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# Assessing the effect of hydrogen on the electronic properties of 4H-SiC

Yuanchao Huang(黄渊超)[1,2], Rong Wang(王蓉)[1,2,†], Yiqiang Zhang(张懿强)[3], Deren Yang(杨德仁)[1,2], and Xiaodong Pi(皮孝东)[1,2,‡]

[1] *State Key Laboratory of Silicon Materials and School of Materials Science and Engineering, Zhejiang University, Hangzhou* 310027, *China*
[2] *Institute of Advanced Semiconductors & Zhejiang Provincial Key Laboratory of Power Semiconductor Materials and Devices, Hangzhou Innovation Center, Zhejiang University, Hangzhou* 311200, *China*
[3] *School of Materials Science and Engineering & College of Chemistry, Zhengzhou University, Zhengzhou* 450001, *China*

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As a common impurity in 4H silicon carbide (4H-SiC), hydrogen (H) may play a role in tuning the electronic properties of 4H-SiC. In this work, we systemically explore the effect of H on the electronic properties of both n-type and p-type 4H-SiC. The passivation of H on intrinsic defects such as carbon vacancies ($V_C$) and silicon vacancies ($V_{Si}$) in 4H-SiC is also evaluated. We find that interstitial H at the bonding center of the Si–C bond ($H_i^{bc}$) and interstitial H at the tetrahedral center of Si ($H_i^{Si-te}$) dominate the defect configurations of H in p-type and n-type 4H-SiC, respectively. In n-type 4H-SiC, the compensation of $H_i^{Si-te}$ is found to pin the Fermi energy and hinder the increase of the electron concentration for highly N-doped 4H-SiC. The compensation of $H_i^{bc}$ is negligible compared to that of $V_C$ on the p-type doping of Al-doped 4H-SiC. We further examine whether H can passivate $V_C$ and improve the carrier lifetime in 4H-SiC. It turns out that nonequilibrium passivation of $V_C$ by H is effective to eliminate the defect states of $V_C$, which enhances the carrier lifetime of moderately doped 4H-SiC. Regarding the quantum-qubit applications of 4H-SiC, we find that H can readily passivate $V_{Si}$ during the creation of $V_{Si}$ centers. Thermal annealing is needed to decompose the resulting $V_{Si}$–$n$H ($n = 1$–4) complexes and promote the uniformity of the photoluminescence of $V_{Si}$ arrays in 4H-SiC. The current work may inspire the impurity engineering of H in 4H-SiC.

**Keywords:** 4H-silicon carbide, hydrogen, electronic properties, passivation

**PACS:** 61.82.Fk, 61.72.–y, 71.15.Mb **DOI:** 10.1088/1674-1056/ac4234

## 1. Introduction

As a leading third-generation semiconductor, silicon carbide (SiC) is leaping in an explosive development to meet the increasing demand of electrical vehicles, 5G communications and renewable-energy systems. There exist over 250 polymorphs for SiC, among which 4H-SiC has attracted great attention owning to its wide bandgap, high carrier mobility, high thermal conductivity, and high stability.[1–3] 4H-SiC ingots are usually grown by the physical vapor transport (PVT) method, during which hydrogen gas ($H_2$) is used to optimize the surface of the seed crystal and tune the growth condition of 4H-SiC.[4–7] 4H-SiC epilayers are often homoepitaxially grown by chemical vapor deposition (CVD), during which $H_2$ is widely used as the carrier gas.[8–11] It should be also noted that H impurities are frequently incorporated during the processing of 4H-SiC-based devices.[12–15] Therefore, understanding the effect of H on the electronic properties of 4H-SiC is critical to the development of 4H-SiC technologies.

