Toward Defect-Free Doping by Self-Assembled Molecular Monolayers: The Evolution of Interstitial Carbon-Related Defects in Phosphorus-Doped Silicon

(Supplementary information)

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Supplementary Note 1. X-ray photoelectron spectroscopy measurements

P 2s narrow scans in Figure 1b and S3 indicate that phosphorus–containing molecules have been successfully bonded onto silicon surface. In addition, surface molecules as shown in Figure S1 can be derived by C 1s narrow scans.

Figure S1. Phosphorus-functionalized silicon surface. Number 1 indicates aliphatic carbon. Number 2 indicates carbon bonded with oxygen or carbon adjacent to carbonyl. Number 3 indicates carbon in carbonyl.

Figure S2. XPS measurements. (a) Full spectrum of P-functionalized silicon surface. (b) Enlarged spectrum from 400 eV to 50 eV. 1 indicates Si 2s plasmon loss and 2 indicate Si 2p plasmon loss.
XPS is a surface-sensitive technique for measuring the element composition and the chemical states in molecular monolayers. XPS full scan detects all the elements with concentration higher than 0.1%. XPS full scan in Fig. S2a shows peaks of Si, O and C, detecting no obvious contamination. In our experiment, P 2s are measured other than the commonly-used P 2p, because P 2s is less affected by silicon plasmon loss, as shown in Fig. S2b. Since P-containing molecular monolayer on silicon surface is very thin (< 2 nm), interference from the Si bulk can be suppressed at small takeoff angle (Fig. S3).

![Figure S3](image)

**Figure S3.** Angle-resolved XPS spectra. P 2s narrow scans of P-functionalized silicon surface with takeoff angles of 90° (a), 75° (b), 60° (c), 45° (d), and 30° (e).

**Supplementary Note 2. Van der Pauw measurements**

When we carried out SAMM-doping on silicon substrate, one piece 1.5 mm × 1.5 mm intrinsic silicon chip (resistivity > 10 kΩ·cm) was paired with the 1.5 mm × 1.5 mm n-type Si sample
(resistivity of ~3.2 $\Omega\cdot cm$). By testing the sheet resistance of SAMM-doped intrinsic silicon samples, doping effect on n-type silicon was estimated. A control sample is an intrinsic silicon sample which went through all the SAMM-doping process except that the P-containing molecules (monododecylphosphate) was not added during the esterification process.

Sheet resistance of blank sample, control sample, 2-min sample and 10-min sample were measured on the square-shaped samples shown as below by van der Pauw technique$^2$. Voltage is applied on corner 1 and 2, flowing current ($I_{12}$) across the sample, then voltage between corner 4 and 3 ($V_{43}$) was measured. Resistance $R_{12-43}$ was defined as $V_{43}/I_{12}$ by Ohm’s law. Similarly, resistance $R_{43-12}$, $R_{14-23}$, and $R_{23-14}$ were measured (Fig. S4). Sheet resistance can be calculated by eq. S1.

$$\exp\left[-\frac{\pi (R_{12-43}+R_{43-12})}{R_s}\right] + \exp\left[-\frac{\pi (R_{14-23}+R_{23-14})}{R_s}\right] = 1 \quad \text{S1}$$

Where $R_s$ is the sheet resistance.

Table S1. Sheet resistance by van der Pauw measurements.

| Sample description                        | Sheet resistance (k$\Omega$/□) |
|-------------------------------------------|---------------------------------|
| Blank sample                              | 309                             |
| Control sample                            | 243                             |
| SAMM-doped sample annealed for 2min       | 5.6                             |
| SAMM-doped sample annealed for 10min      | 1.7                             |
Figure S4. (a) I-V curves from van der Pauw measurements on blank sample. (b) I-V curves from van der Pauw measurements on control sample. (c) I-V curves from van der Pauw measurements on 2-min sample. (d) I-V curves from van der Pauw measurements on 10-min sample.

Supplementary Note 3. Ionized charge profiles of Schottky diodes
Ionized charge profiles in silicon substrate (n-type Si with resistivity of ~3.2 Ω cm), 2-min sample and 10-min sample can be derived from C-V curves in Fig. 2b according to eq. S2 and S3.3

\[ W_{\text{dep}} = \frac{\varepsilon A}{C} \quad \text{S2} \]
\[ N_c = \frac{2}{q \varepsilon A^2 \frac{d}{dV}} \quad \text{S3} \]

Where \( W_{\text{dep}} \) is the depletion width, \( \varepsilon \) the dielectric constant of silicon, \( A \) the area of electrode, \( C \) the capacitance, \( q \) the unite charge and \( V \) the voltage.

**Figure S5.** (a) Schottky diode fabricated on P-doped Si. (b) Ionized charge profiles of blank sample (black curve), 2-min sample (red curve) and 10-min sample (blue curve) derived from C-V.

**Supplementary Note 4. DLTS measurements**

Peak amplitude of C,H was found to vary with the bias voltage applied during the cooling process from 300 K to 50 K. When the sample was cooled with bias of -2 V, the peak at ~ 94.5 K (at a rate window of 200 s \(^{-1} \)) has a relatively higher amplitude on DLTS spectra measured with bias pulse of -0.5 V ~ 0.2 V. However, when the sample was cooled with bias of 0 V, the peak at the same position almost disappear on DLTS spectrum measured in the same condition. This can be explained by the charge state controlled-metastability of C,H, which is also observed by Kamiura *et al.*4.
Figure S6. DLTS spectra measured on 2-min SAMM-doped sample with bias pulse of -0.5V ~ 0.2 V at a rate window of 200 s⁻¹. Bias voltages of 0 V (black curve) and -2 V (red curve) was applied respectively during the cooling process.

