Unusual Reactivity of Group 14 Hydrides toward Organic Halides: Synthetic Studies and Application to Functional Materials

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Abstract: Extensive investigation of functional organosilicon and organogermanium compounds has identified various valuable applications in organic chemistry and advanced materials. This review summarizes the major developments of metal–mediated coupling reactions between group 14 hydrides and organic halides during the last decade with an emphasis on our own studies. High reactivity and selectivity have been achieved for C–Si and C–Ge bond formations under mild conditions. This transformation shows good functional group compatibility, and can serve as a powerful tool for the synthesis of medicinal, pharmaceutical, agrochemical, electrical, and photoluminescent compounds. Ground- and excited-state properties of fluorescence materials have been investigated by DFT and TD–DFT calculations, and several important aspects of the experimental observations have been validated. Direct functionalization of H–terminated Si and Ge surfaces has been demonstrated utilizing Pd(II)–mediated arylation reactions, illustrating the potential for further development of the Pd–catalyzed reactions for the organic modification of semiconductor surfaces.

Key words: C–Si bond formation, group 14 compounds, cross-coupling, palladium, rhodium, platinum, samarium, σ–π conjugation, photoluminescence, surface functionalization, self-assembled monolayer.

1. Introduction

The formation of C(sp³)–E (E=Si, Ge) bonds is a fundamental organic reaction, and has attracted much attention in fields such as medicine, pharmacology, agrochemistry, and material science. Arylsilanes or arylgermanes are generally prepared by reacting halosilanes or halogermanes with corresponding organometallic reagents. However, this approach suffers from poor functional group tolerances when the starting substrates bear reactive functional groups. In addition, these starting materials are moisture-sensitive, corrosive, and difficult to handle. They are also often accompanied by substantial salt formation and side reactions. Therefore, the development of new, easier methods for the synthesis and modification of group 14 compounds is highly desirable.

The activation of Si–H and Ge–H bonds with transition metal complexes is a fundamental step in several catalytic transformations of organosilanes and organogermanes. Reduction and hydrolylation are representative chemical synthesis. Palladium, platinum, and rhodium catalysts are frequently used in these reactions. Another type of transformation is still a challenge in the field of organometallic chemistry to form C(sp³)–E bonds. Transition metal–catalyzed C(sp³)–E formation reactions with group 14 hydrides appears to be highly promising for the synthesis of functionalized group 14 compounds. Recently, silylation of aryl C–H bonds with hydroxilanes has been reported in the presence of transition metal catalysts. However, there are still problems such as substrate scope, need for an excess of aromatic substrates, and high temperature in this reaction.

This review considers the synthesis and functional properties of novel organosilicon and organogermanium compounds based on the unusual reactions of group 14 hydrides toward organic halides in the presence of a catalytic amount of transition metal complex and a stoichiometric amount of organic base. This reaction shows wide scope for organic halides and group 14 hydrides. An area with great potential is synthetically useful compounds such as biologically active silicon ones. Effective synthesis of some organosilicon–based pharmaceuticals and crop protection agents which are already on the market was described by the use of this transformation. Some group 14 compounds prepared by this reaction have shown high solid–state fluorescence intensity, and the relationship between fluorescence and structure has been investigated by X-ray diffraction analysis and theoretical calculations. We have also demonstrated the application of this transformation to the immobilization of aromatic compounds on hydrogen-terminated silicon and germanium surfaces.

2. Transition Metal–catalyzed Synthesis of Group 14 Compounds via Coupling Reaction between Aryl Halides and Group 14 Hydrides

