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Iridium single atom tips fabricated by field assisted reactive gas etching

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Abstract

We present a simple, reliable method to fabricate Ir single atom tips (SATs) from polycrystalline wire. An electrochemical etch in $CaCl_2$ solution is followed by a field assisted reactive gas etch in vacuum at room temperature using oxygen as an etching gas and neon as an imaging gas. Once formed, SATs are cooled to liquid nitrogen temperatures and their underlying structure is examined through evaporation of the apex atoms. Furthermore, a method is developed to repair Ir SATs at liquid nitrogen temperatures when apex atoms evaporate. This method may be used to fabricate Ir SAT ion sources.

1. Introduction

Atomically defined tips have attracted much study because of their potential applications in scanning ion microscopy (SIM) and focussed ion beam (FIB) systems. Of particular interest are single atom tips (SAT) whose ion beams originate from a single atom at the apex of the tip. Single atom tips have been prepared using multiple methods of fabrication, but most recently, the field controlled chemical etch method and the thermal build up method have gained popularity.[1-12] The field controlled chemical etch method has so far only been used to etch tungsten metal tip precursors, although the mechanism should be universal for most materials given an appropriate imaging and etching gases. Tungsten tips have been favoured in helium ion beam generation because of the high field evaporation point of tungsten, allowing for larger fields and greater current generation while maintaining a stable last atom.

However, tungsten may have some limitations in generating ion beams of other gases, such as oxygen, because of its corrosive nature. Oxygen ion beams would be very beneficial for SIMS measurements because of its high sputter and secondary ionization rate. For use in corrosive gas environments, noble metal tips such as iridium have been proposed. Iridium SATs have been prepared on facetted tungsten (111) and with the use of oriented iridium (210) single crystal wire and have been shown to produce helium, hydrogen, nitrogen and oxygen beams at various temperatures.[10, 11] However, SATs for iridium have not been shown to operate above 20K for high field ionization gases.

In this manuscript, the field assisted reactive gas etching procedure is utilized to prepare iridium SATs from polycrystalline iridium wire. The SATs were prepared at room temperature. We also examined the underlying structure of (100) Ir SATs fabricated in this manner and outline a method to repair these SATs at liquid nitrogen temperatures.

2. Material and Methods

Polycrystalline Ir tips were electrochemically etched in a two-step process using a $CaCl_2$ solution.[1, 13] The first consisted of dipping the tip in a solution of $CaCl_2$ and applying 35 – 10Vrms until drop-off occurred. The second was a micro-polish of the first few micrometers of the apex performed in a bubble of solution suspended in a loop of tungsten wire. The etching was observed beneath a microscope and the applied voltage was 1Vrms for this stage. The sharpness of the wires were evaluated in a field emission test system, after degassing of the tip to ~800 °C, by measuring the field emission current to a plate approximately 2mm from the tip apex. Tips were considered sharp when a field emission current of ~10nA was measured with an applied voltage between -200 and -600V. Tips were then transferred to the field ion microscope (FIM).

The FIM system had a base pressure of $<1e^{-10}$Torr. The cooling system consists of a flow through cryostat using liquid nitrogen cooled nitrogen gas; a gas mixing system with warm nitrogen gas allowed for control of tip temperature. The tip was placed 2 cm from a Hamamatsu microchannel plate (MCP) coupled with a phosphor screen to amplify tip signals. The images were captured with a high sensitivity 12-bit camera.

Prior to FIM, the tip was degassed at ~900C for a few minutes. For FIM imaging, He or Ne gases were introduced at the uncorrected partial pressure of $1e^{-5}$Torr. The voltage of the tip is then increased until a clear apex crystal structure was visible.