Considerable efforts have already been devoted to investigate H in 4H-SiC.[16–30] For n-type 4H-SiC, it was found that H–ion implantation, $H_2$-plasma treatment, and high-temperature $H_2$ annealing could reduce the concentration of electrons and increase the resistivity of 4H-SiC.[20–22] The reduction of the electron concentration was controversially attributed to the formation of $N_C$–H complexes, as well as the creation of electron traps such as H interstitials and intrinsic defects.[20] The hole concentration of p-type 4H-SiC also decreased after high-temperature $H_2$ annealing,[22–25] as a result of $H_2$ annealing-induced decomposition of $Al_{Si}$–H complexes and the creation of positively charge H,[22–24] which differed from the behavior of H in n-type 4H-SiC. $H_2$-plasma treatment was found to reduce the photoluminescence of both Al-related defects and N–Al complexes.[25] But the underlying mechanism remains ambiguous. Moreover, intrinsic carbon vacancies ($V_C$) were found to seriously reduce carrier lifetime in 4H-SiC.[26–29] It was experimentally found that $H_2$-atomsphere annealing was actually not capable of passivating $V_C$ in 4H-SiC.[32,33] However, it was theoretically proposed that H might passivate $V_C$.[34–36] It is apparent that a clear picture on H in 4H-SiC remains elusive.

In this work, we systemically explore the effect of H on the electronic properties of both n-type and p-type 4H-SiC. The passivation of H on intrinsic defects such as $V_C$ and silicon vacancies ($V_{Si}$) in 4H-SiC is also evaluated. We find that

†Corresponding author. E-mail: rong_wang@zju.edu.cn
‡Corresponding author. E-mail: xdpi@zju.edu.cn

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interstitial H at the bonding center of the Si–C bond ($H_i^{bc}$) and interstitial H at the tetrahedral center of Si ($H_i^{Si-te}$) dominate the defect configurations of H in p-type and n-type 4H-SiC, respectively. For n-type 4H-SiC, the compensation of $H_i^{Si-te}$ is found to pin the Fermi energy and hinder the increase of electron concentration in highly N-doped 4H-SiC. Reducing the concentration of unintentional incorporated H is highly desired to improve the n-type doping and reduce the resistivity of n-type 4H-SiC. In p-type 4H-SiC doped by Al, we find that the compensation of $H_i^{bc}$ on the p-type doping of 4H-SiC is negligible compared to that of $V_C$. Nonequilibrium H-incorporation approaches may passivate $Al_{Si}$ by H, and degrades the performance of p-type 4H-SiC. The degradation can be easily eliminated by thermal annealing, because of the low binding energy of $Al_{Si}$–H in p-type 4H-SiC. We have further examined whether H can passivate $V_C$ and improve the carrier lifetime in 4H-SiC. It turns out that nonequilibrium passivation of $V_C$ by H is effective to eliminate the defect states of $V_C$, which enhances the carrier lifetime of moderately doped 4H-SiC. Regarding the quantum-qubit applications of 4H-SiC, we find that H can readily passivate $V_{Si}$ during the creation of $V_{Si}$ centers. Thermal annealing is needed to decompose the resulting $V_{Si}$–$n$H ($n$ = 1–4) complexes and promote the uniformity of the photoluminescence of $V_{Si}$ arrays in 4H-SiC.

## 2. Computational methodology

First-principles calculations are carried out by the projector-augmented wave (PAW) method, as implemented in the Vienna *ab initio* simulation package (VASP).[37,38] The wave functions are expanded by using the plane waves up to a kinetic energy cutoff of 500 eV. The Perdew–Burke–Ernzerhof revised for solids (PBEsol) functional with the GGA exchange correlation is adopted for the structural relaxation.[39] The supercell size and atomic positions are fully relaxed until the total energy per cell and the force on each atom converge to less than $1 \times 10^{-6}$ eV and 0.01 eV/Å, respectively. For accurate bandgap energy and defect level description, the hybrid density functional of Heyd, Scuseria, and Ernzerhof (HSE06), which mixes 25% of screened Hartree–Fock exchange to the PBE exchange functional, is employed during the calculation of electronic properties.[38] H impurities are modeled in 128-atom 4H-SiC supercells. For Brillouin zone integration, the Monkhorst–Pack scheme with a $\Gamma$-centered $2 \times 2 \times 2$ special $k$-points mesh is used.[39] Defect formation energies of H are calculated by the well-established mixed $k$-point scheme.[42,43]

## 3. Results and discussion

### 3.1. Configurations

As shown in Fig. 1, the configurations of H in 4H-SiC include substitutional H at C sites ($H_C$), substitutional H at Si sites ($H_{Si}$), as well as interstitial H at the bonding center of Si–C ($H_i^{bc}$), interstitial H at the tetrahedral center of Si ($H_i^{Si-te}$) and C ($H_i^{C-te}$), and interstitial H at the octahedral center ($H_i^{oc}$). We note that the nonequivalent lattice sites of Si and C in 4H-SiC include the quasihexagonal ($h$) and quasicubic ($k$) sublattice sites. The difference of the formation energy of $H_C$ ($H_{Si}$) at the $k$-site and $h$-site is negligible. So, we just construct $H_C$ and $H_{Si}$ at the $k$-site as a representative.

