Supplementary materials for "Atomic and electronic structures of the β-$FeSi_2$/Si(001) interface"

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I. THE β-FESI$_2$/SI(001) INTERFACE STRUCTURE

In order to determine the β-FeSi$_2$ /Si(001) interface structure, we examined several models by optimizing their structures by DFT calculation and simulating STEM images. Figure S1 shows selected three slab models: (a) a β-FeSi$_2$ slab and a Si(001) slab are bonded through Si dimers, (b) a β-FeSi$_2$ slab is simply stacked on a Si(001) slab without modifications, (c) a β-FeSi$_2$ slab and a Si(001) slab are bonded another configuration of Si dimers.

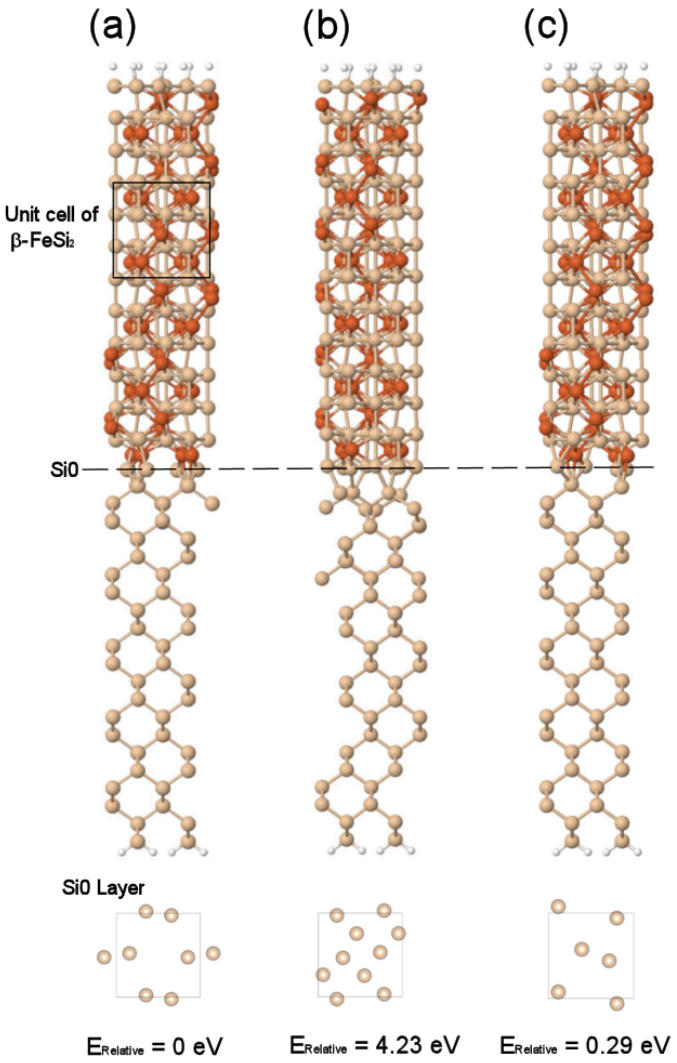


FIG. S1. Representative slab models used for the DFT calculations of the β-FeSi$_2$/Si(001) interface. (a) is the model that yields the best agreement with STEM observations and the most stable structure among examined models. Each energy represented is the total energy relative to that of the slab in (a).

Figure S2 shows the detailed atom configurations of the β-$FeSi_2$/Si(001) interface determined in this study. Their fractional atomic coordinates are represented in Table S1.

