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Low-temperature, ultrahigh-vacuum tip-enhanced Raman spectroscopy combined with molecular beam epitaxy for in situ two-dimensional materials’ studies

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Tip-enhanced Raman spectroscopy (TERS), which combines scanning probe microscopy with the Raman spectroscopy, is capable to access the local structure and chemical information simultaneously. However, the application of ambient TERS is limited by the unstable and poorly controllable experimental conditions. Here, we designed a high performance TERS system based on a low-temperature ultrahigh-vacuum scanning tunneling microscope (LT-UHV-STM) and combined with a molecular beam epitaxy (MBE) system. It can be used for growing two-dimensional (2D) materials and for in situ STM and TERS characterization. Using a 2D silicene sheet on the Ag(111) surface as a model system, we achieved an unprecedented $10^9$ Raman single enhancement factor in combination with a TERS spatial resolution down to 0.5 nm. The results show that TERS combined with a MBE system can be a powerful tool to study low dimensional materials and surface science.

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I. INTRODUCTION

Raman spectroscopy is a powerful, nondestructive technique for investigating the vibrational properties of molecules and solid materials. However, the very small Raman scattering cross section, about $10^{-28}$-$10^{-30}$ cm$^2$ per molecule, makes trace detection very challenging.1,2 The adsorption of molecules on a coarse or nanostructured metal surface can result in remarkable enhancement of the Raman signal by localized surface plasmon resonance, known as surface-enhanced Raman spectroscopy (SERS).3 However, the spatial resolution of SERS is still limited by the light diffraction or the nanoparticle size.4,5 In contrast, tip-enhanced Raman spectroscopy (TERS) utilizes an atomically sharp scanning probe microscope (SPM) tip to enhance the Raman signal in a more controllable manner, with a well-characterized tip and tip-surface separation. Since the first TERS experiment reported in 2000,6–8 it has attracted great attention from different research fields. Theoretically, the electromagnetic enhancement factor can exceed $10^9$ in TERS,9,10 which, combined with the resonance Raman enhancement and chemical effects, can result in a total TERS enhancement factor as high as $10^{12}$.4,11 Such high enhancement provides TERS with single molecule sensitivity, capable to retrieve the chemical fingerprint of a single molecule underneath the tip while observing its structure by SPM. However, early TERS experiments were mostly conducted in ambient condition and at room temperature (RT), with the typical spatial resolution being 10-50 nm, in the same order with the spatial extent of localized surface plasmons.12–15

The environmental contamination results in unstable instrumental performance, strongly limiting its application.

Ultrahigh-vacuum (UHV) is a prerequisite for TERS to perform well-defined experiments on a pristine substrate surface. In addition, it prevents the degradation of the plasmonic metals, including the tip and substrate, from oxidation and absorbing contaminations. It was until 2008 that the first single-molecule TERS was performed by Steidtner and Pettinger in an UHV-TERS, combined with simultaneously scanning tunneling microscopy (STM) images.12 In addition to ultrahigh-vacuum, low temperature (LT) is also critical for high-performance TERS. Spectra bleaching and blinking are usually unavoidable at RT16–18 due to the molecule desorption, diffusion, and unstable adsorption configuration on the substrate. The blinking behavior had been used as evidence of single molecule TERS, when direct imaging of the individual molecule was not possible.4,18,19 while with LT STM, it is possible to resolve individual molecule in high-resolution STM images simultaneously when acquiring the TERS spectrum, thus enabling a direct correlation between the single-molecule geometry and its Raman spectrum.20,21 Recently, remarkable improvements in the spatial resolution have been achieved down to the sub-nanometer scale, allowing TERS to image the inner chemical structures of a single molecule and carbon nanotube via LT-UHV-STM on Ag(111) surfaces.21,22

So far, very limited LT-UHV-TERS instruments with high performance have been demonstrated.20,21,23 Moreover, most high resolution TERS experiments have been demonstrated with organic molecules or carbon nanotubes. With the emerging two-dimensional (2D) materials in recent years, it is of great interest to study the atomic scale TERS spectra of these...
materials, such as the local vibrational properties of single-atom defects, dopants, and domain boundaries. However, *in situ* growing 2D materials is more challenging than adsorbing organic molecules on a surface. It usually requires the integration of a molecular beam epitaxy (MBE) system into the LT-STM-TERS system without affecting the performance of the STM-TERS, which is nontrivial. Here, we report on our originally designed TERS system based on a homemade LT-UHV-STM system, which is combined with a MBE system for *in situ* growing 2D materials. The system has demonstrated high performance in studying low dimensional materials, such as silicene, silicon nanoribbons and cluster, and borophene on a silver surface.\(^{24–26}\) A TERS enhancement factor of \(10^9\) and a 0.5 nm spatial resolution have been achieved, which are among the best records so far.\(^{21–24,27,28}\)

