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A single-atom sharp iridium tip as an emitter of gas field ion sources

Hong-Shi Kuo[1], Ing-Shouh Hwang[1,3], Tsu-Yi Fu[2], Ying-Siang Hwang[2], Yi-Hsien Lu[1], Chun-Yueh Lin[1], Jin-Long Hou[1] and Tien T Tsong[1]

[1] Institute of Physics, Academia Sinica, Nankang, Taipei, Taiwan, Republic of China
[2] Department of Physics, National Taiwan Normal University, Taipei, Taiwan, Republic of China

E-mail: ishwang@phys.sinica.edu.tw

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Abstract

We report a reliable method for preparing a pure Ir single-atom tip by thermal treatment in oxygen. The atomic structure of the tip apex and its ion emission characteristics are investigated with field ion microscopy. We have shown that the Ir single-atom tip can be a good field ion emitter, capable of emitting a variety of gas ion beams, such as He^+, H_2^+, N_2^+, and O_2^+, with high brightness and stability. In addition, this tip can easily be maintained and regenerated in vacuum, ensuring it has sufficient lifetime for practical applications.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Ion beams have been widely used in a large number of scientific and technological applications, such as surface and thin film analysis, imaging, ion implantation, sputtering, etc. In principle, focused ion beams (FIBs) can extend the above applications to a much higher spatial resolution [1]. This would provide powerful tools to image and analyze materials as well as to fabricate novel structures and devices with desired functions. Current FIB systems mainly use a liquid metal ion source (LMIS), in which a liquid metal is supplied and field evaporated from a cusp above the liquid Taylor cone formed on a tungsten base tip. Among all LMISs, Ga^+ has been adopted in most commercial FIB systems because of its good ion beam stability and simplicity of operation. Typical Ga-FIB systems can achieve a resolution of ∼20 nm with a brightness of $\sim 10^9$ A m^{-2} sr^{-1}. The resolution and the brightness are mainly limited by the relatively large virtual source size (50 nm), the large opening angle, and the wide energy spread of the ion beams (ΔE: 5–50 eV).

Even though Ga-FIB systems have been used in research as well as in the integrated circuit industry for fabrication of nanostructures, micro-machining/deposition [2], TEM sample preparation [3], and mask repair [4], there are strong demands for FIBs using other elements and FIB systems with a better spatial resolution. For example, various methods in ion beam analysis, such as secondary ion mass spectroscopy (SIMS) and Rutherford scattering, are important for characterization of materials. Gallium is not the most suitable element for these analysis methods. In addition, precision ion implantation of certain elements may allow us to fabricate novel devices. Recent research has shown that the spin states of individual nitrogen-vacancy (N-V) centers in diamond can rapidly be polarized, preserved, and read out even at room temperature, making the room temperature qubits possible [5, 6]. Precision implantation of a single nitrogen ion in diamond can provide a mean to fabricate such a crucial device in a quantum computer.

Another type of ion source for FIB is a gas field ion source (GFIS), which uses a very sharp emitter for field ionization of gas molecules attracted to the tip apex. The virtual source size (∼1 nm or smaller) and the energy spread (<1 eV) are at least one order of magnitude smaller than those of LMISs. This implies that GFIS-FIB systems may achieve a much better resolution than the current Ga-FIB systems. In addition, the metal ion contamination problem often encountered in LMIS-FIB systems may be avoided if a noble gas ion source is used. For an LMIS-FIB system, usually one should change the emitter in order to change the ion

[3] Author to whom any correspondence should be addressed.

species. An important advantage for GFIS-FIB systems is that the same emitter is capable of producing different ion beams simply by changing the gas species. Many different gases can be chosen according to the desired functions. For example, focused helium or hydrogen ion beams would be good for scanning ion microscopy because of their low masses and low sputtering rates. In addition, the focused helium ion beam can be used to carry out Rutherford scattering spectroscopy on materials with lateral resolution down to a nanometer. A focused Ar ion beam is suitable for ion milling and fabrication of nanostructures because of its large mass. A focused oxygen ion beam has the highest secondary ion yield, which is very useful for SIMS. The focused nitrogen ion beam is highly desirable for direct nitrogen implantation. Evidently, GFISs provide a very different category of ion beams and will greatly extend the application fields of current FIB technology.

