Supporting Information for:

Tight-Binding Quantum Chemical Molecular Dynamics Simulations for the Elucidation of Chemical Reaction Dynamics in SiC Etching with SF_6/O_2 Plasma

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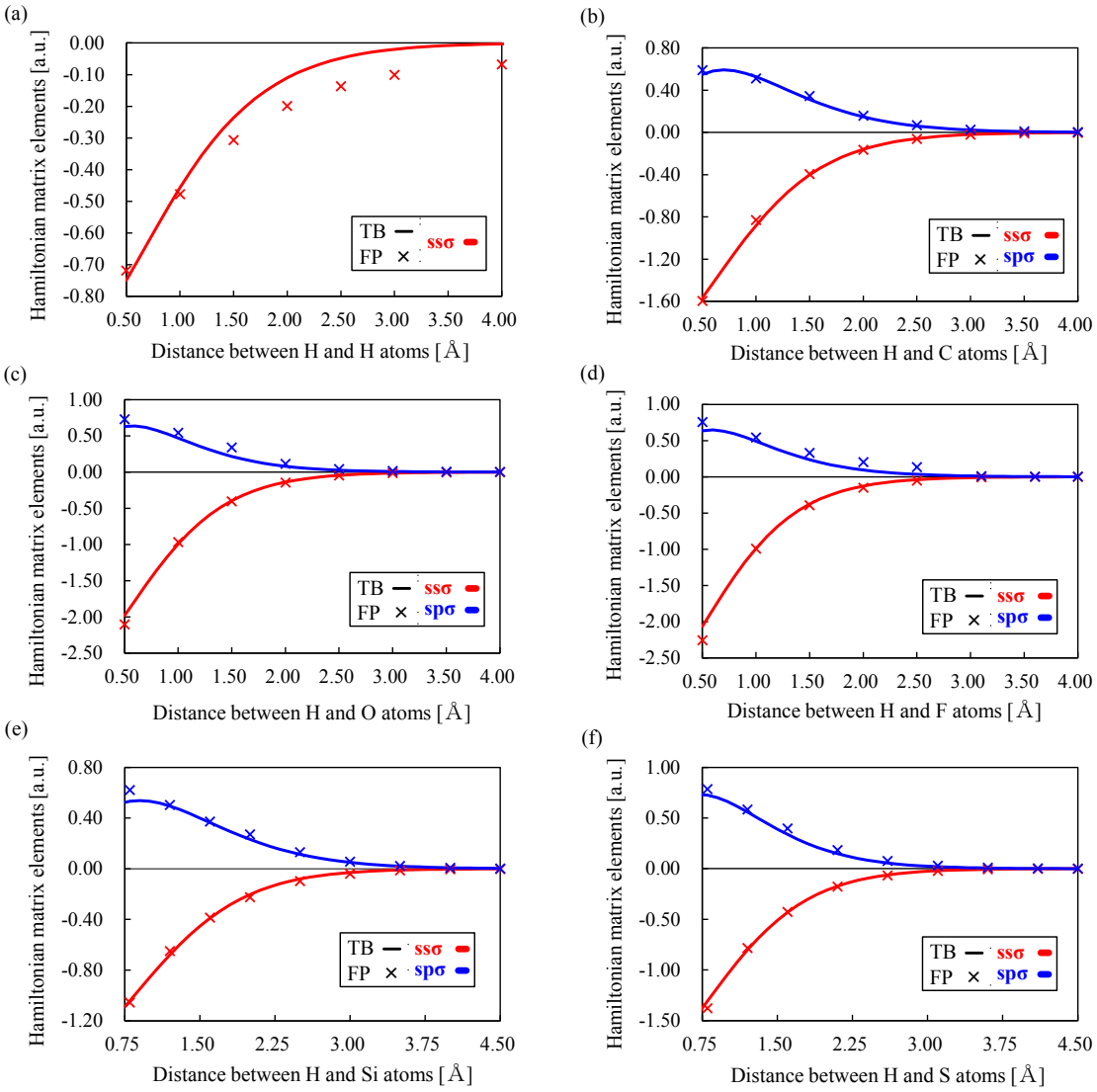

Figure S1. Hamiltonian matrix elements calculated by using the TB-QCMD (TB) with the parameters in Table 2 of the main text and the first-principles (FP) method. Since the TB-QCMD is performed with a minimal basis set, the Hartree-Fock method with the STO-3G basis set is employed as a first-principles method. Figures (a) through (u) show interactions of H-H, H-C, H-O, H-F, H-Si, H-S, C-C, C-O, C-F, C-Si, C-S, O-O, O-F, O-Si, O-S, F-F, F-Si, F-S, Si-Si, Si-S, and S-S atom pairs, respectively.

