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# Tailoring the Sharpness of Tungsten Nanotips via Laser Irradiation Enhanced Etching in KOH

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***Abstract*****—**Controlled modification of appropriate sharpness for nanotips is of paramount importance to develop novel materials and functional devices at a nanometer resolution. Herein, we present a reliable and unique strategy of laser irradiation enhanced physicochemical etching to manufacture super sharp tungsten tips with reproducible shape and dimension as well as high yields (~80%). The corresponding morphology structure evolution of tungsten tips and laser-tip interaction mechanisms were systematically investigated and discussed using field emission scanning electron microscope (SEM) and physical optics statistics method with different fluences under 532 nm laser irradiation. This work paves the way for exploring more accessible metallic tips applications with tunable apex diameter and aspect ratio, and, furthermore, facilitates the potential sharpening enhancement technique for other materials used in a variety of nanoscale devices.

***Keywords*****—**Tungsten tip sharpening, Laser irradiation, Physicochemical etching, Light-matter interaction.

## I. INTRODUCTION

SUPER sharp tips are featured typical tip radius as small as less than 10 nm and higher aspect ratios at the tip apex. They are predominately used for applications in various fields like atomic force microscope for enhanced probing and imaging of surface science, nanofabrication, nanolithography, low-voltage field emitters, nanoelectronics and bio-sensing, *etc* [1]. Among all the commercialized nanotips, tungsten (W) nanotip is one of the most favored conductive nanotips due to its robustness and high density, amenable to chemical etching, tunable tip geometric shape, and highest melting point of all the non-alloyed metals as well as its relatively good oxidation resistance in air, *etc* [2]. In recent years, interest in super sharp tips dramatically increased due to overwhelming demand of the prerequisite testing for transistors and nano-circuits in semiconductor industry communities. However, nanotip fabrication turns out more and more challenging for W tips when meet the phenomenal progress in increasing circuit performance by reducing device dimensions at a rate commonly referred to as Moore’s law (where the number of transistors that fit on a computer chip doubles every 18 months) has been curtailed by practical and fundamental limits. Thus, there is a keen interest in developing ultimate reliable fabrication of large amount of super sharp tips, like super sharp conductive W nanotips. Moreover, sophisticated setup requirement and high cost of the conventional tip sharpening methodologies, e.g., sputtering with inert gas [3], chemical reverse etching [4], thermal field treatment [5], field-assisted reaction [6] and filed induced low temperature oxidation [7] *etc*. hampered the super sharp nanotips usage population and marketing. Here, in this letter, we demonstrate a simple laser irradiation enhanced physicochemical etching approach toward a new route to surmount the limits of traditional technologies to produce W super sharp nanotips (~10 nm in radius) with a very good control in tip apex radius and tip aspect ratio as well as a high yield (~%80). Furthermore, a detailed discussion of how laser interacts with W tip mechanism was discussed in length, which strongly correlates the laser irradiation process which accounts for heat gradient generation to enhance the physicochemical etching procedure in KOH solution.

## II. EXPERIMENTAL PROCEDURE

Fig.1 represents the experimental setup used for performing laser irradiation enhanced etching process within KOH solution. The tapered shape W tips were initially prepared from commercialized W wires with a diameter of ~0.25 mm by using an ac electrochemical method. To eliminate the inconsistency of the initial tips profile, the nanotip apex radius was inspected and measured with a scanning electron microscopy (SEM). The tips with the same radius of curvature (ROC) with ~40 nm were employed for comparative studies. The W tips were mounted in an upright position and placed in a Teflon container, which was then positioned on the revolving stage, and it can translate along X-Y-Z axis. Diluted KOH solution with concentration ~0.5 M was used as the etchant. Tip holder carries multiple W tips was immersed in the KOH solution. 532 nm Nd:YAG laser beam with pulse duration of ~6 ns was irradiated to the W tip apex long the axial direction. The maximum output energy of excitation laser was optimized to be ~0.6 mJ. The laser pulse energy was adjustable and an electrical shutter was utilized to switch the laser beam on and off during physicochemical etching. All the tips were given a single-pulse laser treatment in KOH, and the tip profiles were characterized using SEM before and after laser irradiation. All the experiments were carried out at the room temperature in the atmosphere ambient.