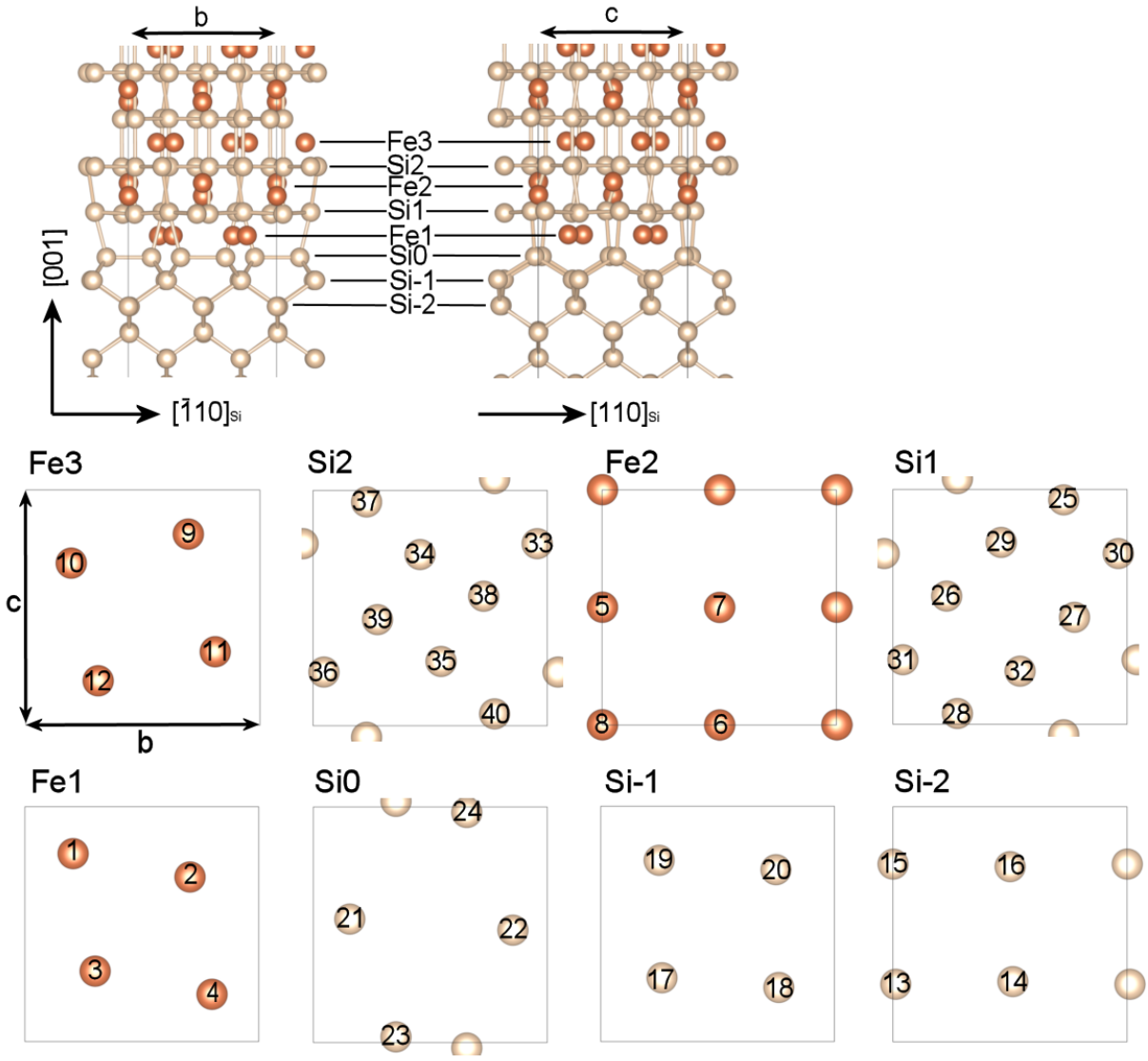


FIG. S2. Detailed structure of the β-$FeSi_2$/Si(001) interface determined in this study.

TABLE S1. Fractional atomic coordinates (x, y, and z) of β-$FeSi_2$/Si(001) for a unit cell size of $\boldsymbol{a}$ = 0.986 nm for β-$FeSi_2$ and $\boldsymbol{b}$ and $\boldsymbol{c}$ = 0.731 nm for Si, calculated using the PBE functional. The atom numbers correspond to those labeled in Fig. S2.

