

## STM-Induced Luminescence from Polysilane Thin Film Using Tip-Detection Method

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We succeeded in the *tip*-detection of STM-induced luminescence from a thin-film silicon-based polymer, poly[bis(*p*-butylphenyl)silane] (PBPS), for the first time, where we used a *transparent* STM tip designed for nanometer-scale photon detection as well as STM-current injection. From the dependence of the luminescence intensity on excitation energy up to 9 eV, we found that the luminescence is not injection-type electroluminescence (EL), but is purely intrinsic EL. The energy dependence of the luminescence intensity will be an experimental constraint on the quasi-1D band structure of the PBPS molecule. Moreover, the tip-position dependence of the luminescence intensity suggests the possibility that our method presents a nanometer-scale STM-induced luminescence map of polysilanes.

Key words: polysilane, STM-induced luminescence, tip detection, intrinsic EL

### 1. INTRODUCTION

The optoelectronic properties of organic molecules have been extensively studied [1]. Berndt *et al.* succeeded in detecting the luminescence from C<sub>60</sub> molecules on gold substrate and obtained STM-induced luminescence maps with nanometer resolution for the first time [2]. Recently, Alvarado *et al.* extensively performed the STM-induced luminescence studies for organic materials [3] such as tris(8-hydroxyquinolato)aluminum ("Alq3") [4] and poly(*p*-phenylenevinylene) ("PPV") [5], and they also have yielded nanometer-scale luminescence maps. In contrast to their lens-collection method, a method of detecting the emitted light by a *transparent* STM tip has been developed [6]. This method presents nanometer-scale STM-induced luminescence maps with signal-to-noise ratio better than the usual lens-collection method yields. On the other hand, among quasi-1D molecules of Si-based polymers ("polysilanes"), poly[bis(*p*-butylphenyl)silane] (PBPS) is found to be suitable [7] for the study of STM-induced luminescence, mainly because of the greater quantum efficiency (about 0.1%), even at room temperature (RT). To the best of our knowledge, however, the STM-induced luminescence with *tip*-detection method has never been used to investigate the optoelectronic properties of polysilanes.

In this paper, we report the *tip*-detection of STM-induced luminescence from a PBPS thin film for the first

time. From the dependence of the luminescence intensity on excitation energy up to 9 eV, we found that the luminescence is not injection-type electroluminescence (EL), but is solely intrinsic EL. The energy dependence of the luminescence intensity will be an experimental constraint on the quasi-1D band structure of the PBPS molecule. Moreover, the tip-position dependence of the luminescence intensity suggests the possibility that our method presents a nanometer-scale STM-induced luminescence map of polysilanes.

### 2. EXPERIMENTAL SETUPS

After a *p*-type Si(111) substrate was etched by NH<sub>4</sub>F solution to remove the insulating surface SiO<sub>2</sub> layer, a synthesized PBPS in toluene solution was spin-coated on it. The thickness of the film was estimated to be 50 nm. The sample was placed in a vacuum of less than 2×10<sup>-10</sup> Torr and was shielded from optical light from outside the vacuum chamber so that its quality would not deteriorate.

An ordinary STM unit was used to control the tunneling current and the distance between the tip and the surface of the sample. The transparent STM tip used consists of a pointed multimode optical fiber coated with In<sub>2</sub>O<sub>3.5</sub>. The tip detection is made possible by the transparency of the In<sub>2</sub>O<sub>3.5</sub> and the current injection by its conductivity. The light detected by the tip is fed to a

photomultiplier via a multimode optical fiber. Throughout the measurements, the sample was kept at RT and the tip was fixed at one point. The bias voltage  $V$  of the tip was varied between -2 V and -9 V. At every  $V$ , both the photon count  $P_b$  and the tunneling current  $I_t$  were recorded as a function of time.

### 3. RESULTS

At a given position of the tip, we clearly observed nonzero values of photon count  $P_b$  at greater values of the tunneling current  $I_t$ . Thus, at each  $V$ , we obtained the  $P_b$  values by setting  $I_t = 12$  nA. Moreover, we observed that  $P_b$  was proportional to  $I_t$ . Although the standard deviation of  $I_t$  was sufficiently small (less than 1 % for all  $-V$ ), we normalized the  $P_b$  values as  $P_b/I_t$  for each measurement time. This normalization was performed to eliminate the effect of fluctuation of  $I_t$  on the values of  $P_b$ . It should be noted that this proportionality not only proves that the luminescence originates from STM-current excitation, but also validates the normalization procedure. At each  $V$ , the luminescence intensity was represented by the value of  $P_{TL}$ , which is defined as an averaged value of  $P_b/I_t$  on the measurement time. Figure 1 shows the dependence of  $P_{TL}$  on excitation energy  $-V$ . One can see a threshold energy  $E_{th} = 4.5$  eV above which  $P_{TL}$  starts to increase markedly with increasing  $-V$  with downward-convex dependence. Below this  $E_{th}$ , luminescence is not clearly observed. The least-squares fit of the dependence yields

$$P_{TL} \propto [(-V)-3.1]^\alpha$$

$$\alpha = 2.3 \pm 0.3.$$

Note that the value of 3.1 eV corresponds to the gap energy  $E_g$  estimated from the 395-nm wavelength of the monochromatic absorption spectrum of PBPS [7].