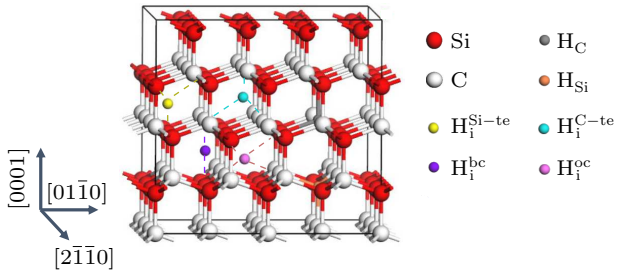



**Fig. 1.** Relaxed structures of H in 4H-SiC. $H_C$, $H_{Si}$, $H_i^{bc}$, $H_i^{Si-te}$, $H_i^{C-te}$, and $H_i^{oc}$ are denoted by gray, orange, purple, yellow, cyan, and pink balls, respectively. Si and C atoms are denoted by red and white balls, respectively.

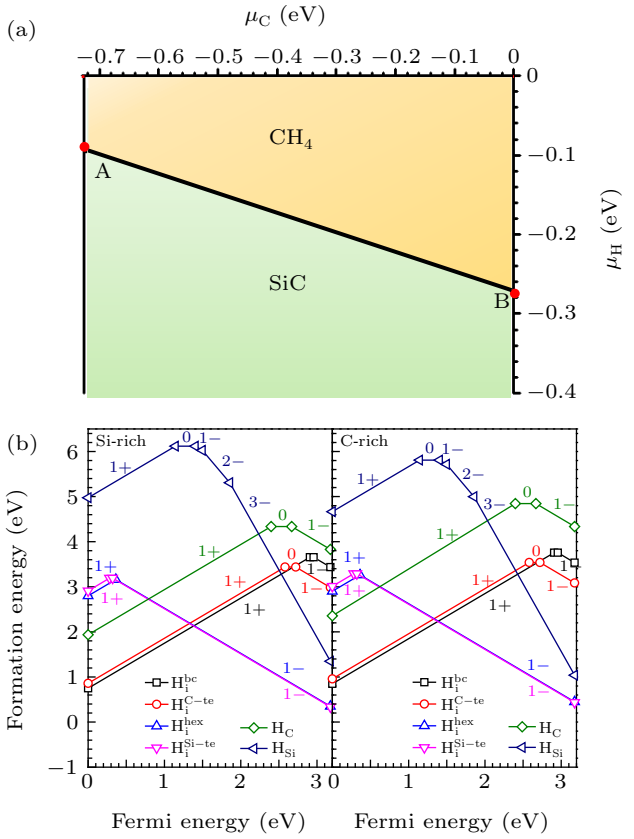



**Fig. 2.** (a) Accessible range of chemical potentials (green area) for equilibrium incorporation of H in 4H-SiC, (b) calculated formation energies of H in 4H-SiC.

During the incorporation of H in 4H-SiC, thermodynamic equilibrium growth conditions require a series of limitations

on the achievable values for chemical potentials of the constituents ($\mu_i$). Firstly, the values of $\mu_{Si}$ and $\mu_C$ are limited to maintain the stable 4H-SiC:

$$\mu_{Si} + \mu_C = \Delta H_f(\text{4H–SiC}), \tag{1}$$

where $\Delta H_f$(4H–SiC) is the formation energy of 4H-SiC. The calculated $\Delta H_f$(4H–SiC) is −0.73 eV for formula which is in good agreement with experiments (−0.68 eV, −0.75 eV or −0.771 eV for formula[44]). Secondly, to avoid the precipitation of elemental host phases and the elemental H, the values of $\mu_i$ are limited by

$$\mu_{Si} \leq 0, \quad \mu_C \leq 0, \quad \mu_H \leq 0. \tag{2}$$

Finally, $CH_4$(g) has the lowest formation energy. Due to this, the formation of $CH_4$(g) should be avoided. The values of $\mu_i$ are limited by

