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Robustness of tungsten single atom tips to thermal treatment and air exposure

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ABSTRACT

Experiments aimed at assessing the robustness of nitrogen-etched, single-atom tips (SATs) prepared using W(1 1 1) single crystal wire were performed. Our experiments showed that single-atoms tips sustain minimal damage when exposed to atmospheric conditions and can be readily and quickly nitrogen-etched to single-atom tips thereafter. The SATs can be annealed at temperatures up to 1100 °C with minimal shape changes. Moreover, annealing temperatures in excess of 1200 °C resulted in an apex faceting which may prove important in further single-atom tip creation. Procedures for warming of the SATs from operating temperatures of 80 K were also evaluated to determine conditions that limit tip contamination. These results show that SATS could be fabricated in a dedicated vacuum system and subsequently transferred to other instruments where they would undergo a brief conditioning procedure to recover the single-atom apex configuration prior to being subjected to operating conditions.

1. Introduction

Research on gas field ion sources (GFISs) evolved from the invention of the field ion microscope and such emitters have attracted scientific interest because of their potential technical applications in electron and ion microscopy, and nanofabrication [1]. The recently-developed helium ion microscope offers advantages over the scanning electron microscope such as high resolution (sub-nanometer), elemental contrast, long depth of focus, and excellent sensitivity to the sample surface thanks to the smaller interaction volume of helium ions with the substrate [2,3]. Moreover, nanomachining capabilities using neon ion beams have also been demonstrated [4].

The imaging and nanomachining performance depends crucially on the reliability of the ion-emitter tip, i.e. the GFIS it employs, as does its ease of operation. A variety of processes have been developed for creating tips terminating in an atomically sharp apex. Studies aimed at investigating the ion emission properties of GFIS candidates such as supertips, fine protrusions located on the apices of rounded field emitters, date back to the late 1980s [5–7]. More recently gas-assisted etching and field evaporation process using etchant gases such as nitrogen [8–11], oxygen [12–14] and water [15] have proved successful in producing nanotips. In addition to these, other methods for creating atomically sharp tips are predicated due to the fact that adsorbates can induce faceting of crystal surfaces [16,17]. Nanotips were also prepared by the deposition of noble metals (Pd, Au, Pt, Rh, and Ir) on W(1 1 1) tips followed by subsequent annealing [18–28]. Such tips exhibit stable three-sided pyramidal apices and may terminated with a single atom or a trimer. The atomic structures as well as their electron/ion emission properties have been investigated.

Although there is a growing number of methods to prepare atomically defined nanotips as GFISs, there have been few reports of the robustness of tungsten SATs to exposure to environmental conditions. TEM studies have shown that the general shape of gas etched nanotips is maintained after transfer between instruments, but the exact atomic structure was not investigated after air exposure [14,15]. Air exposure experiments of rhodium coated tungsten tips have been evaluated using field emission studies [28]. There, air exposure caused significant change to the field emission current and patterns. However, annealing experiments were able to recreate a tip with similar performance prior to air exposure indicating a recovery strategy for Rh coated tips. The effects of air exposure will be important if one plans to create a SAT in a dedicated vacuum system and then transport the tip to an installation where only a brief conditioning procedure aimed at restoring the nanotip apex would be required. This method may also be beneficial for nitrogen etched tips by limiting the exposure of the ion gun to etchant gases.

The present paper investigates the robustness of single-atom W(1 1 1) tips obtained by nitrogen-assisted etching process in a field ion microscope. The robustness of the SATs were evaluated under various conditions such as warming and cooling cycles with

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Table 1
List of tested protocols to ramp-down HV and warming up to RT in order to remove prepared nanotips from the UHV system.

Experiment	Voltage	Tip temperature	Result
I	SAT BIV	Warming to RT	Excessive field evaporation occurred
II	85% BIV	Warming to RT	Minimal contamination/nanotip remained sharp
III	50% BIV	Warming to RT	Heavy contamination/high tip voltage required to recover recognizable FIM pattern
	50% BIV	Cold/LN_2	Minimal contamination/nanotip remained sharp
IV	HV off	Warming to RT	Minimal contamination/nanotip remained sharp

and without high voltage applied, annealing temperatures and exposure to air. Methods were developed to perform minor repairs to the SATs when required.

2. Experiments and discussion

The tungsten tips used in our experiments were obtained from single-crystal W(1 1 1) wires using the electrochemical etch procedure in 2 M NaOH solution. After having been inspected under the optical microscope to ensure they were not visibly blunt, the tips were mounted inside the ultrahigh vacuum (UHV) field ion microscope operating at base pressure $<7 \times 10^{-11}$ Torr. Tips were degased at temperatures of approximately 800 °C for several minutes. FIM images were amplified by a Hamamatsu multichannel plate (MCP) and recorded by a high-sensitivity 12-bit camera. The entire fabrication process was controlled and monitored by a PC computer to ensure reliability and reproducibility. FIM imaging was performed at liquid nitrogen temperature by passing cold nitrogen gas through the cryostat. Warming of tips was performed with room temperature gas.