Initial attempts at etching followed a similar procedure to that proposed in the literature.[5, 6, 14] However, it was quickly determined that the use of helium as the imaging gas prohibited fine control over the etching of the iridium because the evaporation field of iridium (5V/ Å) is close to the best imaging field (BIF) of the imaging gas helium (4.4 V/ Å). This created some limits in the ability to controllably etch and observe simultaneously. Switching to neon (3.5 V/ Å BIF) as the imaging gas alleviated the problem. A second issue that arose was the effect of temperature on the iridium etching. Etching at low temperature (77K) did occur to some degree, but the corrosion process was slow and provided for more adsorption of the etchant gas with less control over the etching or no etching at all. In order to achieve a degree of control and an acceptable etching rate (tip preparation in approximately 1 hour) etching was performed at room temperature with oxygen as the etchant gas and neon as the imaging gas.

3. Results and Discussion

In order to etch the tip at room temperature, the apex was first field evaporated until a large region of crystal was visible, utilizing an appropriate pressure of neon gas. This usually required an applied voltage between 5-10kV and provided clean ordered tips with radii approximately 7 to 10nm. O_2 was then introduced at $5x10^{-6}$ to $1x10^{-8}$ Torr (lowered as etching progresses). The etching proceeded in the usual manner as describe previously.[6, 14] A general description is as follows. The high electric field at the apex ionizes oxygen molecules before they can reach the surface atoms. This protects those apex atoms from reaction and etching. Because of the shape of the tip, the electric field is lower at the perimeter and shank of the tip where oxygen can penetrate the field. Once oxygen molecules reach the surface they can react with the tungsten surface atoms, create protrusions which are more volatile and are then field evaporated from the tip surface. The removal of shank atoms leads to a sharpening of the tip. The tip voltage is initially kept constant until evaporation of shank atoms becomes evident. As the tip sharpens, the etching regions migrate to the apex[3]. The sharpening of the tip increases the electric field at the apex. In order to avoid field evaporation of apex atoms, the voltage is as the etching process continued. Once only a few atoms are left at the apex, the oxygen pressure is lowered in order to slow the etching process during the last steps in the SAT formation. Once the SAT was formed, the oxygen gas is removed from the vacuum chamber.

A specific example is shown in figure 1. Figure 1a shows a neon image of an iridium tip at room temperature. The tip was imaged at 4.6kV and has a radius of curvature of ~7.5nm. This is the tip prior to introduction of oxygen. Oxygen was then introduced ($5x10^{-6}$ Torr) allowing the tip to etch. Figure 1b shows the tip after some etching. During etching the voltage is lowered in steps of 200V in order to maintain the best imaging voltage at the apex atoms. Because the tip is sharpening, the voltage must be lowered in order to keep a consistent electric field. The image in figure 1b was acquired at 3.6kV. It is evident that the observable iridium atoms have been reduced because of etching of the perimeter atoms. The fuzzy imaging ring observed is due to the oxygen gas in the chamber becoming ionized close to the tip surface. No fuzziness is observed over the apex atoms, indicating that they are substantially protected from oxygen attack because of the high field at the apex. Figure 1c and 1d show snapshots after further etching. The observation of the apex atoms is shrinking. Figure 1e shows a very small apex and was acquired at 2.8kV. The pressure of oxygen was then reduced to $1x10^{-8}$ Torr, and the observation of oxygen gas ionization has almost disappeared in figure 1f, where only three apex atoms are observed. A single atom is removed resulting in figure 1g, and the removal of another atom, leaves the SAT in figure 1h.

All Ir SATs were prepared at room temperature and could subsequently be cooled to a different operating temperature. In most cases, the tips were cooled to liquid nitrogen temperatures. In some instances adsorbed gases were observed during the cooling of the tip. These could be removed by applying voltage pulses with a magnitude of 500 – 1000V above the imaging voltage for a time duration of 500us. An image of an SAT after cooling to 77K is shown in figure 2a, with the observation of some

weak satellites. In some cases, asymmetry of spots were observed and is likely due to gas adsorption near the apex atoms.[15]

To examine the tip structure, the apex atom was evaporated with voltage pulses of magnitude 1 to 2kV and a duration of 500us. The evaporation of the apex atom revealed the underlying structure shown in figure 2b. Although not a perfect structure, the remaining apex atoms are derived from an arrangement of Ir atoms from the original Ir (100) oriented tip.