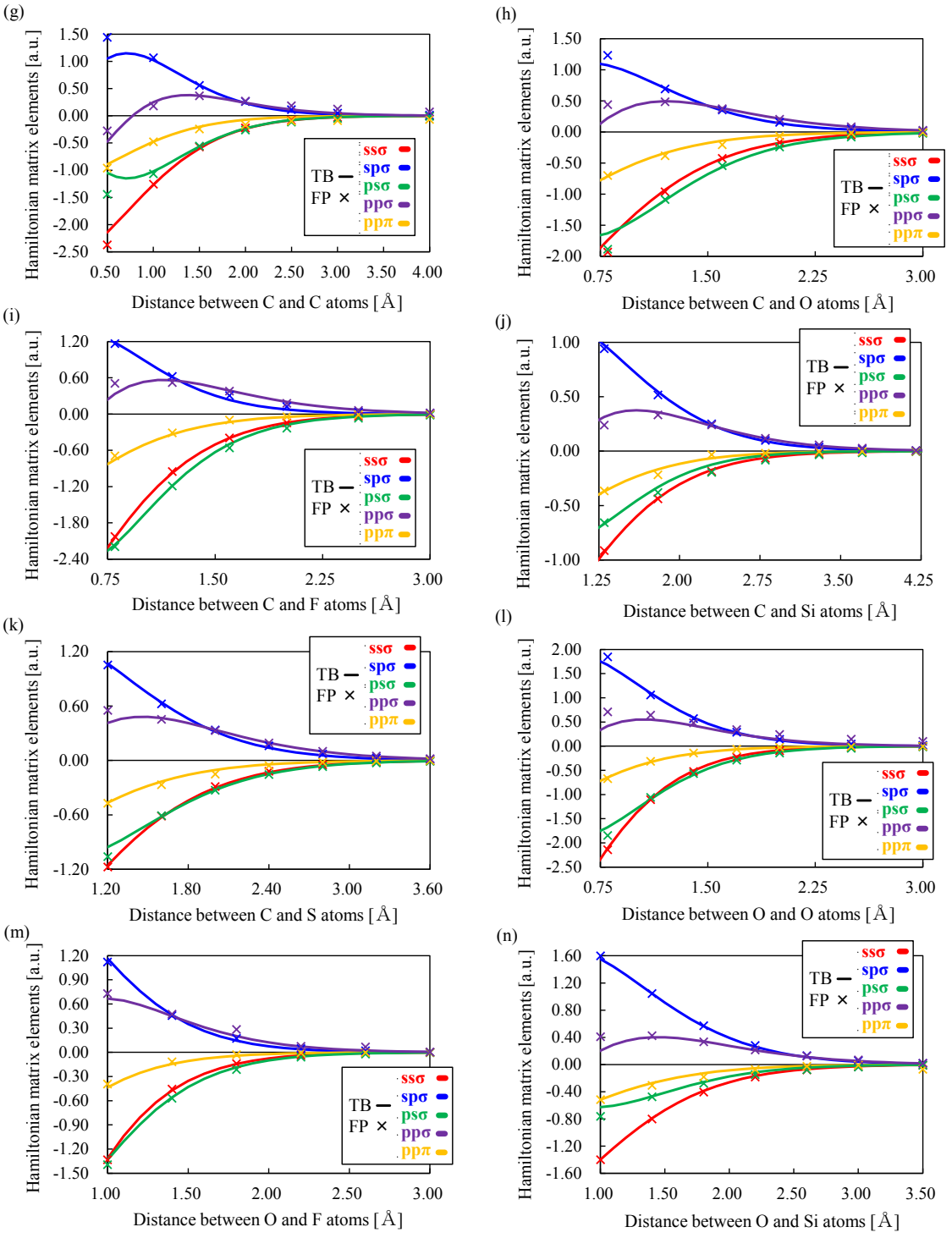

Figure S1. (*Continued*)