In order to assess the robustness of single-atom tips a series of experiments were performed to evaluate SATs performance with respect to ambient exposure as well as annealing temperatures. Testing required to complete several steps: (i) tip warm-up and voltage ramp down after initial SAT fabrication, (ii) degassing and SAT recovery, and (iii) SAT robustness with respect to annealing temperature which could be either performed during degasing phase or subsequently after SAT recovery. In the following three sections we will examine each step to find an optimal solution for maintaining sharp nanotips after ambient exposure.

2.1. Voltage ramp-down and warm-up procedure

The single-atom tips were prepared in the field ion microscope at nominally liquid nitrogen temperature (approximately 80 K) using the nitrogen etching procedure [8–10]. The first step was to remove high voltage which was applied during the tip etching process as well as to warm the SAT to room temperature (RT). The imaging gas was also removed from the vacuum system to avoid possible contamination due to residual impurities in He imaging gas. After warming to RT overnight, the tip was then cooled down, without any high temperature annealing step, in order to assess any contamination and/or damage from this process. Several scenarios were explored to select an optimal protocol to minimize SAT evaporation or contamination due to condensation on a cold tip or field assisted adsorption and/or diffusion. The tested processes are summarized in Table 1. In all cases of tip warming to room temperature, the experiments were allowed to occur overnight to assure a warm tip and to allow the vacuum to recover from any cryo-pumped gases.

In experiment I (see Table 1), the best imaging voltage for the SAT was maintained during the tip warm up to prevent contamination. However, significant field evaporation occurred effectively destroying the SAT since the field required to remove atoms at RT is lower compare to LN_2 temperature [29–31]. Although the SAT was recovered using the gas-assisted etching after the tip was cooled down, this process was far from ideal (figures not shown).

Experiment II resulted in minimal tip apex modification during warm up. After initial warm up under conditions described in Table 1, the atomic arrangement was found to be nearly identical after subsequent tip cool down and applying tip voltage to image using FIM. Results of the experiment II are demonstrated in Fig. 1. The original tip (Fig. 1a) was terminated with a trimer (tip voltage was 5.8 kV) was allowed to warm up overnight while tip voltage was reduced to 5.0 kV. 5.0 kV was chosen as the warming voltage as zero or minimal field evaporation would be expected [29]. After subsequent cool down to liquid nitrogen temperature the next day the tip voltage was restored to the best image value of 5.8 kV (Fig. 1b). Only two additional adsorbates were observed, which suggests that the electric field at the apex is high enough to protect the apex from contamination but low enough to avoid evaporation.

In order to further evaluate the effect of the voltage application the experiment was repeated, but at a further reduced voltage. In experiment III, during the warm up procedure, the tip voltage was lowered to 50% of the BIV. After cooling to liquid nitrogen temperatures, FIM imaging was again attempted. In this case, while the SAT had originally imaged at 8.9 kV, it was not until the voltage reached 15.8 kV (177% of the SAT) that one could observe the central hexagonal atomic arrangement typical of W(1 1 1)-oriented nanotip (Fig. 2a). Around this arrangement only randomly scattered bright spots (adsorbates) against a black background could be seen; the underlying lattice structure was not visible at all, suggesting substantial apex contamination.

The experiment was then repeated with the tip being maintained at liquid nitrogen temperature overnight while at a voltage of 50% of the BIV (experiment IIIB), in order to evaluate the effect of raising and lowering the temperature. Upon ramping up the voltage after the overnight vacuum exposure in order to evaluate whether or not the SAT (imaging at 6.5 kV) had undergone any considerable changes, a recognizable crystal pattern (the hexamer) was observed at 7.3 kV, at only 112% of the SAT BIV. We continued evaporation to 170% of the original BIV and were able to observe a larger recognizable pattern, although still with tip perimeter contamination.

The required increase in operating voltage to image the tips in Fig. 2 are likely due to contamination of the tip. However, the required voltage increase for the RT tip compared to the LN_2 tip suggests that more adsorbates covered the tip at room temperature. This indicates that the majority of contaminants did not arrive from the gas phase as under these conditions. It would be expected that the cold tip would have more contaminants due to higher sticking coefficient. It was therefore concluded that adsorbates migrated from the shank of the tip (similar to the process of imaging gases) to contaminate the apex. Cold tips would limit migration towards the apex, while at room temperature the thermal vibrational energy permitted adsorbates to overcome the barriers in the potential landscape of the tungsten substrate to diffuse towards the tip apex and/or undergo a thermally-driven reaction with tungsten surface atoms. It may also be that most of the contamination took place during the act of warming the tip as condensed contaminants become mobile during the warming period prior to their desorption. Several hours were required to bring the tip to room temperature.

Experiment IV involved warming of the tip in the absence of any applied voltage. Fig. 3A shows the SAT at 9.2 kV just prior to the