DLTS simulation was performed according to the basic working principle of boxcar DLTS.⁵ Capacitance transient ΔC starts at the end of excitation pulse and then decays exponentially as the electrons are thermally emitted. Capacitance transient with a given rate window $e_n$ can be described by eq. S4.

$$\Delta C = \Delta C_0 \left( \exp(-e_n t_1) - \exp(-e_n t_2) \right)$$

S4

Where $\Delta C_0$ is the initial capacitance transient (capacitance transient at the end of excitation pulse), $e_n$ the emission rate. $t_1$ and $t_2$ define the rate window.

For the bump area where several peaks overlap, capacitance transients are summed up as shown in eq. S5. For 2-min sample, the bump ranging from 100 K to 300 K in DLTS spectrum detected with the pulse of -2 V ~ 0.2 V can be simulated as shown in Fig. S5. When the rate window is 5 s⁻¹, $t_1$ is 0.122172 s and $t_2$ is 0.30543 s.

$$\Delta C = \sum \Delta C_{0i} \left( \exp(-e_{ni} t_1) - \exp(-e_{ni} t_2) \right)$$

S5

And the emission rate $e_n$ is given by Eq. S6.

$$e_n = (\sigma_n (\nu_n) N_c / g) exp \left( -\frac{E_n}{kT} \right)$$

S6
where $\sigma_n$ is the capture cross-section, $\langle v_n \rangle$ is the mean thermal velocity of electron, $g$ is the degeneracy factor (chosen 2 here), $N_c$ is the effective density of states related to the semiconductor band structure, and $k$ is the Boltzmann constant.

In Figure S7, peak 1 with energy level of 0.147 eV was ascribed to C,H (substitutional carbon bonded with hydrogen). Peak 8 is present in arsenic-doped substrate but absent in phosphorus-doped substrate, therefore we attributed peak 8 as C$_i$-As$_s$ (interstitial carbon bonded with substitutional arsenic). Peak 2–peak 7 were from the conclusion in our previous publication$^1$. Each simulated peak in Figure S7 stands for a defect detected in P-doped silicon. The gap between experimental (black) and simulation (red) is due to surface states and atomic disorder.

**Figure S7.** DLTS simulation on 2-min sample with bias pulse of -2 V ~ 0.2 V at rate window of 5 s$^{-1}$. 

![DLTS Simulation Graph](image-url)
**Figure S8.** DLTS spectra measured at different rate windows and corresponding Arrhenius plots. (a) DLTS spectra and (b) Arrhenius plot on 2-min sample with bias pulse of -2 V ~ -0.5 V. (c) DLTS spectra and (d) Arrhenius plot on 10-min sample with bias pulse of -2V ~ -0.5 V.

**Supplementary Note 5. Simulation on band structures and DLTS detection regions**

Band structures and DLTS probe regions at different bias voltages were predicted using Atlas device simulator by Silvaco. One dimensional mesh was generated on cross-section of the 500 μm silicon substrate with fine mesh in SAMM-doped region while coarse mesh in substrate. Dopant concentration in the n-type silicon substrate is $1.8 \times 10^{15}$ cm$^{-3}$. Phosphorus doped by SAMM was input from the front surface, depth profile of which is derived from SIMS and ionized charge profiles in Fig. 4a, 5a and S5. Gold front electrode with work function of 5.1 eV was applied. Ohmic contact between Al back electrode and silicon substrate is simulated with contact command.

Electron drift and diffusion is governed by eq. S7.\(^6\)

$$J_n = e(\mu_n n \varepsilon + D_n \nabla n) \quad S7$$

Where $J_n$ is the electron current density, $e$ the unit charge, $\mu_n$ the electron mobility, $n$ the electron concentration, $\varepsilon$ the internal electric field, and $D_n$ the electron diffusion coefficient.

The Poisson equation is shown in eq. S8.

$$\nabla^2 \varphi = -\nabla \varepsilon = -\frac{e(-n+\text{Nd}^+)}{\varepsilon_r \varepsilon_0} \quad S8$$

Where $\varphi$ is the electric potential, $\text{Nd}^+$ the ionized donor concentration, $\varepsilon_0$ the vacuum permittivity, and $\varepsilon_r$ the relative permittivity.

Temperature dependence of the ionized donors is simulated according to eq. S9.\(^6\)

$$N_{D^+}^t = \frac{N_D}{1 + 2 \exp\left(\frac{E_F - E_d}{kT}\right)} \quad S9$$

Where $N_D$ is the donor concentration, $E_F$ the Fermi level, $k$ the Boltzmann constant, $T$ the temperature, and $E_d$ the activation energy of phosphorus.
Figure S9. Silvaco simulation of Schottky diode on 2-min SAMM-doped sample at 300 K. (a) and (b) are band structure and electron distribution with reversed bias of -2 V. (c) and (d) are band structure and electron distribution with applied bias of -0.5 V. (e) and (f) are band structure and electron distribution with applied bias of 0.2 V.
Figure S10. Silvaco simulation of Schottky diode on 10-min SAMM-doped sample at 300 K. (a) and (b) are band structure and electron distribution with reversed bias of -2 V. (c) and (d) are band structure and electron distribution with applied bias of -0.5 V. (e) and (f) are band structure and electron distribution with applied bias of 0.2 V.

Supplementary Note 6. Temperature-dependent metastability of C$_t$-D$_s$
**Figure S11.** A comparison of DLTS spectra of 2-min sample before (black line) and after heat treatment (red line) at 340 K for 10 min. During DLTS measurements, the applied pulse is -0.5 V ~ 0.2 V and the rate window is 200 s⁻¹.

**Reference**

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