# Prism-Coupled Scanning Tunneling Microscope Light Emission Spectroscopy

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# 論文内容要旨

The invention of scanning tunneling microscope (STM) by Binning and Rohrer in early 1980's has revolutionized the field of microscopy and found immediate wide spread applications in surface studies of semiconductors and metals. The atomic resolution capabilities of STM made possible the real space imaging of conducting and semi-conducting surfaces down to the atomic scale and allowed direct visualization of individual atomic or molecular adsorbates. In spite of all these capabilities, STM bears the disadvantage of not being able to identify the nature of the atomic or molecular species being manipulated by it. The efforts to develop a technique to study the nature of surface species appearing in STM images resulted in the introduction of STM light emission (STM-LE) spectroscopy. STM when coupled with light emission spectroscopy not only allows the determination of surface topographic imaging, but also the characterization of chemical, electronic and optical properties of surfaces of metals with atomic-scale spatial resolution. By correlating the observed light emission spectra with the size and shape of the structures determined by STM, information about the individual nanostructures may be obtained.

An important application of STM-LE might be in the study of molecular layer covered metal substrates. The study of molecular monolayers on metal surfaces has developed rapidly in the viewpoint of applications in electronic devices. Recently, tunneling has been identified as the main conduction mechanism for alkanethiol self-assembled monolayers (SAMs) formed in a nanometer-scale junction. Key to understanding electron transfer is the ability to make quantitative measurements on single molecules, their features, and components.

STM-LE will be a very useful tool to study the SAM films, but it inherently suffers a problem of weak signal owing to the low efficiency of excitation by electron tunneling. Moreover, inelastic tunneling probability drastically decreases with an increase in tip-sample gap distance. When metal substrate is covered by a molecular layer, it causes an increase in the barrier thickness between tip and sample which is followed by a decrease in inelastic tunneling probability in the relevant visible spectral range. Thus it further adds to the difficulty of detecting an already weak signal. The techniques employed so far for overcoming this difficulty have mainly concentrated on optical means to improve the efficiency of light collection, e.g., light collection using an elliptical mirror, a fiber bundle, a multiple-fiber system or a conductive transparent STM tip. In spite of all these efforts, a satisfactory signal-to-noise ratio still remains unresolved.

In the current study we consider a different method to enhance the signal level. It is well known that the STM-LE from metallic samples is radiated by localized surface plasmons (LSPs) excited by tunneling electrons. Even though surface plasmon polaritons (SPPs) are simultaneously excited, they scarcely contribute to the signals in the conventional STM-LE measurements. This is because of the existence of a wave vector mismatch between SPPs and light propagating in the vacuum. This mismatch prevents coupling between them on flat surfaces. Prism-coupled STM-LE geometry may eliminate the wave vector mismatch. In this configuration, a metal thin film is deposited at the bottom of a hemispherical glass prism. Since the light propagating in the glass has a wave vector whose magnitude is larger than that of SPPs localized at the metal-air interface, its wave vector component parallel to the interface can be matched to that of SPPs by adjusting the propagation angle of the light. SPPs become radiative with the adjusted angle on the prism side. The signal level of STM-LE is thus expected to enhance owing to the contribution of SPPs by utilizing the prism-coupled STM-LE.

It must be emphasized that for STM-LE spectroscopy, it is not the signal level only but also the attainable spatial resolution, which are important. Spatial resolution depends on types of sample materials targeted and functioning mechanisms of STM-LE. Electromagnetic spatial resolution of the tip-side emission is given by lateral sizes of LSP. The prism-side emission is caused by not only LSP but also SPP localized at the sample surface. It is important to understand whether electromagnetic spatial resolution of prism-side emission is given by lateral sizes of LSP or by propagation lengths of SPP. If SPP is directly excited by electron tunneling, the latter would apply. In this case, the prism-side emission is inappropriate for nanometer-scale investigations of surfaces because propagation lengths of SPP are a few hundred nanometers in the visible spectral range. Therefore the current study also focuses on the spatial resolution of STM-LE in prism-coupled geometry.

