



Modulation of porphyrin photoluminescence by nanoscale spacers on silicon substrates



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ABSTRACT

We investigate photoluminescence (PL) properties of quasi-monolayered tetraphenyl porphyrin (TPP) molecules on silicon substrates modulated by three different nanoscale spacers: native oxide layer (NOL), hydrogen (H)-passivated layer, and Ag nanoparticle (AgNP) thin film, respectively. In comparison with the PL intensity from the TPP molecules on the NOL-covered silicon, the fluorescence intensity from the molecules on the AgNP-covered surface was greatly enhanced while that for the H-passivated surface was found dramatically suppressed. Time-resolved fluorescence spectra indicated shortened lifetimes for TPP molecules in both cases, but the decay kinetics is believed to be different. The suppressed emission for the H-passivated sample was attributed to the weaker decoupling effect of the monolayer of hydrogen atoms as compared to the NOL, leading to increased nonradiative decay rate; whereas the enhanced fluorescence with shortened lifetime for the AgNP-covered sample is attributed not only to the resonant excitation by local surface plasmons, but also to the increased radiative decay rate originating from the emission enhancement in plasmonic “hot-spots”.

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1. Introduction

The interaction between organic molecules and silicon is an important issue in Si-based molecular devices and has attracted much attention for various investigations [1–7] including photoluminescence (PL) [8,9]. The surface of silicon wafers is normally covered by a thin native oxide layer (NOL) of ~2 nm in thickness [10]. This dielectric layer can be used as a natural spacer to block direct charge transfer from molecules to the Si substrate, thus avoiding fluorescence quenching. However, when silicon wafers are used in electronic devices, the thin oxide layer on the surface is usually removed and the surface is then passivated by hydrogen (H) to saturate Si dangling bonds [11]. Such H-passivated Si surface is a promising platform for molecular optoelectronics since recent studies suggest that a monolayer (ML) of H atoms may electronically decouple the molecular states from the Si substrate [12], thus enabling to access the intrinsic molecular properties. On the other hand, metallic nanostructures such as silver nanoparticles (AgNPs) have been used to improve the efficiency of organic optoelectronics devices such as organic solar cells [13] and organic light emitting diodes [14]. This is because metallic nanostructures are

known capable of modifying the excitation and emission properties of nearby molecules thanks to enhanced local fields associated with surface plasmon resonances [15–20]. However, while extensive researches have been carried out for molecules on metal surfaces, the PL study of organic molecules near silicon is relatively limited. To list a few scattered examples, Zhang et al. [21] investigated tip enhanced PL of diindenoperylene molecular films on Si substrates; Chouket et al. [22] explored the energy transfer between porous silicon and Rhodamine molecules; and Choi and Buriak [23] found enhanced PL of porous silicon by decorating the surface with organic layers. In principle, all these optical phenomena can be understood in term of the Purcell effect [24], which states that the decay behavior of an emitter depends on not only the nature of the emitter itself but also its local environment [15,18–20,25].

In this work, we modify the local environment of tetraphenylporphyrin (TPP) molecules on Si by using three different spacer layers (i.e., the NOL, the H-passivated layer, and the thin film composed of AgNPs) and investigate their modulation on the PL decay behavior. In comparison with the PL intensity from the TPP molecules on the NOL-covered Si surface, the molecular fluorescence from the AgNP-covered surface was found enhanced, whereas the TPP fluorescence from the H-passivated Si surface was found dramatically suppressed. Time-resolved fluorescence studies revealed shortened lifetimes of the TPP molecules on both H-passivated and AgNP-covered Si surfaces. We shall discuss briefly

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Fig. 1. (a) Schematic of the TPP/Spacer/Si sample with the molecular structure of TPP shown on the right. (b) Schematic flowchart for the fabrication of nanoscale spacers. (c) AFM image (500 nm \times 250 nm) of AgNP film on the hydrogen-passivated Si. (d) STM image (2.5 V, 10 pA, 20 \times 10 nm²) of the first-monolayer TPP molecules on Ag (111).

the origin of such lifetime shortening and present a qualitative explanation on the enhancement and suppression of the molecular fluorescence in either case.