II. EXPERIMENTAL SETUP

A. The LT-UHV-STM system

Figure 1(a) shows an overview of our homemade experimental setup. It contains three vacuum chambers: (1) a tiny fast load-lock chamber, through which the sample or tip can be loaded into the UHV chamber without breaking the UHV, (2) a molecular beam epitaxy (MBE) chamber, where 2D materials can be grown *in situ* for STM and Raman characterization, and (3) the LT STM chamber, where STM topography imaging and the scanning tunneling spectroscopy (STS) measurements are performed. The top part of the STM chamber is a homemade, double-Dewar UHV cryostat, where a home-designed, Pan-type STM head was mounted on the bottom of the cryostat. Depending on the cooling agent, the STM can work at liquid nitrogen (78 K) or liquid helium (4 K) temperature. All the experiments in this paper were performed at liquid nitrogen temperature. The main chambers (STM and MBE) have a base pressure of \(2.0 \times 10^{-10}\) mbar.

In conventional STM setups, spring suspension and eddy current damping are usually needed to isolate the STM scanner from environmental noise. However, we designed our STM scanner without spring and eddy-current damping, and the STM scanner has a hard-contact to the cryostat [Fig. 1(b)]. We designed this specifically for two reasons: First, considerable space can be reserved for installing lens and piezoelectric motors to drive the lens for focusing. Second, a direct contact to the cryostat can significantly improve the efficiency of heat exchange between the STM scanner and the cryostat, thus stabilizing the scanner temperature and reducing the thermal drift due to laser illumination (about 0.3 nm/h at 78 K). To compensate for the insufficient noise isolation in the STM scanner part, we designed three-level damping system outside the STM chamber. First, the inner Dewar is connected with the outer Dewar through a welded bellow on the top and supported by three legs sitting on soft rubber blocks, as shown in Fig. 1(b). This is like hanging the whole inner Dewar with spring from the outside. Second, the system frame is supported by four air legs, and third, the whole system is placed on an 8-ton concrete platform, which is inside a 3-m-deep hole in the basement, and supported by four pneumatic feet and isolated from the ground. The three-level damping system effectively isolated the mechanical noise coming from the ground. Apart from mechanical isolation from the ground, a shielding room was built to block the acoustic noises from surroundings, with pyramid-shape, sound-absorbing sponge covering the inner walls of the room, as shown in the photograph in Fig. 1(c). The STM and Raman electronics were all placed outside the shielding room to leave a quiet and dark environment for the system. Apart from the external damping systems mentioned earlier, the STM head was also designed to have a tiny and rigid body. After these optimizations, the STM can reach a high stability with a mechanical noise below 1 pm.
The STM tip and sample can be optically accessed through two viewports (V1 and V2). The Raman optics is coupled to STM through the viewport V1. The optical parts of the Raman system were arranged in a dark box and fixed on the system frame [Fig. 1(a)] and connected with the laser and spectrometer through fibers. A telescope was installed outside viewport V2 to monitor the positions of the tip and sample for STM coarse approaching, as well as for adjusting the position of the laser spot on the tunneling junction, as shown in Fig. 1(a).

B. The optical part

Combining the Raman optics with a LT-UHV-STM system is challenging. To date, only a few groups have introduced TERS into UHV systems\(^{29-31}\) and even less have achieved the LT-UHV-TERS with a desirable performance.\(^ {20,21,23}\) Because of the limited space around the STM scanner, side illumination with a lens of long focal length is often used; thus, the numerical aperture (NA) is unavoidably decreased.\(^ {30}\) Moreover, an effective mechanism to align the laser onto the tip apex accurately and confocal with the collective Raman light is particularly important and difficult.