**The purpose of the present work is to develop a technique for the study of organic layer covered metallic surfaces by improving the light emission from scanning tunneling microscopic (STM) process.**

In order to achieve this goal, prism-coupled geometry was employed to improve the signal level of STM-light emission process. The prism-coupled STM-LE geometry was examined both theoretically and experimentally. In this geometry, metal film was deposited on the flat bottom of a hemispherical prism, and the STM light emissions from the tip-sample gap into the vacuum (tip-side emission) and into the prism (prism-side emission) were measured. The theoretical calculation was based on the dielectric theory of STM-LE. Tunneling current is modeled by an oscillating current source with the inelastic tunneling spectrum given by:

$$|I(\omega)|^2 = \frac{2me^2}{h^3}\left[(eV-\hbar\omega)\int_0^{\varepsilon_F-(eV-\hbar\omega)} dE_x \exp\left\{-\int_0^1 dx\left[K(x)+Q(x)\right]\right\} + \int_{\varepsilon_F-(eV-\hbar\omega)}^{\varepsilon_F} dE_x(\varepsilon_F - E_x)\exp\left\{-\int_0^1 dx\left[K(x)+Q(x)\right]\right\}\right]$$

Tip is modeled as sphere and sample as a flat substrate. Then, electric filed in the tip-sample gap region (i.e., near-field) is calculated using the Poisson equation (neglecting the retardation). We call this localized field as "localized surface plasmons (LSP)." LSP can be equivalently replaced by a dipole. The radiation from the dipole is calculated on both tip and prism sides by solving the Maxwell equation. The parameters input to the calculation are the radius $a$ (100 nm) of the curvature of the tip

front, the thickness of the Au substrate $t$ (40 nm), the tip-sample gap distance $d$ (1 nm), the work and dielectric functions of the tip and the sample materials, and the dielectric function of prism (BK7). First of all, the angle dependence of STM-LE intensity both for the tip- and prism-side emission was calculated respectively. The angle dependence calculations clearly indicates that the tip-side emission is almost independent of the emission angle, on the other hand prism-side emission is strongly dependent on the angle of emission. The strength of emission near the vicinity of 43° is around 20 times or larger than that of the tip-side. Then the theoretical spectra for the emission angles θ i.e., the spectra for θ = 75° (tip-side emission) and θ = 43° (prism-side emission), was calculated respectively. The spectrum of the tip–side emission has a single peak at a photon energy of 2.1 eV, showing that the resonance energy of LSPs confined in the gap between the tungsten (W) tip and Au film sample is 2.1 eV. The spectrum of the prism-side emission has a peak at a photon energy of 1.8 eV and a shoulder at a photon energy of 2.1 eV. The photon energy of the shoulder position agrees with the resonance energy of LSPs, showing that LSPs contribute to the prism-side emission but this contribution is not dominant. As previously reported, the wave vector of SPPs localized at the Au film surface matches that of light propagating in the prism with θ = 43° at a photon energy of approximately 1.8 eV. The total intensity of the prism-side emission is approximately 32 times larger than that of the tip–side emission. Hence, the theoretical calculations based on the dielectric theory of STM-LE predicted that the prism-side emission can be much stronger than the tip-side emission for the specific emission angle of 43°. Theoretical analysis also revealed that this enhancement of emission intensity is caused by the SPPs localized at the Au surface which becomes radiative on the prism side. This light emission from SPPs results in an increase in the signal intensity on the prism-side. As there is no SPP signal on the tip-side, the light is only from LSP and thus very weak.

