Time-resolved scanning tunneling microscope light emission spectroscopy of Sb_2Te_3

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ABSTRACT

We have successfully added ps temporal resolution to scanning tunneling microscope (STM) light emission spectroscopy. STM light emission spectra of Sb_2Te_3 were measured in the configuration that the tip - sample gap of the STM is irradiated by a pair of pump and probe laser pulses with a duration less than 2 ps each, and were analyzed as a function of optical delay time between the pump and probe pulses. We found that the peak energy of the STM light emission, which is excited via electronic transitions of Sb_2Te_3 (Y. Uehara et al., , Solid State Commun., **149**, 1902 (2009)), is shifted toward the higher energy side when the optical delay time is in the range between around 2 ps to 13 ps. This result demonstrates that the proposed method has temporal resolution of ps.

Keywords STM light emission spectroscopy, ps time-resolution, chalcogenide alloys

1. Introduction

Scanning tunneling microscopy (STM) possesses excellent spatial and energy resolution, i.e., atomic spatial and meV energy resolution. However, its temporal resolution is poor; temporal resolution of conventional STM measurements is in the range of μs or much worse. This feature is intrinsic because a current amplifier with a relatively high gain (10^8 or higher) has to be used in the feedback circuit of STM. Since bandwidths of amplifiers are inversely proportional to their gains, temporal resolution of STM is limited to such a level.

Gimzewski et al. reported in 1988 that visible light is emitted from the tip-sample gap of a STM. [1] Since the light excitation is carried out by the well focused tunneling electron beam emitted from the tip, spatial resolution of STM light emission is comparable to STM itself. [2] It should be noted that temporal resolution attainable in optical measurements is not limited by intensity of light to be measured. Even though the intensity is in a photon counting level like STM light emission, its temporal behavior can be measured with temporal resolution of ps or better. Thus, STM light emission will be a candidate for a novel technique possessing ps temporal as well as atomic spatial and meV energy resolution.

We previously investigated temporal behaviors of light emitted from the STM tip-sample gap irradiated by ps laser pulses with a streak camera. [3] In this configuration, not only the light excited by tunneling electrons (i.e., STM light emission) but also one directly excited by the laser pulses (we call this light direct component hereafter) are emitted. That is to say, the direct component has to be removed from the observed spectra to obtain the STM light emission. This is possible because the STM light emission and direct component have different tip-sample gap bias voltage V_o dependence from each other. [3] Figure 1 shows the temporal behaviors of (a) laser pulse and (b) STM light emission obtained in this manner. (The sample was an evaporated Au film.) While the attainable temporal resolution of the streak camera used in the measurements was 2 ps, the sweep mode adopted determined the temporal resolution to be 100 ps in Fig. 1. One can see that the STM light emission is synchronized with the laser pulse.

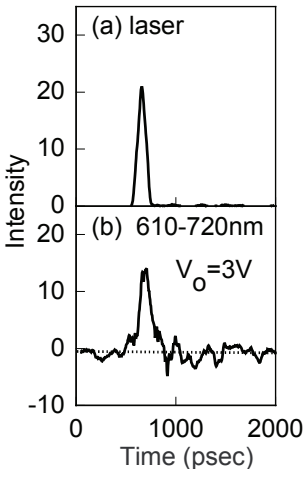

Fig. 1 Temporal behaviors of (a) laser pulse and (b) STM light emission.

On the basis of the finding described just above, we propose novel STM light emission spectroscopy having ps temporal resolution. In this

method, STM light emitted from the tip-sample gap irradiated by a pair of pump and probe pulses is analyzed as a function of optical delay time T_{delay} between them; the time evolution of material properties of sample that is initiated by the pump pulse are traced by STM light emission synchronized with the probe pulse. In this paper, we report about the results obtained from Sb_2Te_3. Noted that descriptions about properties and mechanisms of STM light emission from Sb_2Te_3 in the resultant section are a digest of the corresponding ones in Ref. 4 and 5.