Although palladium–mediated Si–C bond formation using cross-coupling between hydroxilanes and organoiodine compounds has been reported by Kunai et al., progress in the catalytic arylation of hydroxilanes has been limited. Due to the electronegativity (H: 2.20, Si: 1.74), halosilanes were preferentially obtained by transition metal catalysis through hydride–halogen exchange reactions. Murata and Masuda were the first to report the use of trialkoxysilanes as precursors to prepare aryltrialkoxysilanes in the presence of transition metal catalysts. Similar reactions were subsequently developed by Komuro, DeShong, and Denmark. However, Murata and Masuda mentioned that triethylsilane was not suitable as a silylating reagent because of its strong reducing power in the palladium–catalyzed silylation of aryl halides. Our group focused on the arylation of trialkysilanes with aryl halides in the presence of a Pd(0) catalyst containing the bulky alkyl phosphate ligand. The trend of the reactivity is Ar–H > Ar–Br > Ar–Cl in this reaction. The steric and elec-
tronic nature of the phosphine ligand greatly affected its reactivity. Screening of palladium catalysts indicated that Pd(P(t-Bu))₂ was effective for this transformation. To evaluate the utility of the Pd-catalyzed Si–C bond formation, a series of aryl iodides and tertiary silanes were tested (Table 1). Aryl iodides bearing electron-donating groups showed good results in producing the corresponding arylated silanes (1–6). Hindered aryl iodide substrates in the ortho position gave poor results, probably because of the steric repulsion between the ligand and the ortho substituents. For example, 1-iodo-2,4-dimethyloenzene and 2-iodoanisole, both sterically demanding substrates, led exclusively to the catalytic deiodination product (7 and 8). Aryl iodide bearing an electron-withdrawing group did not show good result (9). Further improvement was considered to expand the scope and to overcome limitations of this method.

Table 1. Pd(P(t-Bu))₂-catalyzed Si–C bond formation with hydrosilanes and aryl iodides.

<table>
<thead>
<tr>
<th>Ar</th>
<th>MeO-</th>
<th>MeO-</th>
<th>MeO-</th>
<th>H-</th>
<th>1, 84%</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>2,65%</td>
<td>5,76%</td>
<td>6,51%</td>
<td></td>
<td>7, trace</td>
</tr>
<tr>
<td>8, Trace</td>
<td>9, not obtained</td>
<td></td>
<td></td>
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</table>

The reaction tolerated a wide range of aryl iodides bearing electron-donating substituents at ortho, meta, and para positions and electron-withdrawing substituents at meta and para positions and gave satisfactory yields in the presence of Rh catalyst (Table 2, 8, 10 and 11). This method is compatible with a range of functional groups, such as ester, amino, and hydroxyl ones, which is in sharp contrast to the limitations of classical method using organometallic reagents (12–17). We used this C–Si bond formation to synthesize TAC–101 analog 20 using Rh-catalyzed Si–C bond formation as a key step.

Scheme 1. Shorter alternative synthetic route to the TAC–101 analog 20 using Rh-catalyzed Si–C bond formation as a key step.

Reagents and conditions: (i) 4-H₂NC₆H₄CO₂Me, EDC- HCl, Et₃N, HOBT, DMF, 50 °C, 2 d, 81%; (ii) [Rh(cod)₂]BF₄ (5 mol%), Et₃SiH, DMPU, rt, 4 d, 68%; (iii) aqueous NaOH/ EtOH, rt, 1 d, 99%.

We reported that the arylation of secondary or primary silanes with aryl iodides in the presence of Pd(P(t-Bu))₂ provided the corresponding arylated products in good to excellent yields (Table 3). The coupling reaction of secondary silanes and aryl iodides gave the corresponding tertiary silanes (single arylated products) and quaternary silanes (double arylated products) by controlling reaction conditions. Similarly, coupling reaction of primary silanes and aryl iodides also gave secondary silanes (single arylated products), tertiary silanes (double arylated products), and quaternary silanes (triple arylated products). The same reactivity was observed for a series of tertiary, secondary, and primary germanes with aromatic and aliphatic substituents. The important feature of this method is the one-pot sequential double arylation of secondary silanes or germanes with two different aryl iodides. Two aryl iodides Ar⁻¹–I and Ar⁻²–I were cross-coupled with secondary or primary group 14 hydrides to produce unsymmetrically substituted group 14 compounds (21–26) by controlling equivalent of aryl iodides. Pd-catalyzed double arylation had an application for the synthesis of flusilazole, a widely used antifungal agent.

This methodology allows easy and versatile synthesis of
unsymmetrical disiloxanes with high functional group compatibility. Siloxanes, linked by SiO\textsubscript{2} bonds, have been studied for use in liquid crystals or starting materials for Hiyama coupling. Symmetrical disiloxanes are obtained from monomeric organoalkoxysilanes by hydrolysis, followed by condensation. However, there are few reports on the synthesis of unsymmetrical siloxanes with reactive functional groups. We have developed the stepwise Pd\textsuperscript{2} catalyzed arylation of siloxane containing Si\textsuperscript{2} bonded hydrogens (1,1,3,3\textsuperscript{2}tetramethyldisiloxane) to prepare unsymmetrical siloxanes. The stepwise arylation proceeded in higher yields in less polar solvent (toluene). Cooler reaction conditions also gave higher yields due to the suppression of reduction of aryl iodides and double arylation of siloxane. Under optimized conditions, they were prepared in up to 82% yield with a broad range of functional groups and substitution positions (Table 4, 27\textsuperscript{2}30\textsuperscript{2}).

