Fabrication of Au and Ag – Coated AFM Probes for Tip-Enhanced Raman Spectroscopy

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Abstract. In this work, approaches for fabrication metal coated probes for Tip Enhanced Raman Spectroscopy (TERS) are considered. It was proposed to use optical characterization of probes to achieve the effective TERS of semiconductor nanoobjects. The shape and size of the metal cluster at the tip apex determines the position of the localized surface plasmon resonance, the electromagnetic field enhancement and, thus, TERS performance. The possibility of optimizing the characteristics of the probes for TERS studies of nanoobjects has been investigated.

1. Introduction

Tip Enhanced Raman Spectroscopy – is a unique research technique that allows to obtain simultaneously information on the surface topology and its chemical state with a nanometer spatial resolution [1, 2]. TERS has become increasingly popular in recent years in various fields of science, including physics, chemistry of low-dimensional systems, biology, and pharmaceuticals [3, 4]. Usually TERS experimental setup combines scanning probe microscope such as scanning tunneling microscope (STM) or atomic force microscope (AFM) with a Raman spectrometer. To record the TERS signal from an object, a laser spot is focused onto the tip apex, exciting a localized surface plasmon, thus produce an “electromagnetic hotspot” at the tip apex. The TERS enhancement and spatial resolution depend strongly on the tip parameters (materials, radius, surface roughness and cone angle). At the moment, various methods for fabricating TERS tips have been proposed, including vacuum evaporation, chemical deposition of metals on silicon probes [5, 6], attachment of plasmonic nanoparticles to the tip, selective deposition [7], electrochemical etching [8, 9]. Despite remarkable progress, development effective techniques for the fabrication of stable probes for TERS measurements are still under demand. The goal of this work is to develop approaches for fabricating TERS probe that are capable of providing the high enhancement of the TERS signal and high spatial resolution for TERS mapping.

In this work, we have considered the possibility of fabricating gold and silver coatings on silicon probes for the implementation of TERS studies. Gold and silver are the two most widely used metal for TERS tips due to their high free electron density, strong LSPR effect in the visible region and relative chemical stability. Ag-coated probes allow higher field enhancement in TERS mode than Au-coated probes. However, silver sulfide or silver oxide films rapidly grow on the Ag-coated tip, thus greatly reducing the lifetimes of such a probe. The shape and size of the metal cluster at the tip apex determines the spectral position of the localized surface plasmon resonance (LSPR) and the enhancement factor of the local electromagnetic field. However, the SEM image of a probe which demonstrates the presence of a metal cluster of the required size on its tip is no guarantee of sufficient TERS enhancement. Therefore,
we use optical characterization of TERS tips in combination with direct structural analysis and demonstrate TERS images of certain nanoobjects.

2. Experimental
A TERS setup consisting of the AFM AIST-NT coupled with Raman spectrometer (Xplora, Horiba) was used for the TERS experiments. Solid–state lasers with the wavelengths of 638 and 785 nm were used as an excitation source. A power of the laser radiation was 1.6 and 0.16 mW for excitation of Au and Ag probe, respectively. To create TERS probes, we used standard semicontact silicon AFM probes of the Vit_P series [10] with optical access from above. The metal coating (Ti, Au, Ag) of the probe was formed by vacuum deposition process. Before metal deposition some of Si probes were covered with 5 nm thick SiO₂. The SiO₂ layer was formed by the oxidation of monosilane in a tubular reactor at a temperature of 350°C and a pressure of 0.95 Torr. To ensure better adhesion of the gold film to silicon or SiO₂, a 20 nm thick Ti layer was previously deposited on the probes. A thin layer of gold (5 nm) was deposited on an Ag coated probe to protect against a rapid degradation. SEM measurements were carried out on a Hitachi SU8220 setup.

3. Results and discussion
A silver or gold metal film with a thickness of 100-250 nm was deposited on the tip of the initial silicon probes. The morphologies of the tip of the probe were characterized by scanning electron microscopy. SEM images of the apexes of TERS probes covered with Au without intermediate layer of SiO₂ (Fig 1a), covered with Au with intermediate layer of SiO₂ (Fig 1b), and covered with Ag (Fig 1c) are shown in Figure 1. For comparison, the SEM image of the tip of a commercially available Horiba TERS probe is presented in Fig 1d. For simplicity these cantilevers are denoted as Au-Si, Au-SiO₂, Ag-Si, and Au-H, correspondingly.

It can be seen from the Fig 1a-d) that a single metal nanocluster is formed at the tip apex of all probes. The size of the metal cluster is 80 nm for the Ag-Si probe, ~70 nm for the Au-Si probe, ~100 nm for the Au-SiO₂ probe, ~50 nm for the Horiba probe.