2. Experiments

Figure 2 shows a schematic drawing of the present experiments. The light source for the pump-probe measurement is a mode-locked ps Ti:sapphire laser with a repetition rate of 80 MHz, a pulse width less than 2 ps. After passing through an optical delay line for creating a pair of pump and probe pulses, the laser beam is directed onto the tip-sample gap region. The light emitted from the gap is collimated by a plano-convex lens, and is refocused onto the entrance split of a spectrograph by a second plano-convex lens to be analyzed in the spectral range from 1.45 to 3.50 eV by an image-intensified one-dimensional charge-coupled-device (CCD) camera attached to the spectrograph.

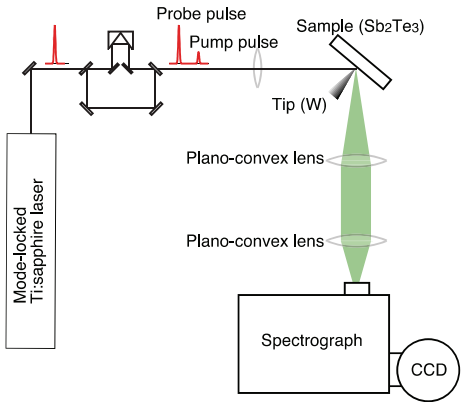

Fig. 2 Schematic drawing of experimental setup.

The sample was a crystallized Sb_2Te_3 thin film of 200 nm-thick. The Sb_2Te_3 film was deposited in an Ar gas at a pressure of 0.5 Pa using a radio frequency (RF) magnetron sputtering apparatus operated at an input power of 100W, and was annealed at 200˚C for 2 minutes in an Ar gas atmosphere for crystallization. The STM tip was made of W using an electrochemical method. The STM tip and sample were set in a low-temperature (LT) STM housed in an ultra-high vacuum (UHV) chamber. The STM was operated at 77 K throughout the experiments. The laser was tuned at a wavelength of 920 nm (i.e., at a photon energy of 1.345 eV). We measured STM light emission spectra as a function of T_{delay} (i.e., as a function ooptical delay time between the pump and probe pulses). As mentioned in the introductory section, the direct components are subtracted from the spectra shown in the resultant section.

3. Results and Discussion

Figure 3 shows the STM light emission spectrum of Sb_2Te_3 measured without laser irradiation of the tip-sample gap. [4, 5] The sample voltage V_o was set at +2.3 V with respect to the tip (tunneling electrons are injected from the tip into the sample for this bias polarity). Figures 3(a) and 3(b) show the same spectrum over the spectral range from 1.5 to 2.5 eV and from 1.55 to 1.65 eV, respectively. From Fig. 3(a), we see that the STM light emission spectrum consists of two components, a single peak with a narrow spectral width at 1.63 eV and a broad spectral feature. The broad component rises near the quantum cutoff [1] eV_o = 2.3 eV (where e is the charge of the electron) and spreads continuously toward the lower-energy side. From this feature, we concluded that this broad component originates from inelastic tunneling processes [5].

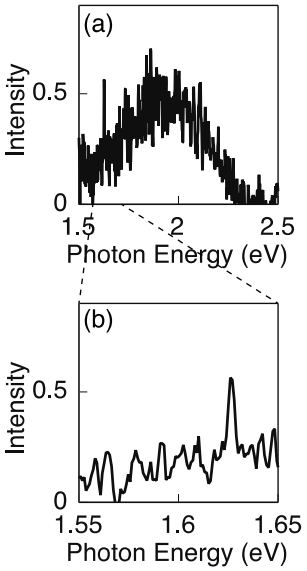

Fig.3 Conventional STM light emission spectrum. The same spectrum is shown in the spectral range (a) between 1.5 and 2.5 eV and (b) between 1.55 and 1.65 eV. (after Ref. 5)

We previously reported that the single peak of Fig. 3(b) originates from the electronic structure having the direct gap-like shape with the band gap of around 1.6 eV. [4, 5] The light emission mechanism of this single peak is illustrated in Fig. 4(a). The single peak comes from edge transitions between the bottom of the upper electronic band (UEB) and the top of the lower electronic band (LEB). These bands are separated by the band-gap energy. Electrons are supplied to the upper band via electron tunneling from the STM tip, and holes are created in the lower band via impact ionization processes [4] induced by the tunneling electrons. The peak in Fig. 3(b) results from the recombination of these carriers. When the bias polarity is

reversed, the peak seen in Fig. 3(b) disappears. The spectrum is not shown here; please see Figs. 1 and 2 in Ref. 4 for details. This bias-polarity dependence is reasonable because electrons are not supplied to the upper band when the sample is biased negatively with respect to the tip; therefore, the peak is absent.

