Phonon detection using scanning tunneling microscope light emission

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ABSTRACT

We have found that the phonon energy of Sb_2Te_3 can be determined from scanning tunneling microscope (STM) light emission spectroscopy combined with picosecond laser pulse irradiation of the tip-sample gap. STM light emission (STM-LE) from Sb_2Te_3 is excited by electronic transitions taking place in the local electronic structure having a direct gap-like shape with a band gap of around 1.6 eV. Hence, a single peak with a narrow spectral width (original peak hereafter) is seen at the gap energy in the spectra measured in the conventional (i.e., no laser pulse irradiation) configuration. When the tip - sample gap in the STM is irradiated with picosecond laser pulses, several peaks are added to the original. These peaks including the original are separated from the adjacent peak(s) by an equal photon energy. The amount of the separation read from the spectra agrees with one of the reported phonon energies of Sb_2Te_3 , showing that one can determine phonon energy of Sb_2Te_3 by STM-LE spectroscopy.

Keywords STM, light emission spectroscopy, vibrational spectroscopy, chalcogenide alloys

INTRODUCTION

Some chalcogenide alloys including Sb_2Te_3 attract strong attention because of their potential for data-storage devices with ultra-high capacity. Optical storage devices using the super-resolution-readout phenomenon [1][2] found in these materials will have a capacity much higher than that of current blu-ray disks. Recently, these materials have been intensively studied for the use in resistive layers of phase change random access memory (PCRAM), which is one of the candidates for the next generation of nonvolatile electrical memory. In order to advance the development of such devices, it is highly desirable that properties of the underlying material are explored and understood with the spatial resolution comparable to targeted sizes of read and write units. Vibrational spectroscopy is a powerful tool for characterizing materials. However, the spatial resolution of conventional ways, such as Raman and infrared spectroscopy, is limited to submicrometers due to the diffraction limit of optical measurements. Much higher spatial resolution is required for the intended applications.

When electrons (or holes) are tunneled from the tip of a STM into the sample, light emission is excited (hereafter we call this emission STM-LE). Since the electron tunneling beam from the STM tip is well focused up to an atomic scale and the beam energy and current are very low, one can obtain the light emission spectra of individual targeted nanostructures on the surface without modifying them. By correlating the observed spectra with the size and shape of the structure as determined by the usual STM operation, one can obtain material information about individual nanostructures. Recently we found that vibrational energies of individual adsorbates and surface nanostructures are determined from their STM-LE spectra (e.g., [3][4]), showing that vibrational spectroscopy is possible by STM-LE spectroscopy with the spatial resolution of STM. In this paper, we focus on the determination of phonon energies of Sb_2Te_3 by STM-LE spectroscopy.

EXPERIMENTS

A Sb_2Te_3 film with thicknesses of 100 nm was deposited on a quartz substrate in an Ar gas atmosphere using a radio frequency (RF) magnetron sputtering apparatus, and was annealed at 200°C

for 2 min for crystallization in an Ar gas atmosphere. Then the sample was set in the STM, which is housed in an ultra-high vacuum (UHV) chamber. The STM was operated in a constant current mode at a tip and sample temperature of 80 K. The tip was made of a tungsten wire by an electrochemical method.

Figure 1 shows a schematic illustration of the experimental setup for the present experiments. The tip - sample gap of the STM is irradiated with a mode-locked picosecond Ti : sapphire laser with a repetition rate of 80 MHz and a pulse width less than 2 picoseconds. The STM light is analyzed by the conventional intensified charge coupled device (CCD) camera attached to a spectrograph. All the STM–LE spectra shown below are averages of 5–10 spectra taken for a tunneling current of 2 nA with an accumulation time of 100 s.