In the early 1970s, GFIS was once considered by Levi-Setti and co-workers for use in a prototype scanning transmission ion microscope [7]. Later, they realized that a sufficiently bright and reliable GFIS would be the determining factor for the feasibility of the high resolution ion microscope. In the 1960s, Gomer suggested that formation of a tiny protrusion on the rounded field emitter might show a lens effect to confine the beam angular divergence, which could effectively increase the angular intensity and beam brightness [8]. Besides, the smaller emitter source size was also beneficial to achieve a higher resolution. Many groups followed this concept and proposed various approaches to build up a small protrusion on the tip apex [9–17]. Although their experiments clearly confirmed that a nano-protrusion on a base tip indeed improved the beam brightness, those methods were tedious, unreliable, and often required special facilities to get a nanotip. Most importantly, the nano-protrusions so prepared were not thermally stable and their lifetimes were too short for practical applications.

In 2001, Fu and Tsong proposed that the surface faceting of Pd/W(111) can generate a nano-pyramid on a tip and form a single-atom tip (SAT) with high reproducibility [18]. Since faceting is a thermodynamics process, the single-atom sharpness can be recovered even if the tip is contaminated or damaged. Later, such noble-metal covered W(111) SATs were confirmed experimentally to be bright and reliable electron/ion beam emitters [19–22]. These findings indicate that the adsorbate-induced faceting can provide an effective way to prepare a thermally stable nanotip and solve the unreliability of conventional nanotips. Iridium is a very special metal that can sustain high temperature annealing, high positive electric fields and chemical attack. In this paper, we present a reliable method for preparation of a pure iridium SAT based on oxygen-induced crystal faceting of the Ir(210) [23] and demonstrate its capability to emit high brightness of several different ion beams, including reactive gas ions. Once an Ir-SAT is formed, we have determined the atomic structure of the tip apex using the atom-by-atom analysis of the field ion microscopy (FIM). Ion emission characteristics of several gaseous ion beams are also measured.

2. Experimental details

An Ir wire with a diameter of 0.1 mm was electrochemically polished in molten salt ($NaNO_3$:KOH = 1:1) with the AC mode (7–9 V (rms)) to make an Ir needle with a radius of about 200 nm. The Ir needle is loaded in a homemade ultra-high vacuum-FIM (UHV-FIM) (base pressure $\sim 1 \times 10^{-8}$ Pa), which has been described elsewhere [21]. The needle is thermally flashed at 1500 °C for several times, and then cooled down to 20 K with a closed-cycled cryostat (Advanced Research System, Inc.) for FIM imaging. Normally, a helium gas of 2×10^{-3} Pa is admitted as an imaging gas. Applying a proper high positive voltage to the Ir needle, ionization of the absorbed helium occurs at the Ir tip apex. These helium ions are accelerated by the strong electric field and impinge onto a grounded micro-channel plate (MCP, Hamamatsu photonics) to reveal the atomic image of the tip apex. The asperities or contaminants on the tip surface can be field evaporated by applying a higher voltage until a clean, smooth and crystalline symmetrical end form is obtained.

3. Results and discussion

3.1. Apex characterization

Figure 1(a) shows a typical fcc FIM micrograph of a pristine Ir tip surface with the tip biased at +10.2 kV. The center (210) plane is surrounded by two {311} and one (110) facets. This Ir tip is then annealed at 400–600 °C for 5 min in an oxygen atmosphere of 2.6×10^{-5} Pa. Figure 1(b) shows an FIM image taken at the tip voltage (V_{ext}) of +7.1 kV after the oxygen thermal treatment. Interestingly, only one bright spot with a half angle of 0.8° is detected at a much lower tip voltage than that in figure 1(a), suggesting formation of an iridium single-atom tip. This single spot indicates that emission occurs only from the topmost atom. The small source size and the small opening angle (compared with 25° for Ga-LMIS) are particularly favorable for achieving high angular intensity, high brightness, and low spherical aberration, which are important characteristics for an FIB system.

