10^{-5} torr is admitted as the image gas. The tip is heated by a DC power supply. The tip temperature is determined by either resistance measurement of the tip-mounting loop with two potential leads or by an optical pyrometer.

3. Results and discussion

An FIM image of the pyramidal single-atom tip is shown in Fig. 1a. One can further study the atomic structures below the topmost atom using field evaporation [12]. One entire layer of atoms at the tip apex can be evaporated by applying a higher electric field. The next layer exposed is then imaged with the FIM. By this method, the second layer consisting of three atoms and the third layer consisting of 10 atoms are observed as shown in Fig. 1b and c. After this procedure, the tip apex is destroyed. However, the single-atom tip can be regenerated by simply annealing it to 1000 K for several minutes as demonstrated in a previous study [7]. This process can be repeated many times and we find that the regenerated tip is identical to the initial one in case of Pd-covered W (1 1 1) single-atom tips. However, for Rh-covered W (1 1 1) single-atom tips a second type of stacking is also frequently observed. For convenience, the original 1-3-10 atom stacking is called type 1 and the second stacking order is called type 2. Fig. 1d–f show the top three layers for the type 2 structure with layers of 1, 6, and 15 atoms, respectively. Type 2 corresponds to the regular BCC stacking with 1-6-15 atoms for the top three layers. Hard sphere models of these two types of pyramidal single-atom tips are illustrated in Fig. 1g and h. Similarly, Ir covered W (1 1 1) single-atom tips also give two kinds of structures alternately. Fig. 2a–c shows the atoms of top three layers for type 1 Ir covered W (1 1 1) single-atom tip, and Fig. 2d–f shows those for type 2.

Although there exists two types of structures for both Rh and Ir covered W (1 1 1) single-atom tips, the regenerating process leads to their structural differences. In Tables 1

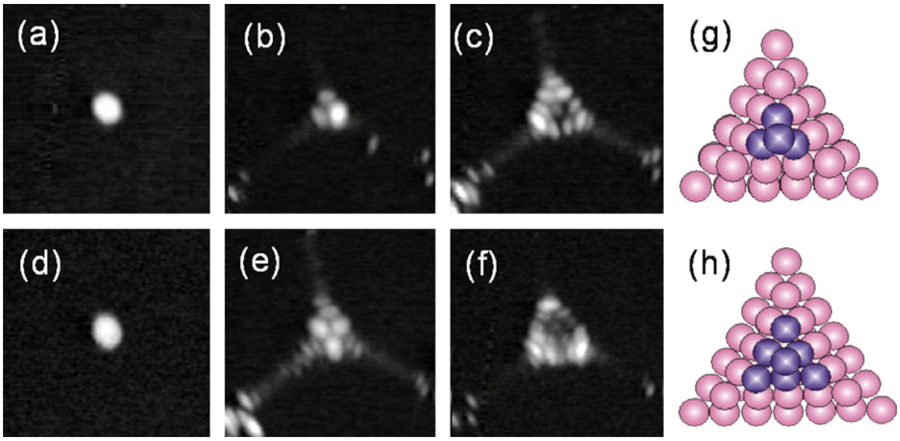

Fig. 1. FIM images and hard sphere models showing the type 1 and type 2 structures of Rh covered single-atom W pyramidal tips. (a)–(c) Type 1 structure: (a) the top layer consists of only one atom, (b) the second layer consists of three atoms and (c) the third layer consists of ten atoms. (d)–(f) Type 2 structure: (d) only one atom is found in the first layer as before, (e) however, now the second layer consists of six atoms, and (f) the third layer consists of fifteen atoms. (g) Top view of a hard-sphere model showing the atomic structures near the top of the type 1 single atom tip and (h) the atomic structures near the top of the type 2 single atom tip.