Preparation of Sb doped SnO_2 SPM tips and their use as transparent probes in STM induced light hybrid microscopy.

T. Tätte*, V. Jacobsen**, M. Paalo*, R. Branscheid**, M. Kreiter**, U. Mäeorg***, K. Saal*, A. Lõhmus* and I. Kink*

*Institute of Physics, University of Tartu, 142 Riia St., 51014 Tartu, Estonia
**Max Planck Institute for Polymer Research, D-55021 Mainz, Germany
***Institute of Organic and Bio-Organic Chemistry, University of Tartu, 2 Jakobi St., 51014 Tartu, Estonia

ABSTRACT

Development of various kinds of sharp needles has been in focus of investigators since their application as sensors in scanning probe microscopy. Although transparent and conductive tips lead to several fascinating applications like STM/SNOM hybrid microscopy, they have stayed somewhat out of focus mainly because of difficulties in preparing such tips. Recently as a potential breakthrough in this field we proposed a new method based on pulling of Sb doped SnO_2 tips from the mixture of stannoxanes. We showed that stable STM image with atomic vertical and nanometre lateral resolutions are possible with the tips. Also, electric potential more than 7-8 volts between the tip and surface caused emission of photons generated by tunneling current. Since these photons are characteristic for confined spot they can be used to map the scanned area. In this work we present new results on optimizing tips preparing process. The influence of pulling speed, humidity and viscosity on the tip radius and angle has been studied.

Keywords: SNOM tips, STM, tunnelling induced luminescence, optical fibres, sol-gel

1 INTRODUCTION

Demand for better optical resolutions than classical λ/2 has led to new techniques that enable to focus light more than optical lenses do.

Metal-coated SiO_2 needles are the most frequently applied for this purpose. By now different methods based on cutting and etching of silica fibres have been developed and commercialized. By a crude division two different kind of tips, aperture and aperturless, are designed for use as SNOM probes [1]. Surprisingly metal oxides have found very limited attention as sensor materials, although they have many of interesting and potentially valuable properties like extremely high strength in the case of HfO_2, electrical conductivity simultaneously with optical transparency in the case of doped SnO_2, high-yield fluorescence in the case of TiO_2, etc. Therefore, we have made many efforts for finding possibilities to sharpen such metal oxide fibres down to nanometer scale needles and use them as SPM probes. In our first paper we presented a technology to prepare Sb^{3+} doped SnO_2 tips from thermally degraded $Sn(OBu)_4$ with tip radius less than 50 nm [2]. Afterwards we found that suitable precursors for tips can be obtained by slow addition of water to $Sn(OBu)_4$. Then we improved universality of the method by preparing sharp needles from TiO_2. In our recent paper we focused on luminescence generated by tunnelling current when operating in STM mode and applying voltages higher than 7 volts between the tip and surface.

2 EXPERIMENTAL

$Sn(OBu)_4$ used in our experiments was prepared by method described previously [2]. All chemicals were distilled prior usage, except $Sn(OBu)_4$, which decomposes when heated [2].

Tip precursors were prepared by droping ~5% solution of water in butanole to acidified $Sn(OBu)_4$ at boiling temperature of butanole, until it turned to suitable viscous matter. Viscosity of obtained materials was measured in closed vessels by Stokes method using metal balls with diameter 1mm and mass 0.032 g. Tips were obtained by pulling material to the atmosphere at room temperature and relative humidity 25-35%. Pulling speed of tips was varied from 0.004 to 4,2 m/s.

After keeping tips some days at room conditions, final mechanical stability and conductivity were attained by baking at 520 ^{0}C for 2 hours.

Prepared tips were glued to top of metal wire with conductive epoxy [4,5]. For testing STM operation with Sb doped SnO_2 tips an atomically flat Au(111) surface coated by self-assembled octanedithiol were prepared by method described in Ref. [3].

Samples for STM/tunnelling induced photon experiments were prepared by thermally evaporating gold onto an indium tin oxide coated microscopy slide. Average thickness of the layer was 5 nm, however, it consisted of separated gold nanoparticles rather than forming of a continuous film. These particles show a strong STM-induced electroluminescence due to plasmonic excitation of the particles.