The atomic structure of the under-layers of the Ir-SAT can be characterized by controlled field evaporation and subsequent observation. After applying a higher tip voltage, the topmost atom is field evaporated and the second layer with three atoms is revealed, as shown in figure 1(c). After the second layer is field evaporated, the third layer and three atomic ridges stretching toward {111} and (001) show up, indicating that the original smooth top shown in figure 1(a) has been transformed into a three-sided pyramid after the thermal treatment (figure 1(d)). Although the tip apex is destroyed by the successive field evaporations, the single-atom sharpness can be recovered simply by repeating the annealing process in the oxygen atmosphere again. We find that the Ir-SAT can be regenerated many times and the successive generations retain the same atomic structure as the first generation. An atomic hardball model based on the FIM observation is shown in figure 1(e). It is a perfect wedged pyramid terminated with only one atom protruding from a (210) plane.

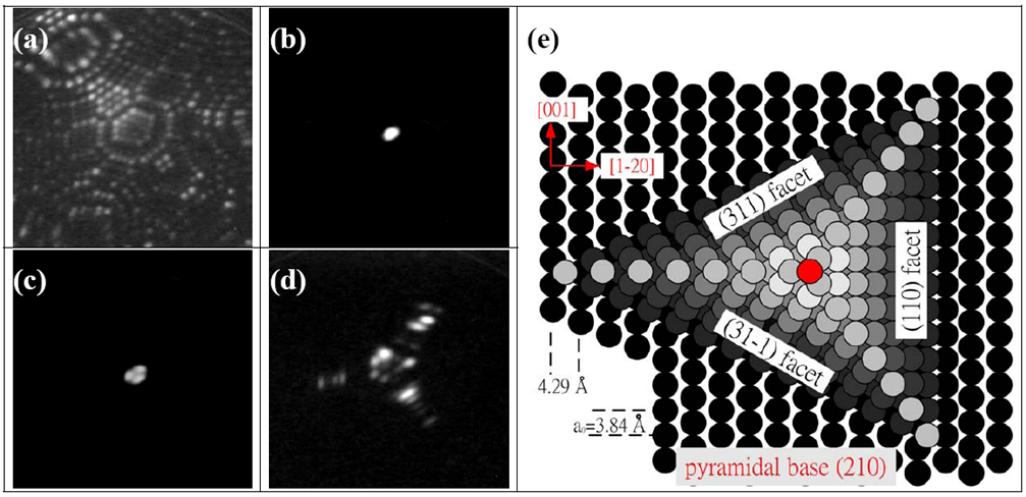

Figure 1. (a)–(d) FIM images with He as the image gas showing the atomic structure of an Ir(210) tip: (a) pristine Ir surface obtained by repeated thermal flash and field evaporation ($V_{ext} = 10.2$ kV); (b) after a thermal treatment in oxygen, the tip apex ends with only one atom ($V_{ext} = 7.1$ kV); (c) the second layer of the tip apex consists of three atoms ($V_{ext} = 7.9$ kV); (d) the third layer and the three ridges showing a pyramidal structure ($V_{ext} = 8.7$ kV); (e) a hardball model of the nano-pyramid.

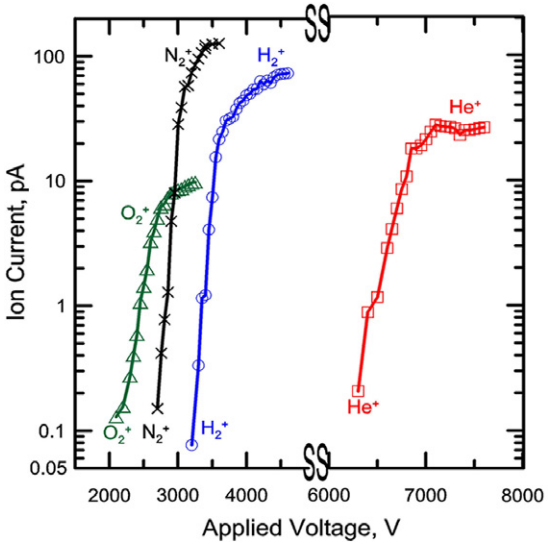

Figure 2. I–V characteristics of various ion beams field emitted from an Ir-SAT at a gas pressure of 1.3×10^{-2} Pa. The tip temperature is 20 K, 20 K, 70 K, and 85 K for He^+, H_2^+, O_2^+, and N_2^+ ion beams, respectively.

