

Method of creating a Pd-covered single-atom sharp W pyramidal tip: Mechanism and energetics of its formation

Tsu-Yi Fu,¹ Lung-Chieh Cheng,¹ C.-H. Nien,² and Tien T. Tsong²

¹*Department of Physics, National Taiwan Normal University, 116, Taipei, Taiwan, Republic of China*

²*Institute of Physics, Academia Sinica, 115 Taipei, Taiwan, Republic of China*

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Single-atom sharp pyramidal W tips, wrapped in a Pd overlayer, having atom-perfect wedges can be routinely and repeatedly created using a surface-science technique. This single-atom tip is thermally stable up to 1000 K because of the exceptionally large surface-energy anisotropy of the Pd covered W(111) surface. We conclude from atom-by-atom analysis that the W tip is covered with only one physical monolayer of Pd. We also investigate the mechanism and energetics of the atomic processes involved in its formation.

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Single-atom sharp tips are among the most important materials in nanoscience, because of their unique properties and potential wide range of applications.¹ First, they can be used as a point electron and ion source with spatial resolution in units of angstroms. Second, when used as an electron source, electrons emitted are coherent, thus 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. Third, in scanning-probe microscopy, the spatial resolution for both imaging and atomic manipulation, and the reproducibility of measurements depend on the sharpness and stability of the tip. Fourth, easy regeneration of single-atom tips can greatly facilitate their use in field-emission flat-panel displays. It is therefore of great importance that single-atom sharp tips of exceptional thermal and chemical stability can be reliably produced, and easily regenerated when they are damaged after long use.

Earlier, Fink² reported a method of creating a single atom W tip by first using a field- and thermal-induced tip-forming process to produce a three-atom island on the (111) facet of a clean W tip, followed by thermal deposition of a W atom on top of this island. Other similar methods have also been reported.² All these methods require tedious procedures, great technical skills, and very high temperature. Not only is there no clear evidence of single-atom sharpness in most of these tips, they are also thermally unstable and therefore impossible to regenerate, thus these methods are rarely used where single-atom sharp tips are needed. Here we report a simple method of creating atomically perfect, single-atom pyramidal tips based on impurity and thermal-induced faceting of a crystal face. We make an atom-by-atom analysis of the tip and study the mechanism and energetics of the atomic processes involved in its formation as well as the thermal stability.

It is well known in surface science that the adsorbate can induce faceting and other morphological changes of a crystal surface.³ Madey and co-workers found and observed with scanning-tunneling microscopy⁴ that three-sided pyramids of a few nanometers 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. The driving force of the pyramidal faceting is attributed to

the enhanced anisotropy of the surface free energy of the Pd-covered W surfaces. By taking into account the accompanied increase in the total surface area in this faceting process, along with the involved kinetic factor for the significant mass transport, they also explained why the resultant surface morphology is dominated by {112} facets instead of {011} ones (having a steeper shape of pyramids). We have succeeded in using this surface-science method to create a Pd-layer-covered single-atom sharp pyramidal W tip with atom-perfect wedges on the (111) face of a W field-emitter tip, and to confirm the facets to be the {112}. The procedure is very simple and the tip can also be easily regenerated after the top few layers are removed by field evaporation. We also clarify the structure by an atom-by-atom analysis of the tip, and the mechanism and energetics of the atomic processes involved in its formation. This investigation also establishes that single-atom sharp crystal corners and wedges can exist even at 1000 K.

All observations were made with a UHV FIM (field-ion microscope). The instrument has already been described in detail elsewhere.⁵ Annealing of the field emission tip to high temperature is done by two methods. An electronically controlled pulsed-current power supply, which can heat up the tip-mounting loop in less than 0.5 sec, is used to heat the tip up to 700 K. For higher temperatures, a DC power supply operated either in constant voltage or current mode, is used. Temperature is determined by a resistance measurement of the tip-mounting loop with two potential leads or by an optic pyrometer. Pd is thermally deposited from a well-degassed Pd wire coil (0.1 mm diameter).

The W tips are prepared by electrochemical polishing with saturated KOH (aq.) of a piece of thin W wire of 0.1 mm diameter. After careful degassing and low-temperature field evaporation, about 1–2 monolayers of Pd is deposited on the clean W tip. 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). Field evaporation of this atom reveals the second layer to consist of three atoms as seen in Fig. 1(b). If field evaporation is continued, the third layer consisting of seven atoms is seen as in Fig. 1(c). Keeping 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. Interestingly, the tip can be

