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Graft and characterization of 9-vinylcarbazole conjugated molecule on hydrogen-terminated silicon surface

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Abstract

Using wet chemical reaction between *N*-vinylcarbazole and hydrogen-terminated silicon surface, we present a new and simple route to directly bond π-conjugated organic molecule on silicon surface. The Si can be in the form of single crystal Si including heavily doped p-type Si, intrinsic Si, heavily doped n-type Si, on Si(1 1 1) and Si(1 0 0), and on n-type polycrystalline Si. The covalent bond between 9-vinylcarbazole and silicon surface was confirmed by reflectance FTIR, XPS and contact angle measurement, respectively. A data-encompassing explanation for the mechanism discusses the possible route of the reaction. This simple and low-costly reaction offers an attractive route to attach functional conjugated molecules onto the semiconductor surface which aims to create some unique molecular device in the future.

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Keywords: Graft; Covalent bond; *N*-vinylcarbazole; Silicon surface

1. Introduction

Traditionally, molecular electronic efforts, both theoretical [1–6] and experimental [7–12], have been driven by thiol-gold chemistry to molecules bonded to gold substrates. However, several recent experiments have demonstrated the feasibility of attaching various molecules on silicon surfaces [13–17]. The marriage of organic functionalities with silicon-based device technologies has recently attracted much attention, possibly enabling us to design and create hybrid silicon-molecular electronics. It offers potential opportunities to combine high chemical, mechanical, and thermal stabilities with attractively electronic or optical properties into existing device technologies [18–22]. In addition, the reactions of organic molecules with silicon surfaces play important roles in preparing silicon-organic thin films [23–25]. For example, covalently bound organic monolayers may offer a way to form ultrathin organic films, particularly feasible if the monolayers possess a variety of chemical functionalities. Furthermore, the covalent integration of organic monolayer with semiconductor surfaces, such as silicon, constitutes a convenient strategy for achieving stable and high-quality hybrid junctions [57,58]. This covalent link should enhance the electronic transmission between the two components [59].

To establish the molecular linkages at the interfaces, it is important to understand the reactivity of organic functionalities with silicon surfaces. Over the past 10 years, several methods have been developed to prepare organic monolayers on various morphologies of hydrogen-terminated silicon. The hydrogen-terminated surfaces in general offer many advantages, including their excellent chemical homogeneity (>99% H termination), being stable enough to handle at atmospheric pressure in the presence of solvent vapors, inert gas impurities, and other contaminants and yet reactive enough to undergo chemistry [26]. On the basis of the bond strength of the Si–H bond, a minimum energy of 3.5 eV is required to perform Si–H bond cleavage [26]. Previous studies show that Si–C bond attached monolayers have been successfully achieved by making use of thermal conditions [27–31], UV irradiation [32–35], electrochemistry [36–38], and chemomechanical scribing [39–41]. These studies have allowed a proper characterization of such monolayers, and now allow a focus on the integration of functional groups in monolayers on the silicon surfaces.

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On the other hand, for organic light-emitting diodes (OLEDs), a prominent class of materials that fulfills all conditions is the class of carbazoles. Carbazole is a well known hole-transporting unit. Many carbazole derivatives have sufficiently high triplet energy to be able to host red [42–45], green [46,47], and in some cases even blue [48,49] triplet emitters. Carbazole derivatives can be used as host material for both small-molecule and polymer OLEDs. *N*-vinylcarbazole consists of a vinyl group with carbazole unit attached at side. As such, *N*-vinylcarbazole can be treated as a collection of carbazole molecules. Regarded as the reaction between active hydrogen on silicon and vinyl group, *N*-vinylcarbazole provides a way to introduce carbazole on silicon. Thus, as a typical carbazole molecular, exploring its reactivity on silicon will offer the necessary flexibility in the functionalization and modification of silicon surfaces and the feasibility in the combination of OLEDs and semiconductor.

In this paper, we develop a novel and simple route to directly bond π-conjugated organic molecule on silicon surface. The reaction mechanism of *N*-vinylcarbazole on silicon surface was studied with the objectives of elucidating the nature of *N*-vinylcarbazole/silicon interface. X-ray photoelectron spectroscopy (XPS) provides information on chemical shifts of the C 1s and N 1s core levels. ATR-FTIR was used to characterize the vibrational properties of 9-vinylcarbazole on silicon surface.