3.2. Emission characteristics of gaseous ion beams

We have evaluated the emission characteristics of several ion beams on the same Ir-SAT by changing the gases inside the chamber. Emission patterns with a small opening angle as in figure 1(b) are seen when we change the gas species. The I–V characteristics of He^+, H_2^+, O_2^+, and N_2^+ at a pressure of 1.3×10^{-2} Pa are shown in figure 2. Since the ion current is in the range of 10^{-13}–10^{-11} A, small currents are measured through amplification of an MCP. The amplification gain is calibrated in the high current regime, where direct current measurement is possible. As shown in figure 2, two different slopes can be seen in the I–V characteristics of the four gaseous ion beams. Similar I–V characteristics are also seen for normal hemispherical tips [24]. In the low-field regime, the ion current increases steeply with the electric field. When the voltage is raised beyond a certain value, the current increases at a slower rate and eventually reaches a plateau. As seen in figure 2, the Ir-SAT is capable of emitting a nitrogen ion beam with a current higher than 100 pA at a gas pressure of 1.3×10^{-2} Pa. It is four times larger than that of the He ion beam, suggesting that this source is a good candidate for precision N_2^+ implantation in diamond [5] and other ion beam applications. Table 1 summarizes the beam current, angular intensity, and the estimated brightness. The normalized brightness of these ion beams is estimated to be 10^{13}–10^{14} A m^{-2} sr^{-1} Pa^{-1}. In comparison, the brightness of typical LMISs is 10^9 A m^{-2} sr^{-1}, equivalent to that of these GFISs at a gas pressure of 10^{-4}–10^{-5} Pa^{-1}. Therefore, the brightness of these GFISs can easily surpass that of LIMS by operating at a higher gas pressure.

Table 1. Characteristics of various ion beams emitted from an Ir ⟨210⟩ single-atom tip.

	He^+	H_2^+	N_2^+	O_2^+
Temp. at cryostat (K)	20	20	85	70
Ion current (pA at 1.3×10^{-2} Pa)	27	66	120	6.6
Angular intensity[a] (μA sr^{-1} Pa^{-1})	3.5	8.1	14.7	0.8
Brightness[a] ($\times 10^{13}$ A m^{-2} sr^{-1} Pa^{-1})	4.8	11.4	20.8	1.2

[a] Normalized to gas pressure (Pa).

It has been known that the ion current in the low-field regime is mainly determined by the ionization probability, which is exponentially proportional to the applied field. In the high-field regime, the saturation ion current is mainly determined by the gas supply function. Figure 2 shows that the saturation ion beam currents of the four tested ions are in the range of 10–120 pA. These values are equivalent to

that of a normal metal emitter [24], suggesting that the total gas supply functions are approximately the same for these two types of emitters. However, a normal metal emitter has hundreds of individual emitting centers. An example is seen in the FIM image shown in figure 1(a), where each spot indicates an emitting center. These ionization centers share the total gas supply, leading to the low angular intensity. In contrast, the oxygen thermal-treated Ir-SAT, as shown in figure 1(b), has only one protruding point at the topmost atom of the pyramid. The field enhancement makes all the coming gas molecules preferably ionized at this topmost atom. In other words, the single-atom tip neither changes the field ionization mechanism nor changes the gas supply function around the tip apex. Instead, the SAT simply reduces the number of ionization centers from hundreds to only one, and thus the beam brightness can be improved by a few orders of magnitude.

After the oxygen thermal treatment, there are oxygen molecules presumably adsorbed on the Ir surface. Ermanoski *et al* suggested that a further thermal treatment in hydrogen or carbon monoxide could remove the oxygen and get a pristine iridium surface [23]. For the applications of Ir-GFISs, the adsorbed oxygen can easily be removed by the applied electric field. As can be seen in figure 2, oxygen can be ionized at a lower voltage than the other three gases. The best image field of oxygen is estimated to be 17 V nm^{-1}. Before the working gas is ionized, the adsorbed oxygen has been field desorbed and a pristine surface is exposed for the working gas.