Figure 1 shows the experimental setup employed to measure STM-LE in the prism-coupled geometry. Two types of samples were prepared. One is a bare Au film and the other is a Au film covered with alkanethiol SAMs. The Au film was evaporated onto a thin glass slide in a high vacuum ($2\times10^{-6}$ Torr) for both of the samples. The Au film thickness $t$ was determined to be 40 nm by ellipsometry. To prepare the sample covered with alkanethiol SAMs, the Au-evaporated glass slide was immersed in a 1 mM ethanol solution of butanethiol ($C_4H_9SH$), octanethiol ($C_8H_{17}SH$), and dodecanethiol ($C_{12}H_{25}SH$) for approximately 24 h at room temperature. Following the preparation process, the sample was pasted to the flat bottom of the hemispherical prism made of BK7 using an index-matching oil. The STM tip made of W was prepared by electrochemical etching. The radius $a$ of curvature of the tip front was determined to be 100 nm by scanning electron microscopy. The STM head shown in Fig. 1 was set over a rotation stage with the tip front over the rotation axis, which enabled us to detect STM-LE

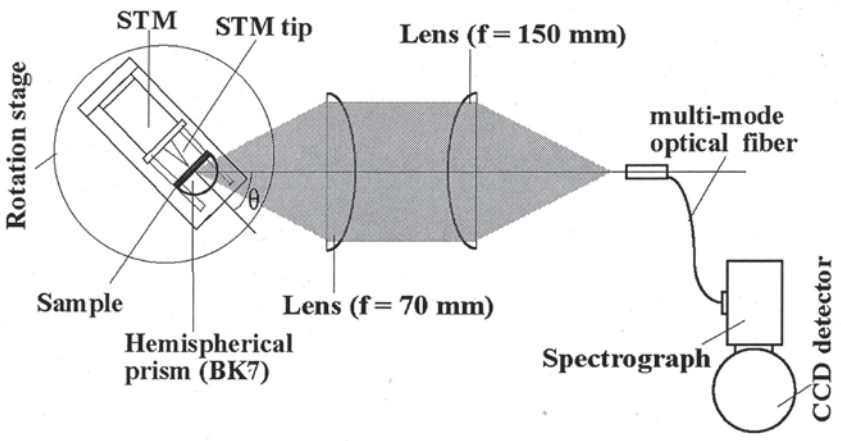


**Figure 1** Schematic of experimental setup for STM–LE measurements in the prism–coupled geometry.

as a function of emission angle θ measured from the sample surface normal. The light emitted from the tip-sample gap in the direction of θ was collected by a lens with a focal length $f = 70$ mm and was focused by a lens with $f = 150$ mm onto the entrance surface of the optical fiber with a core diameter of 1 mm. The light was then guided by the optical fiber to the spectroscopic system consisting of a spectrograph and a liquid-nitrogen-cooled charge-coupled device (CCD). The experimental spectra were taken for STM biasing conditions of 2.5 V and 2 nA with an exposure time of 500 s. The dark signals were subtracted from each experimental spectrum. All the experiments were carried out in air.

The experimental STM–LE spectra were measured for the emission angles $\theta$ corresponding to those for the theoretical calculations i.e., the spectra for the bare Au film for emission angles of 75° (tip–side emission) and 43° (prism–side emission), respectively. Despite the fact that both emissions are excited by the *same* electron tunneling, notable differences in total intensity (i.e., photon-energy integrated intensity) and spectral peak position are observed; the total intensity ratio of the tip-side emission to the prism-side emission is approximately 1:8, and their spectral peaks are positioned at 1.8 and 2.0 eV, respectively. Thus, it can be concluded from the above discussion that the theoretical predictions were confirmed experimentally.

Next, the spatial resolution of STM-LE in a prism-coupled configuration has been probed using a finite difference time domain analysis. It was revealed that the spatial resolution of the prism-side emission was controlled by the lateral size of LSP similar to the conventional STM-LE and not by the propagation lengths of SPP. Thus, it can be conclude that by using the prism-coupled configuration, signal levels of STM-LE improve without loss of spatial resolution attained in the tip-side emission. Hence, the targeted sample structure can be investigated with intended spatial resolution by the prism-coupled STM-LE.