Optically active silicon-stereogenic organosilanes are promising for use as chiral auxiliaries, reagents, resolving agents, and drug candidates. Despite much investigation into the preparation of enantioriched organic compounds with a carbon-stereogenic center, the available strategies are restricted to the desymmetrization of prochiral organosilanes. We reported a palladium/phosphoramidite catalyzed asymmetric arylation of prochiral secondary silanes with aryl iodides to give tertiary silanes in up to 76% enantiomeric excess (ee). In this reaction, ortho substituted aryl iodides are required to achieve high enantioselectivity (Table 5, 33\textsuperscript{2}38\textsuperscript{2}).

A possible mechanism for the reaction is depicted in Figure 1 based on the experimental results. This transformation gave better results using electron-donating aryl iodide as a substrate, which exhibited a reactivity to aryl iodides different from typical Pd\textsuperscript{2} catalyzed C-C bond formation. From the observation of H NMR in THF-d\textsubscript{4}, the metal–hydride peak was observed at high magnetic field region during the course of stoichiometric reaction. Accordingly, hydrosilane (H–SiR\textsubscript{3}) Scheme 2. Palladium-catalyzed triple–stepwise arylation of 3-((dimethylsilyloxy)-1,1,3,5,5–pentamethyltrisiloxane.\textsuperscript{a}

Table 3. Stepwise arylation of primary and secondary group 14 hydrides.\textsuperscript{a}

Table 4. Palladium–catalyzed stepwise arylation of 1,1,3,3–tetramethyldisiloxane.\textsuperscript{a}

Table 5. Catalytic enantioselective arylation of secondary silanes.

\textsuperscript{a} Reaction conditions: (i) Pd(P(t-Bu)\textsubscript{3})\textsubscript{2} (0.025 mmol), 3-((dimethylsilyloxy)-1,1,3,5,5–pentamethyltrisiloxane (0.50 mmol), 4-todoanisole (0.50 mmol), (i-Pr\textsubscript{2}EtN (1.0 mmol), toluene (2.25 mL), 0 °C, 2 h; (ii) (i-Pr\textsubscript{2}EtN (1.75 mmol), 2-iodoethene (0.875 mmol), 0 °C, 4 h; (iii) (i-Pr\textsubscript{2}EtN (1.75 mmol), 1-(n-butyl)4-iodobenzene (0.875 mmol), 0 °C, 1 d. \textsuperscript{b} Yield was based on 4-todoanisole.

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adds oxidatively to the Pd(0) center to generate hydrido silyl complexes (H\textsuperscript{+}Pd(II)\textsuperscript{+}SiR \textsubscript{3}) at the initial stage. Then, a pathway through \(\sigma\)-bond metathesis between the Pd(II) species and aryl iodide or a pathway through further oxidative addition of Ar-I to generate Pd(IV) species would lead to arylsilanes, although this step remains poorly understood. Finally, reductive elimination gave arylsilanes by the aid of base along with the generation of catalytic species (path I). During the transformation, another cycle that produces the reduced product is competitive with this route through I-Pd(II)-Ar intermediate (path II). Steric and electronic factors of phosphine ligand have a significant effect on this step.

Our metal-mediated system is not limited to using only aryl iodides as coupling partners. Next, we focused on forming Si-C(sp\textsuperscript{3}) bonds using iodoalkanes as coupling partners (Table 6). In the presence of Pt(P(r-Bu))\textsubscript{2}, coupling reactions of tertiary silanes with 1-iodoalkane provided alkylated quaternary silanes in good yield (39-43). This reaction worked well for a broad range of functional groups such as ester and cyano moieties (44 and 45). To highlight its practical utility, we used it in the synthesis of silafluoren (46), an agricultural insecticide. The optimized Pt-catalyzed alkylation of arylsilanes with alkyl iodide gave silafluoren in 42% yield, demonstrating suitability of this reaction for the simple preparation of biochemical components.