Layer	Atom Number	x	y	z
Fe1	1	0.205	0.801	0.115
	2	0.705	0.701	0.115
	3	0.301	0.300	0.115
	4	0.801	0.201	0.015
Fe2	5	0.002	0.501	0.397
	6	0.502	0.000	0.397
	7	0.502	0.500	0.328
	8	0.002	0.001	0.328
Fe3	9	0.693	0.813	0.612
	10	0.193	0.689	0.612
	11	0.810	0.313	0.612
	12	0.310	0.189	0.612
Si-2	13	0.014	0.245	-0.261
	14	0.514	0.256	-0.261
	15	0.000	0.756	-0.261
	16	0.499	0.745	-0.261
Si-1	17	0.264	0.274	-0.123
	18	0.763	0.227	-0.123
	19	0.249	0.773	-0.123
	20	0.749	0.728	-0.123
Si0	21	0.155	0.525	0.000
	22	0.853	0.476	0.000
	23	0.353	0.025	0.000
	24	0.655	0.976	0.000
Si1	25	0.730	0.955	0.242
	26	0.230	0.546	0.242
	27	0.775	0.455	0.241
	28	0.276	0.046	0.242
	29	0.462	0.775	0.231
	30	0.962	0.727	0.231
	31	0.044	0.275	0.231
	32	0.544	0.226	0.231
Si2	33	0.957	0.774	0.483
	34	0.457	0.727	0.483
	35	0.547	0.274	0.483
	36	0.047	0.227	0.483
	37	0.229	0.951	0.484
	38	0.729	0.551	0.484
	39	0.275	0.451	0.485
	40	0.775	0.051	0.485

II. STM OBSERVATION OF THE β-FESI$_2$ SURFACE

Figure S3 represents an STM image of the β-$FeSi_2$ surface, which exhibits surface undulation of approximately 0.1 nm. The image clearly shows that the β-$FeSi_2$ surface, covered with the $p(2 \times 2)$ superstructure, displays continuous height variation without the formation of steps.

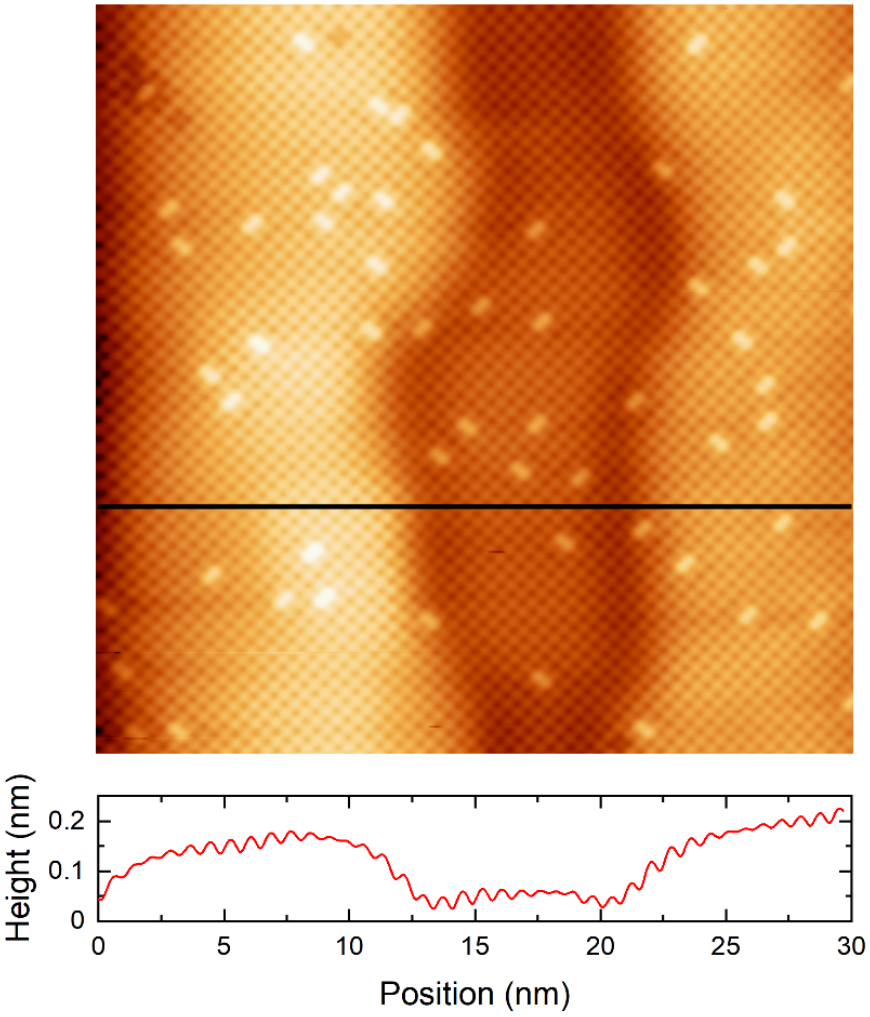


FIG. S3. STM image of the β-$FeSi_2$ surface and a line profile along the black line in the STM image. White dots are unknown defects. Imaging parameters: sample bias of +1.0 V, tunneling current of 50 pA, and sample temperature of 4.3 K, The image dimensions are 30×30 nm^2.