$$\mu_C + 4\mu_H \leq \Delta H_f(CH_4) = -0.79, \tag{3}$$

where $\Delta H_f(CH_4)$ are formation energy of $CH_4$. By solving Eqs. (1)–(3), we can get the accessible range for values of the chemical potentials, as shown by the green regions in Fig. 2(a). We then take the Si-rich limit [point A in Fig. 2(a)] and the C-rich limit growth condition [point B in Fig. 2(a)] to calculate the formation energies of H in 4H-SiC.

As shown in Fig. 2(b), the formation energies of H interstitials are lower than those of substitutional H, as a result of the steric effect. $H_i^{bc}$ and $H_i^{Si-te}$ dominate the configurations of H in p-type and n-type 4H-SiC, respectively. For $H_i^{bc}$, the neutral charge state is never stable, because of the Coulumn effect between $H_i^{bc}$ and its neighboring atoms. When the Fermi energy increases up to 2.80 eV, the charge state of $H_i^{bc}$ charges directly from 1+ to 1−. $H_i^{Si-te}$ also acts as a negative-$U$ center, with the charge transition from 1+ to 1− occuring at 0.34 eV. We find that $H_i^{bc}$ and $H_i^{Si-te}$ introduce deep defect states under the conduction band minimum (CBM) and above the valance band maximum (VBM) of 4H-SiC, respectively. These defect states are both occupied by one electron, indicating H may capture carriers and affect the performance of 4H-SiC (Fig. 3). More importantly, electron transfer between H and other defects (*e.g.*, dopants and intrinsic defects) would give rise to H-passivation of these defects. Unintentional H passivation of dopants would change the electronic properties of semiconductors.[45] During the processing of semiconductor devices, passivation of H is also frequently adopted to suppress the negative effect of intrinsic defects.[46,47] Therefore, we evaluate the effect of H passivation of the common n-type dopant (N), p-type dopant (Al), and intrinsic defects ($V_C$ and $V_{Si}$) on the performance of 4H-SiC. Because the growth conditions for both the single crystal growth and homoepitaxy of 4H-SiC are Si-rich, and the growth condition does not significantly affect the formation energies of H in 4H-SiC [Fig. 1(b)], we investigate the effect of H on the electronic properties of 4H-SiC under the Si-rich limit.

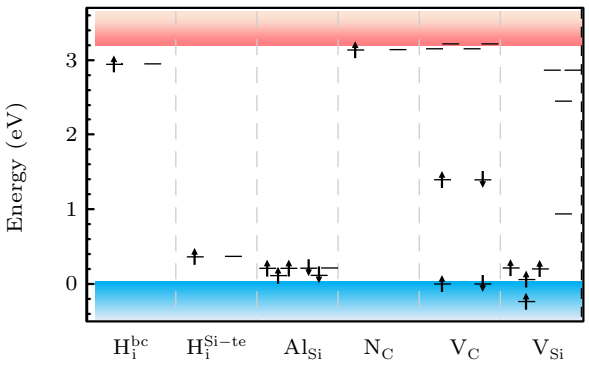



**Fig. 3.** Single-electron levels of dominant H interstitials, dopants, and intrinsic defects in 4H-SiC. Pink and blue regions indicate the CB and the VB of 4H-SiC, respectively. The up and down arrows denote the occupied spin-states of electrons on the defect levels.

### 3.2. H in n-type 4H-SiC

The high dopability of N in 4H-SiC endows 4H-SiC a great success in high power electronics. For n-type 4H-SiC substrates, the resistivity in the order of $10^{-3}$ Ω·cm is highly desired to guarantee its conductivity. During the homoepitaxy of n-type 4H-SiC layers, the electron concentration of the n-type buffer layer should be as high as possible to guarantee the conversion efficiency of basal plane dislocations.[48,49] However, the doping efficiency of N still lags behind the demand of ideal power-device applications. In this section, we evaluate the effects of compensation (or passivation) of H on the electronic properties of n-type 4H-SiC.