In our setup, the optical path mainly contains three parts: (1) the aspheric lens and the 3D piezoelectric motor to drive the lens inside the UHV chamber, (2) the optical part in the dark box outside the UHV chamber, and (3) the laser and the spectrograph system. The schematic of the optical path for the TERS setup was illustrated in Fig. 2(a), and the optical part in the dark box in Fig. 1(a) was shown in the dashed blue line box. A linear p-polarized 532 nm laser (Cobolt, Sweden) was connected to the optical part through a single mode polarization-maintaining fiber and became the collimated beam (diameter about 1 mm) with a fiber collimator. The laser was then introduced through a laser line filter to remove the stray light and passed through a half wavelength plate to achieve a polarization direction along the tip shaft. The laser was expanded through a 5× beam expander and focused onto the junction by the in situ aspheric lens (Edmund optics), which is 25 mm in diameter, with a working distance of 24.17 mm (focal length 30 mm), and NA of 0.42. The lens was mounted on a homemade 3D piezoelectric motor, which can move in the x, y, and z directions in a range of ±4.5 mm, with a precision less than 100 nm. The scattered light was collected in a backscattering configuration through the same lens and then passed through two edge filters to remove the residual laser light, collected by an achromatic lens and coupled into a multimode fiber. The scattered light incidents into the spectrograph through a slit and is dispersed by a grating (1200 grooves/mm) and then detected by a liquid nitrogen cooled CCD with a spectral resolution of 1.6 cm\(^{-1}\) (Princeton Instrument, SP2300i). The slit width is 200 µm for all the experiments presented in this paper.

After the alignment of the external optical path, we focus the laser onto the junction by fine controlling the lens position by the 3D motor. The tip and the focused laser spot can be monitored in situ through a video camera by a beam splitter (BS, with a 10:90 reflection transmission ratio) to separate tenth white light for imaging, which can give a clear tip (down) and its mirror (top) image with laser illuminated on the junction, as shown in Fig. 2(a). It also maintains a high efficiency since 90% Raman signal can transmit the BS and be collected. Compared with the other side-illuminated LT-TERS setups, our design has an in situ high NA lens inside the UHV chamber in contrast to Van Duyne’s design where all optics are outside the chamber\(^ {20}\) and Dong’s design where an oblique tip-sample system forms;\(^ {21,22}\) thus, the scanner stability is largely improved.

C. Preparation of Ag tips

The STM tip plays a crucial role in STM imaging and TERS measurement. The material, size, and shape of the tip apex strongly influenced plasmon resonance in the tip-sample nanocavity. Ag and Au tips, with their appropriate dielectric response at the visible region, have been widely used in TERS experiments. Especially, Ag is so far the best material for TERS spectroscopy in the visible range and for STM-induced electroluminescence in UHV systems.\(^ {32-34}\) Au is more suitable for red laser systems and favorable in air for its inertness.\(^ {32}\)
A high-quality TERS tip usually has a sharp end and smooth surface to reduce the laser scattering and unexpected hot spots on the tip shaft.\textsuperscript{35,36} A sharper tip gives a higher enhancement and a better spatial resolution. Compared with Au and W tips, chemically etched Ag tip with reproducible high quality is still a challenge.\textsuperscript{32} Here, we improved the fabrication method by single step etching of a Ag wire (Alfa Aesar, 99.9985%, 0.5 mm), with perchloric acid and ethanol solution in a 1:4 volume ratio.\textsuperscript{37} It is notable that using a Pt-Ir ring as the cathode is not preferred since it results in dirty etching products easily attached to the tip surface. Instead we use a U-type glass cathode is not preferred since it results in dirty etching products easily attached to the tip surface. Instead we use a U-type glass tube as the etching cell, which is more easily attached to the tip surface. Instead we use a U-type glass tube as the etching cell, which is more

**III. RESULTS AND DISCUSSIONS**

**A. STM imaging and in situ Raman spectroscopy**

We examined the STM performance and the optical efficiency at the liquid nitrogen temperature using a Si(111) surface prepared in the MBE chamber. Figure 4(a) shows a STM image of a Si(111)-(7 × 7) surface, we can see a clear atomic resolution with low noise. The Raman spectrum of the Si(111) sample was shown in Fig. 4(b), with an acquisition time of 1 s and the laser power at 10 mW. It shows that our setup has a high collective efficiency with the aspherical lens inside the UHV chamber, and the second order (2TO) Raman peak of Si(111) can also be observed clearly.

The normal Raman spectrum of monolayer silicene on Ag(111) was measured as a model system, as shown in Fig. 4(d). The signal-to-noise ratio is acceptable even though the signal is very weak from such a monoatomic layer film. While there are two coexisting, ordered silicene phases (4 × 4 and √3 × √3) on the Ag(111) surface [Fig. 4(c)], it is impossible to distinguish the two phases by the normal Raman spectrum due to the µm size of the laser spot. In addition, the Raman mode at about 300 cm\(^{-1}\) and 440-480 cm\(^{-1}\) is usually attributed to amorphous silicon.\textsuperscript{38} In our in situ TERS experiments, these modes all can be detected in the well-defined silicene structures, as will be discussed later.