Preferential carbene insertion into Ge-H was compared with other heavier group 14 hydrides. Metal carbenoids are usually prepared from metals (e.g., Zn, Al, Sm, etc.)\textsuperscript{25} and 1,1-dihaloalkanes, and their insertion into heteroatom–hydrogen bonds is a well-established process. Although excellent yields can be obtained by carbenoid insertion into Si-H bonds, chemoselective carbene insertion into group 14 hydrides has not been reported. To compare the reactivity in a competitive environment, an equimolar solution of triphenylsilane, triphenylgermane, and triphenylstannane was treated with Sm carbenoids prepared by samarium metal and bromoiodomethane in situ (Figure 2(a)). Surprisingly, samarium carbenoid was found exclusively to attack triphenylgermane to give triphenylmethylgermane (47) in 85%, although Zn and Al carbenoids led to a statistical mixture of products. To demonstrate the synthetic utility of this methodology, we selectively inserted a carbene into a compound containing both Si-H and Ge-H moieties in the same molecule (48). As expected, the Sm carbenoid exhibited complete Ge-H selectivity, and the Si-H functionality remained unaffected during the transformation (49, Figure 2(b)).

### Table 6. Substrate scope of the Pt-catalyzed alkylation of tertiary silanes with 1-iodoalkanes.

<table>
<thead>
<tr>
<th>R\textsubscript{3}Si=H (3.0 equiv)</th>
<th>Pt(P(r-Bu))\textsubscript{2} (5 mol%)</th>
<th>R\textsubscript{3}Si=H (1.0 equiv)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CH\textsubscript{2}Br/THF</td>
<td></td>
</tr>
<tr>
<td></td>
<td>–78 °C to rt</td>
<td></td>
</tr>
<tr>
<td>Ph\textsubscript{3}SiH</td>
<td>Ph\textsubscript{3}GeH + Ph\textsubscript{3}SnH</td>
<td>Sm (4.0 equiv)</td>
</tr>
<tr>
<td>Ph\textsubscript{3}GeH</td>
<td>Ph\textsubscript{3}SnH</td>
<td>CH\textsubscript{2}Br/THF (4.0 equiv)</td>
</tr>
<tr>
<td></td>
<td>99 : 1 : 0</td>
<td>–78 °C to rt</td>
</tr>
<tr>
<td></td>
<td>(47, 85%)</td>
<td></td>
</tr>
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</table>

**Figure 2.** (a) Chemoselective methylene insertion with samarium carbenoid. (b) Selective carbene insertion into the Ge-H group of 49.

### 3. Application to Fluorescent Materials

The introduction of various heteroatoms into the backbone of organic compounds is interesting approach for exploring new materials because it is expected to provide unusual electronic structures and photophysical characteristics. Especially, bridging an aromatic ring by Si or Ge atoms influences the spectroscopic properties due to hyperconjugation which

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often enhances the fluorescence intensity. To expand the scope of the transformation, we examined the possibility of its application to group 14 fluorescent materials.

π-Conjugated group 14 metallole units have recently been recognized and extensively studied for their potential applications in organic light-emitting diodes (OLEDs). The σ* orbital of the Si–C bond can effectively interact with the π* orbital of the butadiene fragment, decreasing the LUMO energy level. The traditional synthesis of these compounds often suffered from low functional group compatibility owing to the use of stoichiometric organometallic reagents, and catalytic Si–C or Ge–C bond formation has emerged as a new strategy for the synthesis of group 14 metalloles. A series of group 14 dibenzometalloes was synthesized from the corresponding dihydrides and 2,2′-diiodoarenes using Pd-catalyzed bond formation to investigate their photophysical properties.

Table 7. Synthesis of functionalized dibenzosiloles and dibenzogermoles.

