# 26 Mechanism and Method of Single Atom Pyramidal Tip Formation from a Pd Covered W Tip

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## 1. INTRODUCTION

Single atom tips have many applications in nano-sciences, because of their unique properties (Crewe *et al.*, 1970). They can be used as a point electron or ion source with coherent electrons and high spatial resolution. How to produce and regenerate single atom tips reliably and easily is important. Fink (1986) reported a method of creating a single atom W tip by using a thermal-induced tip-forming process to produce a three-atom island on the (111) facet of a W tip, followed by thermal deposition of a W atom on top of the island. This method requires very tedious procedures, great technical skills, and very high temperature. It is difficult to reproduce and impossible to regenerate, thus it is difficult to be routinely applied to where needed. We find single atom pyramidal tips with single atom sharp wedges of noble metal, Pd, can be routinely and repeatedly created on a W tip using a surface-science technique based on impurity and thermal induced faceting of a crystal face. Nieh *et al.* (1999) found and observed with STM that three-sided pyramids of a few nanometer size with either {112} or {011} facets can be formed on the W (111) surface by annealing the surface covered with a few monolayers of thermally deposited Pd. Fu *et al.* (2001) use the similar method to create a single atom pyramidal Pd tip on the (111) face of a W field emitter tip. The procedure is very simple and also the tip can be regenerated after the top atom is field evaporated. The mechanisms and the energetic of atomic processes involved in the formation of single atom tips and the thermal stability are also studied using field ion microscopy (FIM).

## 2. EXPERIMENT

All observations were made with a UHV FIM. Tsong (1990) has already described the instrumentation. The procedures used in this investigation are the same as those used in the past. The only special procedure used here is the annealing of the field emission tip to high temperatures. Heating can be done by two methods. An electronic controlled pulsed current power supply, which can heat up the tip-mounting loop in less than 0.5 s, is used to heat the tip up to 700 K. For higher temperatures, a DC power supply, which can operate either in constant voltage or current mode, is used. The temperature is determined by a resistance measurement of the tip mounting loop or by an optic pyrometer. Pd is deposited from a well-outgassed thermal evaporation source. The W tips are prepared by electrochemical polishing with saturated KOH (aq.) of a piece of thin W wire of 0.1 mm diameter.

## 3. RESULTS AND DISCUSSIONS

After careful degassing and low temperature field evaporation, about 1~2 monolayer of Pd is deposited on the clean W tip in the UHV chamber. Immediately after the tip is annealed to about 1000 K for 3 min, a single atom pyramidal tip can be observed at the (111) face as shown in Fig. 1(a). After field evaporation of the atom of the top layer, the second layer consists of three atoms is

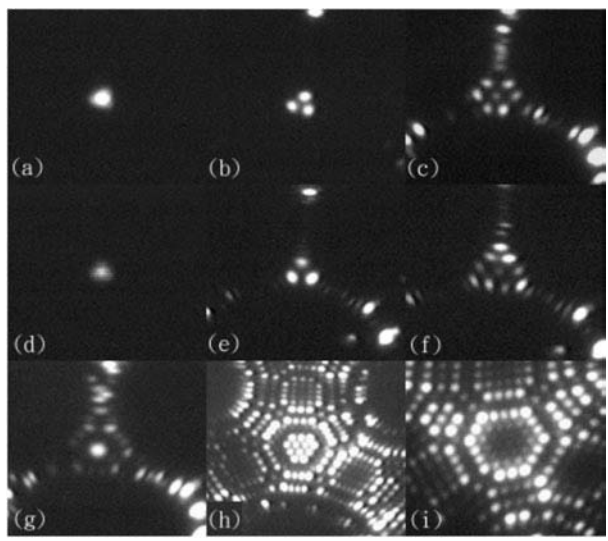


Fig. 1 FIM images illustrated the structures of the single atom tip: (a) only one atom on the first layer, (b) the second layer consists of three atoms, (c) the third layer consists of seven atoms, three corner atoms losing for ten atom layer, (d)-(f) a reformed single atom tip by 1000 K annealing 3 min, (g) only one atom left on the third layer during the field evaporation, the atom should be W atom, (h) we can observe the size of (211) facets increases after field evaporating many layers, compared to (i) clean W sample without extra treatment of forming single atom tip.