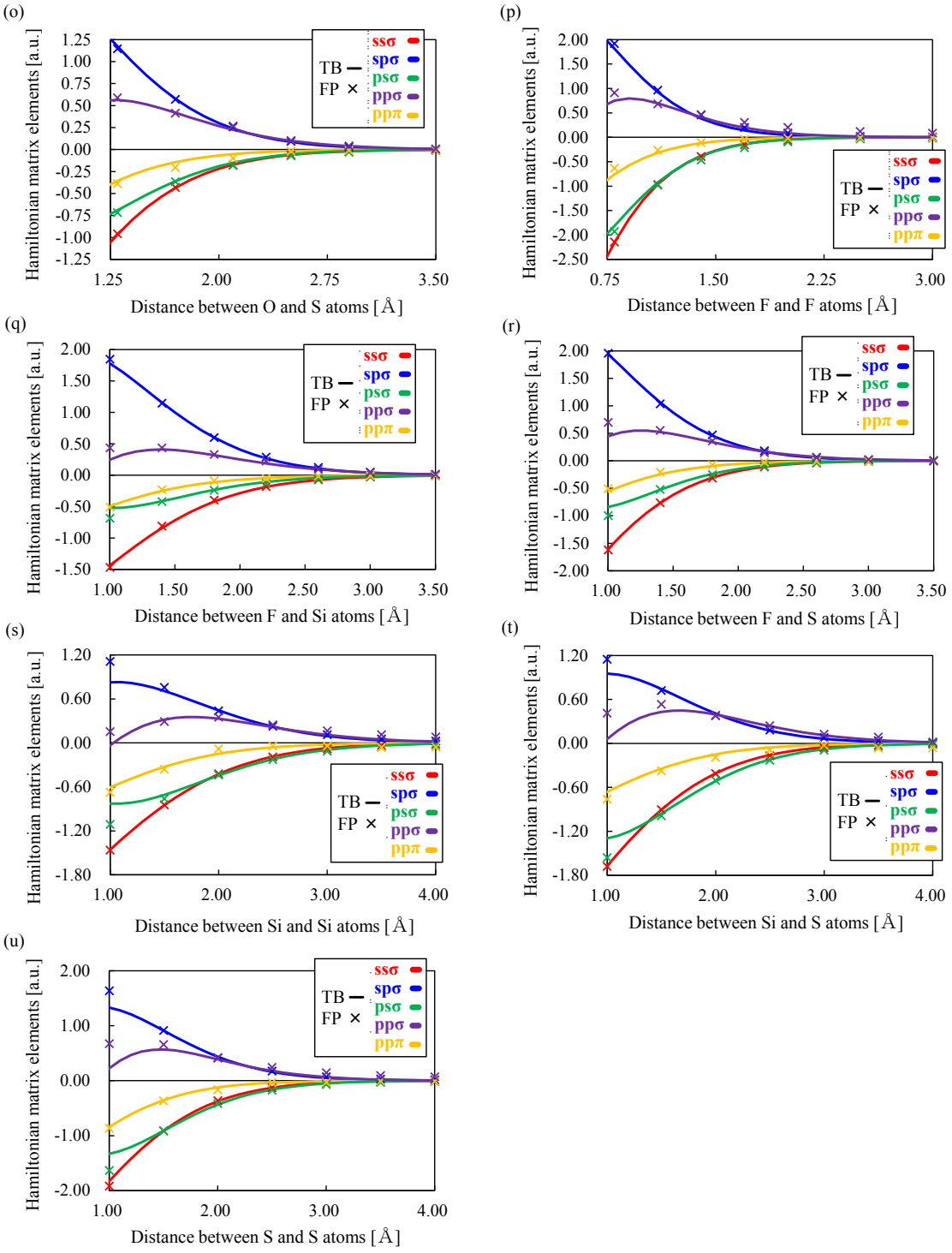

Figure S1. (*Continued*)

Table S1. Bond lengths (Å) calculated by using the TB-QCMD and first-principles methods. First-principles calculations are performed with Dmol^3 code [49] and Gaussian 03 program [S1]. DFT calculations within the generalized gradient approximation (GGA) with the Perdew-Wang exchange correlation functional (PW91) and within the local density approximations (LDA) with the Vosko-Wilk-Nusair (VWN) functional using double zeta plus polarization function (DNP) basis set are performed by using Dmol^3 code. By using Gaussian 03 program, B3LYP/6-311G, MP2/6-311G, and Hartree-Fock(HF)/6-31G calculations are also performed.

