# Tip-enhanced Raman scattering microscope using quartz-tuning-fork AFM probe

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Tip-enhanced Raman scattering (TERS) microscopy is one of the powerful scanning probe microscopy, which enables Raman analysis at nanoscale beyond the diffraction limit of light [1]. Applications by using TERS microscopy to a variety of samples, such as carbon materials, semiconductors and bio-molecules, have been reported. Typically, the distance between the metal tip and samples are controlled by contact-mode atomic force microscopy (AFM) to obtain the sufficient Raman enhancement in a moderate exposure time. However, the contact-mode AFM can limit the range of applications. It is difficult to measure samples which are soft or unfixed on a glass substrate, because the tip can damage or drag the sample. Moreover, a laser beam which is used to detect a cantilever deflection can interfere with Raman measurements in visible wavelengths. We believe that the introduction of advanced AFMs can expand the applications and contribute to commercialization.

Here, we present a TERS microscope using a quartz-tuning-fork (QTF) AFM probe. The QTF is known as one of the probes for frequency-modulation (FM-) AFM [2]. The QTF has a much higher spring constant (> $10^3$ N/m) than that of the Si cantilever, which realizes an extremely small oscillation amplitude (< 1 nm) in dynamic-mode operation. The dynamic-mode operation enables us to measure soft or unfixed samples. The small amplitude below 1 nm contributes to obtain the Raman enhancement as high as that obtained by the contact-mode AFM operation. Moreover, the QTF has piezoelectricity, and thus the oscillation of the QTF is detected by electrical signals. This non-optical detection scheme does not affect Raman measurements, and is easy to be handled by users.

We have developed a TERS probe shown in Figure 1. An oxidized Si cantilever whose tip is coated by silver nanoparticles is attached on the end of the QTF. The ensemble of the metal nanoparticles has been shown to work as an optical antenna leading to the strong Raman enhancement [3]. The QTF is controlled by a home-made FM-AFM with the amplitude of below 0.8 nm. A home-made Raman microscope is combined with the FM-AFM, and TERS experiments were performed.

First, we report a result taking advantage of the use of the QTF-FM-AFM. The Q-factor of the QTF is quite high (~10000) even in ambient condition, thus the force between the tip and samples is preciously measured as the resonance frequency shift $\Delta f$ of the QTF. The relationship between TERS spectrums and the force is an interesting topic, because the tip might induce strain in the sample [4]. Therefore, simultaneous measurements of TERS spectrums and the force are quite informative. We measured TERS spectrums and the $\Delta f$ simultaneously, changing the tip-sample distance $z$. Semiconductor single-walled carbon nanotubes (CNTs) are employed as the sample, and excited by a laser of wavelength $\lambda$=488 nm. As a result, the G band intensity $I$ showed an exponential increase as $z$ approached to 0. Notably, the distance $z$ showing the increase of $I$ corresponded to $z$ at which the $\Delta f$ switched from a negative to a positive value. This means that the effective Raman enhancement is expected when the tip approaches to $z$ at which a repulsive force acts between the tip and the sample. Moreover, we observed difference in the distance dependence of $I$ between $G^+$ and $G^-$ modes [5]. The simultaneous measurements of TERS spectrums and the force can be a new method to study material properties. In addition, although our CNTs are not fixed on the substrate, we have succeeded to observe TERS images of $G^+$ band intensity with a spatial resolution of approximately 16 nm.

Our TERS microscope is now extended for experiments using deep-ultraviolet (DUV) light. We expect that a DUV-TERS microscope is useful for studying bio-molecules or wide-gap semiconductors at the nanoscale, because a resonant Raman scattering is expected due to the absorption in the DUV region. As a preliminary result, we have succeeded to observe DUV-TERS spectrums on a monolayer graphene by using an aluminum tip excited by a laser of wavelength $\lambda$=266 nm. The details are shown in the presentation.

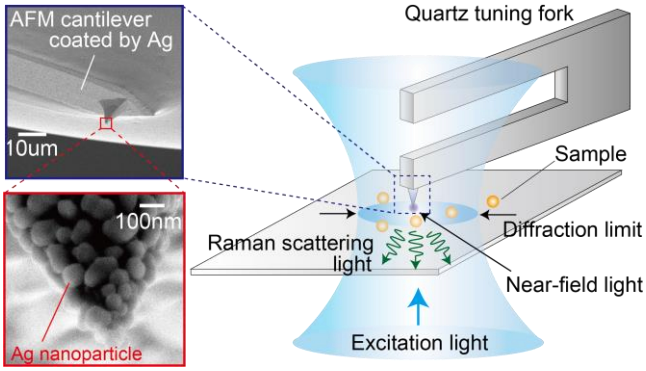


Fig.1: Our TERS probe using a quartz-tuning-fork.

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