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Tip-induced band bending and its effect on local barrier height measurement studied by light-modulated scanning tunneling spectroscopy*

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Local barrier height (LBH) of Si(001) surface was studied using light-modulated scanning tunneling spectroscopy (LM-STS), which enables the observation of the tip-sample-dependent LBH with or without photoillumination simultaneously. The bias voltage and tip-sample distance dependence of LBH were comprehensively understood by the tip-induced band bending (TIBB), which influences the scanning tunneling microscopy and spectroscopy (STM/STS) in measurement of the local electronic structures of semiconductors. A marked decrease in surface photovoltage caused by photocarrier tunneling at shorter tip-sample distance was also shown. On the basis of these results, a method to measure LBH free of TIBB is discussed. [DOI: 10.1380/ejssnt.2006.192]

Keywords: Scanning Tunneling Microscopy; Si(001); local barrier height; surface photovoltage; tip-induced band bending

I. INTRODUCTION

As the scale of target materials decreases, scanning tunneling microscopy and spectroscopy (STM/STS) has been playing an important role as a powerful method of analyzing physical and chemical phenomena because of its high potential to probe the local electronic structures of materials. Actually, since its development, a considerable number of studies have been devoted to the utilization of STM/STS for analyzing the characteristics of electronic structures such as local band structures [1] and local barrier height (LBH) [2–4].

However, as has been pointed out, STM/STS parameters, such as bias voltage, tunneling current and tip-sample distance, influence the sample characteristics [5, 9]. One of the critical problems is the tip-induced band bending (TIBB). As is discussed in this paper, it is difficult to accomplish spectroscopic analysis on semiconductor surfaces by conventional methods because the bias voltage between the tip and the sample induces band bending in the sample surface underneath the STM tip [6].

Figure 1 illustrates the characteristics of TIBB depending on tip-sample distance. The measurement conformation among the STM tip, tunnel gap and semiconductor surface forms a metal-insulator-semiconductor (MIS) structure. When the tip-sample distance is sufficiently large, since the bias voltage is mostly applied to the tunnel gap between the sample and the tip, the band bending in the sample surface is small as shown in Fig. 1(c). However, as the tip-sample distance decreases, the bias voltage begins to impinge on the inner part of the sample surface, resulting in the induction of TIBB as shown in Figs. 1(b) and 1(a). The TIBB increases with the total applied bias voltage. Although this effect is well recognized and suggested by some experimental results [6], its characteristic properties have not yet been well examined experimentally because these issues are directly related to the STM/STS measurement mechanism itself.

A useful way of examining TIBB is to measure surface photovoltage (SPV). When the tip-sample distance is not sufficiently large and the STM/STS measurement is performed in the dark, TIBB appears as shown in Fig. 2(a), where a *p*-type semiconductor sample is used. When the sample below the STM tip is photoilluminated with a sufficient intensity, the introduction of photoexcited carriers reduces the band bending, resulting in the flat-band condition shown in Fig. 2(b). This band bending change in the MIS structure is defined as a SPV. The effective bias voltage applied between the STM tip and the sample surface (tunnel gap) increases by the amount of SPV under photoillumination as shown in Fig. 2, resulting in the lowering of the net barrier height (BH) for the tunneling of electrons at the valence band maximum by SPV/2.

Since the pioneering work by Hammers et al. [7], this technique has been developed and extensively applied to the analysis of semiconductor devices [6–8]. However, since the tip-sample distance cannot be maintained constant when the bias voltage is changed [5], these conventional methods cannot be used for the detailed analysis of TIBB.

In this study, we analyzed TIBB on a Si(001) surface by measuring LBH using light-modulated scanning tunneling spectroscopy (LM-STS) [9]. Since this method enables the observation of the tip-sample-dependent LBH with or without photoillumination simultaneously, we can precisely analyze the tip-sample dependence of TIBB.

II. EXPERIMENTAL

Measurements were performed under ultrahigh vacuum (T=300 K) for a Si(100) 2×1 clean sample surface (*p*-type, 10 Ωcm). A laser diode (635 nm) or a He-Cd laser (442 nm), mechanically chopped at 100 Hz, was used for photoillumination to perform LM-STS.