Generally, spectra of STM light emission excited via inelastic tunneling processes are strongly affected by electronic density of states at the sample surface, and ones via electronic transitions by electronic band structure of the sample. While both kinds of spectra contain valuable material information on the targeted sample, we focus on the latter spectra (i.e., peak component) and do not discuss the former in the following argument. That is to say, we examine STM light emission spectra in the spectral range between 1.55 and 1.65 eV.

Figure 5 show STM light emission spectra from the laser-irradiated tip-sample gap. Not the paired-pulse train shown in Fig. 2 but the single-pulse train was irradiated to the gap at this stage. The sample bias polarities are positive for Fig. 5(a) and negative for Fig. 5(b) with respect to the tip, respectively. The dotted vertical lines indicate the energies of the peaks in Fig. 5(b) and are to guide the eye.

The spectrum of Fig. 5(a) exhibits a single clear peak, which is similar to that found in Fig. 2(b), at the photon energy of 1.63 eV, indicating that the laser irradiation does not significantly affect the STM light emission due to the electron-hole recombination for this bias polarity. The rest of the spectrum (i.e., other than the peak at 1.63 eV) may be the result of the inelastic tunneling processes, although the signals are so scattered that it is difficult to clarify the spectral profiles.

Contrary to the positively biased case, the spectrum of Fig. 5(b) has several peaks in addition to the peak at 1.63 eV. These peaks (including the one at 1.63 eV) are separated from their neighboring peaks by 18 meV. All peaks in Fig. 5(b) must be excited via electron tunneling processes because of the following reasons. Firstly, any signal from the direct component, i.e., one produced by laser irradiation alone has already been subtracted as already mentioned. Secondly, STM light emission via inelastic tunneling does not strongly depend on bias polarity. However, clear bias-polarity dependence is seen between Figs. 5(a) and 5(b). Thus, we can conclude that inelastic tunneling processes are not involved in the emission of these peaks. These results strongly suggested that all peaks originate from the electron-hole recombination mechanism.

Here we consider why STM light emission occurs via electron-hole recombination even for negative-bias polarity, when the tip-sample gap is irradiated by the laser beam. Figure 4(b) shows the light emission mechanism for this case. Since Sb_2Te_3 is a narrow gap semiconductors or more rigorously from its theoretical band diagram [7], we see that the laser-beam photon energy of 1.34 eV suffices to excite electrons from the occupied electronic bands to the unoccupied bands that are higher in energy than the upper band of the 1.63 eV radiation. Thus, electrons can be supplied to the upper band by laser irradiation (i.e., via a kind of light ionization process shown in Fig. 4(b)). Holes are created in the lower band via electron tunneling from the sample to the tip. Consequently, STM light emission at 1.63 eV is excited even for the negative polarity.

Next, we discuss the origin of the periodic structures seen in Fig. 5(b). Similar phenomena are seen in the STM light emission spectra of streaky Ni(110)-(2x1) H [8] and Ag nanoparticles capped with myristate [9]. In both cases, periodic structures appear in the STM light emission spectra, and their periods agree with the vibrational energies of hydrogen adsorbed on the Ni(110) surface and the myristate,

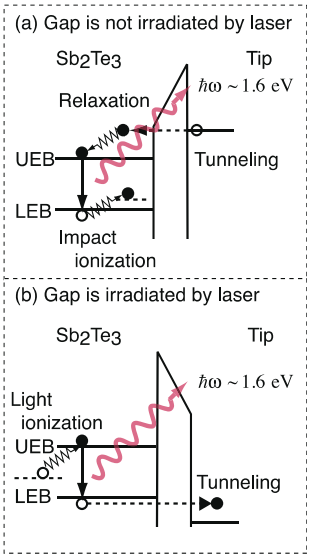

Fig. 4 Schematic drawings of two STM light emission mechanisms that function when the gap (a) is not and (b) is irradiated by the ps-laser light, respectively. (after Ref. 5)

