Hansen Solubility Parameters of Stacked Silicanes Derived from Porous Silicon

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ABSTRACT: Exfoliated nanomaterials could spur great interest as a new paradigm in materials science. Therefore, we have sought organic solvents to obtain high-quality two-dimensional nanomaterials and enable their adoption in large-scale applications. However, recent approaches in liquid-phase exfoliation are based on empirical trial-and-error strategies. Here, we show that the dispersibility of stacked silicanes is discussed on the basis of Hansen solubility parameters (HSPs). Using these parameters, we demonstrate that silicanes can be efficiently dispersed in bromonaphthalene and can be exfoliated as individual sheets (1–6 nm in thickness and up to 2 μm² in area). During the exfoliation process, the oxidation state of the obtained sheets is affected by the nature of the solvents. Furthermore, HSPs of the stacked silicanes are compared with those of graphene and hydrogen-terminated germanane.

1. INTRODUCTION

Although graphene is ultimately excellent in terms of electron mobility, it is a zero-band gap semiconductor, which means that graphene is not suitable for use in switching devices. In contrast, silicene and germanene (allotropes of three-dimensional (3D) Si and 3D Ge) have been reported as two-dimensional (2D) semiconductors with finite band gaps. However, pristine silicene and germanene (with unsaturated dangling bonds) are prone to oxidation in the ambient atmosphere, necessitating that oxidation-resistant methods for the liquid-phase exfoliation of other 2D materials. One such method that has been established is the 3D-Si technology. However, pristine silicene and germanene (allotropes of three-dimensional (3D) Si and 3D Ge) have been reported as two-dimensional (2D) semiconductors with finite band gaps. Furthermore, their physical and chemical compatibilities with Si allow the easy hybridization of their 2D devices and well-established 3D-Si technology. However, pristine silicene and germanene (with unsaturated dangling bonds) are prone to oxidation in the ambient atmosphere, necessitating that silicene and germanene can be synthesized and treated in ultrahigh-vacuum conditions. Therefore, silicene and germanene have not been used in the fabrication of actual devices.

To improve the oxidation resistance of silicene and germanene in the ambient atmosphere, researchers have developed organo-modified silicene and germanene, which have covalent bonds without unsaturated dangling bonds. Recently, the scalable synthesis of stacked silicanes without organic modifications has led to the development of a method for leaching lithium from Li₁₃Si₄ alloy. In a previous report, we reported the Hansen solubility parameters (HSPs) for hydrogen-terminated germanane (GeH) where we proposed that HSPs will be useful in developing a method for the liquid-phase exfoliation of other 2D materials.

In the present study, we explore suitable solvents to efficiently exfoliate stacked silicanes. To accomplish this exploration rationally, we experimentally determined the HSPs of stacked silicanes via dispersibility experiments of a porous silicon powder in various probe liquids. Through this investigation, the appropriate solvents for producing stacked silicanes are identified, which will contribute to the fabrication of feasible low-cost, high-speed 2D-silicon switching devices.

2. RESULTS AND DISCUSSION

2.1. Liquid Exfoliation. Figure 1 and Figures S2 and S3 show photographs of stacked silicane dispersions in the probe liquids after 20 min of sonication and after the subsequent sedimentation procedures (2 h, 1 day, and 2 days). The raw data of light intensity transmitted through the stacked silicane dispersions (just below the air–liquid interfaces) and the background intensity (measured through the probe liquids before the sonication procedure) were taken from the image data in Figure 1; the results are summarized in Tables S2–S4. The T values calculated by eq 1 are also listed in Tables S2–S4.