III. BAND STRUCTURE OF THE β-FESI$_2$/SI(001) INTERFACE.

A. Pseud-hydrogen atom terminaion on the topmost surface of the slab

Before initiating band calculations, we investigated the effect of hydrogen termination on Si atoms on the topmost surface of a β-$FeSi_2$/Si(001) slab. Since the top layer of the β-$FeSi_2$ slab terminated with Si atoms also has a metallic electronic state [1], its band diagram exhibits a complex band structure near the Fermi energy, complicating the identification of bands originating from the β-$FeSi_2$/Si(001) interface. To mitigate this complexity, reducing the charges on the top Si atoms via hydrogen termination is effective. However, the precise charge values on the Si atoms in the β-$FeSi_2$ surface are unknown. Therefore, we examined the effect of termination using pseud-hydrogen atoms with different charges (q = 1.0, 1.25, 1.5, 1.66, and 1.75).

Figure S4 shows the projected density of states (PDOS) for atoms in varisou layers of the Slab. In the normal β-$FeSi_2$/Si(001) slab, the Si atom in the first layer exhibits significant charge densities around the Fermi energy, with these charges penetrating several layers deep into the β-$FeSi_2$ slab. The application of pseud-hydrogen termination with a charge of 1.5 effectively reduces these charges. Consequently, we utilized this termination for our band calculations. It is important to note that pseud-hydrogen termination, regardless of the charge value, does not impact the electronic state at the β-$FeSi_2$/Si(001) interface.