Bond	Experiments[S2]	TB-QCMD	GGA PW91/DNP	LDA VWN/DNP	B3LYP /6-311G	MP2 /6-311G	HF/6-31G
H - H	0.741	0.730	0.748	0.763	0.742	0.737	0.730
H - C	1.087	1.051	1.096	1.097	1.089	1.092	1.082
H - O	0.958	0.981	0.969	0.971	0.971	0.969	0.950
H - F	0.917	0.921	0.931	0.933	0.940	0.937	0.921
H - Si	1.480	1.432	1.489	1.495	1.493	1.501	1.492
H - S	1.336	1.284	1.355	1.357	1.385	1.381	1.353
C - C	1.530	1.544	1.547	1.530	1.555 [b]		
C - O	1.160	1.219	1.175	1.168	1.185	1.202	1.161
C - F	1.323	1.367	1.340	1.323	1.371	1.379	1.341
C - Si	1.874	1.886	1.896-1.911	1.875-1.890			
C - S	1.553	1.644	1.569	1.558	1.591	1.606	1.584
O - O	1.207	1.278	1.224	1.211	1.256	1.325	1.195
O - F	1.405	1.450	1.428	1.399	1.475	1.515	1.418
O - Si	1.663	1.712	1.631-1.632	1.617-1.618	1.656 [b]		
O - S	1.431	1.488	1.479	1.464	1.604	1.622	1.555
F - F	1.412	1.468	1.422	1.394	1.469	1.506	1.413
F - Si	1.553	1.533	1.582	1.565	1.636	1.637	1.625
F - S	1.561	1.558	1.614	1.587	1.760	1.767	1.676
Si - Si	2.359	2.352	2.370	2.340	2.415 [b]		
Si - S	2.145	2.098	2.155	2.133			
S - S	2.070	2.062	2.092	2.065	2.254	2.269	2.211

Reference S2: D. R. Lide, *Comprehensive Handbook of Chemical Bond Energies*, CRC Press, USA, 2009.

Mark b: B3LYP/6-31G (diamond, silicon dioxide, and silicon crystals)

Table S2. Reaction energies (kcal/mol) of main molecules and radicals used in the etching simulation. The first-principles calculations are performed with Dmol^3 code [49] and Gaussian 03 program [S1]. The DFT calculations within GGA PW91 and LDA VWN functional using DNP basis set are performed by using Dmol^3 code. By using Gaussian 03 program, B3LYP/6-311G, MP2/6-311G, and Hartree-Fock(HF)/6-31G calculations are also performed.

Reaction							TB-QCMD	GGA PW91	LDA VWN	B3LYP	MP2	HF
SF_4	+	SF_2	→	$2SF_3$			-78.55	-16.40	-21.54	-69.55	-61.27	-73.77
SF_5	+	SiF_3	→	SF_4	+	SiF_4	140.40	112.28	114.03	88.07	123.13	123.00
SF_3	+	SiF_2	→	SF_2	+	SiF_3	32.28	33.34	30.70	68.51	93.61	92.02
SF_2	+	SiF	→	SF	+	SiF_2	54.55	61.08	61.51	66.26	79.54	75.78
SF_4	+	CF_3	→	SF_3	+	CF_4	77.05	40.90	42.28	34.05	48.26	40.53
SF_3	+	CF_3	→	SF_2	+	CF_4	155.60	57.30	63.82	103.60	109.53	114.30
SF_2	+	CF_2	→	SF	+	CF_3	29.32	0.85	1.47	17.72	42.73	42.83
SiF_2	+	CF_2	→	SiF	+	CF_3	-25.23	-60.23	-60.05	-48.54	-36.81	-32.96
CH_4	+	CH_2	→	$2CH_3$			19.49	4.50	2.41	22.80	27.58	37.26
SiH_4	+	SiH_2	→	$2SiH_3$			-22.52	-17.05	-20.00	-13.33	-2.19	-6.40
CH_3	+	SiH	→	CH_2	+	SiH_2	-35.65	-38.57	-40.48	-66.89	-69.51	-72.36
COF_2	+	COH_2	→	2CO	+	2HF	-49.30	-17.42	-39.60	-12.63	21.69	8.15
$2COH_2$			→	CO_2	+	CH_4	87.76	63.35	66.82	54.08	47.04	49.43
$2COF_2$			→	CO_2	+	CF_4	37.58	22.58	23.17	22.14	27.48	28.51
SiH_4	+	OH	→	SiH_3	+	H_2O	15.14	30.86	39.48	-2.10	9.15	-4.09