Applying the criterion to divide the probe liquids into good/poor solvents, we plotted the HSPs of the good (blue circles) and poor (red squares) solvents, as shown in Figure 2. Figure 2a–c represents the HSP plots based on the data corresponding to 2 h, 1 day, and 2 days of sedimentation, respectively. The HSP spheres and HSP center values obtained by the SPHERE method are drawn with the green wire frame and solid green circle in Figure 2, respectively. The good solvents inside and outside the HSP spheres were plotted as solid blue circles and open blue circles, respectively, whereas poor (red squares) solvents were plotted as open red circles and red circles, respectively.
the poor solvents outside and inside the HSP spheres were plotted as solid red squares and open red squares, respectively. The good/poor solvents outside/inside the HSP sphere are deemed as anomalies, likely resulting from uncertainties in the official HSPs, limitations of the HSP theory (e.g., insufficient treatment of acid–base interactions), and/or unexpected experimental errors. Although a considerable number of anomalies are observed (19, 16, and 13 for 2 h, 1 day, and 2 days of sedimentation, respectively), the obtained HSP spheres are still considered useful, as will be discussed later.

The HSP values obtained by the SPHERE method are summarized in Table 1 and Figure 3. The "stacked silicane #1", "stacked silicane #2", and "stacked silicane #3" are based on the data obtained after 2 h, 1 day, and 2 days of sedimentation, respectively. Although the HSPs (especially $\delta D$ and $\delta H$) of stacked silicanes #2 and #3 are slightly greater than those of stacked silicane #1, they are similar to each other. Because the FIT values' were $0.34-0.48$ (where FIT = 1 represents a perfect fit with no anomaly) as a result of the considerable number of anomalies, the accuracy of the HSP values should be considered poor. However, the tendency of the HSP terms to be high (extremely high for the $\delta D$ term) was consistent for all of the results; therefore, the exfoliated stacked silicanes must have high cohesive energy (strong intersheet interactions). In addition, the HSP values of the stacked silicanes were consistent with those of the ionic liquid 1-butyl-3-methylimidazolium tetrafluoroborate ($[\delta D, \delta P, \delta H] = [23, 19, 10]$ [J/cm$^3$]$^{1/2}$), which can effectively diffuse into CaSi$_2$ and CaGe$_2$ source materials to form bilayer silicene$^{10}$ and bilayer germanene.$^{11}$

Comparing the three HSP terms of the stacked silicanes with those of graphene (as a 2D-material analog)$^{6,12}$ reveals that the $\delta D$, $\delta P$, and $\delta H$ values of the stacked silicanes are much larger than those of graphene. In particular, the $\delta D$ values for the stacked silicanes ($21-26$ [J/cm$^3$]$^{1/2}$) are extraordinarily large compared with those of common chemical compounds ($15-20$ [J/cm$^3$]$^{1/2}$) composed mainly of hydrocarbons, oxygen, and nitrogen. The $\delta D$ value is dependent upon the size of the constituent atoms (i.e., atoms larger than carbon, such as chlorine, sulfur, and bromine, lead to larger $\delta D$ values)$^9$ as well as upon the molecular size and the atomic bonding state. More precisely, the $\delta D$ is correlated with the polarizability of the functional groups of constituents.$^{13}$ Although the polarizability values of graphene and stacked silicanes are unknown, the polarizability values for the ground-state atoms of carbon and silicon have been calculated to be $1.67 \times 10^{-24}$ and $5.53 \times 10^{-24}$ cm$^3$, respectively; thus, the extraordinarily large $\delta D$ value of stacked silicanes might be attributable to the large polarizability of the silicon atom.

The $\delta H$ value of stacked silicanes ($14-18$ [J/cm$^3$]$^{1/2}$) was larger than that of graphene ($\sim 7$ [J/cm$^3$]$^{1/2}$). However, these $\delta H$ values are not extraordinarily large; they are comparable to the moderately large $\delta H$ values of hydroxyl compounds such as alcohols and polyols. This moderately large $\delta H$ value of
Table 1. HSPs Obtained for Stacked Silicanes with the Different Sedimentation Times and Those for H-Terminated Germanane (from Ref 7) and Graphene (from Ref 8) for Comparison