Figure 3 is an example of LM-STS for SPV measurement. After setting the tip position under the conditions of $V = -3.0$ V and $I = 1$ nA, an *I-V* curve was obtained under chopped photoillumination [9]. The tunneling current oscillates with the chopping frequency between two envelopes that correspond to the *I-V* curves obtained un-

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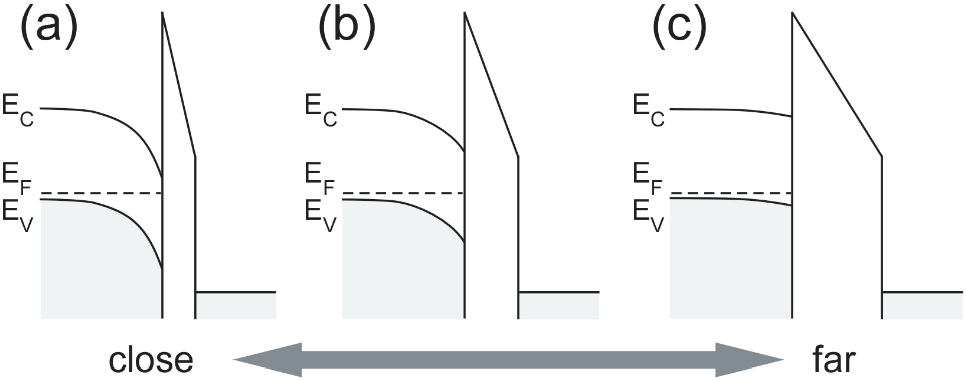

FIG. 1: Characteristics of tip-induced band bending (TIBB) depending on tip-sample distance.

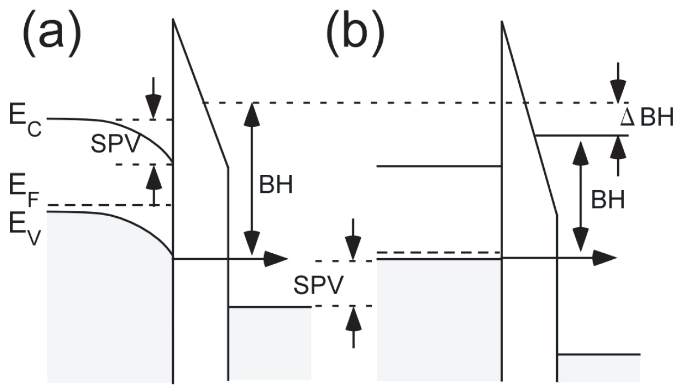

FIG. 2: Schematic illustrations of MIS structures in cases (a) without and (b) with photoillumination.

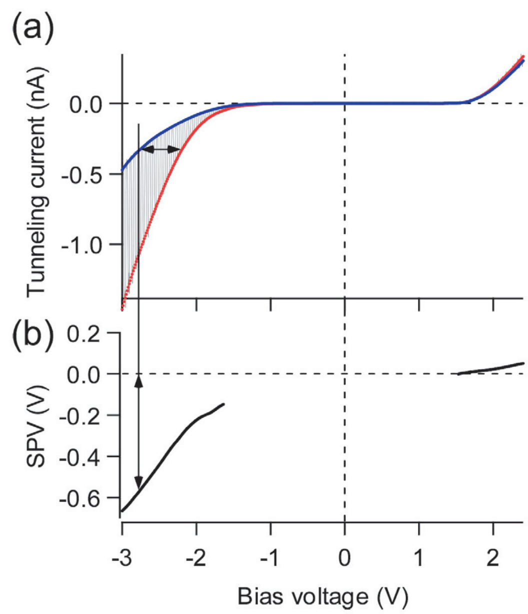

FIG. 3: LM-STS spectrum obtained for Si(001) sample.