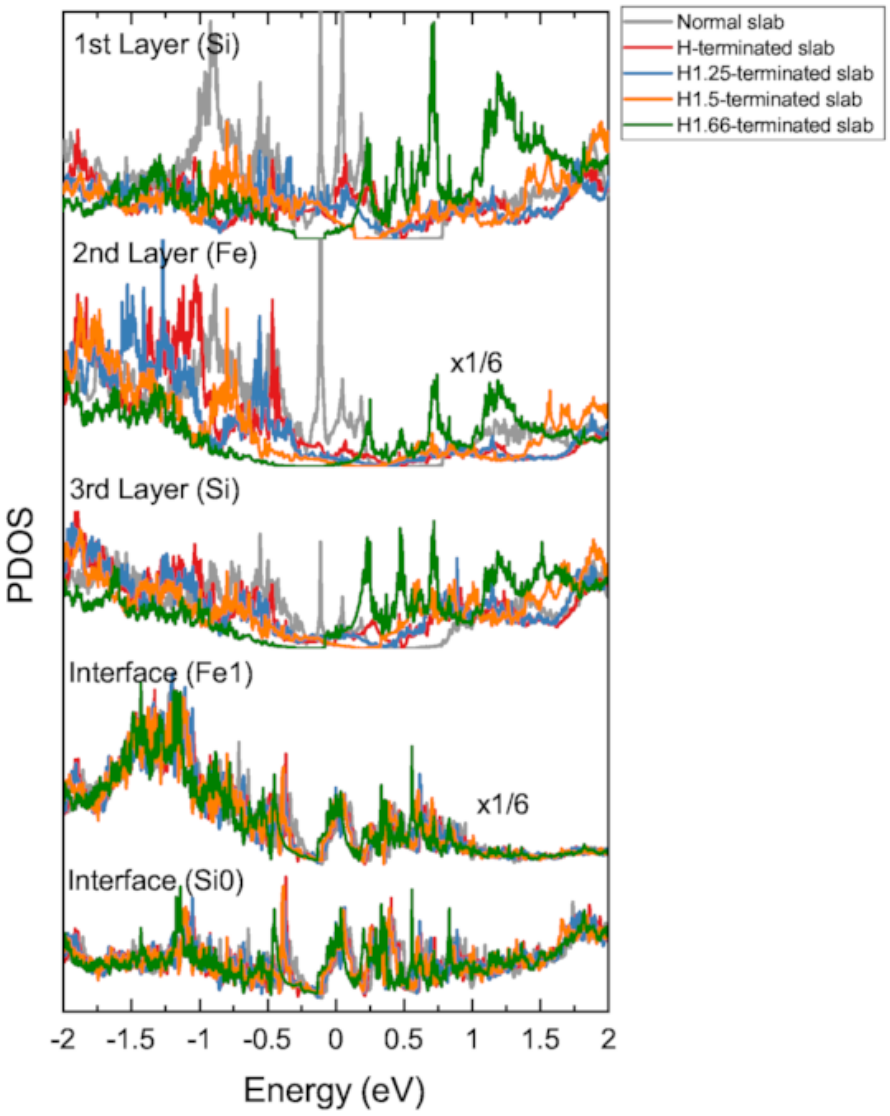


FIG. S4. The effect of pseud-hydrogen atom termination on the β-$FeSi_2$ surface.

B. Band assignment

The origin of the bands was examined by plotting charge densities for each eigenvalue. Figure S5 represents the charge density distributions for representative positions of the bands: the β-$FeSi_2$/Si(001) interface, the bulk β-$FeSi_2$, and bulk Si. The charges for the interface states are well localized on the Fe1 atoms and extend along the interface. These states are also situated within the band gaps of both the bulk β-$FeSi_2$ and bulk Si. The decay depth of these states into the β-$FeSi_2$ film is examined by plotting PDOS for Fe atoms in different layer near the interface (Fig. S6). The result shows that the states associated

with these bands decay to 46% in the Fe2 layer and further diminished to 6% in the Fe3 layer. The orbital-decomposed PDOS for the Fe1 and Si0 atoms, displayed in Fig. S7, reveals that these bands originate from 3d orbitals of Fe and 2p orbitals of Si.

C. Spin-polarized band calculations

The band structure for the β-$FeSi_2$/Si(001) interface was investigated using both non-spin-polarized and spin-polarized calculations. The bulk bands of β-$FeSi_2$ projected onto the (001) plane exhibit completely degeneracy between the up and down spin bands [Fig. S8]. However, according to the result of the slab calculation, this degeneracy is significantly lifted for the interface bands and slightly for the bulk β-$FeSi_2$ bands.

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[1] K. Sagisaka, T. Kusawake, D. Bowler, S. Ohno, Emergence of metallic surface states and negative differential conductance in thin β-$FeSi_2$ films on Si(001), Journal of Physics: Condensed Matter **35**, 135001 (2023).