| sample                                      | HSP ([J/cm^3]^{1/2}) | fit  | remarks |
|---------------------------------------------|-----------------------|------|---------|
| stacked silicane #1 (20 min exfoliation + 2 h sedimentation) | 20.41 15.91 14.09 13 | 0.338 | G/T = 32/55 |
| stacked silicane #2 (20 min exfoliation + 1 day sedimentation) | 23.76 18.65 14.13 17.1 | 0.45 | G/T = 18/55 |
| silicon nanosheet #3 (20 min exfoliation + 2 day sedimentation) | 26.03 16.74 17.85 19.9 | 0.476 | G/T = 13/55 |
| germanane #1 (literature, 10 min exfoliation + 1 h sedimentation) | 23.24 14.61 13.98 17.9 | 0.526 | G/T = 19/34 |
| germanane #2 (literature, 10 min exfoliation + 1 day sedimentation) | 24.69 11.21 17.73 17.9 | 0.51 | G/T = 10/34 |
| graphene (literature) | 20 11.2 7.3 6.7 1 |  | G/T = S/12 |

Figure 3. Comparison of experimentally obtained HSPs of stacked silicanes (this study), H-terminated germanane (ref 7) and graphene (ref 8).

Figure 4 shows the dependences of the light transmittance T through the stacked silicane dispersions on the relative energy difference [RED = \( R_\text{fi} \) (HSP distance between stacked silicanes and solvent)/\( R_\text{HR} \) (interaction radius of stacked silicanes)], where RED = 1 indicates the threshold to divide good/poor solvents. In all of the results corresponding to sedimentation carried out for 2 h, 1 day, and 2 days, the RED threshold does not perfectly divide good/poor solvents; however, a correlation between the dispersibility and the RED value is apparent (i.e., a smaller RED (better compatibility in terms of HSP) resulted in lower light transmittance (better dispersibility of stacked silicanes in the solvent)). Therefore, we speculate that the HSP framework still works well in this system. The large dispersion of data points might be attributable to the experimental error, that is, degradation via oxidation and/or hydrolysis, likely resulting from the presence of a water impurity in the probe liquids (residual concentrations of water impurities in probe liquids were not controlled in this study).

2.2. Characterization of Stacked Silicanes. Figure 5a, b and Figure S4 show the AFM images of the exfoliated stacked silicanes obtained using ethanol and bromonaphthalene coated on a SiO\(_2\) (300 nm)/Si substrate. Although we could not determine the tendency of the thickness depending on the types of probes, the sheet thickness is \( \sim 1 \)–6 nm with flat surfaces and sharp edges. Based on the thicknesses, the exfoliated sheets were composed of 3–20 silicon layers (the thickness of one structural silicon monolayer is \( \sim 0.3 \) nm). A sheet size histogram of 285 arbitrarily selected flakes demonstrated that the number of frequency of >50% of seats is lesser than 0.4 \( \mu \)m\(^2\) (Figures S5 and S6, Supporting Information).

stacked silicanes implies that the stacked silicane surface is partially oxidized and/or hydrolyzed; the surface is therefore partly terminated by hydroxyl groups. In general, because moisture in the atmosphere and water in organic solvents function as efficient oxidizers, the treatment of stacked silicanes in dry air and/or in dehydrated solvents might be beneficial to achieve a dispersion of high-quality stacked silicanes without degradation via oxidation and/or hydrolysis.

