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Optimizing Germanium-Selective Functionalization on Patterned SiGe Substrates with Thiol-Based Molecules: The Critical Role of Oxygen-Free Conditions †

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Abstract: Germanium offers attractive optical properties despite being an indirect bandgap semiconductor, and new Ge-based devices are being optimized for sensing and photonics applications. In particular, considering the use of Ge as a sensor, improving its selectivity via organic grafting offers new alternatives that are still under investigation. In this work, we focus on the selective functionalization of germanium in SiGe-patterned alloys using a custom thiol-based luminescent molecule, namely 6-[2,7-bis[5-(5-hexyl-2-thienyl)-2-thienyl]-9-(6-sulfanylhexyl)fluoren-9-yl]hexane-1-thiol. The process selectively targets regions with Ge, while leaving Si-rich areas uncovered. Moreover, this study emphasizes the importance of an oxygen-free environment, as performing the functionalization in an inert atmosphere significantly improves surface coverage.

Keywords: germanium; silicon; SiGe; functionalization; grafting; semiconductor

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1. Introduction

Silicon (Si) has been the preferred semiconductor for a wide range of electronic and microelectronic applications for over 40 years, largely due to its stable oxide (SiO_2). However, as modern microelectronics rapidly advance, there is increasing interest in germanium as a potential replacement for silicon in future generations of optoelectronic devices [1–3]. This is because germanium exhibits higher carrier mobility and a narrower bandgap. Nonetheless, the limited use of a germanium platform as a sensor is attributed to its unstable surface, including poor passivation, thermal instability, and water-soluble oxide [4,5]. Within this framework, achieving stable and high-coverage surface functionalization is essential for tuning and enhancing the material properties needed for these advanced technologies.

The functionalization of silicon surfaces involves well-established protocols [6–10], and several molecules are reported to form stable monolayers on Si; meanwhile, the current literature on germanium surface functionalization is quite limited. Additionally, the literature on SiGe functionalization is even more restricted, with only few available examples [11–13].

The thiol group generally proposed as the best grafting system for Ge substrates is also the most promising candidate for the selective functionalization of SiGe surfaces.

To study functionalization, we synthesized a luminescent model molecule with terminal thiol groups, which is easily detectable with confocal microscopy. The SiGe substrates are pre-treated with halide passivation (performed using HCl), leaving a Cl-terminated Ge. The substrates are then functionalized with the thiol-based 6-[2,7-bis[5-(5-hexyl-2-thienyl)-2-thienyl]-9-(6-sulfanylhexyl)fluoren-9-yl]hexane-1-thiol molecule.

In our work, we show that this process selectively functionalizes the SiGe pattern, where Ge is present while leaving the SiO_2 area almost uncovered, confirming the selective properties of the organic grafting. Here, we optimized conditions for effective SiGe grafting, highlighting the crucial role of oxygen. The study shows that performing the functionalization procedure in an oxygen-free atmosphere significantly enhances the extent of coverage on the substrate, highlighting the importance of an inert environment in achieving optimal functionalization results. For selectively functionalizing germanium fractions on substrates made of SiGe patterns on a SiO_2 background, we have chosen to follow, as a reference. a protocol similar to the one used for the functionalization of germanium. In the literature, three main methods of functionalizing germanium are present: (i) Grignard chemistry [14,15], (ii) alkanethiol passivation [16,17], and (iii) hydrogermilation [18]. Both the Grignard chemistry and hydrogermilation approaches result in the formation of a Ge-C bond but can also result in a Si-C bond formation, while the alkanethiol passivation results in the selective creation of Ge-S bonds [19–21].

An additional challenge that needs to be addressed concerns the characterization technique used to evaluate the quality of surface grafting. Contact angle measurements and techniques such as XPS may not be sufficiently sensitive to detect grafting, which, in the case of complete surface coverage in a SiGe 30% system, would involve only 30% of the available surface. One of the most sensitive techniques is luminescence; for this reason, we decided to develop a luminescent molecule that could provide an immediate assessment of grafting quality. Among the most widely used luminescent molecules, fluorene-based compounds play a crucial role due to their ease of functionalization and high photoluminescence efficiency [22–24].

We have synthesized a custom thiol-based fluorene derivative designed to specifically meet our requirements: (i) selectively functionalize germanium by forming a Ge-S bond, and (ii) being easily detectable by fluorescence microscopy due to its fluorescent properties. The molecule we designed is a thiophene-fluorene-based molecule with a thiol-terminal alkyl chain, namely 6-[2,7-bis[5-(5-hexyl-2-thienyl)-2-thienyl]-9-(6-sulfanylhexyl)fluoren-9-yl]hexane-1-thiol (Bis-TTF).