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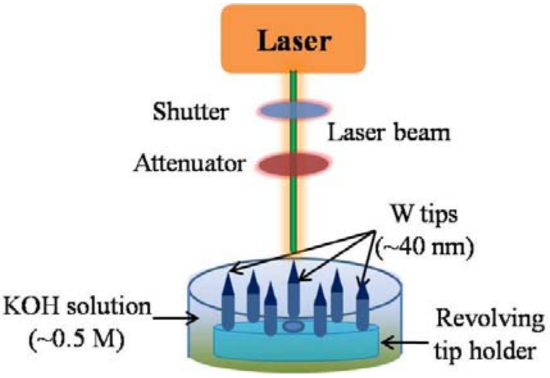


Fig. 1 Schematic illustration of experimental setup employed for laser-enhanced physicochemical etching

## III. RESULT AND DISCUSSION

As shown in Fig. 2, the SEM images demonstrate the geometry and the dimension variation of the W nanotip (a) before and (b) after a single-pulse laser treatment at a power density of ~62 mJ/cm$^2$. Compared with the tip profile after laser irradiation as illustrated in (b), the region in (a) which was defined by the white dotted lines and the solution represents the amount of W removed by KOH after single-pulse 532 nm Nd:YAG laser irradiation. The tip apex radius was reduced from 40 nm in (a) to 10 nm in (b).

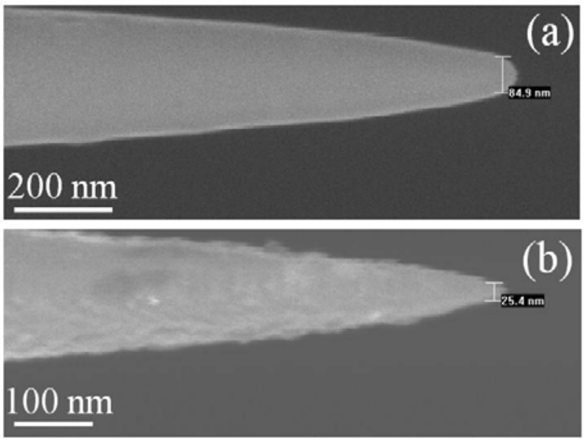
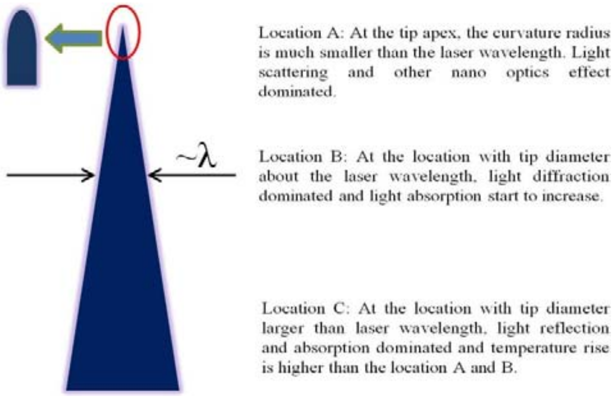


Fig. 2 SEM images of the W nanotip (a) before and (b) after laser treatment at a laser fluence of 62 mJ/cm$^2$