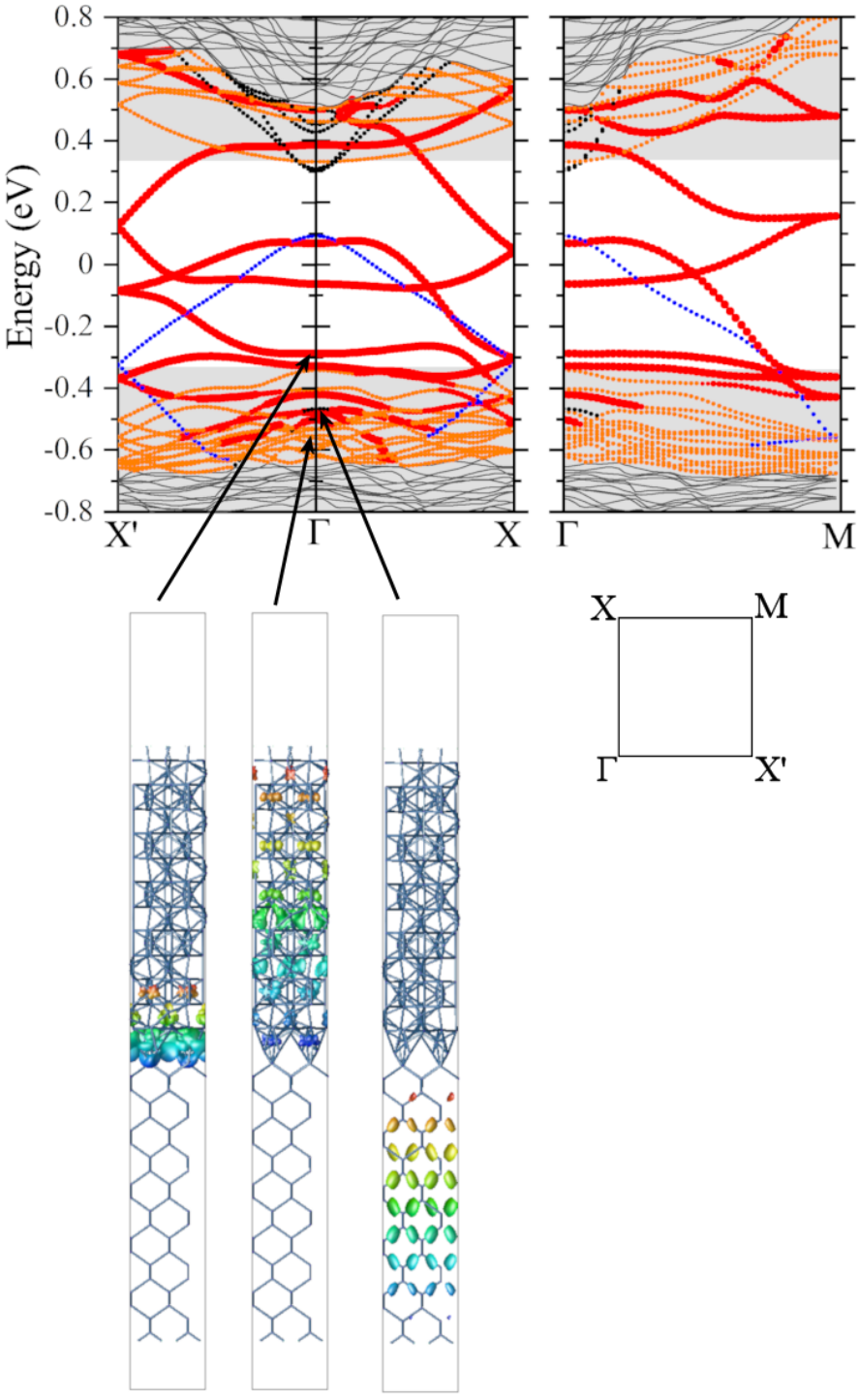


FIG. S5. Non-spin polarized bands and charge density distributions of the β-$FeSi_2$/Si(001) slab. Charge densities are visualized with the isosurface values of 0.005 e/Å^3. Color scale represents height in z direction.

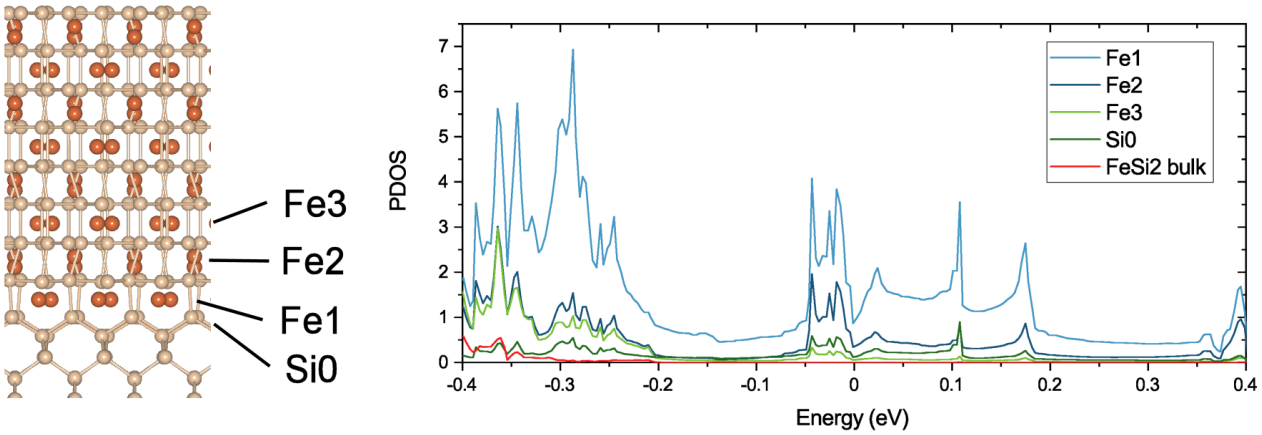


FIG. S6. PDOS for various layers near the interface.