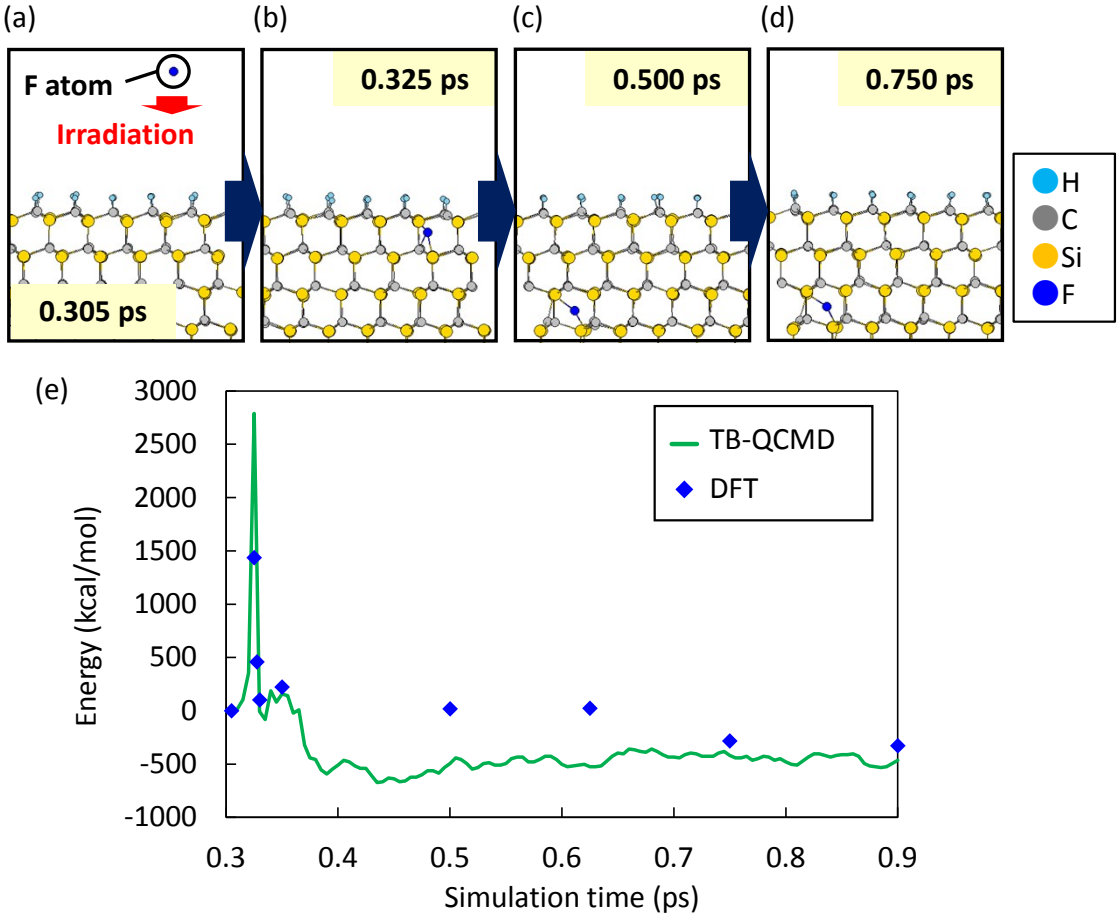

Figure S2. Time evolution of the energy (kcal/mol) during the irradiation of F atom to the SiC surface terminated by H atoms. Snapshots of the TB-QCMD simulation at (a) 0.305 ps, (b) 0.325 ps, (c) 0.500 ps, and (d) 0.750 ps are shown. (e) Energy change during the TB-QCMD simulation and energies by the static DFT (GGA PW91/DNP) calculations. The static DFT calculations are performed with the structures of the TB-QCMD simulations at 0.305, 0.325, 0.328, 0.330, 0.350, 0.500, 0.625, 0.750, and 0.900 ps.