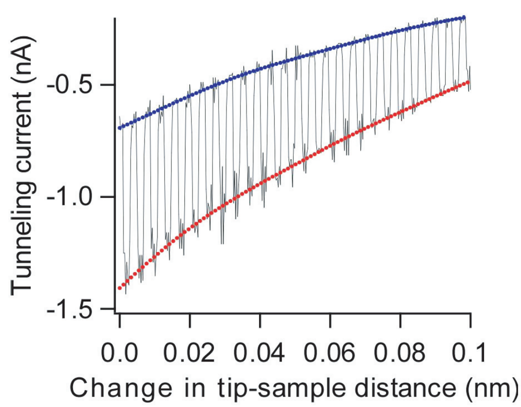

FIG. 4: I-Z curve (Z: tip-sample distance) measured under chopped photoillumination. Horizontal axis represents the distance of tip retraction from the set point.

der photoilluminated (red) and dark (blue) conditions. Bias-dependent SPV is determined by calculating the lateral shift of the two I-V curves as related to bias voltage for the I-V curve under the dark condition (blue one), which is presented in Fig. 3 (b). The central part of the spectrum (-1.5 to +1.5V in Fig. 3) is missing due to the difficulty in calculating the shift of the two I-V curves for that region. The existence of the bias-voltage dependence of SPV is clear. For the forward bias (positive sample bias) voltage condition, the SPV is small because the Fermi level is close to the valence band edge.

By combining LM-STS with LBH measurement, we have developed a new method to observe the tip-sample dependence of LBH with or without photoillumination simultaneously. Figure 4 is an example of the tip-sample distance dependence of the LM-STS spectrum. The I-Z curve was obtained under chopped photoillumination. With a similar process to that employed for SPV analysis, two I-Z curves under photoilluminated (red) and dark (blue) conditions are obtained simultaneously from the LM-STS spectrum as shown in Fig. 4. Thus, each value of LBH is calculated as

$$\mathrm{LBH} = \frac{\Phi_{tip} + \Phi_{sample} - V}{2} = \frac{h^2}{32\pi^2 m}\left(\frac{d(\ln I)}{dz}\right)^2. \quad (1)$$

Here, Φ_{tip}, Φ_{sample}, V and h represent the work functions of the STM tip (W) and the Si sample, the applied bias voltage and Planck constant, respectively.