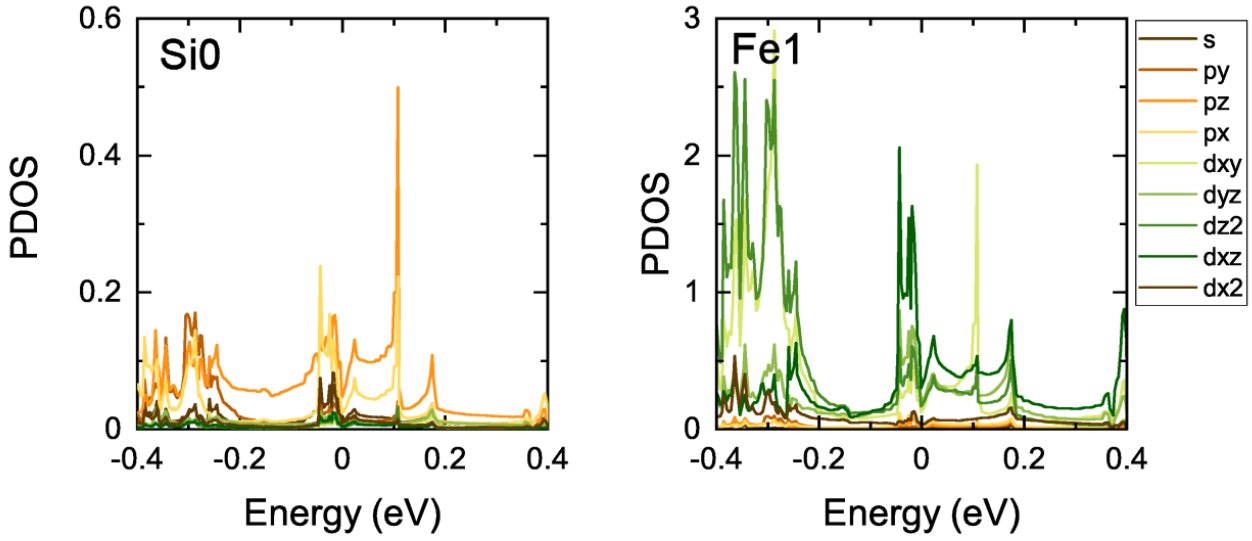


FIG. S7. PDOS decomposed to electron orbitals for the Si dimer in the S0 layer and the Fe atom in the Fe1 layer.