Figure 3 shows the current stability of four different gas ion beams emitted from an Ir-SAT. Obviously, they are very stable with instability (standard deviation/mean current) below 5%. The current fluctuation of a GFIS is mainly due to the adsorption and ionization of impurity atoms. The contamination molecules adsorbed on the tip shank may either form a new emitting center sharing the gas supply, or may block the diffusion path. Both lead to a noisy beam and a lower angular intensity. Although a GFIS is normally operated at a higher gas pressure (10^{-2}–10 Pa) in the gun chamber, a UHV chamber (base pressure $<1 \times 10^{-7}$ Pa) is highly recommended for stabilizing the beam current as well as for extending the source lifetime. Furthermore, it is not recommended to switch off the high voltage to turn off the ion emission. It would be better to evacuate the gas from the gun chamber to diminish the ion beam while keeping the tip cool and the high voltage on (for example, at the best image field of helium) all the time. As most gases have lower ionization field than helium, the high electric field at the apex can effectively remove the adsorbed impurity molecules and keep the tip apex clean.

During gas ionization, the tip apex atoms are also under a very high electric field (10–50 V nm^{-1}). For generation of a helium ion beam, the tip atom should be able to sustain a field higher than 45 V nm^{-1}; otherwise the tip atom would be removed below the field that is required for ionization of helium atoms. Tungsten is the most commonly used material for field electron/ion sources because of its high evaporation field and thermal stability. However, if there are reactive gas molecules, such as oxygen, nitrogen, or water, adsorbed on the tungsten tip, the threshold evaporation field for tungsten atoms would be dramatically reduced [15, 25]. This field enhanced etching effect can greatly reduce the tungsten tip lifetime. Our current work clearly indicates that the Ir-SAT not only can sustain high electric field, but also shows high corrosion resistance for many reactive gases. Especially, nitrogen is the most corrosive gas ever known for field ionization from a sharp metal tip. Our results strongly suggest that this Ir-SAT should be able to emit many other gas ions. The high ion current stability and the sufficient tip lifetime can fulfil the strict requirements for applications in FIB systems.

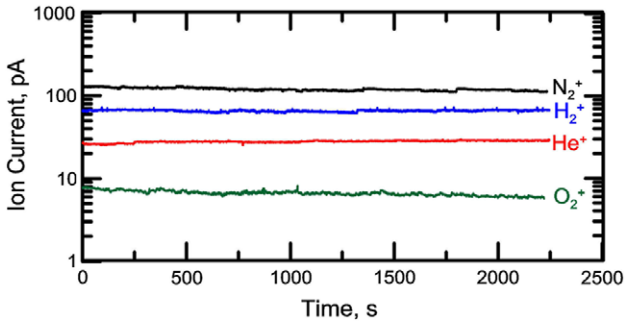

Figure 3. Typical N_2^+, H_2^+, He^+, and O_2^+ ion beam currents as functions of time. We note that the slightly higher instability for the O_2^+ ion beam is mainly due to the O_2 condensation on the cryostat head, which makes our gas pressure control more difficult.

Recently, a commercial helium ion microscope based on a point helium ion source has been released and it demonstrates a better resolution (∼0.75 nm) and higher contrast than that of a scanning electron microscope [26–28]. It uses a sharp tungsten tip to field emit a high-brightness helium ion beam. However, the pristine tungsten tip is susceptible to the etching of reactive gases, such as H_2, N_2, and O_2, and thus cannot be the emitter of these GFISs. Our work demonstrates that the use of an Ir-SAT as the emitter in a FIB system may greatly extend the application of FIBs to precision ion implantation, element analysis, and fabrication of many novel devices.

4. Conclusions

To conclude, we have successfully developed a preparation method of a thermally stable Ir single-atom tip. We have also demonstrated that this tip can emit several high-brightness ion beams with good current stability, making it a very promising GFIS emitter for future FIB applications. It is anticipated that GFIS-FIB systems will become powerful and versatile tools for processing and characterization in nanoscience and nanotechnology, which will make possible many important applications which are simply out of reach with current technology.

Acknowledgments

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