Under laser irradiation, the electrons in the W tip gain energy from the photon and transit to higher energy states. The excessive energy will be released in the way of heat generation and relaxation. Considering the mean free time between collisions for electrons is of the order of $10^{-14}$ to $10^{-13}$ s in W tips, the electrons will be involved numerous collisions both among themselves and with lattice phonons for times order of $10^{-9}$ to $10^{-8}$ s [8]. The energy absorbed by electrons will be distributed and transferred into the lattice. Thus the laser irradiation energy will be turned instantaneously into heat within the volume in which the laser is absorbed. The study of how light interacts with matter is called physical optics [8]. Scattering is a process that conserves the total amount of energy. Absorption is a process that removes energy from the incident light beam by converting it to another form. Extinction (or attenuation) is the net effect of scattering and absorption and describes the effect of the interaction between the radiation and the matter upon which it impinges [9]. Both scattering and absorption cause the incident laser beam to be diminished as it is projected through an assemblage of W atoms, some decrease due to redirection of rays by scattering, some decrease due to loss of the photons by absorption. This reduction in the energy of the incident laser beam leads to the concept of extinction (i.e., sum of scattering and absorption), which is the degree of attenuation of the incident light energy. Wherein, scattering comprises reflection, refraction and diffraction. The interaction between laser and W tip induces the temperature gradient from the bulk to tip apex. A larger cross sectional area at the base inevitably translates to a greater extent of electronic excitation that can subsequently decay to heat [10]. As depicted in Fig. 3, location A which is at the tip apex has a diameter that is at least 10 times smaller than the wavelength of the incident laser beam (~532 nm). As a result, most of the laser beam incident at A is reflected or scattered with little or no energy absorption. Consequently, the temperature rise at A due to absorption of incident laser energy is low. At location B, where the tip diameter is close to the value of the incident laser wavelength, light diffraction dominates and the amount of incident beam absorption increases relative to A. Since material temperature increases with the amount of light absorbed, the temperature at location B will be higher than that at location A. Finally, at location C where the local tip diameter is, at least, several times larger than the incident laser wavelength, light absorption and reflection dominate. This translates to a greater amount of laser energy being absorbed by the nanotip at location C compared to location B. As a result of the increase in energy absorption with tip dimension, a temperature gradient is developed across the length of the nanotip. Location C with the largest diameter absorbs the most incident laser energy is the hottest among the three locations, while location A having the smallest diameter absorbs the least amount of energy is the coolest. Since etching rate varies as a function of temperature, the chemical etch rate along a nanotip, under laser irradiation, will also vary based on the temperature gradient established from the tip bulk (fast etch) to tip apex (slow etch). And further specific relationship of the tip sharpness against the laser fluence applied was also compared and shown in Fig. 4. Within the range of fluences from 4.8 to 96 mJ/cm$^2$ investigated, all tips showed a dramatic reduction in the tip sharpness, and the mechanisms involved were dominated by interfacial interactions. Beyond 96 mJ/cm$^2$, more vigorous thermal interactions at the W solution interface occurred, resulting in major morphological modifications.[1]



Location A: At the tip apex, the curvature radius is much smaller than the laser wavelength. Light scattering and other nano optics effect dominated.

Location B: At the location with tip diameter about the laser wavelength, light diffraction dominated and light absorption start to increase.

Location C: At the location with tip diameter larger than laser wavelength, light reflection and absorption dominated and temperature rise is higher than the location A and B.

Fig. 3 Schematic illustration of three different laser-W tip interaction schemes

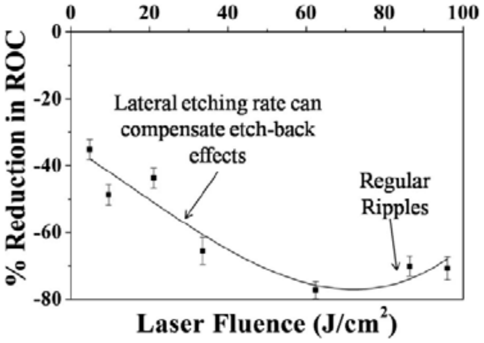


Fig. 4 Dependence of reduction in ROC of W nanotips on the laser fluence during laser-enhanced physicochemical etching

## IV. CONCLUSION

In summary, we have demonstrated the feasibility of sharpening conical W nanotips using a pulsed Nd:YAG laser enhanced physicochemical etching in diluted KOH solution. Etching mechanisms vary with the extent of laser light–matter interaction as the radius decreases from the micrometer range at the tip base to less than 40 nm at the tip apex. With the incident laser positioned in the axial direction to the tip apex, the generated temperature gradient from the tip base to the apex resulted in the slowest rate of material removal at the nanometer-scale tip apex. By applying an acceptable range of laser fluence, lateral etching of the W nanotips could be controlled to further sharpen the original nanotips. This makes laser physicochemical etching a potential sharpening enhancement technique for tips used in a variety of nanoscale applications.

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