As shown in Fig. 4(a), the +/0 transition energy level of N locates at 0.06 eV below the CBM of 4H-SiC, which agrees well with theoretical and experimental results.[1] We find that the Fermi energy of 4H-SiC tends to shift toward its CBM as the concentration of N increases [Fig. 5(a)]. For n-type 4H-SiC, the formation energy of the negatively charged $H_i^{Si-te}$ becomes lower than that of $N_C^+$, which leads to the compensation of negatively charged $H_i^{Si-te}$ on the n-type doping of 4H-SiC. The Fermi energy would be pinned in the mid-gap of 4H-SiC when the concentration of unintentional induced H becomes nonnegligible.

We also evaluate whether H can passivate $N_C$ in n-type 4H-SiC. As shown in Fig. 4(a), the formation energy of $N_C$–H complex is much higher than those of individual $N_C$ and $H_i$, indicating that the passivation of H at $N_C$ is unlikely to happen under thermodynamic equilibrium growth conditions. We also calculate the binding energy of the $N_C$–H complex [$E_b$ ($N_C$–H)] by $E_b$ ($N_C$–H) = $\Delta H_f$ ($N_C$) + $\Delta H_f$ ($H_i$) − $\Delta H_f$ ($N_C$–H). The negative value of $E_b$ ($N_C$–H) throughout the bandgap of 4H-SiC indicates that the $N_C$–H complex is not stable against decomposition. This indicates that the compensation of $H_i^{Si-te}$ exerts more significant effect on the properties of n-type 4H-SiC. Reducing the concentration of unintentional

induced H is highly desired to improve the n-type doping and reduce the resistivity of highly N-doped 4H-SiC.

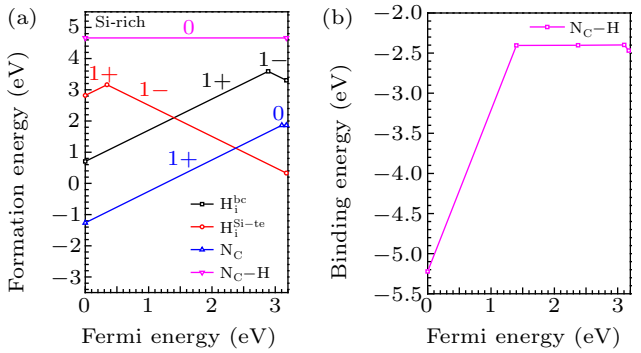



**Fig. 4.** (a) Calculated formation energies of $N_C$, $N_C$–H, $H_i^{Si-te}$, and $H_i^{bc}$ in 4H-SiC, (b) calculated binding energy of the $N_C$–H complex in 4H-SiC.

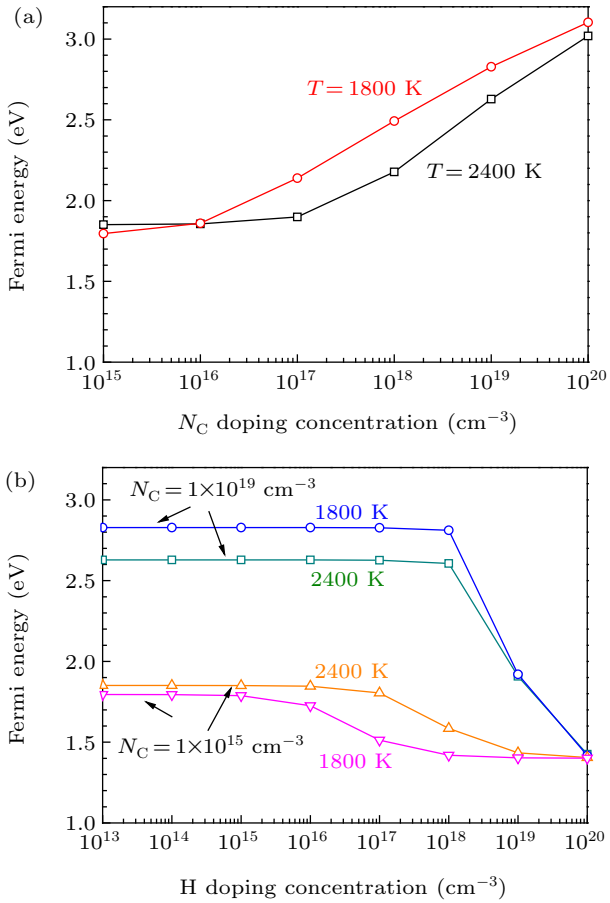



**Fig. 5.** (a) Fermi energies of 4H-SiC grown at 1800 K and 2400 K as functions of the concentration of N, (b) Fermi energies of 4H-SiC grown at 1800 K and 2400 K as functions of the concentration of H under different background concentrations of N.