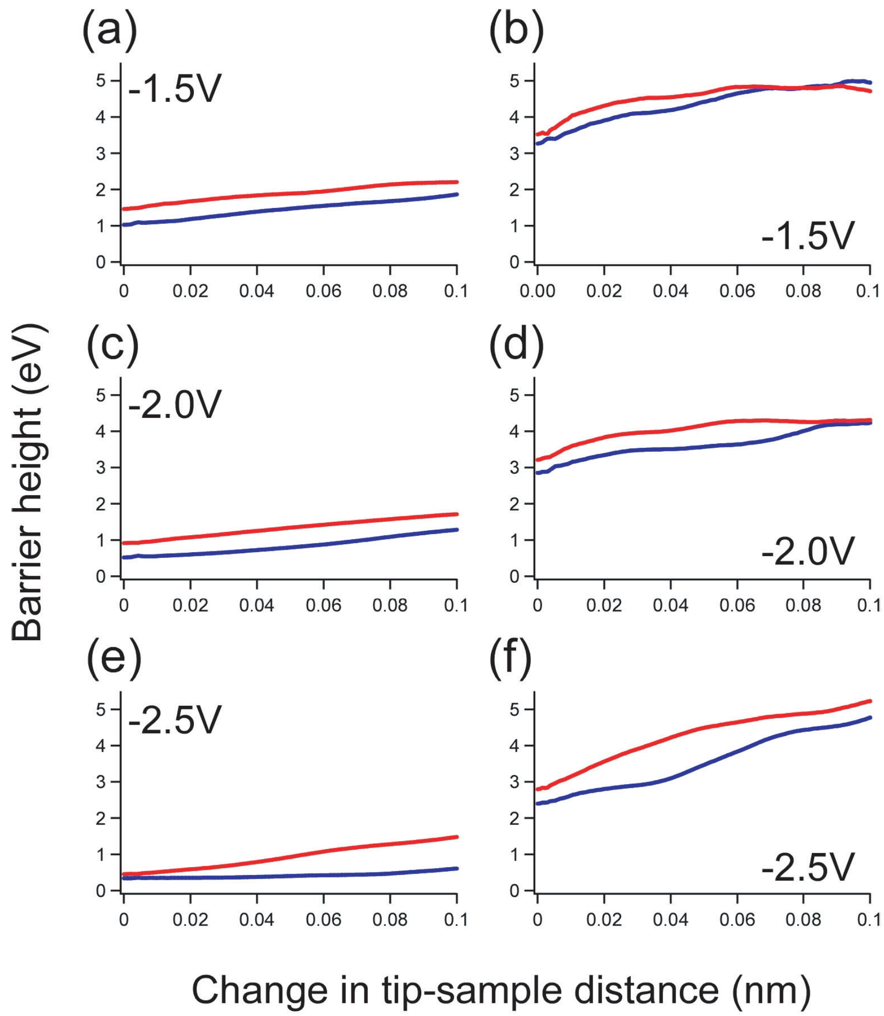

FIG. 5: Tip-sample distance and bias-voltage dependences of LBH obtained using two different tips ((a), (c) and (e) for the first tip and (b), (d) and (f) for the other) under dark (blue) and photoilluminated (red)) conditions, respectively. Horizontal axis represents the distance of tip retraction from the set point.

III. RESULTS AND DISCUSSION

Now, let us examine TIBB by LM-STS. The tip-sample distance dependence of LBH was measured by the method explained in section 2 using several tungsten tips.

Figure 5 shows the tip-sample distance of LBH obtained for two different tips ((a), (c) and (e) for the first tip, and (b), (d) and (f) for the other tip) under dark (blue) and photoilluminated (red) conditions, respectively. To examine the bias dependence of LBH, we obtained *I-Z* curves at various bias voltages, three of which are shown here. With this method, since LBH with or without photoilumination can be obtained simultaneously, the tip-sample dependence of TIBB can be analyzed as the effect of SPV taken into consideration together. After setting the STM tip with the conditions of sample bias voltage (-2 V) and tunneling current (1 nA), we wait for a while with a weak feedback under a chopped light to settle the tip position just to measure 1 nA (center of the two *I-V* curves in Fig. 4). Then, feedback is turned off completely and the bias voltage is changed to that used in the experiment. With this process, we can keep the same tip-distance of the set point throughout the measurements for different bias voltages. Thus, LM-STS spectra were obtained as the tip-sample distance was increased from the set point.

Due to the steep change in the tunneling current depending on the tip-sample distance, the change in distance was limited to 0.1∼0.2 nm for each measurement. The tip-sample distance dependence was slightly different between these two tips, which is probably caused by the difference in the tip shape that changes the set point of its position determined by the tunneling current and bias voltage. Taking advantage of this variation, we were able to observe the tip-sample distance over a wider range, despite the limited distance change of 0.1 nm for one tip.

Note that the LBH in Fig. 5 is not a real one, but an apparent LBH, which is deduced from the derivative of *I-Z* curves (Eq. (1)). If there is no TIBB, LBH should be constant because the slope of *I-Z* curve should be constant. In contrast, the decrease in LBH in Fig. 5, with the decrease in the tip-sample distance, indicates the increase in TIBB that lowers the intensity of tunneling current resulting in a deviation from the exponential function in Eq. (1) [10].

Let us see the results obtained under dark condition first. In Fig. 5(b), the LBH is almost flat at a large distance (0.08-0.1 nm) and is approximately 4.5 eV, indicating that there is little TIBB. The decrease in LBH with further decrease in the tip-sample distance indicates the increase in TIBB. In Fig. 5(a), the LBH is lower than that in Fig. 5(d), even in the large-distance region, which suggests that Fig. 5(a) shows the change obtained at a tip-sample distance shorter than that shown in Fig. 5(d). Therefore, Figs. 5(a), 5(c) and 5(e), and Figs. 5(b), 5(d) and 5(f) are considered to show the changes in TIBB appearing in the regions shown in Figs. 1(c) and 1(b), and Figs. 1(b) and 1(a), respectively.