Before TERS experiments, the optical property of the Ag tip also can be examined by STM induced luminescence (STML) on the Ag(111) surface [Fig. 4(e)]. It shows a bias-voltage dependent behavior, with a threshold voltage and the strongest luminescence at a moderate bias voltage,\textsuperscript{39} as shown in Fig. 4(f). The electroluminescence is attributed to the radiative decay of the plasmon through inelastic tunneling excitation. Its energy can be tuned into resonance with the Raman scattering light by in situ voltage pulsing the tip on a bare Ag(111) substrate surface, thus giving a strongest enhancement of the Raman signals.\textsuperscript{21}

**B. TERS enhancement factor and spatial resolution**

A monolayer silicene film epitaxially grown on the Ag(111) surface was used as a model system to show the performance of our TERS setup. Figure 5(a) shows a gap-distance dependent TERS spectra of the silicene √3 × √3 phase. One can see that the A\(^1\) and A\(^2\) modes are largely enhanced when the tip is close to the silicene surface, and the E mode which is the dominant peak in the normal Raman spectrum [Fig. 4(d)] becomes insignificant. In addition, there are additional peaks appearing at ∼300 cm\(^{-1}\), 440 cm\(^{-1}\), and 480 cm\(^{-1}\) when the gap is small enough.\textsuperscript{24} It illustrates that the peaks are inherent properties of silicene structures rather than from amorphous silicon.\textsuperscript{38}

Figure 5(b) shows the pure near field and far field Raman spectra of silicene, with different acquisition time. The intensity of near field Raman signal (I\(_\text{near}\)) is about 10\(^2\) times enhanced compared with the time-normalized far field A\(^1\) mode intensity (I\(_\text{far}\)). The TERS spatial resolution is as high as 0.5 nm, with a 10%-90% intensity contrast of the A\(^1\) mode, as shown in Fig. 5(d). The A\(^1\) mode TERS intensity profile along the blue dot line follows the abrupt morphology change. The TERS enhancement factor (EF) can be estimated by \(EF = I_{\text{near}}/I_{\text{far}} \times A_{\text{near}}/A_{\text{far}}\), where A\(_{\text{near}}\) is the area contributed to the near field signal, which is set as a circular area 2 nm in diameter based on the sub-nanometer TERS resolution. A\(_{\text{far}}\) is the size of the focused laser spot (about 12 µm in diameter),
and C is the silicene coverage on Ag(111), being 0.6 ML in the present measurement. The estimated EF is as high as $2 \times 10^9$. It is notable that the thus estimated EF is in general an underestimated value, since the laser spot is usually larger than that estimated by the geometric configuration, due to the spherical and chromatic aberrations of the single lens system, unavoidable under or over focusing, and slight off-axis of the incident laser. For a similar configuration from Dong’s group (NA = 0.44), the diameter of the focus laser spot was estimated to be 100 µm; thus, $A_{\text{far}}$ is about $10^2$ times larger than ours.²²

By subtracting the far field signals, the enhancement here is a pure physical enhancement contribution, which can be considered as the fourth power of the electric field enhancement.³ We have simulated the electric field distribution at the nanogap. The curvature radius of the Ag tip apex is set to $R_{\text{tip}} = 40$ nm (according to the typical SEM picture of the Ag tip). The gap distance between the tip and Ag surface is 1 nm, typical for a STM tunneling gap.⁴⁰ The fourth power of the electric field component in the z direction $|E_z|^4$ at the nanocavity is enhanced more than $3.5 \times 10^9$, as shown in Fig. 5(e).