<table>
<thead>
<tr>
<th>R</th>
<th>Ph</th>
<th>Yield</th>
</tr>
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<tbody>
<tr>
<td>El: 50</td>
<td>51</td>
<td>88%</td>
</tr>
<tr>
<td>El: 54</td>
<td>55</td>
<td>81%</td>
</tr>
<tr>
<td>El: 56</td>
<td>57</td>
<td>68%</td>
</tr>
<tr>
<td>El: 58</td>
<td>59</td>
<td>64%</td>
</tr>
<tr>
<td>El: 60</td>
<td>61</td>
<td>55%</td>
</tr>
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</table>

Our method could be useful for constructing other types of luminescent material. Organic molecules containing conjugated six-membered rings are less well investigated due to limitations of the synthetic methodology. We obtained silicon-containing six-membered ring compounds, 9,10-dihydro-9,10-disilaanthracenes, in acceptable yields (up to 43%) via palladium-catalyzed coupling reactions between 1,2-bis(dimethylsilyl)arenes and 1,2-diiodoarenes using the simple one-pot procedures listed in Table 8 (62–69). This reaction provides a rare example of unsymmetrical 9,10-dihydro-9,10-disilaanthracenes. We also investigated the fluorescence at room temperature and phosphorescence at 77 K of these compounds and carbon analog 70. Compound 67, bearing ester groups on aromatic ring, displayed blue phosphorescence with ΦP of 0.06; although the carbon analog 70 did not show any phosphorescence at all.

Table 8. Synthesis of 9,10-dihydro-9,10-disilaanthracenes 62–69.

<table>
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<tr>
<th>Ar</th>
<th>Ph</th>
<th>Yield</th>
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<tbody>
<tr>
<td>62</td>
<td>63</td>
<td>27%</td>
</tr>
<tr>
<td>65</td>
<td>66</td>
<td>21%</td>
</tr>
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<td>68</td>
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<td>68</td>
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</table>

* Yield is based on 1,2-diiodoarene used.
gated $\pi$-electrons linked to an electron donor (D) at one end and an electron acceptor (A) at the other have been recognized as a class of electroluminescence and nonlinear optical materials. The replacement of C=C bonds by Si-Si bonds is especially interesting, because they have similar chemical and physical properties. This feature may give rise to unique fluorescence properties of organodisilane compounds. The introduction of electron-donating and -withdrawing groups to the appropriate positions of disilane unit can provide D-Si-Si-A molecules. These unsymmetrical substituted disilanes were obtained by coupling 1-aryl-1,1,2,2-tetramethyldisilanes with aryl iodides in the presence of a Pd catalyst. We studied their photophysical properties and second order nonlinear optical responses (second harmonic generation (SHG)) by a powder method (Figure 4). Compounds 71–76 are stable thermally and chemically, and exhibit a strong emission at room temperature. The introduction of strong electron donors and acceptors is highly sensitive to solvent polarity in fluorescence. Among these compounds, 76 showed intense solid-state blue emission due to the suppression of nonradiative decay from the excited state and the enhancement of emission by the protection of intermolecular stacking in the solid state. Besides, compound 73 showed a moderate $\beta$ value of SHG efficiency. This value is similar to those of traditional push-pull $\pi$ conjugated systems. A single crystal of this compound showed unsymmetrical packing ($P_a$). These unique properties resulted from the through-bond interaction of $\sigma\cdots\pi$ mixing between Si-Si bonds and aromatic $\pi$-systems.

Figure 4. (a) Structures of D-Si-Si-A molecules prepared by Pd-catalyzed arylation. (b) ORTEP drawing of the lattice structure of 73. All hydrogen atoms are omitted for clarity. Displacement ellipsoids drawn at the 50% probability level.

$\pi$-Conjugated D-A-D and A-D-A triads are established as strong emitters and electron transporters due to their strong intramolecular charge transfer (ICT) effects. However, $\pi$-conjugated systems often face several problems such as concentration quenching and low solubility owing to strong $\pi\cdots\pi$ stacking. Motivated by these results, we focused on synthesizing D-Si-Si-A-Si-Si-D (77–81) and A-Si-Si-D-Si-Si-A (82–85) molecules to overcome these problems. The disilane-bridged molecules shown in Figure 5(a) were also prepared by a Pd-catalyzed method. For 76–81, we used benzothiazole and thienopyrazine, nitrogen- and sulfur-containing heterocyclic compounds which are well-known for their strong electron-withdrawing ability. They displayed broad and weak absorption spectra assignable to ICT absorption. Excitation at this band led to weak emission in solution but strong emission in the solid state. This aggregation-induced emission enhancement (AIEE) was first reported by Tang et al., and subsequent works have developed organic compounds showing this phenomena. Compound 80 exhibited marked AIEE fluorescence upon its increasing concentration in water (Figure 5(b)). A solution of 80 was dissolved in THF and water fraction ($f_w$) was gradually increased. The PL intensity was diminished up to water concentration of ca. $f_w<70\%$, after this point the intensity starts increasing up to $f_w=99\%$. The PL intensity at $f_w=99\%$ is three times higher than the solution in pure THF.