Using the fluorescent molecule, we successfully demonstrated the effectiveness of S-H group functionalization through confocal microscopy. Additionally, our experiments revealed that working in the absence of oxygen, under an inert atmosphere (nitrogen) during all the functionalization steps, significantly improves the efficiency of the functionalization, most likely because oxygen competes with thiol functionalization in the reformation of the surface oxide layer.

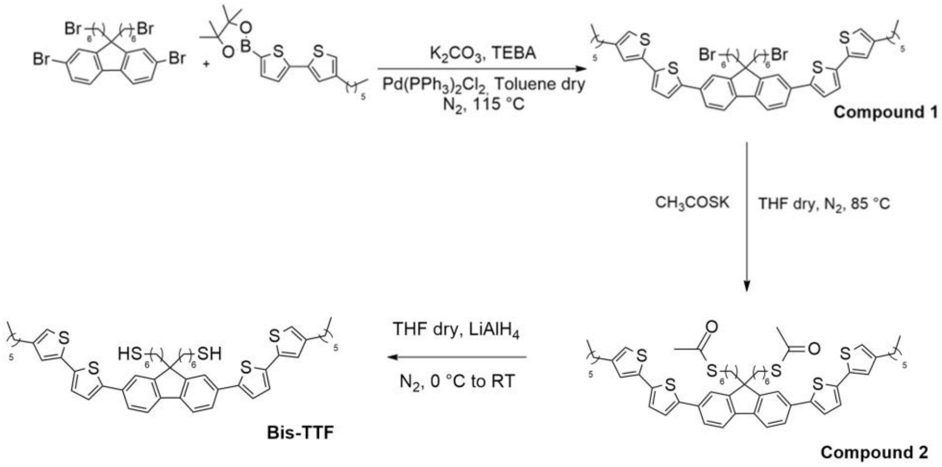
2. Materials and Methods

2.1. Materials

Organic grafting was optimized on an alloy of Si_1-xGe_x, with a Ge content (x) of about 30%. A total of 26 nm of this SiGe alloy was deposited in a molecular beam epitaxy reactor (MBE) on 14 nm thick monocrystalline silicon on an insulator (on 25 nm thick buried oxide, BOX) previously diced in 2 cm × 2 cm samples [25]. To improve the selectivity of the organic grafting to the germanium element, all samples were pre-patterned to obtain germanium zones versus areas covered by thermal oxide or pure silicon. The SiGe or pure Ge areas were patterned by optical lithography and transferred to the SiO_2 films by dry etching (CF_4 plasma) [26]. Specifically, the adhesion promoter Ti prime was spin-coated at 3000 rpm for 5 s, and then the positive resist AZ 5214E was spin-coated in two different steps at 750 rpm for 5 s and at 4000 rpm for 40 s. By reactive ion etching (RIE), roughly 30 nm of SiGe or pure Ge was etched.

2.2. General Information for Synthesis

All reagents were purchased from commercial sources and used without further purification. All solvents have been distilled prior to use. All reactions were carried out in an inert atmosphere. The 1H NMR spectra were recorded with a Bruker ARX 400 MHz spectrometer (Bruker, Karlsruhe, Germany). The reaction path can be followed in Scheme 1 below.



Scheme 1. Reaction scheme for the synthesis of Bis-TTF.

Synthesis of ***compound*** **1.** A total of 260 mg (0.4 mmol) of fluorene, 300 mg (0.8 mmol) of thiophene, and 8.5 mg (3%) of the $Pd(PPh_3)_2Cl_2$ catalyst and TEBA are placed in a Schlenk tube to undergo some nitrogen–vacuum cycles. Then, 6 mL of fresh distilled Toluene and 3 mL of a degassed 2M K_2CO_3 aqueous solution are added under nitrogen. The reaction is heated at 115 °C in an oil bath overnight. The reaction mixture is diluted with EtOAc and washed 3 times with distilled water; then, the organic phase is anhydrificated with sodium sulfate, filtered, and dried in a rotary evaporator. The clean product (M_W = 989.14 g/mol) is obtained after purification through a silica gel column, using as eluent an 8:2 mixture of hexane and dichloromethane with a final yield of 39% (154 mg).