2. Experimental

2.1. Materials

2.1.1. Chemicals

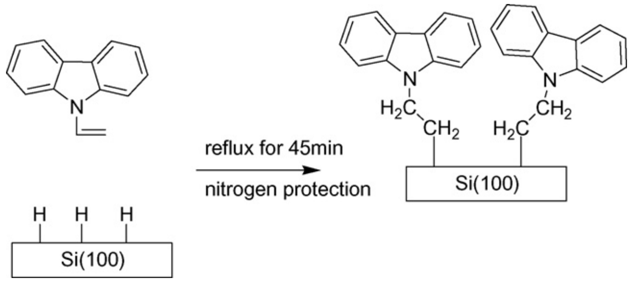
MeOH, EtOH, and CH_2Cl_2 were distilled prior to use. Distilled CH_2Cl_2 was used as a solvent in chemical reactions. *N*-vinylcarbazole was used as received. All reactions were performed under a nitrogen atmosphere.

2.1.2. Wafers

Silicon samples were slices of single-polished wafers. All silicon samples were n-type doped samples (0.1 Ω cm), obtained from Aldrich Chemical Co., WI.

2.2. Preparation of H-terminated silicon surfaces

The silicon samples were firstly cleaned by rinsing with CH_2Cl_2, dried, and then oxidized in 3:1 concentrated H_2SO_4/30% H_2O_2 for 2 h at 100 °C, followed by thorough rinsing with 18 MΩ cm H_2O. The surface was etched in nitrogen-sparged 40% aqueous NH_4F solution for 4 min. We choose NH_4F etching for Si(1 0 0) because this etching solution has been shown to produce the least contaminated and most stable hydrogen-terminated Si(1 0 0) among commonly used etching procedures [50]. After NH_4F etching, the silicon surfaces was rinsed with 18 MΩ cm H_2O for a few seconds and then dried under argon. Upon drying, the crystal was transferred to a glass reaction cell, which was connected to a vacuum line pumped by a diffusion pump. The cell was evacuated to a base pressure of 1×10^{-5} Torr.



Scheme 1. Reaction route between *N*-vinylcarbazole and H-terminated Si(1 0 0) surface.

2.3. Monolayer preparation by thermal method

A solution of *N*-vinylcarbazole was placed in a small three-necked flask fitted with a nitrogen inlet, a reflux condenser with a $CaCl_2$ tube, and a stopper. The solution was refluxed for at least 45 min under a flow of nitrogen. Subsequently, a cleaned and freshly etched sample was added to the refluxing solution, while a slow nitrogen flow was maintained. After 12 h the modified sample was removed from the solution and excessively rinsed with EtOH and CH_2Cl_2, respectively. The reaction route between *N*-vinylcarbazole and H-terminated Si(1 0 0) surface was shown in Scheme 1.

2.4. Analysis of the monolayer

2.4.1. Contact angle measurements

In all cases where modified samples were analyzed by different techniques, a small piece (∼10 mm × 10 mm) was cut from the sample directly after cleaning. Static water contact angles were obtained using an Erma G-1 contact angle meter (volume of the drop of ultra pure water, 3.5 μL). Contact angles of two or three drops were measured. The error of the contact angles is ±1°.

2.4.2. Fourier transform infrared spectroscopy in the attenuated total reflection mode (FTIR-ATR)

The film was grown on the Si(1 0 0) surface. A KRS crystal was sandwiched between the reflective faces of two silicon wafers, and the angle of incident light was set at 45°. All spectra were run for 4000 scans at a solution of 4 cm^{-1}. A spectrum of two clean silicon wafers with a sandwiched KRS crystal was measured as a background correction.

2.4.3. X-ray photoelectron spectroscope

XPS measurements were performed on a VG Ionex system equipped with a Clam II analyzer and a standard Al Kα X-ray source. Spectra were taken in normal emission at 10^{-9} mbar. In the XPS experiments, the Al X-ray source ($h\nu = 1486.6$ eV) was used. All of the spectra presented in this paper are referenced to the binding energy (BE) of 99.3 eV [51] for the bulk Si 2p XPS peak. The spectra of the monolayer were fitted with the software VGX900 (VG Scientific, UK). During the fitting, the full width at half-maximum (fwhm) of each peak was kept at 1.2 eV, which is the typical resolution of the C 1s core level for our XPS system.