As shown in Figs. 5(b), 5(d) and 5(f), the decrease in LBH is sharper with higher bias voltages. The sharper decrease in LBH for the case of -2.5 V compared with that for the lower bias voltages indicates that the electric field impinges on the semiconductor surface for a higher bias voltage, resulting in a sharper tip-sample distance dependent LBH with higher bias voltage. Actually, for the shorter tip-sample cases (Figs. 5(a), 5(c) and 5(e)), the change in LBH in the dark (blue line) is smaller for the high bias voltage (Fig. 5(e)) than that with lower bias voltages (Figs. 5(a) and 5(c)). This can be attributed to the earlier appearance of the pinning effect due to a larger TIBB for a higher bias voltage. However, when the change in TIBB is weakened or stopped, for example, as the band edge meets the Fermi level, the LBH will increase and have again a higher value corresponding to the value of the fixed TIBB. Therefore, although the change in TIBB is slow, the low LBH still indicates the existence of a slight change in TIBB.

When the sample below the STM tip is photoilluminated with a sufficient intensity, the introduction of photoexcited carriers reduces the band bending, resulting in the flat-band condition as shown in Fig. 2(b). Therefore, the decrease in LBH under photoilluminated condition, with the decrease in the tip-sample distance, indicates a decrease in the effect of photoillumination depending on the tip-sample distance.

LBH obtained under photoillumination is almost flat at a large distance (0.05-0.1 nm) as expected. This result clearly shows that the decrease in LBH with decrease in the tip-sample distance in this region observed in the dark is caused by TIBB. Decrease in LBH begins with further decrease in the tip-sample distance, which indicates that the decrease in the effect of photoillumination to reduce TIBB begins near this distance.

Slope in the decrease of LBH is almost the same regardless of photoillumination for the low bias voltages (Figs. 5(a) and 5(c)). However, as shown in Fig. 5(e), the LBH obtained at -2.5 V under photoillumination sharply decreases with the decrease in the tip-sample distance, and is close to the same value for the LBH in the dark at shorter distance. The result indicates that the decrease in LBH under photoilluminated condition, with the decrease in the tip-sample distance, is sharper for the higher bias voltage. Since SPV is expected to be larger for the higher bias voltage, some other mechanism is necessary to explain the lowering in the photoillumination effect. To see this point, we examined the tip-sample dependence of SPV for the cases shown in Figs. 5(a) 5(c) and 5(e).

Figure 6 is the result. The tip-sample distance was varied by setting the bias voltage of the servo condition with a constant tunneling current set point of 1 nA. The green spectrum was obtained at the position of 0 nm in Figs. 5(a), 5(c) and 5(e). Blue and green spectra were obtained at two different positions of -0.35 nm (closer) and 0.24 nm (far) from the set point. The central part of each spectrum is missing due to the difficulty in calculating the shift of the two I-V curves for that region as explained in Section 2.

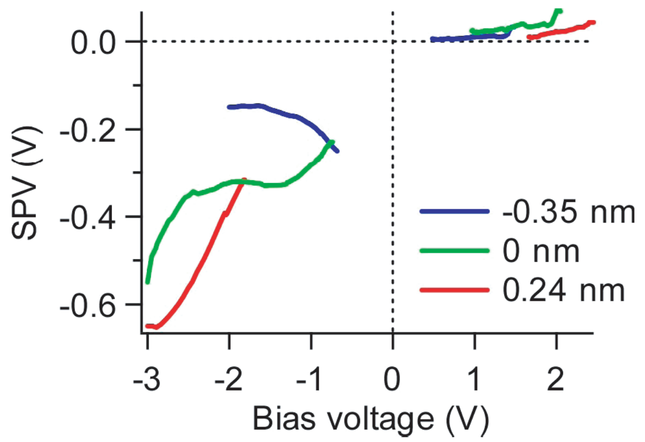

FIG. 6: Tip-sample distance dependence of SPV. The green spectrum was obtained at the position of 0 nm in Figs. 5(a), 5(c) and 5(d). Blue and green spectra were obtained at two different positions of -0.35 nm (closer) and 0.24 nm (far) from the set point. Horizontal axis represents the distance of tip retraction from the set point.

In general, with the increase in TIBB, the SPV increases as the tip-sample distance decreases as expected from the mechanism shown in Fig. 1. However, the SPV decreases with the distance in Fig. 6, which indicates that the effect of photoillumination is reduced as the tip-sample distance decreases.