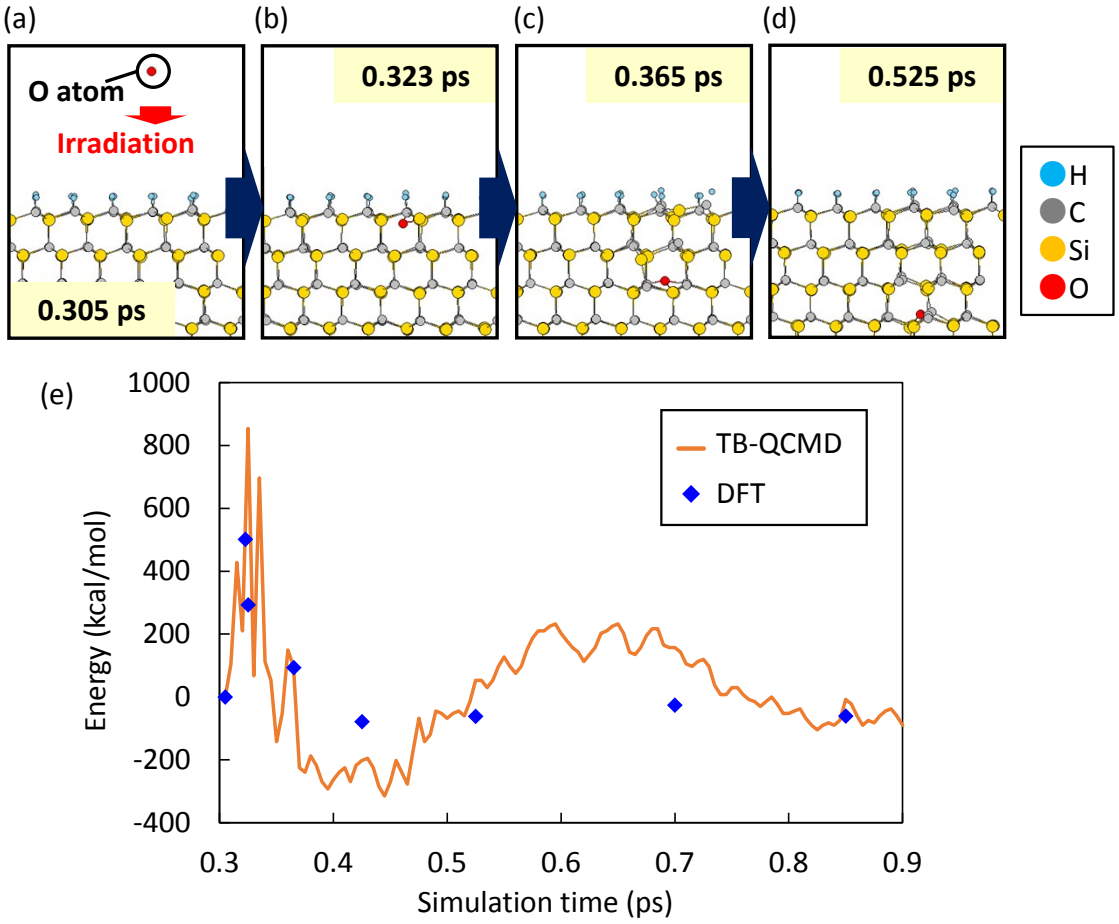

Figure S3. Time evolution of the energy (kcal/mol) during the irradiation of O atom to the SiC surface terminated by H atoms. Snapshots of the TB-QCMD simulation at (a) 0.305 ps, (b) 0.323 ps, (c) 0.365 ps, and (d) 0.525 ps are shown. (e) Energy change during the TB-QCMD simulation and energies by the static DFT (GGA PW91/DNP) calculations. The static DFT calculations are performed with the structures of the TB-QCMD simulations at 0.305, 0.323, 0.325, 0.365, 0.425, 0.525, 0.700, and 0.850 ps.

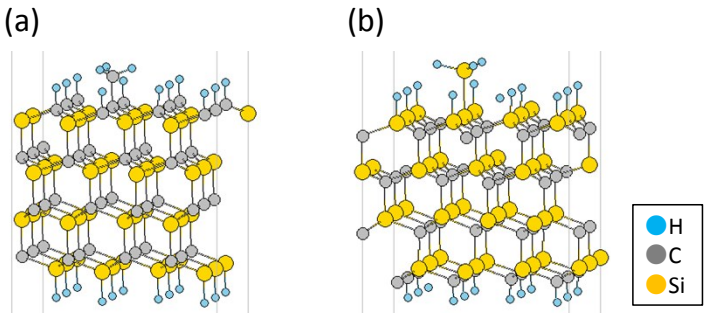

Figure S4. Simulation models for the calculations of binding energies of (a) C-C and (b) Si-Si bonds generated on the SiC surface.

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