The STM measurements were performed using a home-built microscope with a commercial controller unit (SPM1000, RHK technology) operated in air. On the backside of the sample an oil immersion objective (Nikon, NA=1.4, 60x) is attached as depicted schematically in Fig.1. This configuration has a photon detection angle of 5.5 sterad. In addition to Sb-SnO_2 tips ordinary Pt/Ir-tips that were mechanically cut from a Pt(90%)Ir(10%) wire (Mateck), were used for comparison. The photons were counted by a photomultiplier (Hamamatsu, H7421-40) which is sensitive for wavelengths shorter than 700 nm with a maximum quantum efficiency of 40% at λ = 580 nm.

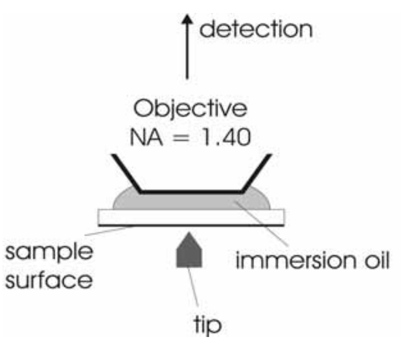

Figure 1: Sketch of the set-up for collecting photons from the tunnelling junction.

3 RESULTS AND DISCUSSION

3.1 Preparation of Tips

Typical shapes of SnO_2 tips prepared from viscous stannoxane solutions are shown in Fig.2. Optimum pulling speed for tips preparation were found to be around 1 cm/s that forms tips with cone angle 10-15^0 from the precursors with viscosities from 500 to some thousand poises. Lower speeds led to larger tip angles and lowered reproducibility of the tip shapes. Higher speeds led to tips with tip angle less than 10^0 that typically were bent and mechanically unstable.

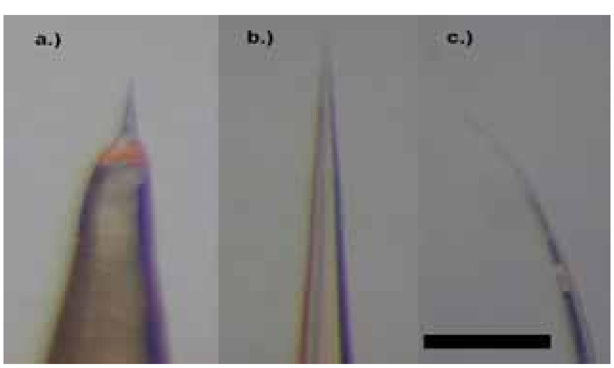

Figure 2: Typical images of fibres pulled at a) 0.25 m/s, b) 1.05 m/s and c) 3.20 m/s from solution with viscosity of 500-2000 poise. The scale bar on the image is around 0.1 mm.

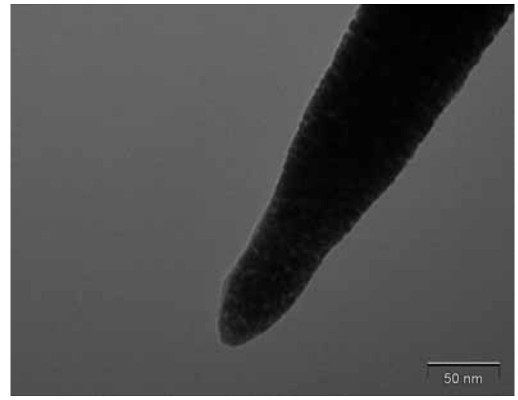

Figure 2: d) TEM image of tip prepared by pulling speed 1.05 m/s from the stannoxane solution with viscosity of 500-2000 poise.

Phenomena of converging of sol jet during the pulling are essential for understanding the mechanism of tip formation. In principle the fibre brakes in a point where its viscosity is the lowest. Viscosity depends on complicated interplay of several phenomena like polymerization of the fibre surface caused by water vapour in air, dynamics of the orientation of the molecules in moving jet, etc. Creation of an exact model remains for future studies.