RESULTS AND DISCUSSION

Let us first see conventional STM-LE spectra of the W tip - Sb_2Te_3 sample gap being not irradiated with the laser pulses. The STM light emission spectrum shown in Fig. 2(a) was observed in the spectral range from 1.55 eV to 1.65 eV for a sample bias voltage of +2.3 V with respect to the tip. A single peak with a narrow spectral width is found at a photon energy of about 1.6 eV. No STM-LE was observed for the reversed bias polarity. From this bias-polarity dependence along with the theoretical electronic structure of Sb_2Te_3 reported by Zhitang et al. [6], the mechanism of the STM light emission is understood as depicted in Fig. 3(a). Sb_2Te_3 has a local electronic structure having a direct gap-like shape, i.e., the structure consisting of upper and lower bands being convex downward and upward, respectively, with a band gap of about 1.6 eV. When the sample bias polarity is positive with respect to the tip, electrons are injected from the tip into the sample and then immediately relax to the bottom of the upper band. Holes are created in the lower band through impact ionization processes initiated by the injected electrons. As a result, STM-LE is excited via recombination of the electrons and holes. It should be noted that the gap energy of Sb_2Te_3 determined by conventional methods is less than 0.5 eV. That is to say, this material electrically functions as a narrow gap semiconductor, showing that the gap detected by STM-LE spectroscopy does not affect its electric properties. However, the optical responses (i.e., its dielectric function) in the visible spectral range [7] are dominantly determined by the electronic transitions in the gap; this gap strongly affects its optical properties.

Next let us see STM-LE spectra of the tip-Sb_2Te_3 sample gap being irradiated with the laser. In this configuration, the bias polarity dependence of STM-LE varies from that of the conventional STM-LE described just above; while STM-LE comes to be detected for both polarities, the signal level is higher for the negative polarity than for the positive. Fig. 2(b) is the STM light emission spectrum for a bias voltage of – 2.3 V. Several peaks appear in addition to the original. These peaks including the original are separated from the adjacent peak(s) by an equal photon-energy. The amount of the separation read from the spectra is 18 meV. This value agrees with one of phonon energies of Sb_2Te_3 [8].

Before elucidating the origin of these multiple peaks, we review our previous work concerning temporal behaviors of STM-LE from the W tip - Au sample gap irradiated with the picosecond laser pulses. [9] In this configuration, the STM-LE becomes a pulse train in synchronization with that of the incident laser as shown in Fig. 4. The pulse width of the STM-LE is the same as that of the laser pulse. Here it should be noted that no thermal effect makes such a pulse train. This is because the repetition rate of the laser (80MHz) is so high that any thermal effect cannot follow the laser pulses. Figure 4 shows that the picosecond laser pulses induce a pulsed tunneling current, by which the pulsed STM-LE is excited.

On the basis of the knowledge described just above, the mechanism responsible for exiting the STM-LE in Fig. 2(b) is concluded as depicted in Fig. 3. While the STM-LE is still excited via the recombination process that is the same as that of the conventional STM-LE, the carriers are created in

a different manner for the negative bias polarity; holes are created in the lower band through the electron tunneling from the sample to the tip for this polarity. Supply of electrons to the upper band is carried out via ionization processes initiated by the incident laser pulses (see Fig. 3). In addition, the incident laser pulses must excite a high density of phonons around the tip-sample gap in the sample. The electrons and holes relaxed to the bottom of the upper band and the top of the lower band, respectively, must interact with the phonons before the recombination. Then phonon replicas of the emission at the photon energy of the gap must be created. As a result, the multiple peaks with the photon-energy separation corresponding to the phonon energy appear in the STM-LE spectra.

CONCLUSION

We have observed the STM-LE spectra of the W tip - Sb_2Te_3 sample gap irradiated with the picosecond laser pulses. The multiple peaks separated from the adjacent peak(s) by the equal energy are found in the STM-LE spectra. Since the amount of the separation agrees with one of the phonon energies of Sb_2Te_3, we conclude that that the phonon energy of this material can be determined by STM-LE spectroscopy combined with picosecond laser pulse irradiation of the tip-sample gap.