2. Experimental

Fig. 1(a) shows the schematic configuration of TPP/spacer/Si samples (Si(111), *p*-type, $<0.01 \Omega \text{ cm}^{-1}$, 380- μm thick) with the TPP molecular structure plotted on the right. As shown in Fig. 1(b) for the flowchart of H- and AgNP-spacer fabrications, the NOL-covered Si substrates were first ultrasonically cleaned with acetone and ethanol, and then treated using the RCA technique [26]. Specifically, the samples were first boiled in a 1:1:5 solution of NH₄OH:H₂O₂:H₂O at 80 °C for 10 min, and then in a 1:1:5 solution of HCl:H₂O₂:H₂O at 80 °C for another 10 min. After rinsing and drying, they were immersed into the NH₄F buffered HF solution [HF (40%):NH₄F (27%) = 1:10] for 3 min to etch away the NOL and at the same time to passivate the Si dangling bonds by H atoms [27]. The AgNP-covered Si surface was prepared by dipping H-passivated silicon substrates into the AgNO₃ solution for 10 s [28], which produced a thin film of AgNPs with an averaged particle size around 20 nm, as shown in the atomic force microscopy (AFM) image of Fig. 1(c). TPP molecules were deposited onto the spacer-covered Si substrates in a vacuum chamber with a base pressure of $\sim 3 \times 10^{-6}$ Torr. The deposition rate is $\sim 0.12 \text{ mL/min}$, which was calibrated by the STM imaging for one monolayer of TPP molecules on the clean Ag (111) surface with a total deposition time of 8 min (Fig. 1(d)), and the same deposition condition was used for the preparation of all molecular samples. It should be noted that the molecules are likely to aggregate to some extent on the spacer surface, producing a quasi-monolayered coverage with aggregated molecular clusters. After deposition, the samples

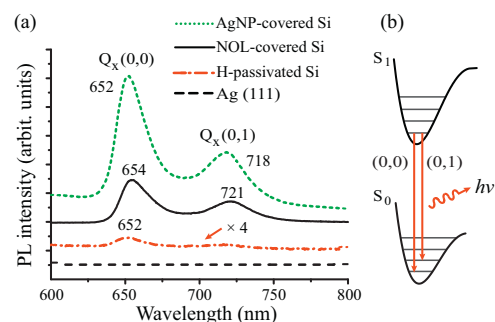


Fig. 2. (a) Steady-state PL spectra of TPP molecules on different surfaces: AgNP-covered Si (dotted curve), H-passivated Si (dash-dotted curve), NOL-covered Si (solid curve), and Ag (111) (dashed curve). Spectra are offset in the figure for clarity. (b) Schematic diagram of the double Q-band emission of the porphyrin molecules from the first excited singlet (S₁) to the ground state (S₀).

were brought out to the air for PL measurements on a home-built optical setup. Steady-state PL spectra were recorded with a liquid-nitrogen cooled charge coupled device spectrometer (Princeton Instruments). Fluorescence lifetimes were measured using the time correlated single photon counting technique with a time resolution of 8 ps using microchannel plate photomultiplier tubes (Edinburgh Instruments). A picosecond pulse diode laser at 405 nm (Hamamatsu) was used for excitation in both steady-state and transient-state spectral measurements. A bandpass filter from 630 to 670 nm was used for the lifetime measurements. Absorption spectra were measured using a Hitachi fluorescence spectrometer.

3. Results and discussion

Fig. 2(a) shows the steady-state PL spectra from the TPP molecules on the NOL-covered Si (solid curve), H-passivated Si (dash-dotted curve), and AgNP-covered Si (dotted curve), respectively. All these spectra were measured in air using the same optical-setup parameters such as the grating, slit size and integration time. As a reference, a PL spectrum for a monolayer of TPP molecules on the atomically clean Ag (111) surface, measured in situ inside ultrahigh vacuum on the sample shown in Fig. 1(d), is also plotted (bottom dashed curve). The absence of molecular emission feature indicates a complete quenching of molecular fluorescence in this case due to rapid charge transfer and dipole transfer between the molecules and metal substrate [15–18,29]. On the other hand, the PL spectrum of TPP on the NOL-covered Si reveals characteristic double Q-band emissions of the porphyrin molecules, originating from $\pi^* \rightarrow \pi$ optical transitions [25,29]. As shown in Fig. 2(b), the emission peak around 654 nm is assigned to the Q_x(0,0) zero-phonon band while the peak around 721 nm to the Q_x(0,1) vibronic overtone. The occurrence of such molecule-specific emissions suggests that the native oxide layer indeed serves as an effective spacer, avoiding the fluorescence quenching effect.

By contrast, on the H-passivated Si surface, although the characteristic Q-band emissions of the TPP molecules are still visible, its fluorescence intensity is dramatically suppressed, about 20 times weaker than that on the NOL-covered Si. The occurrence of molecular fluorescence suggests that the monolayer of H atoms does play the role of electronic decoupling, as reported in Ref. [12], but the suppressed emission indicates that the decoupling is not sufficient to block completely the quenching channel to the Si substrate. There are still weak dipole interactions between the molecules and Si, which provides nonradiative decay channels and leads to the decrease of the fluorescence intensity. Interestingly, the emission intensity from the TPP molecules on the AgNP-covered Si is considerably enhanced, about 3 times stronger than that on the NOL-covered Si. Such enhancement suggests a different

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