shown in Fig. 1(b). If the field evaporation is continued, the third layer is revealed. Fig. 1(c) shows this layer consists of seven atoms. Keep on field evaporating, we can desorb layer after layer and observe the structure of the next layer. Of course, the single atom tip is destroyed after these observations. Interestingly, the single atom tip can be regenerated after it is annealed again. Fig. 1(d) – (f) show the structures of the top three layers of the regenerated single atom tip. In this case, the third layer consists of ten atoms including three corner atoms. During the field evaporation, some special features are noticeable. There is always one atom left on the fourth layer as shown in Fig. 1(g). This atom is apparently harder to be field desorbed than other atoms of the third layer. It can be removed only when the field is high enough to desorb the fourth layer. This is why we cannot show the complete structure below the fourth layer. This higher desorption field indicates the last atom left on the third layer is a W atom rather than a Pd atom. The W atom appears in the third layer of the single atom tip is a clear evidence that only one Pd physical monolayer covers up the pyramidal tip, or only one Pd layer is needed to induce the faceting of the W (111) surface. Compare the W (111) after field evaporation of the single atom tip for several layers [Fig. 1(h)] with that before the deposition of the Pd cover layer [Fig. 1(i)], the {211} facets are noticeably broader. The phenomenon shows the single atom tip constitutes with a 4-atom Pd cluster sitting on the three-side pyramids with {211} facets.

The bcc (111) facet with higher surface free energy should be replaced by other atomically smoother, closed packed substrates, such as: (211) or (110) facets if the temperature is high enough to overcome the thermal activation energy for the atomic rearrangements. The Pd overlayer can decrease the facet formation energy for two reasons. One is larger surface free energy anisotropy of the adsorbate-covered crystal. The other is that it is kinetically favourable. Compare the activation energies of terrace diffusion; the Pd atoms encounter apparently much lower diffusion barrier than W atoms. In the other words, they approach to the stable state under lower temperature annealing. Besides, the (112) channel with the smallest barrier forms an easy path for the atoms to rearrange to pyramid. Other kinetic characters can be found in the potential energy diagram of one Pd atom diffusing near the W (111) step as shown in Fig. 2. The first, the trap energy at the step edge is rather small. The average activation energy for a Pd atom to ascend the step of the W (111) is derived to be $1.84 \pm 0.07$ eV. The average activation energy for a Pd ledge atom to dissociate from a step edge of the W (111) is derived to be $1.72 \pm 0.07$ eV. The extra-trapping barrier is only 0.6 eV; this value is close to the extra-reflective barrier. Thus Pd adatoms can easily jump up the step as well as dissociate from the step by overcoming the trapping energy. The thermal energy at ~600 K is big enough already to overcome these potential barriers. In the temperature range, the probability of descending the step is about the same as that of ascending the step. The behaviour is quite different from other previously studied systems by Fu *et al.* (1998). The second, a potential energy slope ~0.013 eV/4.47 A due to a free energy anisotropy exists. Pd atoms can

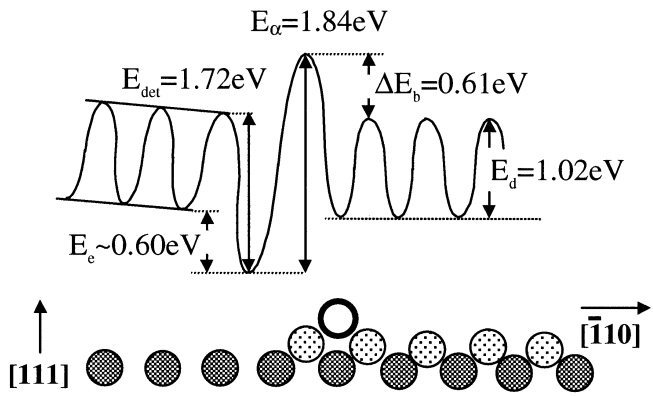


Fig. 2 Potential energy diagrams showing the measured potential barriers for different atomic processes of Pd adatom diffusing across W (111) surface step.

move toward the top surface layer with a greater probability because of the slope of the potential energy. In addition to the small step trap, the energy slope helps Pd atoms to diffuse in the direction of forming an atom-perfect pyramidal shape of the tip. In addition, this investigation thus also establishes the fact that single atom sharp crystal corners can exist at several hundred K. The exceptional thermal stability of the tip is believed to be due to the great binding strength of a 4-atom Pd cluster interacting with the underlying W (111) face.

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