3.2 STM/Tunnelling Induced Light Measurements

In Fig.3, STM-micrographs of the octanedithiol SAM test sample taken with the Sb-SnO_2-tip and with a standard Pt/Ir tip are compared. Firstly, it is clear that STM operation with the transparent tip is possible without any extra effort. Monatomic steps at the edges of gold terraces and at the rim of round etch-pitches are clearly resolved proving that the vertical resolution is significantly better than 2.36 Å, which is the distance between two Au(111) planes. An upper limit for the lateral resolution in the range of a few nanometers is estimated from the width of the steps in the line profile (Fig. 3(b)).

It must be noted that the Sb-SnO_2-tip is not suited to resolve the structure of the octanedithiol film (with a vertical contrast below 1 Å and a lateral periodicity around 1 nm as seen in the reference image taken with the Pt/Ir tip in Fig. 3(d)). One possible reason is a reduced vertical sensitivity due to higher noise level of the tunnelling current, which masks the signal caused by the sub-angstrom corrugation of the molecular pattern.

Imaging performance of the transparent tip is somewhat reduced compared to a Pt/Ir tip but good enough to provide sub-nm resolution in an STM measurement.

It is important to note that stable imaging was possible with this tip for extended times (at least some ten minutes), leading to the conclusion that tip deformation does not occur continuously. Since a degradation of tip conductivity after storage under ambient conditions for some weeks was observed, we propose that the conductivity of the material at the tip surface decreases even quicker, probably carbon-rich coatings which are reported for tin-oxide materials have to be considered as an additional factor, especially after imaging in a scanning electron microscope. Since the feedback mechanism of the STM approaches the tip to the sample until the setpoint current is reached, this surface layer is mechanically removed, exposing fresh tip material. At this point the importance of a massive tip becomes obvious since removing the conducting layer from coated tips makes them useless for STM operation.

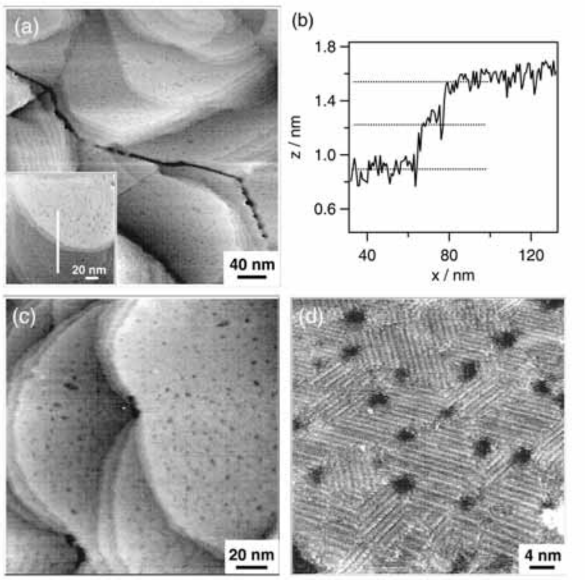

Figure 3: (a) STM-topography of a Au(111) surface passivated with an octandithiol-SAM, imaged with the transparent-conductive tip (V = 350 mV, I = 65 pA), (b) height profile taken within the inlet image in (a), (c) and (d): STM-topography of the same sample imaged by a standard Pt/Ir-tip (V = 331 mV, I = 35 pA in (c) and V = 289 mV, I = 41 pA in (d)).

The next central question for the envisaged applications is whether the Sb-SnO_2-tip can be used to inject hot tunnelling electrons in the sample, which then generate photons in the visible spectral range.

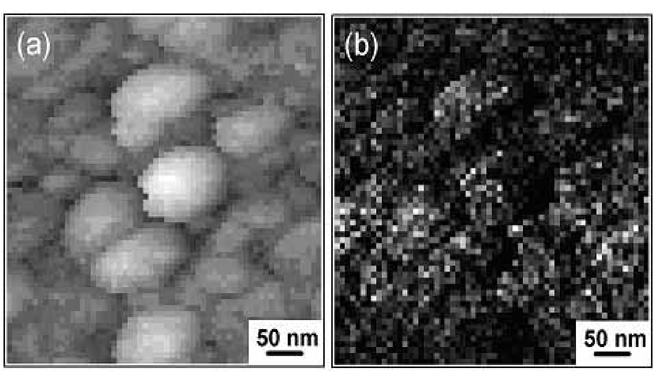

Figure 4: Electroluminescence image of an irregular gold island film with nominal thickness of 5 nm on ITO. (a) topography, (b) photon emission (I = 1 nA, V = 7 V, counting interval per pixel 25 ms, colour scale 0…2000 cps)

In both experimental runs photon emission starts around 7-8 V with an additional pronounced increase in intensity around 10-12 V. From experiments with metallic tips an emission onset is expected at voltages corresponding to the lower limit of the spectral response of the photomultiplier (λ = 700 nm, E = 1.8 V) with additional enhancement at the voltage corresponding to the particle plasmon energy of Au (2.5 V).