While the electric field component in the x-y plane $|E_{xy}|^4$ is only $10^7$ enhanced, which is negligible compared with the $10^7$ area ratio of $A_{\text{far}}$ to $A_{\text{near}}$. The full width of half maximum (FWHM) of $|E_z|^4$ intensity is about 5 nm, much bigger than the actual resolution here. To explain the ultrahigh spatial resolution, we noticed that the lateral resolution and the enhancement are very sensitive to the tip condition, indicating that the most apex of the tip plays a key role in the TERS measurement. In our simulation, the FWHM of $|E_z|^4$ can be reduced to 1.8 nm with a tip radius $R_{\text{tip}} = 2.5$ nm, as shown in Fig. 5(f). Such an atomically sharp tip apex can be achieved in STM by fine-tuning the in situ voltage pulses or soft-touching the tip to the Ag(111) substrate surface. The electrodynamics-quantum mechanical approach shows a similar result that an atomic sharp tip in a quantum size junction can confine the plasmon enhanced field within a few angstroms.⁴¹

C. Selective enhancement and polarization dependent TERS intensity

Our experiment shows that TERS enhancement selectively acts on the $A^1$ and $A^2$ modes of silicene [Fig. 5(a)],
FIG. 5. TERS enhancement factor and the spatial resolution. (a) Gap-distance dependent TERS spectra of the silicene $\sqrt{13} \times \sqrt{13}$ phase (1 V, 50 s for each spectrum). (b) Pure near field (50 s) and far field (600 s) Raman spectra of silicene. (c) STM topography of the $\sqrt{13} \times \sqrt{13}$ phase on the Ag(111) surface; the inset is the enlarged STM image in the black box. (d) $A^1$ mode TERS intensity mapping of the $\sqrt{13} \times \sqrt{13}$ phase on the Ag(111) surface in the inset in (c); the overlapped dots line is the $A^1$ mode TERS intensity along the blue dot line in (c) (1 V, 300 pA). (e) 3D color map of $|E_z|^4$ enhancement at the nanogap between the tip and Ag surface. (f) Calculated $|E_z|^4$ intensity distribution at the nanogap with $R_{tip} = 2.5$ nm and the intensity profile along the line $y = 0$. Reproduced with permission from Sheng et al., Phys. Rev. Lett. 119, 196803 (2017). Copyright 2017 American Physical Society.

while the E mode has negligible enhancement. The different enhancement behavior of A and E modes can be explained by the Raman tensor calculation, as follows. Silicene on Ag(111) processes a $C_3$ symmetry ($C_{6v}$ for $4 \times 4$ and $C_3$ for $\sqrt{13} \times \sqrt{13}$ and $2\sqrt{3} \times 2\sqrt{3}$ phases); the A mode Raman tensor is

$$\mathbf{R}(A) = \begin{bmatrix} a & 0 & 0 \\ 0 & a & 0 \\ 0 & 0 & b \end{bmatrix}.$$
The TERS intensity of the A mode can be calculated by

\[ I_{\text{TERS}}(A) \propto \left| E_{\text{loc}}(\omega_S) \cdot \hat{R}(A) \cdot E_{\text{loc}}(\omega_L) \right|^2 \]

where \( \hat{G}(\omega_S) \) and \( \hat{G}(\omega_L) \) are the enhancement factor of the local field \( E_{\text{loc}}(\omega_S) \) and \( E_{\text{loc}}(\omega_L) \) over the far field \( E_{\text{far}}(\omega_S) \) (scattering Raman light) and \( E_{\text{far}}(\omega_L) \) (incident laser light), respectively,

\[ \hat{G}(\omega_S) = \begin{bmatrix} g_{SS} & g_{ST} & g_{ST} \\ s_{SS} & s_{ST} & s_{ST} \\ g_{SS} & g_{ST} & g_{ST} \end{bmatrix}, \quad \hat{G}(\omega_L) = \begin{bmatrix} g_{LL} & g_{LT} & g_{LT} \\ l_{LL} & l_{LT} & l_{LT} \\ g_{LL} & g_{LT} & g_{LT} \end{bmatrix}, \]

and \( g_{ij}(\omega) = \frac{E_{\text{loc}}(\omega)}{E_{\text{far}}(\omega)} \) for \( i, j = x, y, z \).

The TERS intensity of the A mode can be expressed as

\[ I_{\text{TERS}}(A) \propto \left| \begin{bmatrix} \cos \varphi, 1, \sin \varphi \end{bmatrix} \cdot \hat{G}(\omega_S) \right|^2. \]

\[ \theta \text{ is the polarization angle of the incident laser beam, and } \varphi = 60^\circ \text{ is the angle of the incident laser with the tip axis. For the A mode, the Raman shift (170 cm}^{-1} \text{ for A}^1 \text{ and } 220 \text{ cm}^{-1} \text{ for } A^2 \text{ of the Stokes scattering light (} \omega_S \text{) is small from the laser light (} \omega_L \text{). It can be assumed that the electric field enhancement factor } g_{S,i} \approx g_{L,i} = g_{ij}. \text{ In addition, because the electric filed is enhanced mainly along the z direction, then } g_{zz} \gg g_{ij} (i, j = x, y, z, i = j \neq z). \text{ Ignoring the lower order terms of } g_{zz}, \]

we can get

\[ I_{\text{TERS}}(A) \propto b_z^2 \sin \varphi \cos \theta \left| b_z^2 \sin \varphi \cos \theta \right|^2 = \frac{3}{4} b_z^2 g_{zz}^2 \cos^2 \theta. \]