Since SPV is realized by the photoexcited carriers, the observed change in SPV may be caused by the efficient tunneling of the photoexcited carriers at a shorter tip-sample distance that results in a suppression of the SPV effect [9]. As assumed by the results of LBH, change in SPV is larger at higher bias voltage. This may be due to the fact that tunneling of the photoexcited carriers is more effective for the higher bias voltage because of the decrease in LBH.

To examine the effect of photoillumination on LBH, we measured the tip-sample distance dependence of LBH by changing photoillumination intensity. A setpoint was determined as -2 V and 1 nA. Figure 7 shows the results, where the tunnel gap is photoilluminated continuously without chopping. In such a condition, since thermal expansion effect can be reduced, we can increase the intensity of photoillumination compared to the case of chopped light.

Low-intensity conditions (12.5, 25%) are similar to those used for the other experiments in this paper, where the observed LBHs are very low. This is caused by the efficient tunneling of the photoexcited carriers at a shorter tip-sample distance that results in a suppression of the SPV effect. Actually, with the increase in photoillumina-

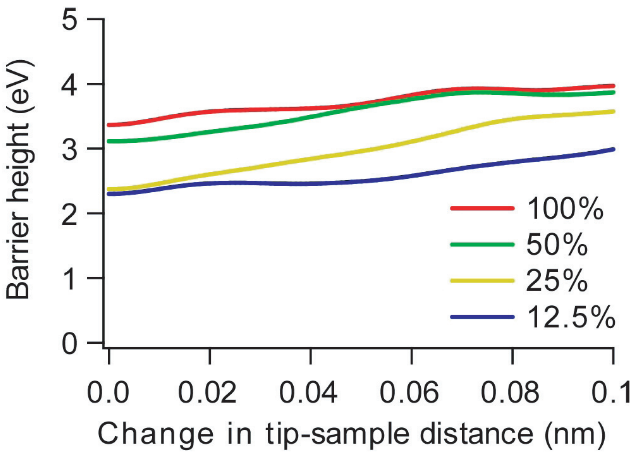

FIG. 7: Tip-sample distance dependence of LBH under various intensities of photoillumination. Horizontal axis represents the distance of tip retraction from the set point.

tion, the LBH increases to close to the flat-band condition as shown in Fig. 2(b). This is due to the reduction of TIBB caused by the increased photo carriers introduced by the increase in photoillumination. Therefore, although it is not perfect, the undesirable effects on LBH measurement can be suppressed by photoillumination of higher intensity. Since tunneling of the photoilluminated carriers at a shorter tip-sample distance suppresses the SPV effect, we should measure LBH at a large distance. A dull tip, which forms a large tip-sample distance as the set point of the tip position determined by the tunneling current and bias voltage, is suitable to measure a better LBH.

When there is no band bending, LBH can be observed correctly regardless of photoillumination. Even in the case where band bending exists, LBH can be observed almost constant if TIBB is weak and little tip-sample distance dependent. In such a case, LBH obtained under photoillumination can be lower than that in the dark, because of the effect of SPV, which is slightly shown for the large distance region in Fig. 5(b). This condition is suitable to measure LBH.

As has been shown, TIBB on a Si(001) surface is comprehensively examined using LM-STS, which enables the observation of tip-sample-dependent LBH with or without photoillumination simultaneously. Analysis on the local electronic structures of semiconductor surfaces, for example, with adsorbed molecules is one of the keys in nanoscience and technology today. Understanding of the photoinduced phenomena is also an important issue. We hope this technique will lead to further development in this field.

IV. CONCLUSIONS

By combining light-modulated STS (LM-STS) with local barrier height (LBH) measurement, we have developed a new method to observe the tip-sample dependence of LBH with or without photoillumination simultaneously. The bias voltage and tip-sample distance dependence of LBH observed on a Si(001) surface were comprehensively explained by the tip-induced band bending (TIBB), which influences the local electronic structures of semiconductors. A marked decrease in surface photovoltage caused by photocarrier tunneling at shorter tip-sample distance was also shown. On the basis of these results, a method to measure LBH free of TIBB was discussed.

Acknowledgments

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