The typical temperatures of PVT growth and CVD homoepitaxy of 4H-SiC are 2400 K and 1800 K, respectively.[1] Therefore, we investigate the effects of H on the Fermi energy and carrier concentration of n-type 4H-SiC at the temperatures of 2400 K and 1800 K. As shown in Fig. 5(a), the Fermi energy of 4H-SiC grown under 1800 K is slightly higher than that of 4H-SiC grown under 2400 K, due to lower concentration of thermally excited electrons at lower temperatures. This indicates that the hole concentration of 4H-SiC grown under 1800 K is higher than that of 4H-SiC grown under 2400 K. When the concentration of N increases from $10^{15}$ $cm^{-3}$ to $10^{16}$ $cm^{-3}$, the increase of Fermi energy of 4H-SiC grown under 1800 K is more significant than that for 4H-SiC grown under 2400 K. For 4H-SiC grown under lower temperatures, the hole concentration is lower, which means that it is easier to tune the Fermi energy of 4H-SiC by increasing the concentration of N. When the concentration of N increases to $10^{19}$ $cm^{-3}$, the Fermi energy of 4H-SiC grown under 1800 K and 2400 K increase to 2.6 eV and 2.8 eV, respectively. Taking 4H-SiC with the N-doping concentration of $10^{19}$ $cm^{-3}$ as an example, we find that the effect of unintentional incorporated H exerts negligible effect on the n-type doping of 4H-SiC. Only when the concentration of H exceeds $10^{18}$ $cm^{-3}$, the Fermi energy of 4H-SiC begins to decrease [Fig. 5(b)]. When the concentration of H increases to $10^{20}$ $cm^{-3}$, the Fermi energy of 4H-SiC is pinned at 1.4 eV due to the self-compensation of H [Fig. 5(b)].

### 3.3. H in p-type 4H-SiC

The p-type 4H-SiC substrates are of great importance to the development of n-channel bipolar devices based on 4H-SiC, which hold great promise for ultra-high voltage (> 10 kV) applications.[50–53] Al owns the lowest ionization energy among all group-III elements in 4H-SiC, which makes it as the most popular p-type dopant in 4H-SiC. It is well known that the lowest defect configuration of Al is $Al_{Si}$. Therefore, we investigate the interaction of H with $Al_{Si}$ in this section, the effect of dominant intrinsic defect of $V_C$ is also taken into consideration.

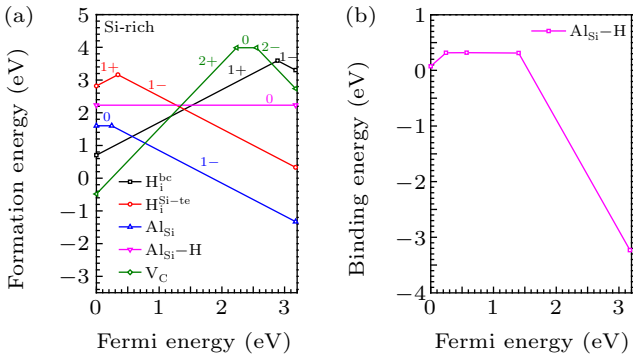



**Fig. 6.** (a) Calculated formation energies of $Al_{Si}$, $Al_{Si}$–H, $V_C$, $H_i^{Si-te}$, and $H_i^{bc}$ in 4H-SiC, (b) calculated binding energy of the $Al_{Si}$–H complex in 4H-SiC.

As shown in Fig. 6(a), the formation energy of $V_C$ is much lower than that of $H_i^{bc}$, indicating the compensation center for p-type 4H-SiC is $V_C$, rather than H. Because the formation energy of $Al_{Si}$–H complex is higher than those of individual $Al_{Si}$ and $H_i^{C-Si}$, H is unlikely to passivate $Al_{Si}$ under thermal equilibrium growth conditions. This ensures the effective doping of $Al_{Si}$ in 4H-SiC. Nonequilibrium approaches, such as H ion implantation or radiation may passivate $Al_{Si}$ by H. The

passivation can be easily eliminated by thermal annealing, because of the low binding energy of $Al_{Si}$–H in p-type 4H-SiC [Fig. 6(b)].