A total of six Ir SATs were successfully etched using this method, ranging in operating voltages from 2.6kV to 5kV. The range in voltage is related to the global structure of the tip.[5] . It is evident that tips can generate neon ion beams at room temperature and this represents the first room temperature Ir SAT images.

Although it was difficult to control the etching of large tips at LN2 temperatures, small apex rebuilds could be achieved. In order to perform SAT repairs at LN2 temperatures, oxygen was reintroduced to a pressure of $1x10^{-8}$ Torr and voltage pulses of 1 - 2kV with durations of 500us were applied. This allowed for removal of satellite atoms. Careful application of the voltage magnitude and duration is required.

A total of three SATs were successfully repaired at liquid nitrogen temperatures using the above method. Figure 3 shows the progress of a tip repair, beginning with the underlying structure of a failed SAT (a) at 5.5kV, and ending with the repaired SAT (b) at 4.5kV. Some disorder in the image of the failed SAT (Fig. 3a) is caused by oxygen adsorption.

4. Conclusions

Iridium SATs have previously been prepared using a faceting method on single crystal W(111) tips. Iridium has been targeted as a desirable material for creating ion beams of gases thought to be corrosive to tungsten, such as nitrogen, oxygen and hydrogen (to some degree) and Ir/W(111) and Ir(210) tips have been shown to produce ions beams for all helium, hydrogen, oxygen and nitrogen.[10, 11]

This is the first time an iridium SAT has been prepared by the field assisted chemical etching method as only tungsten SATs had been prepared previously and the first report of a room temperature operating SAT formed from iridium. The iridium SATs were stable at room temperature while generating ion beams from high field ionization gases, such as neon. We also showed that oxygen is certainly corrosive to iridium under high field conditions required for neon imaging at room temperature. It was also demonstrated that oxygen can also be corrosive at LN_2 temperature, although corrosion at that temperature was slower. Hydrogen gas has also been known to promote field evaporation of iridium atoms under high field conditions, which also indicates corrosive behaviour.[16] The ability to generate stable oxygen and other gas ion beams from iridium is likely due to the lower required electric field for oxygen (1.5 V/Å) and other gases compared to that of helium and neon,

minimizing the corrosion process of field assisted etching. This observation may also be evident for other tip materials, where the imaging gas field is sufficiently low that etching induced evaporation is limited.

In summary, we present a simple, reliable method to prepare Ir SATs using a field assisted reactive gas etching technique at room temperature. The method allows for constant monitoring of the apex structure during fabrication. We show that the SAT is stable at both room temperature and at liquid nitrogen temperatures (cooled after fabrication). We find that our SATs can be repaired at liquid nitrogen temperatures quickly and easily; this greatly improves the practicality of the tip as an ion source.