The AIEE of 80 has been rationalized to stem from the suppression of $\pi\cdots\pi$ stacking interactions in a similar way to that reported for other systems. Its crystal structure packing shows no $\pi\cdots\pi$ stacking which prevents quenching due to aggregation. We concluded that the strong emission of disilane-bridged D-A-D/A-D-A triads in the solid state was caused by the suppression of both non-radiative relaxation and intermolecular interaction.

Figure 5. (a) Structures of D-Si-Si-A-Si-Si-D and A-Si-Si-D-Si-Si-A molecules prepared by Pd-catalyzed arylation. (b) Fluorescence photographs recorded under UV (365 nm) irradiation for 80 in THF/water with $f_w$ from 0 to 99% ($f_w=V_{\text{water}}/(V_{\text{water}}+V_{\text{THF}})$).

Oligothiophenes have been studied for use in organic light-emitting devices and photovoltaic cells, and tris(trimethylsilyl)silyl group ([Me3Si]3Si) is expected to be useful for lengthening the $\sigma\cdots\pi$ conjugation system and suppressing intermolecular interaction in the solid state. We designed and synthesized...
hybridized compounds of oligothiophene and (Me₃Si)₃Si moieties and investigated their photophysical properties (Figure 6, 86–91). The products were prepared by the Pd-catalyzed coupling of (Me₃Si)₃Si-H and diiodooligothiophene in good to moderate yield. Both absorption and emission maxima of the doubly tris(trimethylsilyl)silylated thiophene derivatives (86–89) shifted to longer wavelengths relative to those of unmodified thiophenes. Fluorescence quantum yields in both solution and the solid state were improved generally up to 0.74. DFT calculation revealed that the silylation of oligothiophene mainly affected the HOMO energy level owing to the interaction between Si-Si σ orbitals and aryl π orbitals to decrease the HOMO–LUMO energy gap. The structures of 87, 89, and 91 were determined by X-ray crystallography. Compounds 87 and 91 showed planar aryl structure to contribute to the effective π-conjugation and steric hindrance of tris(trimethylsilyl)-silyl group to suppress the intermolecular π-stacking interaction, resulting to display the high quantum yield in the solid state. Compound 89 did not display high quantum yields due to the distorted structures between its thiophene rings.

Figure 6. (a) Structures of prepared bis(trimethylsilyl)silyl-thiophenes. (b) UV–vis absorption spectra of 86–91. (c) Fluorescence spectra and fluorescence images under UV lamp of 86–91.

4. Application to Immobilizing Organic or Complex Molecules onto an Electrode Surface

Highly ordered organic monolayers on a crystalline silicon surface are potentially useful for many applications, and can be prepared easily by reacting a hydrogen–terminated silicon surface and an olefinic substrate. The most commonly used hydrogen–terminated silicon surfaces are prepared by etching with diluted HF (1–5%) or NH₄F aq. (40%). The surface undergoes reconstruction to form the most stable Si(111)–7 × 7 and Si(100)–2 × 1 surfaces, which have structurally different surfaces (Si–H: dihydride vs monohydride; Figure 7 (a) and (b)). Si(111) substrates are often preferred to Si(100) for the covalent grafting of organic monolayers, because monohydride–terminated Si(111) is atomically flat, whereas dihydride–terminated Si(100) prepared under wet conditions is rough. Therefore, organic functionalization on Si(111) yields densely packed, ordered monolayers with higher surface coverage.

Functionalization of silicon electrodes with aryl films can be achieved via the decomposition of the corresponding diazonium salt (Ar–N₂⁺) as shown in Figure 7(c). UV irradiation decomposes the light–sensitive diazonium group and electrochemical reduction covalently connects residual aromatic groups to the silicon surface. The attachment of aryl groups to the substrate surface can be assigned to the reaction of an aryl radical formed by a one–electron reduction of diazonium salt with the release of N₂. That is, the multilayer formation was assigned to the attack of an aryl radical on the grafted layer along an SiH homolytic substitution reaction. The structure of the layer should look like a substituted polyphenylene if sterically hindered groups at the 3,5–positions were not introduced into aromatic moieties.