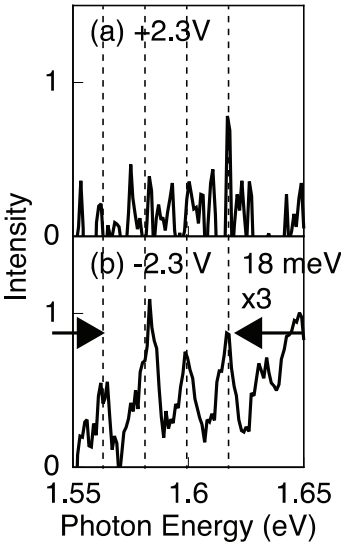

Fig. 5 STM light emission spectra obtained when the tip-sample gap irradaited by the laser pulses. (a) and (b) are for bias voltages of +2.3 V and -2.3 V, respectively.

respectively. From the spectral analogy, we consider that vibrations in Sb_2Te_3 (i.e., phonons) are involved in the appearance of the multiple peaks in Fig. 5(b). In fact, Sb_2Te_3 has an infrared-active phonon mode (A_{2u}) at 145 cm^{-1} = 18 meV [10].

The sample temperature of 77 K corresponds to a thermal energy of 6.5 meV. Thus, the density of thermally excited 18 meV phonons is moderate at this temperature. As a result, only a single peak is seen in Fig. 3(b). Higher density of phonons must be excited by laser irradiation of the gap. Then, couplings between the electronic transitions and the phonons must be significantly accelerated. As a result, the multiple peaks appeared in addition to the original one.

The recombination processes for STM light emission starts afresh with each new ps laser-pulse irradiation and so must finish before the phonons excited by the given laser pulse have decayed. Otherwise, the strong interactions between the edge transitions and phonons that are evidenced in Figs. 5(b) would not exist. The upper and lower electronic bands involved in the peak emission are not the lowest unoccupied and the highest occupied electronic states of this material [7]. The carriers relaxing to these electronic states will be further scattered by phonons into lower states. We conclude that because of this situation, the lifetime of the emission due to electron-hole recombination becomes comparable to or less than the phonon lifetime.

Finally let us describe experimental results about the proposed pump-probe measurements. When T_{delay} was larger than 13 ps, the observed spectra were identical to that shown in Fig. 5(b). On the other hand, when T_{delay} became less than 13 ps, the peak that is originally seen at the photon energy of 1.63 eV was shifted toward the higher energy side; the amount of shift increased up to around 200 meV as T_{delay} decreased. The periodic structure originated from the interactions between phonons electronic transition was not seen in the shifted spectra. Furthermore, the shift was not observed for T_{delay} less than around 2 ps. That is to say, the pump and probe pulses arrived simultaneously at the gap, the spectrum shown in Fig. 5(b) was observed.

As argued above, the STM light emission is excited via the electronic transitions, even when the tip-sample gap is irradiated by the laser pulses. Hence, the shift of the peak energy toward the higher energy side implies that the gap between the upper electronic band and the lower electronic band (see Fig. 4) is enlarged, strongly suggesting that the lattice in the region involved in the STM light emission is deformed. The pump pulse first creates hot electrons in its impinging region in the sample and phonon excitations and cooling of the hot electrons are followed. We consider that the lattice of crystalized Sb_2Te_3 is reversibly deformed during such relaxation processes.

4. Conclusion

STM light emission from Sb_2Te_3 was measured in the configuration that the tip - sample gap is irradiated by a pair of pump and probe pulses, and the results were analyzed as a function of T_{delay}. We found that the peak energy of the STM light emission is shifted toward the higher energy side when T_{delay} is in the range between around 2 ps to 13 ps. This result demonstrates that the proposed method has temporal resolution of ps.

Acknowledgement

This research was supported in part by a Grant-in-Aid for Scientific Research from the Ministry of Education, Culture, Sports, Science and Technology (Contract No. 2234007).

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