

A comparative study of electron transport in benzene molecule covalently bonded to gold and silicon electrodes for pioneering the electron transport properties of silicon quantum dot-molecule hybrid polymers



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ABSTRACT

In order to pioneer the electron transport properties of silicon (Si) quantum dot-molecule hybrid polymers, we investigate the electron transport properties of the benzene molecule in silicon (Si) semiconductor electrodes, based on nonequilibrium Green's function (NEGF) method coupled with density functional theory (DFT), in comparison with conventional gold (Au) metal electrodes, with three different anchoring linker groups: thiol for dithiol-benzene (DTB), methylene for dimethyl-benzene (DMB), and direct bonding for benzene (Ph). It is interestingly found that, due to band gap nature of the Si semiconductor electrodes, the molecular junctions with the Si electrodes show no current up to the bias voltage of around 0.8 V. In addition, the DTB molecular junctions in the Si semiconductor electrodes connected with Si–S bond show higher conducting properties than other DMB and Ph molecular junctions directly coupled to the electrodes with the Si–C bonds (DMB < Ph < DTB). The electron transport properties of the molecules in the two different electrodes are analyzed on the basis of the understanding transmission spectra, projected density of states (PDOS), and molecular orbitals. We believe that the use of thiol linker may open new possibility in the molecular electronics with the Si semiconductor electrodes and the Si QD-molecule hybrid polymers concept.

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1. Introduction

Silicon quantum dot (Si QD) is one of the most attractive nanomaterials that exhibit interesting size-dependent optoelectronic properties due to spatial confinement of exciton in all three-dimensions, because of its many advantages such as nontoxicity, abundance, and compatibility with currently well-established industrial silicon processes, compared to other II–VI or III–V QDs [1]. Surface functionalization of the Si QD has been diversely investigated not only to protect the surface especially from oxidation, but also to tune the optoelectronic properties [2]. Recently, we have found that the surface modification of the Si QD with conjugated organic molecules led to strong electronic coupling between the Si QD and conjugated molecules, resulting in significant alteration of the electronic structure of the Si QD directing to more direct band

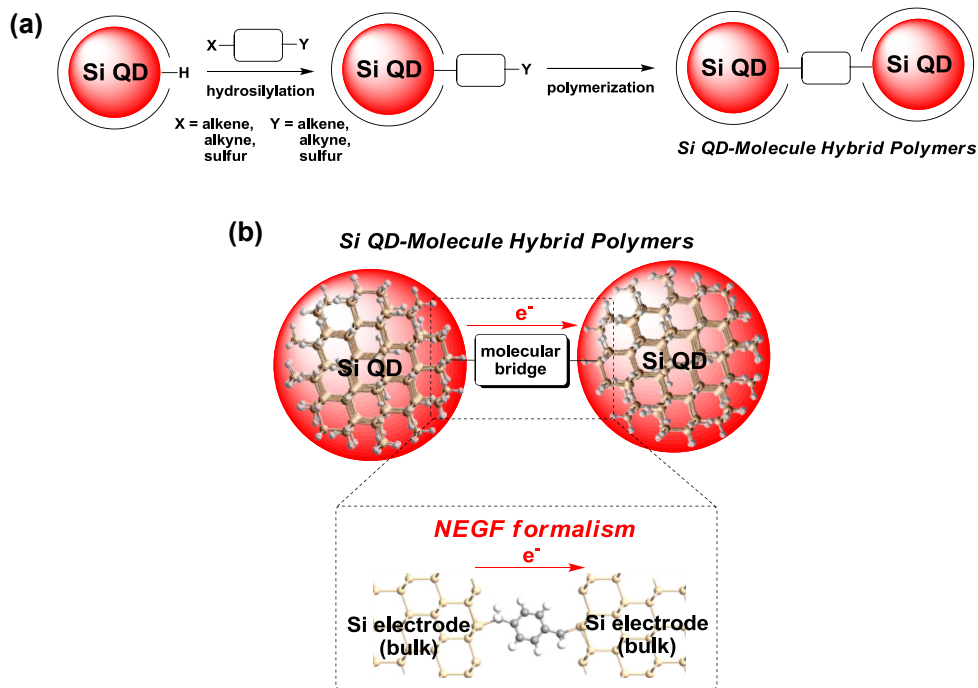
gap character [3]. Also we have demonstrated new material concept, Si QD polymers, in which properly surface-functionalized Si QD by introducing α,ω -bifunctional molecule can be allowed for further chemical reactions [4].