Synthesis of ***compound*** **2.** A total of 154 mg (0.156 mmol) of compound **1** and 10 eq. (166 mg) of Potassium Thio-Acetate are placed in a Schlenk tube to undergo some nitrogen–vacuum cycles. Then, 3.5 mL of fresh distilled THF is added and the reaction is kept at 85 °C in an oil bath overnight. The reaction mixture is diluted with EtOAc and washed 3 times with distilled water and brine. The organic phase is dehydrated with sodium sulfate, filtered, and dried with a rotary evaporator. The product is obtained after a chromatographic column with silica gel using a 6:4 to a 1:1 hexane–dichloromethane eluent mixture, yielding 98 mg (0.1 mmol; 64%) of clean product.

Synthesis of ***Bis-TTF molecule.*** The molecule is obtained through the reduction of the thio-acetate moiety in the thiol group. A total of 2.98 mg of the compound **2** is placed in a Schlenk tube to undergo vacuum–nitrogen cycles, and then fresh distilled THF, 4 mL, is added. A 1 M solution/dispersion of $LiAlH_4$ is prepared under nitrogen in another Schlenk tube in fresh distilled THF:15 mg of reductant (4 eq.), which undergoes nitrogen–vacuum cycles, in 0.4 mL of THF. The Schlenk tube is placed in an ice bath and 0.4 mL of the reductant solution is added; the reaction is kept at room temperature for half an hour and then 1 mL of AcOEt is added to avoid S-S dimer formation for another 30 min. The reaction mixture is then diluted with EtOAc and washed with distilled water, the organic phase is anhydrificated with sodium sulfate, filtered, and dried with a rotary evaporator. The reaction is quantitative, leading to obtaining 87 mg of the final product.

2.3. Substrate Functionalization Procedure

The SiGe substrates were cleaned using the following procedure: 10 min in acetone, 10 min in isopropanol, and then drying under a nitrogen flux. After cleaning, etching was performed by immersing the substrates in a 10% HCl solution for 10 min. The substrates were then rapidly immersed in deionized water and then in isopropanol. Next, the samples were immediately transferred into a solution of 2.25 mM of Bis-TTF molecules in a 6:4 mixture of ethyl acetate and THF at 50 °C for 24 h. Afterwards, the substrates were rinsed with fresh ethyl acetate and THF to remove any possible physisorbed molecule residue from the SiGe surface. Finally, the samples were blow-dried under nitrogen before characterization.

2.4. Characterization

Microscopy fluorescence images were collected with a Nikon Eclipse TE2000-U inverted confocal microscope (Nikon, Tokyo, Japan) via excitation with a 100 W Hg lamp with a 450–490 nm band-pass excitation filter.

3. Results

The passivation of germanium using alkanethiol involves a two-step process. First, the native oxide is removed, and then the passivation step is carried out. The native oxide can be eliminated by using halide acids (HX, where X = F, Cl, or Br) [27–30]. In this case, we used HCl, which results in a Cl-terminated surface. This surface is reactive towards thiols and oxides at a slower rate than an H-terminated Ge surface, allowing the material to be manipulated for a sufficient time in the laboratory [30].

Bis-TTF (Figure 1) was designed to attach to Ge using its thiol moieties. Its presence can be easily monitored using a fluorescence optical microscope because of its good fluorescence typical of fluorene-thiophene-based molecules. We decided to attach a bithiophene to the fluorene instead of a single thiophene to shift the emission to a region that can be easily excited by the lamps of the confocal microscope [31]. This is important because we want to selectively functionalize only the regions of our samples where Ge is present (specifically the SiGe pattern). Therefore, if the attachment is effective and selective, we expect to detect a luminescent pattern where the molecule is attached by shining UV light on the sample.

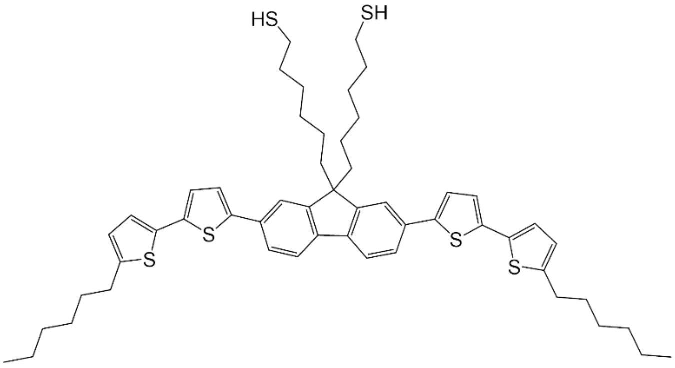


Figure 1. Chemical structure of the grafted molecule.

