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Safe fabrication of sharp gold tips for light emission in scanning tunnelling microscopy

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Abstract

Gold is the optimal tip metal for light emission in scanning tunnelling microscopy (LESTM) under ambient conditions. Sharp Au-tips of ~10 nm radius were produced reliably using a safe, two-step etching method in 20% (w/w) $CaCl_2$ solution. Previous $CaCl_2$-based methods have tended to produce blunter tips, while other etching techniques that do produce sharp Au-tips, do so with the use of toxic or hazardous electrolytes. The tips are characterised using scanning electron microscopy and their efficacy in LESTM is evidenced by high-resolution, simultaneous topographic and photon mapping of Au(1 1 1)- and polycrystalline Au-surfaces. Spectra of the optical emission exhibit only one or two peaks with etched tips in contrast to the more complex spectra typical of cut tips; this feature, together with the highly symmetric geometry of the tips, facilitates a definitive analysis of the light emission process.

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Keywords: Tip fabrication; Scanning tunnelling microscopy; Light emission; Plasmons; Gold

1. Introduction

Electron microscopy and field ion microscopy have driven the development of sharp metallic tip structures during the past 50 years. Melmed, in his review article of 1991 [1], placed structure on what had become a very disparate field, identifying 10 distinct techniques that had been used to form sharp metallic tips. These were traced from the context of field electron emission microscopy, where tungsten tips had apex radii of ~1 μm, through field ion microscopy, where tip radii should be <100 nm, to the procedures borne of scanning probe microscopy. Indeed, tip fabrication received significant impetus in the wake of the invention of the scanning tunnelling microscope (STM) [2] in 1982 and the subsequent development of other scanning probe techniques. A variety of techniques and processes have been developed for different metallic tips, such as W [3–8], Pt [9,10], PtIr [4,7,11], Ag [12–14] and Au [10,15–21]. In the broad-ranging investigations of Lemke et al. [4] and Nam et al. [10] Ir, Cu, Ni, Fe, Pd and Rh were added to the repertoire of tip materials. Tip fabrication requires attention because tip properties are crucial in all forms of scanning probe microscopy—in the context of STM, the size, shape and chemical identity of the tip influence not only the resolution, but also the electronic structure detected [22].

The specific goal of the work reported here is the reproducible, safe fabrication of sharp Au-tips using a simple, economical method. The motivation stems from our work on light emission from the scanning tunnelling microscope (LESTM) under ambient conditions [23–26]. This imposes a number of criteria on the tip properties and thus the fabrication procedure:

- Since our interest lies with STM the general requirement for the tip to be sharp on the nm to atomic scale should be met. Also, the tip should have a low aspect ratio to reduce flexing.

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- Tips for LESTM should be formed from a metal with good optical properties, i.e. small imaginary part of the dielectric function, ε_i. However, the usual choices of tip metal, W and PtIr, are optically absorptive (large value of ε_i) and yield poor light emission. For example, in our initial LESTM investigations [23], it was found that PtIr tips yielded a light intensity that was at least an order of magnitude less than that for a Au-tip/Au-sample combination; W-tips were worse still. These comparisons corroborate those of Berndt et al. [27] who found a factor of 10 improvement in light emission for Au-tips over W-tips used with Au-samples in a UHV environment, while Qiu et al. [28] in their study of STM induced fluorescence from porphyrin molecules, similarly found the light emission intensity with Ag-tips to be a factor of 10 better than with W-tips. Au and Ag are thus established as the preferred tip materials and have been widely used in LESTM studies [23–33]. Furthermore, in LESTM the form of the tip up to an optical skin depth (20–25 nm) back from the end of the structure has a crucial influence on the light output. Thus, the quality criteria for 'good' tips for LESTM pertain not just to the last ~nanometer (as for normal STM imaging) but also to the tip structure on a scale that is an order of magnitude greater.
- In ambient conditions there is the additional requirement that the tip (and sample) should not oxidise or otherwise become contaminated. This leaves Au as the single preferred material for both tip and sample since Ag reacts with sulphur in the atmosphere to form Ag_2S. In our working environment, it was found that Ag tips (and samples) degrade significantly within 1–2 days, with electron tunnelling becoming noisy, then impossible. The presence of Ag_2S degrades not only the electronic properties, but also the optical performance—we have investigated this effect quantitatively for the case of surface plasmon polariton propagation on thin Ag films using a photon STM [34]. Similarly, in the present context, where *localised* plasmon modes of the tip–sample nanocavity are responsible for the light emission [27–29], the formation of Ag_2S has a markedly deleterious effect. In contrast, a Au-tip/Au-sample combination yields a consistently good level of light emission (spectrally integrated signal >1000 counts s^{-1} over the red/near-IR range) for several weeks or more.
- A further requirement is that the tip surface should be smooth. This is a feature that has been highlighted more in the context of tip enhanced Raman scattering [20,35,36] rather than LESTM. A rough tip surface shows an affinity for carbon contamination.

Compared with other tip materials, notably W and PtIr, Au has received relatively little attention in the literature since it is soft and therefore forms tips that are easily damaged. Such tips tend not to be used in general STM work, especially under vacuum conditions. Nonetheless, various methods for the formation of Au-tips by electrochemical etching have been reported [15–20]. A summary of the principal features of the techniques used is given in Table 1, as is a summary of the method employed here. Note that most of the techniques use toxic or hazardous materials such as KCN [18] or HCl [15,16,20]. The etch method outlined by Ren et al. [20], yields similar tip structures to those reported here but with the use of HCl etchant solution; there are clear advantages in using a non-hazardous electrolyte in terms of both safety and convenience. On the other hand, the previous use of safer protocols has generally led to the formation of tips that are blunter or of poorer surface quality. For example, while the use of NaCl [17] or $CaCl_2$ [19] as an electrolyte is much safer, it is reported that the tip formation process is complicated by increased bubbling due to the by-products of the reaction; such tip structures are not ideal for LESTM. Finally, a further method has been to overcoat electrochemically etched W-tips with ~20 nm of Au [21] but this yielded rough tips with apex diameters >150 nm.

2. Experimental

In this work the tip is formed using the 'drop-off' technique as described, for example, by Bryant et al. [37]. A wire is immersed in electrolyte (Fig. 1) and the tip is formed at the air–electrolyte interface when the lower portion of the wire drops off. This proceeds first by 'necking' of the wire, with the drop in the level of the meniscus leading to a characteristic profiling of the necked region. When the weight of the immersed part of the wire exceeds the tensile strength of the necked region, the immersed portion drops off, leading to the formation of a sharp tip. We give a brief, highly specific summary of the overall procedure prior to a more detailed, developmental account in the next section that forms an instructive landscape on the form of Au-tip structures as a function variation in the critical process parameters.

The electrolyte comprises of calcium chloride dihydrate powder (BDH Laboratory Supplies) in deionised water, constituting a 1.8 M solution. The tip is formed from 0.25 mm diameter gold wire of 99.99 + % purity (Birmingham Metals Inc.), a portion of which (~3.5 mm in a total length of 10 mm) has been covered with a protective varnish coating to prevent etching below the electrolyte surface. The counter-electrode is 1 mm diameter Pt wire formed into a 10 mm ring with the tip formation region at its centre (Fig. 1). The reaction scheme for the etching of Au in electrolytes containing Cl^- ions has been investigated in some detail by Ren et al. [20].

The etching proceeds in two stages, an etch under ac bias conditions, followed by a final dc etch to the drop-off point. For the ac stage, a Thurlby Thandar Instruments TG210 function generator is used to control the input voltage magnitude and frequency. This unit also has a dc offset control ensuring that the Au wire is always the