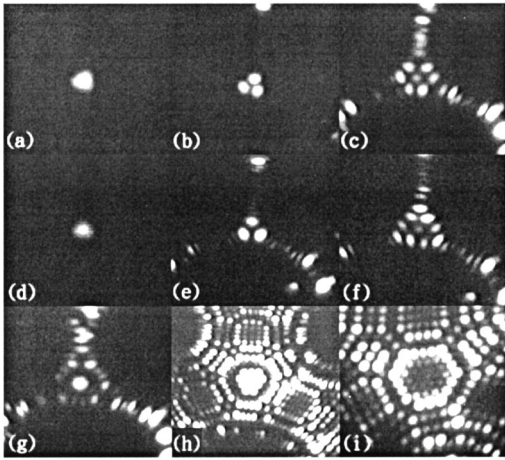


FIG. 1. FIM images showing the structure of a single-atom tip: (a) the top layer consists of only one atom; (b) the second layer consists of three atoms; (c) the third layer consists of seven atoms; (d) a regenerated single-atom tip by annealing to 1000 K for 3 min, again only one atom is in the first layer; (e) the second layer consists of three atoms; (f) the third layer now consists of ten atoms; (g) one field-evaporation-resistant atom is left on the third layer, which should be W atom; (h) we can observe the size of $\{211\}$ facets increase after field evaporating many layers for comparing with (i) a clean W tip without extra treatment of forming a single-atom tip.

regenerated after it is annealed again without a new Pd deposition. Figures 1(c)–1(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, now having additional three corner atoms, or the pyramid is now atom perfect without any missing corner atom. During the field evaporation, some special features are noticeable. There is always one atom left on the fourth layer when the third layer is field evaporated as shown in Fig. 1(g). This atom is much 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 field-evaporation-resistant atom is obviously a W atom rather than a Pd atom. A W atom appearing in the third layer of the single-atom tip is clear evidence that only one Pd physical layer covers up the W pyramidal tip, or only one Pd layer is needed to induce the faceting of the W(111) surface. This is the reason we can regenerate the single-atom tip without a new deposition of Pd since only a few Pd atoms need to be supplied from the surrounding surface to regenerate the single-atom pyramid again. Another interesting feature is that the $\{211\}$ facets surrounding the single-atom pyramid are much larger than those found in the field-evaporation end form of a W tip, as can be seen by comparing Figs. 1(c), 1(d), 1(g), and 1(h) with the regular image of a field-evaporated W tip [Fig. 1(i)]. Most interestingly, the wedges have the width of a single atom. Image spots of wedge atoms are elongated in the direction normal to the wedges due to an image distortion. Image magnification is larger in that direction because of the diverging electric-field lines. Thus the structure is an atom-perfect pyramidal tip of W covered with Pd atoms.

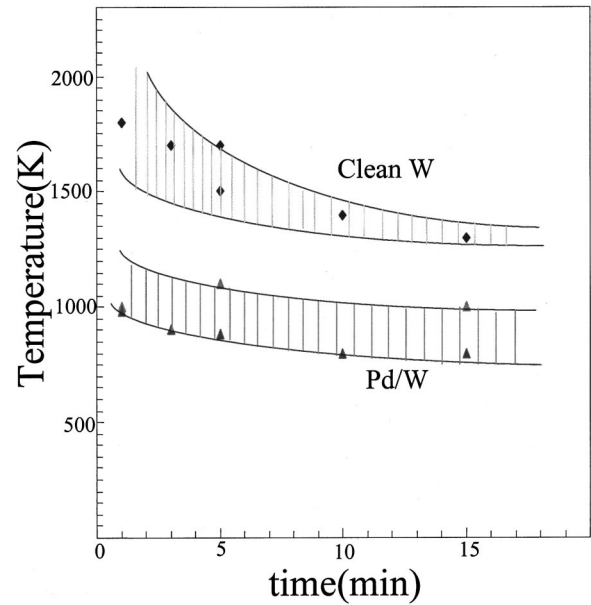


FIG. 2. Diagram showing the temperature and time needed in facet formation for clean W tips and Pd-covered W tips.

The bcc W(111) face is an atomically rough, morphologically unstable surface. Its surface free energy is higher than that of $\{211\}$ or $\{110\}$ faces. From the energetic point of view, the $\{111\}$ facet of a tip should be replaced by other atomically smoother, more closely packed facets, provided the temperature is high enough to overcome the thermal-activation energy of the atomic processes needed for this atomic rearrangement to occur. A pyramid of $\{112\}$ faces do form after heating a clean W tip to ~ 1500 K, although we do have a great difficulty in producing a single-atom tip. Figure 2 is a generalized phase diagram showing the temperature range of facet formation for clean W tips and Pd-covered W tips. We find that a Pd overlayer can reduce the faceting temperature by as much as 700 K, from 1500 K to 800 K. One reason is the larger surface-free-energy anisotropy of the adsorbate-covered crystal. The W(111) substrate becomes unstable when it is covered by one physical monolayer of

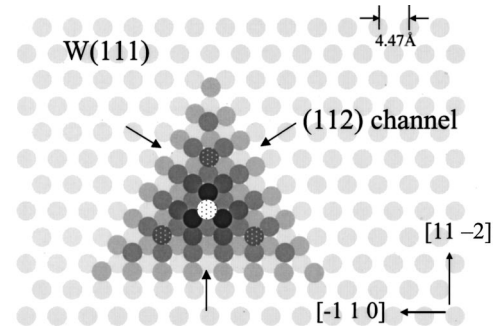


FIG. 3. Top view of a hard-sphere model showing the atomic structures near the top of the single-atom tip. The single atom sits on a pyramid with three $\{211\}$ facets. Atoms can move to upper layers along the $\{112\}$ surface channel as the arrows indicate. The gray spheres with white dots are corner atoms that are missing sometimes as in Fig. 1(c).

