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ScienceDirect
Surface Science 602 (2008) 176–181
SURFACE SCIENCE
www.elsevier.com/locate/susc

STM induced light from nontrivial metal structures: Local variations in emission efficiency

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Received 26 April 2007; accepted for publication 1 October 2007
Available online 9 October 2007

Abstract

Scanning tunneling microscopy is performed on a gold surface which is structured on a length scale of 10–100 nm by colloidal lithography and the light emission induced by the tunneling electrons is investigated. The lithographically defined structure is reflected in a contrast in photon emission. It turns out that a major contrast mechanism depends only on the local geometry of the tunnel contact. Remarkable variations in photon images are observed, dark flat areas and bright slopes as well as the inverted case may be obtained upon imaging with different tips. A qualitative explanation for this behavior is proposed.

Keywords: Scanning tunneling microscope; Light emission; Colloidal lithography

1. Introduction

During the operation of a scanning tunneling microscope (STM), a potential difference is applied externally between the tip and the sample. As a consequence, the tunneling of an electron is accompanied by the loss of the energy corresponding to this potential difference. For ensembles of tunnel junctions it was shown that, provided the externally applied voltage is high enough, for some small fraction of the tunneling electrons this energy is converted in photons which can be detected optically [1], the same mechanism was observed for the single tunnel junction formed in an STM [2]. The detectable photon flux depends both on the local coupling of the tunneling electrons to the electromagnetic field via an effective dipole and on the coupling of this local dipole to outgoing radiation. It has been realized that the latter is strongly dependent on the geometry of the tunnel junction: local electromagnetic resonances, today frequently referred to as plasmon resonances, play an important role in this context. Recently, this concept of the coupling of the local electromagnetic field to outgoing radiation and particularly the balance between photons detectable in the far field and photons dissipated locally has been quantified for light emitted by chromophores [3,4].

These resonances have first been discussed in the context of tunneling between small particles [5] and have been termed tip-modes for the case of tunneling from an STM tip [6,7] to a substrate. These strong geometry dependences in photon emission yield, although complicating the overall picture of light emission, represent a highly promising concept for the study of local optical enhancement itself since the volume where the light emission originates is spatially defined to atomic distances. Thus, the tunnel junction may be regarded as a highly localized light source probing the local optical enhancement. The quantitative understanding of the enhancements at nanoscopic geometrical features, is still an experimental challenge in spite of its paramount importance for surface enhanced spectroscopies [8,9], local sensing [10,11] and related applications [12].

This optical enhancement was first theoretically discussed for STM induced light by modeling the tunnel junction as the gap between a metal sphere and a plane metal

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0039-6028/$ - see front matter
doi:10.1016/j.susc.2007.10.009

surface [5]. In this case, incident plane waves at a certain, geometry-dependent wavelength may lead to strong local fields in the gap [13] which due to optical reciprocity [14] is equivalent to enhanced coupling of a local excitation to outgoing photons.

Several refinements led to more sophisticated models of the tunnel gap geometry. Firstly, more realistic tips were discussed. Analyzing paraboidal shapes it was realized that the tip shape both on the local scale and on the scale of some 100 nm plays an important role [15,16]. On these tips, several optical resonances may exist at different wavelengths with widths and enhancement factors that strongly vary with geometry, resulting in photon emission enhancement at the corresponding wavelengths. This finding was experimentally corroborated by the observation of highly different photon emission efficiency for double tips [17]. Asymmetric tips with multiple resonances at several wavelengths have been reported experimentally [18,19] and their light emission properties could be reproduced in a calculation.