Figure 7. Surface structure of hydrogen–terminated silicon surface: (a) Si(111) and (b) Si(100). (c) Electrochemical grafting mechanism of aryldiazonium cations on a silicon surface.

The catalytic system described above was successfully extended to the modification of electrode surface. Thus, we developed the first example of versatile and efficient methods to form clean organic monolayers with Si–aryl and Ge–aryl bonds on hydrogen–terminated silicon and germanium surfaces via a Pd–catalyzed arylation reaction (Figure 8). This palladium–catalyzed grafting process was effective for 4–ido-phenylferrocene, 5–ido–1H–imidazole, and 9–(4–idoeph- nyl)anthracene, and gave the desired surface functionalization. Cyclic voltammetry (CV), and X–ray photoelectron spectroscopy (XPS) characterized the surfaces and estimated the surface coverage. To demonstrate the scope of this approach, we attempted to construct redox–active metal complex oligomer wire on H–Si(111) surface using subsequent complexation as
described in our previous reports. The preparation of oligomer wire was carried out as shown in Figure 8(b). The oligomer wire growth was observed by AFM, and Figure 8(c) shows AFM image of 10 layers of π-π conjugated complex wire prepared by stepwise construction method. The height was 17.0 ± 0.5 nm, which was consistent with theoretical height. The result suggested that π-π conjugated complex wires were grown vertically through stepwise complexation on the Si surface, and that 4′-(4-iodophenyl)-2,2′:6′,2″-terpyridine was immobilized on Si surface via Pd-catalyzed reaction.

Micro patterning of electrode is an important technology for preparing devices such as memories, sensors, and actuators. Especially, chemical modification of silicon surface via deposition and patterning of organic layers is currently of great interest. Most of the methods for preparing micro sized silicon electrodes are based on lithographic techniques. Electron beam (EB) induced patterning process is one of the most useful method to prepare them. The preparation of micro patterned monolayers on hydrogen-terminated Si(111) surfaces has been reported. However, the electrochemical evaluation of the monolayer is difficult due to the trace amount of current.

To overcome this problem, a representative aromatic group, 4-ferrocenylphenyl one, was covalently bound to a micro-patterned silicon electrode via the arylation of a hydrogen-terminated Si(111) surface formed selectively on a Si wafer. Starting from a Si(100) on insulator wafer, the aromatic monolayer was attached sequentially by spin-coating a resist, electron beam lithography, Cr/Au deposition, lift-off, anisotropic etching with aqueous KOH solution, and Pd-catalyzed arylation (Figure 9(a)). The micro-patterned electrode surface was observed by digital microscope and high-resolution SEM (Figure 9(b)). CV and XPS were used to characterize the coupling reaction between the 4-ferrocenylphenyl groups and the silicon substrate. The data show that this synthetic protocol gives chemically well-defined and robust functionalized monolayers on silicon semiconducting surfaces with small electrodes.

5. Conclusions

This review provides an overview of recent advances in the transition metal-based systems for the synthesis of organosilicon compounds from hydrosilanes and organoiodine compounds. As compared to the previously reported procedures which use organometallic reagents and chlorosilanes, the reaction described here has a broad scope and can be used to prepare a variety of group 14 compounds under mild conditions. The reactivity is the opposite to that expected from the polarity of the Si–H and Ge–H bonds and their hydride character. The umpolung arylation strategy enabled us to achieve a variety of methodologies for the preparation of pharmaceutical, agricul-

Figure 8. (a) Synthetic scheme of the Pd-catalyzed surface reaction to immobilize aromatic group directly onto hydrogen-terminated Si(111) or Ge(111) surfaces. (b) Synthetic procedure of π-conjugated complex oligomer wire: (i) immobilization of 4′-phenyl-2,2′:6′,2″-terpyridine group, (ii) complexation with Fe(BF₄)ₓ, (ii) complexation with 4,4″-((1,4-phenylene)bis(2,2′:6′,2″-terpyridine), and (iv) stepwise complexation. (c) 3D AFM image (1 μm × 1 μm) of 10 layers of π-conjugated complex oligomer on Si(111) electrode.
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**PROFILE**

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