### 3.4. H passivation of $V_C$

When 4H-SiC is applied in power electronics, $V_C$ has been identified as the carrier-lifetime killer in bipolar devices based on 4H-SiC.[26–30] By trapping carriers in its deep defect level, $V_C$ severely reduces the carrier lifetime and thus the blocking voltage of the 4H-SiC drift layer.[53] Various approaches such as carbon ion implantation followed by thermal annealing, thermal oxidation, and annealing with a carbon cap, have been proposed to eliminate $V_C$ in 4H-SiC.[54–57] For the sake of reducing processing complexity and cost, we evaluate whether H can passivate the defect states of $V_C$.

As shown in Fig. 2, passivating $V_C$ by 4 H atoms can effectively eliminate the defect level of $V_C$ and potentially improve the carrier lifetime in 4H-SiC. Therefore, we calculate the defect formation energies of $V_C$–$n$H ($n$ = 1–4) to verify whether H is capable of passivating $V_C$ and enhance the carrier lifetime of 4H-SiC. As shown in Fig. 7(a), the defect formation energies of $V_C$–$n$H ($n$ = 1–4) are all larger than that of pure $V_C$. Although the deep defect states of $V_C$–4H disappears in 4H-SiC, $V_C$–4H has the highest formation energy among all $V_C$–$n$H ($n$ = 1–4) complexes. This indicates that equilibrium incorporation of H cannot eliminate the defect states of $V_C$. Nonequilibrium approaches, such as H ion implantation or irradiation may capable of passivating $V_C$ by H. The binding energy of $V_C$–$n$H ($n$ = 1–4) complexes are calculated by $E_b(V_C\text{–}nH) = \Delta H_f(V_C) + n\Delta H_f(H_i) - \Delta H_f(V_C - nH)$. As shown in Fig. 7(b), when the Fermi energy of 4H-SiC is in the range from 0.44 eV to 3.03 eV, the binding energies of $V_C$–4H is positive, indicating the $V_C$–4H complex is stable against decomposition. This means that nonequilibrium passivation of $V_C$ by H is effective to eliminate the defect states of $V_C$ and thus enhance the carrier lifetime of moderately doped 4H-SiC with Fermi energy ranging from 0.44 eV to 3.03 eV.

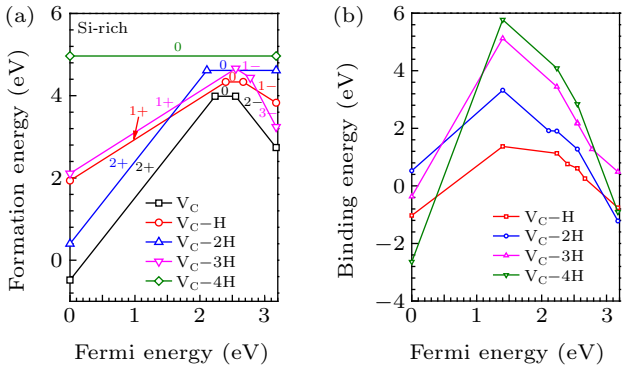



**Fig. 7.** (a) Formation energies and (b) binding energies of $V_C$–$n$H ($n$ = 1–4) complexes in 4H-SiC.

### 3.5. H passivation of $V_{Si}$

Since 2015, $V_{Si}$ has been manipulated as isolated spin qubits for quantum computing.[58–63] Isolated $V_{Si}$ color centers were created by laser writing, ion implantation or electron irradiation.[58] It was found that both the photoluminescence (PL) wavelength and intensity were not uniform throughout the $V_{Si}$ array of 4H-SiC.[64,65] In this section, we evaluate the possible reason of H passivation on the nonuniform PL emission of $V_{Si}$ arrays in 4H-SiC.