By combining these two aspects in tuning of property and chemical functionality via the surface engineering of the QDs, one can create novel functional materials, *Si QD-conjugated molecule hybrid polymers*, consisting of the Si QDs connected or bridged with conjugated organic molecules throughout the materials (Scheme 1(a)). It can be expected that such Si QD hybrid polymers would have unique optoelectronic properties arising from combinational effects from the size-dependent electronic structure of the Si QD, the electronic coupling between the Si QD and surface molecules, and particularly transporting behavior of electrons through the conjugated molecules in the polymers.

Herein, we aim to approach to the understanding of how electrons transport in such novel hybrid materials by looking at the electron transport properties in the conjugated molecules (the simplest conjugated benzene molecule in this study) coupled in

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Scheme 1. (a) Sequential procedure for preparation of Si QD-molecule hybrid polymers; α,ω -bifunctional molecules are attached to the surface of hydride-terminated Si QD by hydrosilylation reaction on one functional group of the molecule then the Si QD is allowed to give the Si QD-molecule hybrid polymers by polymerization on one another functional group. (b) Electron transport properties in molecules coupled with two bulk Si electrodes are considered on the basis of NEGF formalism for ultimately understanding those in molecules bridging the Si QDs.

bulk-type Si electrodes, as a model system, although the bulk Si electrodes are not completely proper to account for the Si QDs, utilizing nonequilibrium Green's function (NEGF) method that has been intensively developed in molecular electronics field (Scheme 1(b)). We believe that such a suggestion of the viewpoint of adopting the theoretical methodology that has been well developed in the molecular electronics field, to the designing and understanding novel functional materials, i.e. Si QD hybrid, in materials science would provide insights widened.

The molecular electronics, utilizing a single molecule in electronic devices as an active component, have attracted great attention since Aviram and Ratner first suggested in 1974 a molecular rectifier that could function by bridging an electron donating π -conjugated molecular part of low ionization potential and an electron accepting π -molecular part of high electron affinity, with a covalent-bonded σ -spacer [5]. The possibility that such molecular devices can replace the conventional silicon-based electronics which are about to be limited in miniaturization below nanometer-scale due to unavoidable quantum-mechanical phenomena such as tunneling, would turn them into ultimate electronic device architectures in the future [6–11]. However, the molecular electronics are still extremely challenging in practical uses due to the insufficiency of reliable methods to make a stable and/or reproducible electrical contact between individual molecules. Thus, computational approach based on theoretical calculations has drawn much consideration for the study on the basic properties of the molecular electronics.

Dithiol-benzene (DTB) or benzene-dithiol molecule within gold (Au) metal electrodes has been mostly investigated since the DTB molecule is the simplest conjugated model system and the thiol end group of the molecule can form stable chemical bond with the Au electrode surface, enabling strong electronic coupling between the molecule and the electrode as well as reproducible electrical

measurements [12,13]. In 1997, Reed et al. first reported the experimental measurement of the electrical conductance of the single DTB molecule sandwiched between two Au electrodes, based on break junction and self-assembly monolayer techniques [14]. In parallel, the DTB molecule has been intensively studied in the theoretical side from the pioneering work [15] to the more advanced ones based on the density functional theory (DFT) coupled with NEGF method [16,17]. It is known that the electron transport properties of the molecular devices are determined by the combination of many factors such as electronic structure of molecules [18–24], electrode materials [24,25], interface between the molecule and electrode including specific contact geometry [26–28] and anchoring groups [29–31], and external bias potential deriving transistor-like behavior [32,33].

To date, most studies on the molecular electronics have been considered on the basis of the metal electrodes, often Au, due to the aforementioned advantages in the device fabrication process with stable Au–S bond that allows strong coupling between the Au electrode and molecule. On the other hand, utilization of semiconductor electrodes in the molecular electronics is emerging and rarely studied in both experimental [34–37] and theoretical [38–41] sides yet, in spite of its significant technological potential such as the possibility of easy integration into conventional Si semiconductor industry, tunability of the band structure -i.e., work function-of the electrodes by doping process, and high stability of chemical bonding of molecules on the Si semiconductor substrate [38,42]. Such a topic, which attempts to combine both benefits of organic molecules with a number of functionality and those of the Si semiconductor technology, is receiving research attention as a field of silicon-molecule hybrid electronics [34–38,42].

There are several pioneering reports on the theoretical description of electronic transport in a molecular junction with semiconductor electrodes [38–41]. In particular, Ratner group

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