Comparing the three HSP terms of stacked silicanes with those of H-terminated germanane (as another 2D-material analog), we observed that the \( \delta D \) and \( \delta H \) values of the stacked silicanes were approximately the same as those of H-terminated germanane (which is thought to be partially oxidized and/or hydrolyzed to form hydroxyl terminal groups), whereas the \( \delta P \) value for the stacked silicanes (16–19 \([J/cm^3]^{1/2}\)) was slightly larger than that of H-terminated germanane (11–14 \([J/cm^3]^{1/2}\)). This comparison suggests that the stacked silicane surface has mixed oxidation states of Si=O, Si−O−Si, and Si−OH, which could result in a higher \( \delta P \) value. Because of this slightly higher \( \delta P \) value for silicon nanosheets, good solvents for exfoliation and dispersion of stacked silicanes are mostly limited to high-bolling-point (BP) solvents, indicating that the coating process of stacked silicane dispersions requires a heat treatment step to evaporate the dispersion solvent. This point can be a weakness of stacked silicanes compared with H-terminated germanane (which can be dispersed in low-BP solvents such as 1,3-dioxolane); therefore, the thermal stability of stacked silicanes should be assessed to achieve feasible stacked silicane-based devices.
To characterize the surface oxidation state of the stacked silicanes exfoliated with ethanol or bromonaphthalene, we recorded partial-fluorescence-yield X-ray absorption near-edge structure (PFY-XANES) spectra (Figure 6). The XANES spectrum obtained from the ethanol dispersion has two peaks at 1842 and 1847 eV, which are assigned to Si–Si and Si–O–Si bonds, respectively, indicating that the sheet exfoliated with ethanol is partially oxidized. By contrast, the spectrum of the bromonaphthalene dispersion has a large peak at 1842 eV and a small peak at 1846 eV, indicating that the sheet is composed almost entirely of Si–Si networks, together with a small amount of SiO. Figure S7 shows a comparison of the Si K-edge spectra obtained using the PFY and the total-electron-yield (TEY) modes. The PFY mode is known to be bulk sensitive, and the TEY mode is known to be a surface sensitive method. As shown in Figure S7, the surface of the sheet exfoliated with bromonaphthalene has one peak at 1847 eV, indicating that the sheet is completely oxidized, with no Si–Si bonding (1842 eV).

To characterize the surface oxidation state of the stacked silicanes exfoliated with bromonaphthalene, we analyzed the samples using X-ray photoelectron spectroscopy (XPS), which is a surface-sensitive measurement. The XPS spectrum displayed Si 2p and Si 2s peaks with binding energies of 101.4 and 152.5 eV (Figure S8), respectively, which suggests that the peak locations for surfaces of bulk Si (99.0 eV) and SiO2 (104 eV)) that the surface of the stacked silicane is partially oxidized. These results are consistent with the TEY-XANES spectra, indicating that the surface of the sheet is oxidized but the core retains Si–Si bonds. The surface of the stacked silicanes is easily oxidized during the exfoliation; therefore, the small amount of contaminant water in the peeling solvent attacks the surface of the sheets. Considering abovementioned results, we propose that although all of the sheet morphologies are similar to each other, more attention should be devoted to sheet oxidation for use in the same applications.

3. CONCLUSIONS

The liquid exfoliation of stacked silicanes was rationally explored on the basis of the consideration of their HSPs. The HSPs of stacked silicanes were determined to be quite large, especially the δD term, which well corresponds to that of an ionic liquid used to form bilayer silicene and bilayer germanene. The extraordinarily large δD value of stacked silicanes might be attributable to greater polarizability of silicon than carbon, whereas the moderately large δH value suggests the partial oxidation of stacked silicanes during treatment in the air and/or solvents, and the slightly large δP value suggests the presence of Si=O, Si–O–Si, and Si–OH terminations. Differing oxidation of the prepared stacked silicanes do not lead to very good fitting in HSP derivation compared to that of graphene. The FIT values show improvement together with the setting time, indicating that the precision will improve after leaching the static oxidation state of the sheets in the various probes. This will form the subject of future work.

4. EXPERIMENTAL SECTION

4.1. Synthesis of Porous Silicon. In a typical stacked silicane synthesis procedure, Li13Si4 crystals were used as precursors, consistent with the previously reported method.6 The alloys were prepared by RF heating of Li and Si pieces; thereafter, Li13Si4 was reacted with ethyl alcohol cooled at 0 °C to remove Li to form the amorphous porous silicon. To crystallize the sample, the as-prepared silicon powder was heated under vacuum at 500 °C for 1 h (Figure S1).