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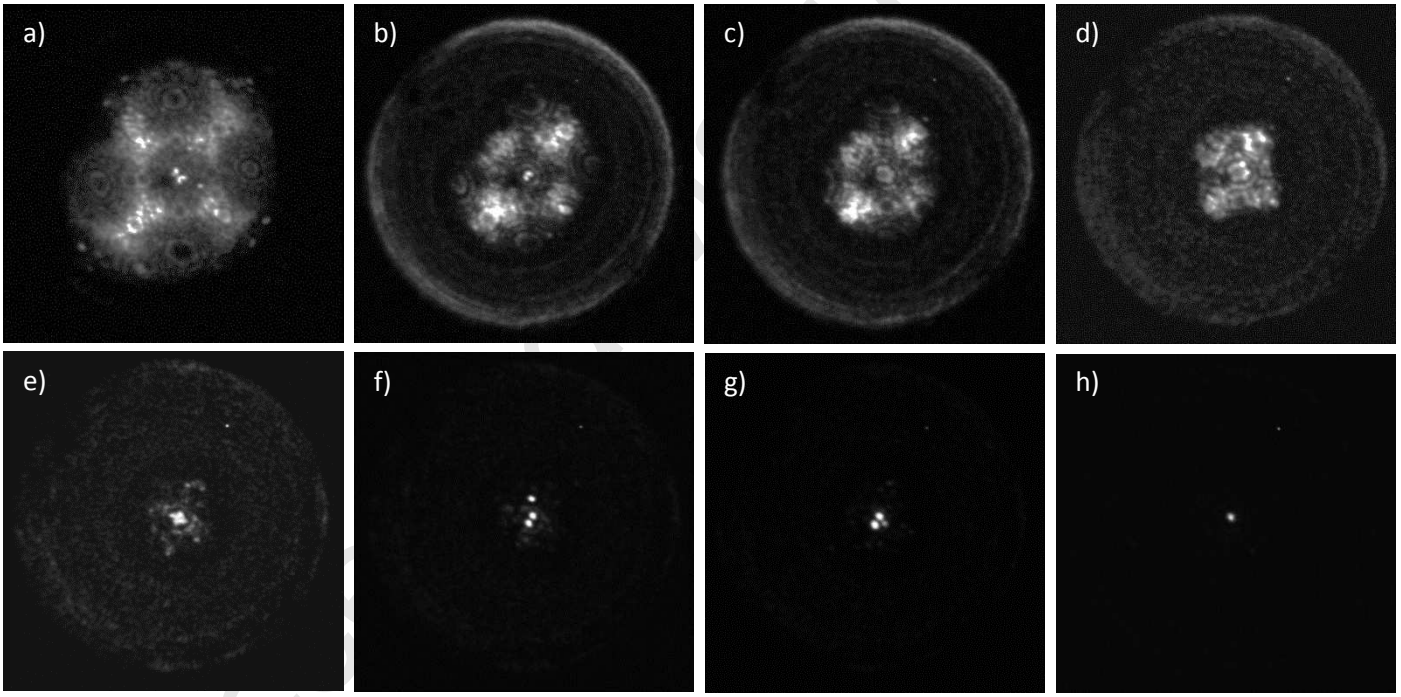


Figure: All images were collected at room temperature using neon as the imaging gas and oxygen as the etching gas. a) Iridium nanotip prior to etching, 4.6kV, R = 7.5nm. b) after etching, the Iridium tip has been sharpened, 3.6kV. Oxygen gas ionization can be observed at the perimeter of the image while the apex is protected against oxygen attack. c, d, e) The apex compresses as the etcing of the shank continues. Imaging voltages are 3.4, 3.0 and 2.8kV respectively. f, g, and h) the oxygen pressure is reduced and the observed oxygen ionization is reduced. f) three atoms remain at the apex. 2.7kV. g) two atoms, 2.7kV. h) Iridium SAT imaged at 2.5kV.

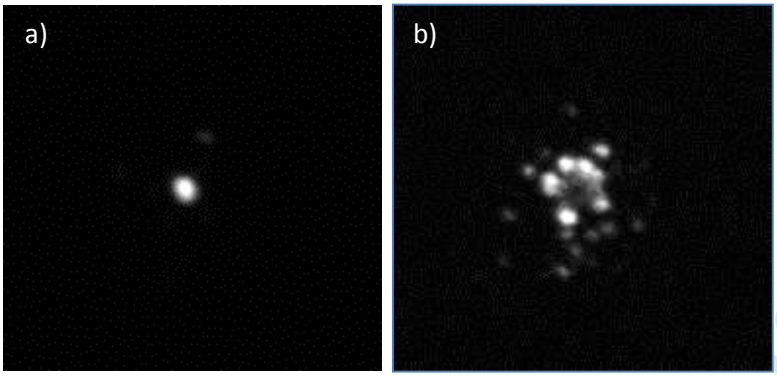


Figure 2: a) SAT after cooling from room temperature to 77K. b) Underlying structure after evaporation of the SAT apex atom. Structure is derived from the original Ir (100) tip.