Here, we assume \( \theta = \pm 90^\circ \) when the electric field component is perpendicular to the tip axis. Thus, for the phonon mode that contains the \( \alpha_{zz} \) Raman tensor, the maximum enhanced intensity would be detected when \( \theta = 0^\circ \), and the enhancement is proportional to \( g_{zz}^2 |\alpha_{zz}|^2 \). For a \( \sqrt{3} \times \sqrt{3} \) phase, with the tip at the position labeled in Fig. 6(a), the TERS intensity of A modes [Fig. 6(b)] can be fitted well by \( \cos^2(\theta + \Delta \theta) \), with a \( \Delta \theta \approx 8^\circ \) between \( A^1 \) and \( A^2 \) modes, which confirms our analysis that the A modes contain a \( \alpha_{zz} \) Raman tensor and with different values for \( \hat{R}(A^1) \) and \( \hat{R}(A^2) \).

For the E mode, the Raman tensor is

\[ \hat{R}(E(x)) = \begin{bmatrix} c & d & e \\ -d & c & -f \\ e & f & 0 \end{bmatrix}, \quad \text{and } \hat{R}(E(y)) = \begin{bmatrix} d & -c & -f \\ -e & c & d & e \\ -f & e & 0 \end{bmatrix}. \]

We can get the TERS intensity of the E mode according to the formula,

\[ I_{\text{TERS}}(E) \propto \left| E_{\text{loc}}(\omega_S) \cdot \hat{R}(E(x)) \cdot E_{\text{loc}}(\omega_L) \right|^2 + \left| E_{\text{loc}}(\omega_S) \cdot \hat{R}(E(y)) \cdot E_{\text{loc}}(\omega_L) \right|^2. \]

For the E (\( \omega_E = \omega_L - \omega_S, -520 \text{ cm}^{-1} \)) mode, it can also be assumed that \( g_{S,i} = g_{L,i} = g_{ij} \), and ignoring the lower order terms of \( g_{zz} \), it can be calculated that the TERS intensity of the E mode is

\[ I_{\text{TERS}}(E) \propto g_{zz}^2 \sum_i (|\alpha_{zz}|^2 + |\alpha_{zz}|^2)(I = X, Y). \]

The enhancement of the E mode (\( g_{zz}^2 \) is about \( 10^4 - 10^5 \)) can be neglected or is just comparable with the area ratio (about \( 10^5 - 10^6 \), now the enhancement is proportional to electric field square, and the contributed near field area is larger) of \( A_{\text{far}} \) to \( A_{\text{near}} \). That is the reason why only the A mode is largely enhanced.

IV. CONCLUSION

We have built a high performance TERS system based on a LT-UHV-STM. To improve the TERS performance, our STM was designed with the scanner having hard-contact

FIG. 6. Laser polarization dependent TERS intensity on silicene. (a) STM image of the silicene \( \sqrt{3} \times \sqrt{3} \) phase and the labeled tip position for TERS measurement. (b) Polar plot of the polarization-dependent TERS intensity of the \( A^1 \) and \( A^2 \) modes (scattered points) and fitted by \( A \cos^2 \theta \) (lines).
to the cryostat, without spring and eddy-current damping. This design allows us to put a big aspheric lens with large NA close to the STM tip, which is driven by a 3D piezoelectric motor for accurate focusing. It also helps us to achieve efficient thermal stability and low drift under laser irradiation. To compensate for the lack of noise isolation inside UHV, a three-level noise isolation system is designed outside the UHV system. Our system demonstrates high TERS performance at the liquid nitrogen temperature, with a 10⁹ TERS enhancement factor and a 0.5 nm spatial resolution. With the combined MBE system, our LT-UHV-TERS is an ideal tool to study local structures and vibration properties, such as strain, defects, and domain boundaries of emerging 2D materials, as has been demonstrated with monolayer silicene as a prototypical system. In the next step, we are aiming to combine our system with a femtosecond laser, to further achieve time-resolved femtosecond stimulated TERS.

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