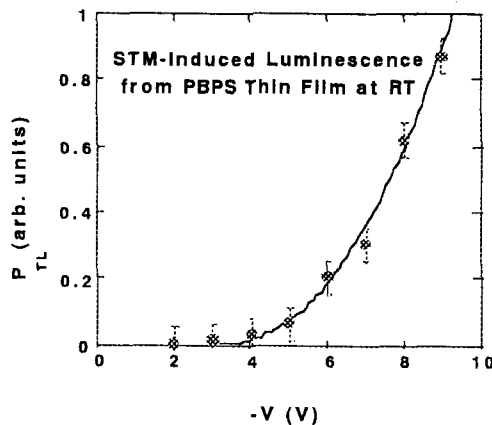


Fig. 1.  $P_{TL}$  versus  $-V$  for PBPS thin film at RT

### 4. DISCUSSIONS

Since we performed the same measurements for a bare Si substrate coated with no PBPS and found that the photon count was less than 2 cps even at  $-V = 9$  eV and  $I_t = 12$  nA, we can safely say that the observed luminescence comes from the PBPS, not from the Si substrate. Note that even if the tunneling current happened to penetrate into the Si substrate through the PBPS thin film, it would be smaller than the current in the bare Si substrate.

Now, we discuss the luminescence mechanisms of the PBPS thin film using the result shown in Fig. 1. When  $-V > E_g$ , electrons emitted from the tip are allowed to go into the conduction band of the sample. Injection-type EL is observed when the injected electrons, that reach the conduction-band edge after releasing their energy due to phonon scattering, directly combine with thermally-excited holes in the valence-band edge. In this case, a plateau should be observed in the dependence of  $P_{TL}$  on  $-V$ , because the luminescence intensity depends on the number of injected electrons, but not on  $-V$ . Indeed, we observed a plateau in the  $P_{TL}$  versus  $-V$  plot for  $p$ -type GaAs [8]. Thus, the absence of a plateau in Fig. 1 indicates that the luminescence is not injection-type EL. When  $-V > E_g$ , some of the injected electrons cause impact ionization. Specifically, the injected electrons excite the valence-band electrons into the conduction band, leaving holes in the valence band. The excited electrons that reach the conduction-band edge form excitons with the holes created in the valence-band edge, which results in intrinsic EL due to the recombination between the electron and the hole of the excitons. Contrary to the injection-type EL, the greater the excitation energy, the greater the amount of impact ionization, which results in the greater luminescence intensity. Thus, the greater  $P_{TL}$  at greater  $-V$  observed in Fig. 1 can be explained in terms of *intrinsic* EL.

In general, intrinsic EL starts to be clearly observed when  $-V > E_{th}$ , where  $E_{th}$  is a threshold energy. Note that  $E_{th} \neq E_g$  but  $E_{th}/E_g = 2-3$ , because, for  $-V$  just above  $E_g$ , the conservation law of momenta of the electrons in concern does not allow the excitation of a sufficient number of electrons into the conduction band [9]. For  $p$ -type GaAs, we actually observed a threshold energy  $E_{th}$  above which the luminescence intensity starts to increase markedly, in addition to the plateau at lower  $-V$  assigned to injection-type EL [8]. Thus, both the absence of a plateau just above  $E_g$  and the substantial increase in  $P_{TL}$  for  $-V > E_{th} > E_g$  indicates that the luminescence is not injection-type EL but *solely* intrinsic EL.

Third, we discuss the values of  $E_{th}$  and  $\alpha$  in the  $-V$

dependence of  $P_{TL}$ . For bulk *p*-type GaAs, we found that  $E_{th}/E_g = 3$  [8] and that the dependence of  $P_{TL}$  on  $-V$  is well-reproduced by a full-band Monte-Carlo simulation in which both a realistic band structure and a generalized dielectric function were taken into account [9]. From the simulation, the value of  $\alpha$  was approximated to be 5.6. On the other hand, in the present case, since Fig. 1 shows  $E_{th} = 4\text{-}5$  eV and the absorption spectrum for PBPS indicates  $E_g = 3.1$  eV [7], we obtain  $E_{th}/E_g = 1.3\text{-}1.7$ . To go further, we need to know whether the PBPS molecules are aligned parallel or perpendicular to the surface of the substrate. According to Kaito and his coworkers [10], most poly[methylhexylsilane] (PMHS) molecules cast on quartz lie parallel to the substrate surface if the thickness of the film is less than 100 nm. Thus, the spin-coated PBPS molecules (the thickness is about 50 nm) are also likely to align *parallel* to the substrate. We believe that the results of  $E_{th}/E_g = 1.3\text{-}1.7$  and  $\alpha = 2.3 \pm 0.3$ , for the case that STM-electrons are injected *transverse* to the PBPS molecules, will be experimental constraints on the quasi-1D band structure of the PBPS.

In addition to the present result, which were obtained by fixing the transparent STM tip at one position, we found that the luminescence intensity depends on the tip position. Specifically, at constant values of  $I_t$  and  $-V$ , the luminescence was not clearly observed when the tip was moved, but further moving of the tip recovered the luminescence intensity again. In addition, we developed a method of grafting single-molecules of polysilanes onto a substrate very recently [11]. Thus, we believe in the possibility that the *tip*-detection method presents an STM-induced luminescence map of a *single* molecule of polysilanes, the resolution and the signal-to-noise ratio of which will be better than those of the map yielded by the usual lens-collection method.

## 5. CONCLUSIONS

For a PBPS thin film, we succeeded in the *tip*-detection of STM-induced luminescence for the first time by using a transparent STM tip designed for both nanometer-scale photon detection and STM-current injection. From the  $-V$  dependence of the  $P_{TL}$  up to  $-V = 9$  eV, we found that the luminescence is solely intrinsic EL. The  $-V$  dependence of the  $P_{TL}$  will be an experimental constraint on the quasi-1D band structure of the PBPS molecule in the case that the STM current is injected *transverse* to the molecules. The *tip*-position dependence of the luminescence intensity suggests the possibility that our method presents a nanometer-scale STM-induced luminescence map of polysilanes.

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