If the sample under investigation is not flat, the description of the electromagnetic response requires a full description of the geometry formed by the tip and the surface. From early observations on irregular surfaces it was inferred that "A curved surface emits more than a flat one" [20,21], later emission enhancement at edges was reported as a general feature of STM induced light experiments [22]. Using very carefully sharpened tips to image silver and gold clusters in the range of 0.4–2 nm, a response was obtained [21] that could be satisfactorily modeled by considering a gap between two spheres [23]. On dense particles layers prepared by thermal evaporation of gold, upon imaging with a Pt/Ir tip, a contrast in emission efficiency was reported and interpreted in terms of different local fields along the particle layer [24]. With electrochemically sharpened Pt/Ir tips, gold clusters on graphite were imaged [25] and an asymmetry was found in the photon map that was attributed to the interaction of an asymmetric tip with the metal spheres. Similar effects were observed with a mechanically sharpened Pt/Ir tip on sputter deposited Ag clusters on Si [26].

These experiments were performed on as grown metal crystallites. A logical further step to the understanding of the role of local field enhancements in the photon emission in an STM consists in the preparation of tailored surface topographies. Here, defined edges, protrusions and slopes can be generated and their influence on photon emission can be studied. Olkovets et al. [27] investigated lithographically prepared gold cylinders and ellipsoids on Si. An increased photon emission on random local protrusions was observed but no correlation of the photon emission with the overall shape of the lithographically prepared objects is evident.

In this paper, we report on another experimental study on lithographically prepared metal structures with nontrivial shapes. Firstly, it is shown that photon emission contrast correlates with the structure as it was defined by the lithographic method (precise to roughly 5–10 nm) and not only on the nm-scaled local structure. Remarkably different photon emission maps are obtained with different tips: some typical scenarios are presented and discussed qualitatively.

2. Experiment

In order to generate a defined sample topography, colloidal lithography was employed [28–33]. Standard microscope cover slides were cleaned by repeated ultrasonication in a 2% detergent solution (Hellmanex) and rinsing with purified water (MilliQ). After a final sonication in ethanol, the samples were dried and a 1.5% suspension of polystyrene colloids (Polybead® Select Certified Size Standards, 400 nm, 2.1%; Polysciences Inc., USA) was applied to the surface and dried under ambient conditions. In some regions of the sample a colloid monolayer was formed. Gold with a nominal thickness of 30 nm was thermally evaporated on the sample, then the colloids were removed by rinsing with tetrahydrofuran and subsequent ultrasonication in ethanol. Finally, a second gold layer (nominal thickness 15 nm) was evaporated on the sample. The resulting surface topography is a regular pattern of roughly triangular elevated areas, referred to as 'nanotriangles' [12].

Two different kinds of probes were used. Pt/Ir tips were prepared by mechanically cutting a Pt/Ir-wire (PT673610, Advent Research Materials Ltd., GB). As a basis for the preparation of gold tips, an optical fiber (DCF SSP5155-125/250, Mitsubishi Cable Industries, Ltd., Japan) was used. After removal of the coating the fiber was etched consecutively in NH_4:HF:H_2O solutions with volume ratios of 1.7:1:1 and 10:1:1, respectively. Each etching was done for 100 min. The first solution with a higher concentration of HF reduces the fiber diameter to about 30 μm. The second solution containing less HF predominantly removes the silica glass cladding while the Ge-doped core is etched much slower. This results in a sharp core tip on the flat cladding end [34] with a radius of curvature of typically 50–150 nm and a roughness of the glass of below 10 nm. These tips are coated by an optically thick gold film by thermal deposition of 6 nm Cr and 120 nm Au. During evaporation, the tip is rotated about its symmetry axis which is oriented at an angle of 45° relative to the direction of the incident gold beam. The resulting gold coating is composed of crystallites with a typical size of 30–100 nm.

A homebuilt inverted STM [35] with a tunneling tip approaching the sample from the lower side and a commercial controller unit (SPM 1000, Fa. RHK Technologies, USA) was used under ambient conditions. The setup owns the advantage that an oil-immersion (Immersol® 518F, Zeiss, Germany) objective with a high numerical aperture (NA = 1.4, 60×, Nikon, Japan) can be used to collect the photons which are mainly emitted to the higher refractive index material [36]. Photons were recorded with a photomultiplier (H7421-40, 40% quantum efficiency at a light wavelength of 580 nm, Fa. Hamamatsu, Japan).