Finally, prism-coupled STM light emission spectroscopy was applied to study STM-LE from alkanethiol self-assembled monolayer (SAM) covered Au film. STM light emissions both for tip- and prism-side were measured. It was found that light through the prism was successfully detected by virtue of the enhancement of the prism-coupled geometry; on the other hand, no signal was detected from the tip-side. The peak intensity was decreased with an increase in the thickness of the covering layer. It was also observed that the cutoff energy of STM-LE spectra shift towards the lower energy side with an increase in the thickness of the SAM film. Various types of models were discussed and analyzed to understand the mechanism of cutoff energy shift. The tip-sample gap structure for each alkanethiol covered Au sample was determined by the *I-z* measurements. On the basis of the gap structure, it is conclude that the red shift is caused by the antenna factor combined with the dielectric function changes at the Au-S interface, which is induced by the adsorption of S on Au.

# 論文審査結果の要旨

シリコンをベースとした大規模集積回路は過去数十年にわたり情報化社会の高度化を支え続けてきた。しかし、更なる微細化への限界が見え始め、新しい材料や動作原理に基づく次世代デバイスの研究が活発になされている。このような研究において特徴的であるのは、当初から高い集積度が求められることであり、デバイス開発と並行してナノスケールでの材料物性評価も重要となる。走査型トンネル顕微鏡（STM）発光は試料と探針間の電子トンネルにより励起される発光であり、そのスペクトル中には探針直下の材料の多様な局所物性が強く反映されるため、有力な局所表面分析法として認識されている。しかし、微弱なトンネル電流で励起される発光は基本的に弱く、この分光法を多様な材料の評価に展開するためには、発光効率の向上が強く求められている。著者は半球プリズムの平坦な底面に試料を配置し、プリズム側に放射されるSTM発光の特性を詳細に研究した。本論文はこれらの成果をまとめたもので、全編5章よりなる。

第1章は序論であり、本研究の背景ならびに目的について述べている。

第2章では、プリズム結合型STM発光の理論予測と実験結果について述べている。プリズム結合型とすることにより、従来の計測配置の場合に比べ1桁以上の発光効率の向上が期待されることを理論的に予測し、実験により確認している。さらに、発光スペクトルの解析から、効率向上をもたらす機構は試料表面に局在する表面プラズモン・ポラリトン（SPP）がプリズム中で発光性になることであると結論している。

第3章では、プリズム結合型STM発光の位置分解能について検討している。SPPの伝搬距離は数$\mu$mにも及び、プリズム結合型STM発光分光の位置分解能がこの距離により決められていたとするならば、この配置はナノメートルの位置分解能での計測には不適切になる。試料と探針の誘電関数を考慮した有限差分時間領域（FDTD）法によりSTM発光スペクトルを詳細に解析し、位置分解能は、SPPの伝搬距離ではなく、試料と探針の間隙に局在した局在プラズモン（LSP）の空間的広がりにより決定されることを見いだした。このことは、プリズム結合型STM発光分光においてもナノメートルの位置分解能が得られることを意味し、ナノ構造物性解析への応用上極めて重要な知見である。

第4章では、アルカン・チオール自己組織化単分子膜で覆われた金表面（SAM-Au表面）試料系への適用について述べている。STM発光が観測されるもっとも高い光子エネルギーはカットオフとよばれ、通常の金属試料の場合にはSTMのバイアス電圧で決まる。しかし、SAM-Au表面の場合にはアルキル鎖長に比例して低エネルギー側にシフトすることを初めて見いだしている。この発見は発光効率の向上による高い信号-雑音比でのスペクトル計測により可能になった。カットオフのシフトをもたらしている機構について詳細に検討し、2つの誘電応答が複合的に関与していると結論している。すなわち、金表面へのイオウ原子の化学吸着により誘起される電子遷移に起因する強い周波数依存性を有する誘電応答と周波数依存性の弱いアルキル鎖の誘電応答が重畳してLSPの共鳴エネルギーを低エネルギー側にシフトさせたというものである。これらの知見は、分子電子工学やナノフォトエレクトロニクスにとって重要かつ有用である。

第5章は結論である。

以上要するに本論文は、プリズム結合型STM発光分光法の開発に関わるものであり、動作特性を理論的に解明するとともに、その有用性を実証する結果を得たものであり、計測工学および電子工学の発展に寄与するところが少なくない。

よって、本論文は博士(工学)の学位論文として合格と認める。