4.2. Liquid Exfoliation. The porous silicon powder (5 mg each) was charged into vials with a capacity of 2 mL, each of which was filled with 55 probe liquids (2 mL each; their HSPs are known). The probe liquids were rationally chosen to cover a wide variety of molecular interactions in terms of HSPs. The vials filled with the stacked silicane source powder and the probe liquids were sonicated for 20 min in an ultrasonic bath (liquid exfoliation) and then photographed after subsequently standing for 2 h, 1 day, and 2 days (sedimentation).

4.3. Characterization of the Stacked Silicane Dispersions. It was reported that the dispersion concentration of stacked silicanes is almost proportional to their absorbance, regardless of sheet diameter and a probe solvent refractive index.8 In this report, we did not focus on nanoparticles or rods but on the nanosheets. Therefore, we used transmittance for estimating the HSP (see Figure S9, Supporting Information). The intensity of the light (divided into three primary colors of red (R), green (G), and blue (B)) transmitted through the dispersions (I_RD, I_GD, and I_BD respectively) and the background light intensity (I_RB, I_GB, and I_BB respectively) were extracted from the image data of the dispersions. The light transmittance T of the dispersions was then calculated using the following equation:
$$T = \frac{I_{RD} + I_{GD} + I_{BB}}{I_{RB} + I_{GB} + I_{BB}}$$

(1)

The $T$ can be transformed to the absorbance per unit length ($A/l$), which directly correlates to the concentration of stacked silicanes exfoliated and dispersed in the probe liquids, via the following equation:

$$A/l = -\log T$$

(2)

In this investigation, the light-traveling length $l$ corresponds to the inner diameter of the vials, which was identical for all of the dispersions in this investigation, ensuring that the light transmittance $T$ is inversely correlated with the concentration of the exfoliated stacked silicanes in the dispersions. Thus, we categorized the probe liquids for the exfoliation and dispersion of stacked silicanes into good ($T < 0.8$) and poor ($T \geq 0.8$) solvents on the basis of the dispersibility of the nanosheets.

4.4. Calculation of HSPs. The HSP is one of indicators for molecular interactions. It is an effective tool to predict and/or examine the compatibility (e.g., dispersibility, solubility, and wettability) of two different materials.9,13–16 The HSP consists of three terms that originate from corresponding molecular interactions: $\delta D$ (London dispersion term), $\delta P$ (polar term), and $\delta H$ (hydrogen bonding term). The compatibility of two different materials (with respective HSPs of $[\delta D_1, \delta P_1, \delta H_1]$ and $[\delta D_2, \delta P_2, \delta H_2]$) can be estimated by the HSP distance $R_s$ which is defined as

$$R_s = \sqrt{4 \times (\delta D_1 - \delta D_2)^2 + (\delta P_1 - \delta P_2)^2 + (\delta H_1 - \delta H_2)^2}$$

(3)

A small $R_s$ value indicates better compatibility of the two different materials. Because the HSPs of typical organic solvents are already known, the HSPs of the probe liquids employed in this investigation were obtained from the official HSP database12 and are listed in Table S1. To determine the HSP of a new material whose HSP is unknown (i.e., stacked silicanes in this case), the SPHERE method has typically been applied.9 In the SPHERE method, experimental compatibility data (such as dispersibility, solubility, or swelling) of the HSP-unknown material with respect to probe liquids must be acquired. From the compatibility data, the probe liquids were divided into “good” or “poor”, and the poor solvents were plotted in the HSP space (i.e., a Cartesian coordinate system comprising axes of $\delta D$, $\delta P$, and $\delta H$). From the HSP plots, a fitting procedure determines the HSP sphere such that it encompasses the good solvents within the sphere while excluding the poor solvents. The center position of the obtained HSP sphere is the HSP value of the objective material. In addition, the radius of the HSP sphere is referred to as the interaction radius $R_0$, which is a tolerance indicator for the objective material to interact with other materials.

In the present study, probe liquids with $T < 80\%$ for the exfoliation and dispersion of stacked silicanes were deemed as good solvents; the HSPs of the stacked silicanes, as determined from the data after 2 h, 1 day, and 2 days of sedimentation, were determined by the SPHERE method.

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