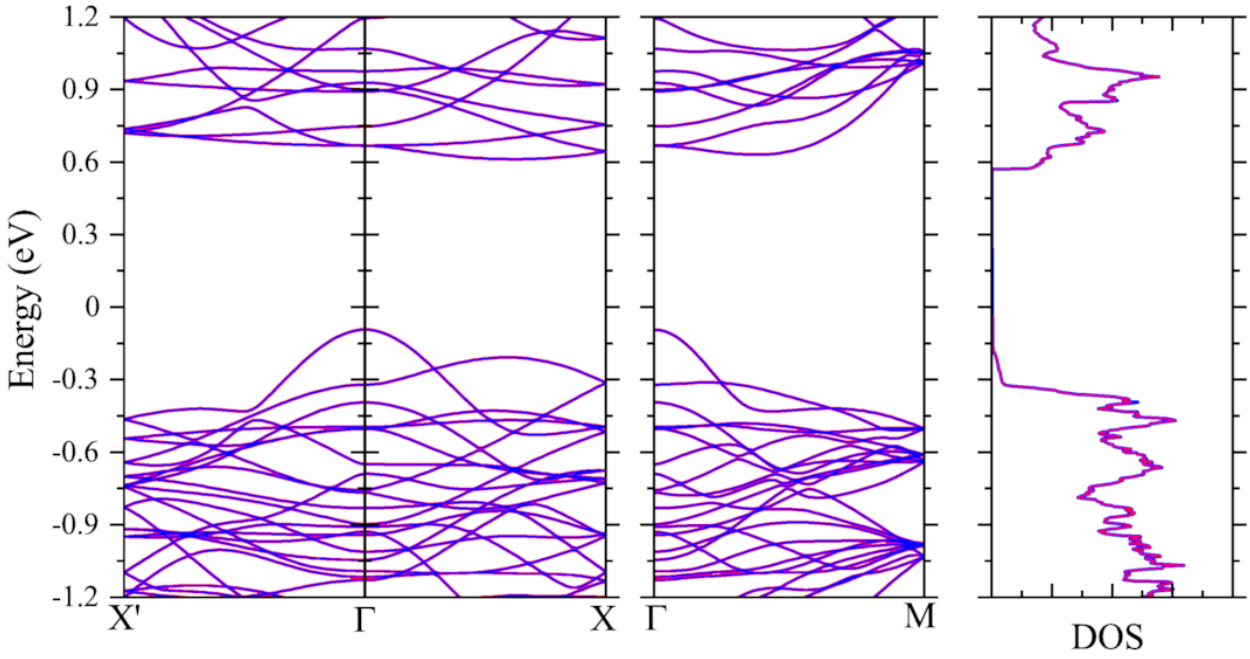


FIG. S8. Spin polarized bands and PDOS calculated with a bulk β-$FeSi_2$ cell. The red and blue curves correspond to bands with up and down spin, respectively.

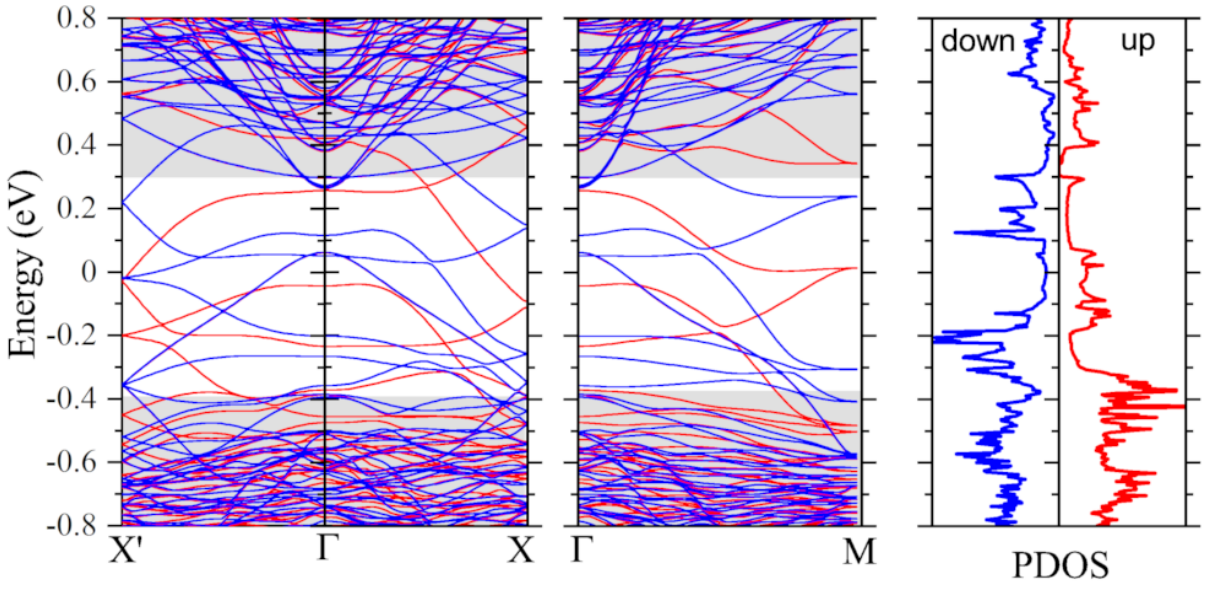


FIG. S9. Spin polarized band structure of the β-$FeSi_2$/Si(001) slab. The red and blue curves correspond to bands with up and down spin, respectively.