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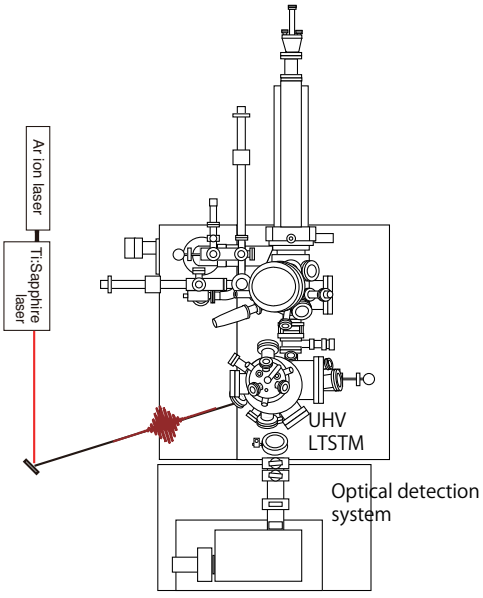

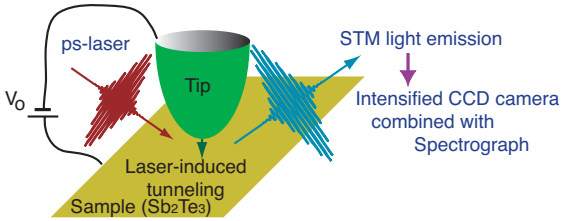

Fig. 1 Experimental setup. The left picture is a top view of the system. The upper right shows optical relations.

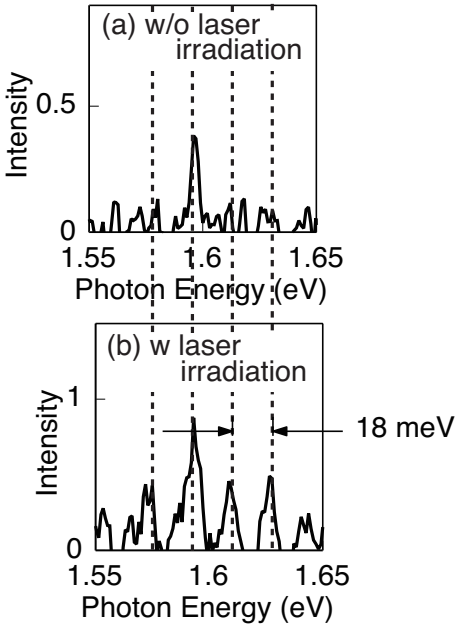

Fig. 2 STM light emission spectra observed when the laser irradiation is (a) off and (b) on. multiple peaks are seen only in (b).

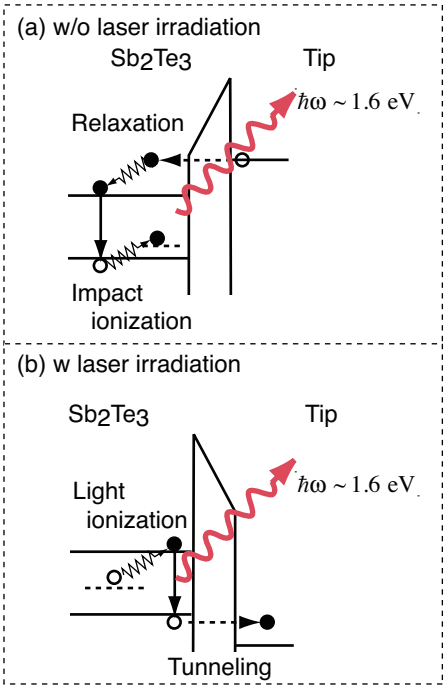

Fig. 3 STM light emission mechanisms operated when the laser irradiation is (a) off and (b) on.

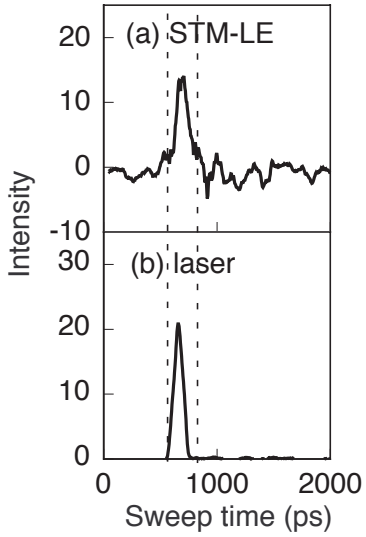

Fig. 4 Temporal behaviors of (a) STM light emission from the W tip-Au sample gap irradiated with the picosecond laser pulses and (b) the picosecond laser pulses themselves. These spectra were measured with a streak camera operated in a mode whose temporal resolution is 100 picoseconds.