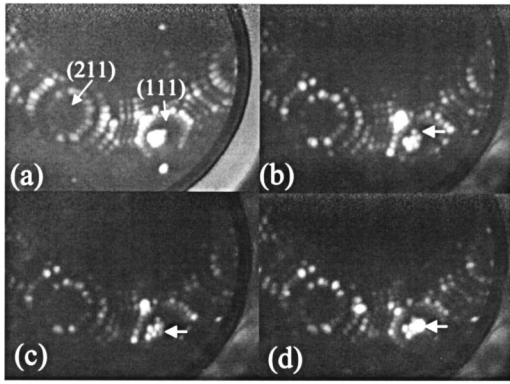


FIG. 4. FIM images showing Pd-atom movement toward the W(111) surface. (a) The top W(111) layer consists of five atoms; (b) one Pd atom, indicated by the arrow, moves to the top layer after heating to 530 K for 10 sec; (c) another Pd atom appears at the top layer; (d) one Pd atom ascends the step of the top layer.

Pd,⁴ and faceting transformation from the (111) to (112) faces is thermodynamically favorable. Theoretical studies⁶ from both embedded-atom and first-principles calculations find that the bcc (211) surface covered by a certain metal film has lower surface free energy than the film-covered bcc (111) surface. In fact impurity-induced faceting has been phenomenon of great interest for many years. The thermodynamic driving force is attributed to the surface-energy anisotropy.⁷ In Pd covered W(111), the energetic advantage is so large that it can compensate for the accompanied increase in total surface area of the forming {112} face pyramid. The other reason is that it is kinetically favorable. Characteristic behavior is found when one of the kinetic processes becomes rate limiting.⁸ The activation energies of terrace diffusion for W (Ref. 9) on W(110), W(211), W(111), and Pd (Ref. 9) on W(110), W(211), W(111) are 0.86 ± 0.09 , 0.76 ± 0.07 , 1.78 eV, and 0.51 , 0.34 ± 0.01 , 1.02 ± 0.06 eV, respectively. Pd atoms with the much lower diffusion barriers are much more mobile than W atoms. In other words, they can approach the stable state at a much lower temperature. These smaller barriers turn out to be a critical factor for forming pyramidal facets and the single-atom tip for two reasons. First, Pd atoms can desorb already at ~ 1100 K.¹¹ Second, the surface-energy anisotropy, which is the thermodynamic driving force, generally decreases with increasing temperature.¹² From the diffusion data, we also notice that Pd atoms diffuse along the (112) surface channel with the smallest barrier.

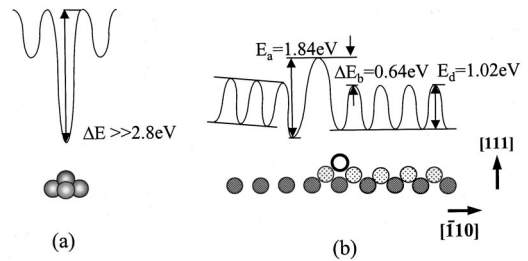


FIG. 5. Potential-energy diagrams showing measured potential barriers for different atomic processes. (a) Structure of the top two layers of Pd/W(111) single-atom tip and the potential-well depth for the top atom. (b) Pd-atom diffusion near the Pd/W(111) step.

One can easily see from the structure model shown in Fig. 3 that Pd atoms can easily move to the upper (111) layers along the (112) surface channels to form a single-atom tip. But, even before the (112) channels are formed, Pd atoms can move toward the W(111) facet and can step up the (111) layers already.¹³ FIM images shown in Fig. 4 provide experimental evidence of the step-up motion. The measured extra reflective barrier for Pd diffusion on the W(110), W(211), W(111) are 0.28 ± 0.03 , 0.30 ± 0.03 , 0.64 ± 0.03 eV, respectively.¹⁰ Although the reflective barriers are quite high, they are not rate limiting above 500 K. Thus Pd atoms can move across different faces toward the (111) face from any part of the W-tip surface. Another kinetic factor of the mass transport favoring a {112} pyramid more than a steeper {011} one is that the latter involves rearrangements of many more atoms from the original surface morphology than the former.

An important question is the stability of the single-atom tip. We find that the top atom routinely appears after annealing at 1000 K for 3 min and will not disappear by further annealing. The trap barrier for the top Pd atom on Pd trimer is therefore much greater than 2.8 eV.¹⁴ This trapping barrier is much larger than either the diffusion barrier or the extrareflective barrier of Pd on the W(111), as shown in Fig. 5. The deep trap is due to the formation of an exceptionally stable four-atom Pd cluster at the pyramid tip driven by the large surface-energy anisotropy of the Pd-covered W surfaces. The formation of a single-atom tip is promoted by a directional walk of Pd adatoms toward the apex position as in a directional-walk experiment.¹⁵ We estimate with a measurement the potential-energy difference toward and away from the tip to be 0.013 eV. This tilt in the surface potential toward the upper (111) layer arises also from the surface-free-energy anisotropy.

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