We conclude that the real tunnelling voltage is lower than the externally applied bias voltage, which is a hint that the resistance of the Sb-SnO_2 material does not vanish in comparison with the tunnelling gap

The photon intensity obtained is high enough to acquire photon maps of the surface. In luminescent areas of the sample >1000 photons per second are detected. The luminescent areas in the photon map displayed in Fig. 4(b) coincide with those in the simultaneously acquired back scan (not shown). The image shows a contrast in the optical image which partly correlates with the topography. Effective light emission seems to be restricted to certain topographic features, thus allowing to determine the local photon emission efficiency for each spot on the surface, possibly due to localised optical resonances. This image is different from earlier STM-generated photon maps that the optical properties of the sample are not significantly influenced by the tip.

4 CONCLUSION

As a result of this study we found that operating at room conditions, tips with most optimal parameters can be pulled from the polymeric stannoxanes with viscosity 500-2000 poises at pulling speed around 1 cm/s.

To our knowledge it has been shown for the first time that doped semiconductor tips like Sb-SnO_2 prepared by a sol-gel method can be used as STM-probes. Visible light emission could be generated with these probes. This opens a promising route to use inelastically tunnelling electrons as a local light source without fundamentally changing the optical near-field as it is unavoidable when metallic tips are used. Though not experimentally shown in this work we want to stress that the same advantage holds for photo-assisted tunnelling microscopy. Optical fields interact with a tunnelling current in manifold ways which for instance enables the detection of optical fields as a demodulated current signal induced by a modulated light illumination. To obtain interpretable information on the optical near-field of the sample a non-metallic tip is of the same importance here as in the case electroluminescence measurements.

Current experimental activities on near-field mapping are assisted by efforts towards an improved shape control of the tip aiming towards an improved stability and conductivity. This should prevent tip changes during scanning and should allow for a more stable STM operation. Imaging of well-defined metal structures that allow for a quantitative modelling is envisaged which is expected to open the door to the understanding optical near fields down to the atomic scale.

5 ACKNOWLEDGEMENTS

We thank G. Glasser (Max Planck-Institut für Polymerforschung, Mainz) who took the electron microscope images and Dr. A.K.A. Aliganga for the preparation of the dithiol-coated Au(111) surface. Parts of this work were financially supported by the Bundesministerium für Bildung und Forschung, (BMBF, Grant No. 03N8702 and 03N6500), Estonian Science Foundation (grants 5545 and 5015), and from the German-Israeli Project on Future-oriented Topics (DIP, Grant D3.1).

REFERENCES

[1] S. Kawata, M. Ohtsu, M. Irie (Eds.), “Nano-Optics,” Springer-Verlag Berlin Heidelberg, 2002

[2] T. Tätte, T. Avarmaa, R. Lõhmus, U. Mäeorg, M.-E. Pistol, R. Raid, I. Sildos, A. Lõhmus, A., “Transparent and conductive Sb-doped tin oxide SPM tips prepared by sol-gel method,” Material Science & Enginering C, 19 (1-2): 101-104.

[3] T. Tätte, V. Reedo, M. Adamovich, T. Avarmaa, R. Lõhmus, U. Mäeorg, M.-E. Pistol, J. Subbi, A. Lõhmus, “Metal oxide based SPM tips prepared by sol-gel method,” Physics of Low-dimensional Structures, 5-6: 31-37 2002.

[4] V. Jacobsen, T. Tätte, R. Branscheid, U Mäeorg, K. Saal, I. Kink, A. Lõhmus, M. Kreiter, “Electrically conductive and optically transparent Sb-doped SnO_2 STM-probe for local excitation of electroluminescence,” Ultramicroscopy, (in press).

[5] V. Jacobsen, Ph.D. thesis, University of Mainz (2004).