Obviously, the TERS probes with nanoclusters having different structural parameters and consisting of various metals should have different LSPR frequencies. The LSPR frequency can be shifted by changing...
the parameters of the metal film deposited on the silicon probe or/and the refractive index a dielectric sublayer preliminary deposited on the probe, for example, SiO$_2$. In this case, an increase in the magnitude of the electric field enhancement and, consequently, the TERS signal is possible. However, the SiO$_2$ sublayer increases the radius of the tip apex (Fig 1b), that leads to decreasing the spatial resolution.

For TERS experiments, it is necessary to excite effectively the LSPR at the tip apex by focusing the laser light. During the alignment process, the tip apex is scanned with a laser beam and the scattered light from the tip is detected. Fig 1e-k shows the Raman spectra from the tips shown in Figs 1a-d, respectively. All spectra shown in Fig 1e-k have a broad peak, which corresponds to the position of the LSPR. The LSPR energy amounts to 1.78 eV ($\lambda_{\text{exc}}=680$ nm) for the Au-Si probe, 1.85 eV ($\lambda_{\text{exc}}=670$ nm) for the Au-SiO$_2$ probe, 1.815 eV ($\lambda_{\text{exc}}=683$ nm) for the Ag-Si probe, 1.828 eB ($\lambda_{\text{exc}}=678$ nm) for the Au-H probe. TERS measurements of semiconductor nanoobjects (carbon nanotubes and CdSe nanocrystals (NCs)) were obtained for all types of probes. However, the TERS intensity was different for different probes. The AFM and TERS images of a carbon nanotube (for G peak 1591 cm$^{-1}$) on an Au surface, measured simultaneously using Au-SiO$_2$ and Au-SiO$_2$ tips, are presented in Fig 2 a, b, respectively. TERS resolution estimated from Fig.2b is about 10 nm. A typical TERS spectrum of carbon nanotube is shown in Fig.2 c.

Figure 2. a, d – AFM morphology and b, e – TERS images of carbon nanotubes and CdSe NCs on Au nanodisk array, correspondingly, measured simultaneously with Au-SiO$_2$ tip. The TERS images of the carbon nanotubes and CdSe were obtained using the G peak (1591 cm$^{-1}$) and LO phonon mode of CdSe (near 200 cm$^{-1}$). The TERS spectra shown in (c) and (i) are taken at positions indicated by red crosses; g, h, i– AFM, TERS images, and TERS spectra of carbon nanotubes obtained by a Horiba tip are shown for comparison. TERS spectra of carbon nanotubes and CdSe NCs were excited with $\lambda_{\text{exc}}=638$ and 785 nm, respectively. The scale bar is 500 nm (a), 100 nm (d) and 200 nm (g).
Using the same probe an intense TERS signal from longitudinal optical (LO) phonons from CdSe NCs was detected at the wavelength of 785 nm (Fig 2 c-e). NCs were deposited on an array of gold nanodisks with a height of 50 nm.

For the first time, TERS images from CdSe NCs on Au nanodisk arrays were demonstrated and described in detail in [11]. As one can see from Fig. 2d, TERS signal originates predominantly from CdSe NCs deposited on Au nanodisks while the signal from the NCs located between Au nanodisks is significantly weaker. The intensity of the TERS map obtained by the Au-SiO$_2$ probe is approximately three times higher than that for the Au-Si probe (not shown in the figure). TERS images of carbon nanotubes obtained using the Au-Horiba probe (Fig. 2f-m) have comparable intensity with those obtained by Au-SiO$_2$ probe (Fig. 2a-e). The Ag-Si tip also has demonstrated effective TERS enhancement from carbon nanotubes deposited on a gold substrate. However, the plasmon enhancement ability of the Ag coated TERS probe rapidly diminishes over time, despite the thin protective layer of gold. Here, the scattering signal from the tip apex can be an important factor for determining the state of the metal coating of the tip.

4. Conclusion
In this paper, Au- and Ag-coatings of AFM probes were deposited and single metal nanoclusters were formed at the tip apexes. Using these metal tips significant enhancement of Raman scattering from LO phonons in CdSe NCs and G-mode in carbon nanotubes was demonstrated and TERS images from semiconductor nanoobjects were recorded. The LSPR wavelength for tip of the probe with gold coating (formed with or without SiO$_2$ sublayer) and silver coating is determined from Raman spectra of the metal probes. The LSPR position of the probes is significantly changed by varying the parameters of the deposited metal film and affects the TERS performance.

Acknowledgment
The authors gratefully acknowledge financial support from RFBR (Project Nos. 19-52-12041_NNIO_a) and the Ministry of Education and Science of the Russian Federation. SEM studies were performed using the equipment of CKP “Nanostructures”. The authors are thankful to Mr. A.S. Medvedev for metal deposition.

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