Fluorescence microscopy images in Figure 2a,b highlight the preferential selective functionalization in atmospheric conditions (moisture and oxygen) mostly occurring in correspondence with the SiGe pattern. It is indeed possible to follow the pattern of an H letter in panels (a) and (b).

To increase the coverage of functionalization on the germanium, we attempted to minimize the presence of oxygen during the procedure by operating with distilled solvents under a nitrogen atmosphere. As mentioned earlier, when exposed to oxygen, silicon and germanium create an oxide layer when exposed to air. It is indeed possible that the formation of germanium oxide could compete with the grafting of thiol molecules, thereby limiting their bonding to the surface.

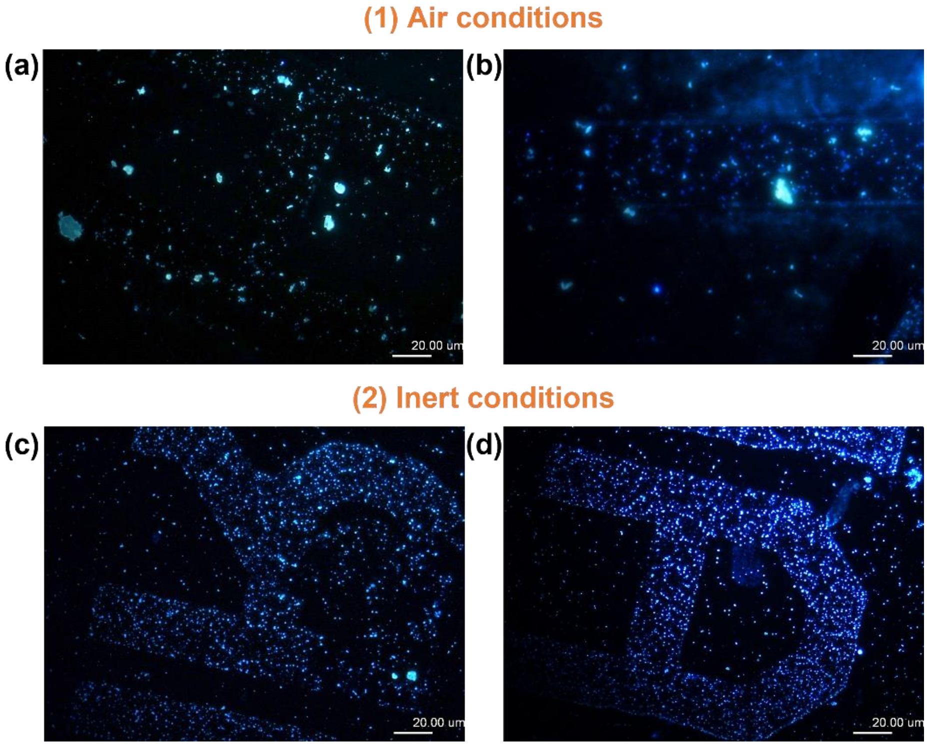


Figure 2. Fluorescence microscopy images of SiGe samples functionalized in (**1**) air, two different sample regions (**a**,**b**) and (**2**) under inert conditions, two different sample regions (**c**,**d**). Samples are irradiated by UV light.

Working in a nitrogen atmosphere results in increased functionalization of the germanium portion, as shown in Figure 2, panels (c) and (d). It is possible to follow the pattern of R and A letters in panels (c) and (d), respectively.

4. Conclusions

Our experiments demonstrate the successful selective functionalization of Ge in prepatterned SiGe films. These findings highlight the effectiveness of confocal microscopy in detecting grafting, made possible through the use of appropriate fluorescent molecules. Furthermore, we observed that, unlike pure Ge surfaces, the elimination of oxygen plays a crucial role in SiGe systems. Specifically, we underscore the detrimental impact of oxygen during the process, as its presence results in reduced substrate functionalization. This may be attributed to the greater susceptibility of Ge to oxidation when present in alloys like SiGe 30%. To mitigate this effect, we have shown that performing the process in a nitrogen atmosphere leads to optimal results. Additional analyses, such as XPS and TOF-SIMS, will be conducted to confirm the presence of Ge-S bonds.

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Data Availability Statement: The data presented in this study are available on request from the authors.

Conflicts of Interest: Author Laura Pasquardini was employed by the company Indivenire Srl. The remaining authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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