As shown in Fig. 8(a), $(V_{Si}\text{–}4H)^0$ and $(V_{Si}\text{–}3H)^-$ complexes have the lowest formation energies in p-type and n-type 4H-SiC, respectively. This indicates that H would passivate $V_{Si}$ and change the optical properties of $V_{Si}$ defects in 4H-SiC. The occupied defect state of $V_{Si}$ lies in 0.72 eV above the VBM of 4H-SiC, which agrees well with experimental and theoretical results.[40,41] When $V_{Si}$ is passivated by 4 H atoms, the defect state disappears from the bandgap of 4H-SiC. This gives rise to the disappear of PL emission of $V_{Si}$. When $V_{Si}$ is passivated by 3 H atoms, the defect states shift to 0.70 eV above the VBM of 4H-SiC. This results in the change of PL emission wavelength and intensity for the $V_{Si}$ arrays in 4H-SiC.[66]

We also calculate the binding energies of $V_{Si}$–$n$H ($n$ = 1–4) complexes by $E_b(V_{Si}\text{–}nH) = \Delta H_f(V_{Si}) + n\Delta H_f(H_i) - \Delta H_f(V_{Si}\text{–}nH)$. As shown in Fig. 8(b), the binding energies of $V_{Si}$–$n$H ($n$ = 1–4) complexes are all positive. This indicates that once the complexes are formed, $V_{Si}$–$n$H ($n$ = 1–4) complexes are stable against decomposition. Because of the low binding energies of $V_{Si}$–$n$H ($n$ = 1–4) complexes, thermal annealing is needed to decompose $V_{Si}$–$n$H ($n$ = 1–4) complexes, and promote the uniformity for the PL properties of $V_{Si}$ array in 4H-SiC.

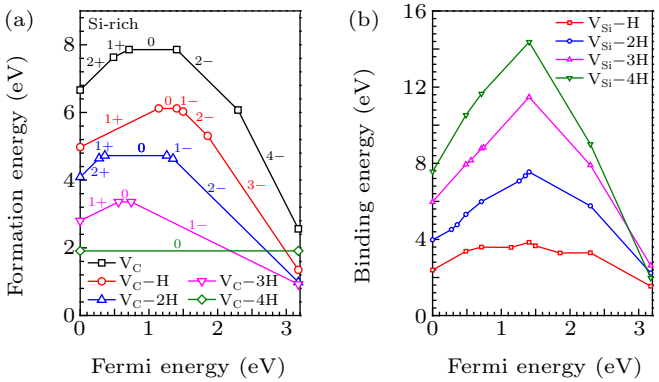



**Fig. 8.** (a) Formation energies and (b) binding energies of $V_{Si}$–$n$H ($n$ = 1–4) complexes in 4H-SiC.

## 4. Conclusion

In conclusion, we have systematically investigated the role of H in the electronic properties of 4H-SiC. We have

found that $H_i^{bc}$ and $H_i^{Si-te}$ dominate the defect configurations of H in p-type and n-type 4H-SiC, respectively. In n-type 4H-SiC, the compensation of $H_i^{Si-te}$ is found to pin the Fermi energy and hinder the increase of electron concentration in highly N-doped 4H-SiC. Reducing the concentration of unintentional incorporated H is critical to further reduce the resistivity of n-type 4H-SiC. For p-type 4H-SiC doped by Al, we find that the compensation of H on the p-type doping of 4H-SiC is negligible compared to that of $V_C$. Nonequilibrium H-incorporation approaches may passivate $Al_{Si}$ by H, and degrades the performance of p-type 4H-SiC. The degradation can be easily eliminated by thermal annealing, because of the low binding energy of the $Al_{Si}$–H complex in p-type 4H-SiC. We find that nonequilibrium passivation of $V_C$ by H is effective to eliminate the defect states of $V_C$ and thus enhance the carrier lifetime of moderately doped 4H-SiC. Regarding the quantum-qubit applications of 4H-SiC, we find that H can readily passivate the silicon vacancy ($V_{Si}$) during the creation of $V_{Si}$ centers. The $V_{Si}$–$n$H ($n$ = 1–4) complexes are stable against decomposition once they are formed. Thermal annealing is needed to decompose the resulting $V_{Si}$–$n$H ($n$ = 1–4) complexes and promote the uniformity of the photoluminescence of $V_{Si}$ arrays in 4H-SiC. The current work may inspire the further development of the impurity engineering of H in 4H-SiC.

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