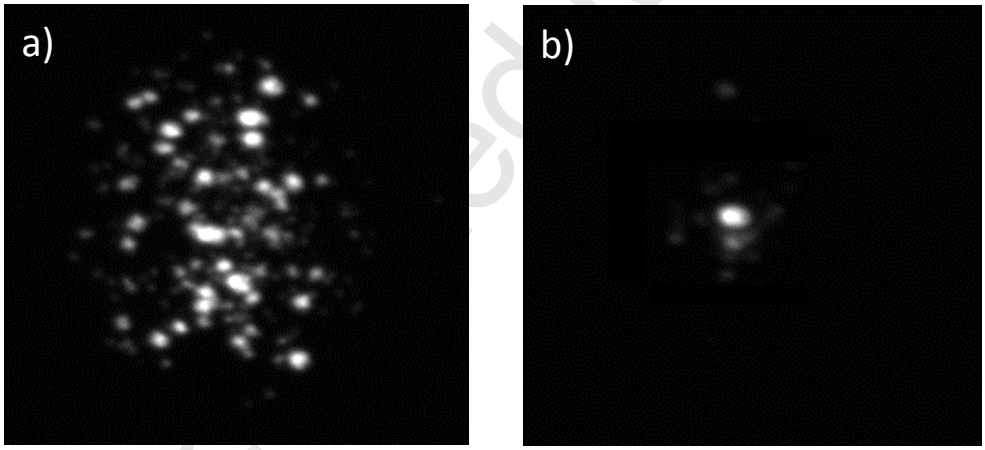
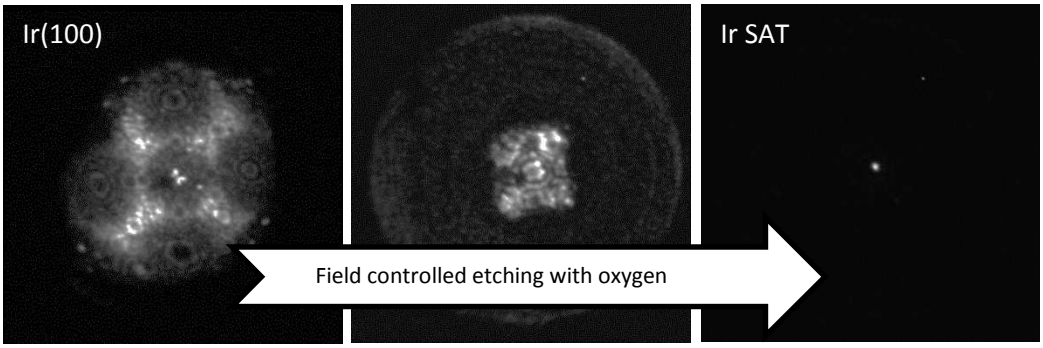


Figure 4: Ir (100) nanotip nepair. a) nanotip at liquid nitrogen temperature temperature before SAT repair, V = 4.8kV. b) SAT after repair at liquid nitrogen temperature, V = 4.5kV.



Iridium single atom tips by field assisted reactive gas etching

John A. Wood, Radovan Urban, Mark Salomons, Martin Cloutier, Robert A. Wolkow, Jason L. Pitters

- Iridium single atom tips (SATs) were prepared
- SATs were be regenerated by field assisted chemical etching using oxygen as an etchant gas
- Oxygen is corrosive to Iridium at room temperature under high field conditions
- Oxygen corrosion rate of Iridium at reduced temperature is slowed
- SATs are stable at room temperature for high field ionization gases such as neon