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Simulation of the atomic and electronic structure of a solid Fe wetting layer on Si(001) obtained by layer-by-layer deposition

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The atomic and electronic structure of the solid wetting layer (SWL) of Fe on Si (001) is studied in the process of layer — by-layer deposition of Fe-monolayer by monolayer by quantum mechanical modeling in the framework of the electron density functional theory. It is shown that Fe atoms in SWL occupy the gaps between the atomic rows along the Si(001)-2×1 dimer chains, and Fe growth occurs by stratification of SWL. In this case, coverage SWL is coated with two-dimensional layers with the structure and composition, respectively, at thicknesses of: $1-2$ ML — (1×1)-FeSi; $2-3$ ML — (2×2)R45°-Fe_3Si; 3 ML, 4 ML and 5 ML — (1×1) — Si, (1×1)-FeSi and (2×1)-Fe_2Si; and $6-7$ ML — (1×1)-Fe. At the same time, starting from the thickness $d = 2$ ML, the substrate atoms change their packing to hexagonal — with packing defects. At the same time, the electronic structure of SWL ischaracterized by (*a*) hybridization of states, (*b*) changing the shape and position of the bands (moving them away from the Fermi level), (*c*) filling in states at the Fermi level, and (*d*) complete disappearance of the band gap.

Keywords: stratification, atomic packing, density of electronic states, quantum mechanical modeling.

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1. Introduction

The ideal ferromagnetic metal-semiconductor interface is of great importance for nanoelectronics and spintronics and depends on the method of its formation. In this regard, quite a large number of studies have been devoted to the formation of the Fe−Si interface not only at room temperature [1–9], but also at a lower substrate temperature [10–12]. However, in these experiments, only the reduced substrate temperature was used, and the reduced vapor temperature was not used. Therefore, such regimes did not lead to the growth of a solid (frozen) Fe wetting layer (SWL) Fe, which can be considered as a „seed layer“ for the formation of a perfect Fe−Si interface.

In [13–16], experiments were performed at a low vapor steam temperature. And In them, SWL Fe was formed. It was found that its formation is accompanied by Si segregation and simultaneous rearrangement of the Si substrate boundary layer Si into the Si metal phase Si (see [15]). Recently, we modeled the growth of SWL in the Fe−Si(001) system using metal deposition in the form of dense „atomic chains“ [17]. It turned out that the growth mechanism in this model differs from that obtained in experiments: mixing and rearrangement of Si occurred much later and without Si segregation. Apparently, the reason for this difference is the deposition of Fe by „atomic chains“.

We assumed that if Fe is deposited as a two-dimensional (2D) layer of atoms rather than „atomic chains“, the mechanism of growth of SWL Fe on Si(001) will be different. As it turned out, under the new conditions, the mechanism of SWL growth better corresponds to the experiment [13]: a Fe−Si mixture is formed up to 3 ML Fe−Si. Moreover, the growth of SWL is accompanied by its stratification, which is manifested in specific features of the electronic structure, and other features.

2. Simulation and calculation procedure

The calculation was carried out on a supercell of size $7.69 \times 7.69 \times 21.16$ Å^3, which contained six monolayers (each of four atoms) of cell Si(001) — 2×1 with a lower fixed layer saturated with hydrogen atoms. Iron atoms were deposited in monolayers ($1\,\text{ML} = 0.68 \cdot 10^{15}\,\text{cm}^{-2}$) of 4 atoms located close to the most favorable positions. The deposition step was one monolayer, and the total number of steps was 7. After each deposition we searched for the equilibrium state of Fe−Si(001) system during its evolution at zero Kelvin (0 K) under the influence of quantum mechanical forces. The calculations were performed using FHI96spin package [18], working on the basis of the density functional theory [19,20], as well as within the framework of the pseudo-potential method [21] and a set of plane waves with using one *k*-point of the Brillouin zone (0,0,0). Pseudopotentials were generated

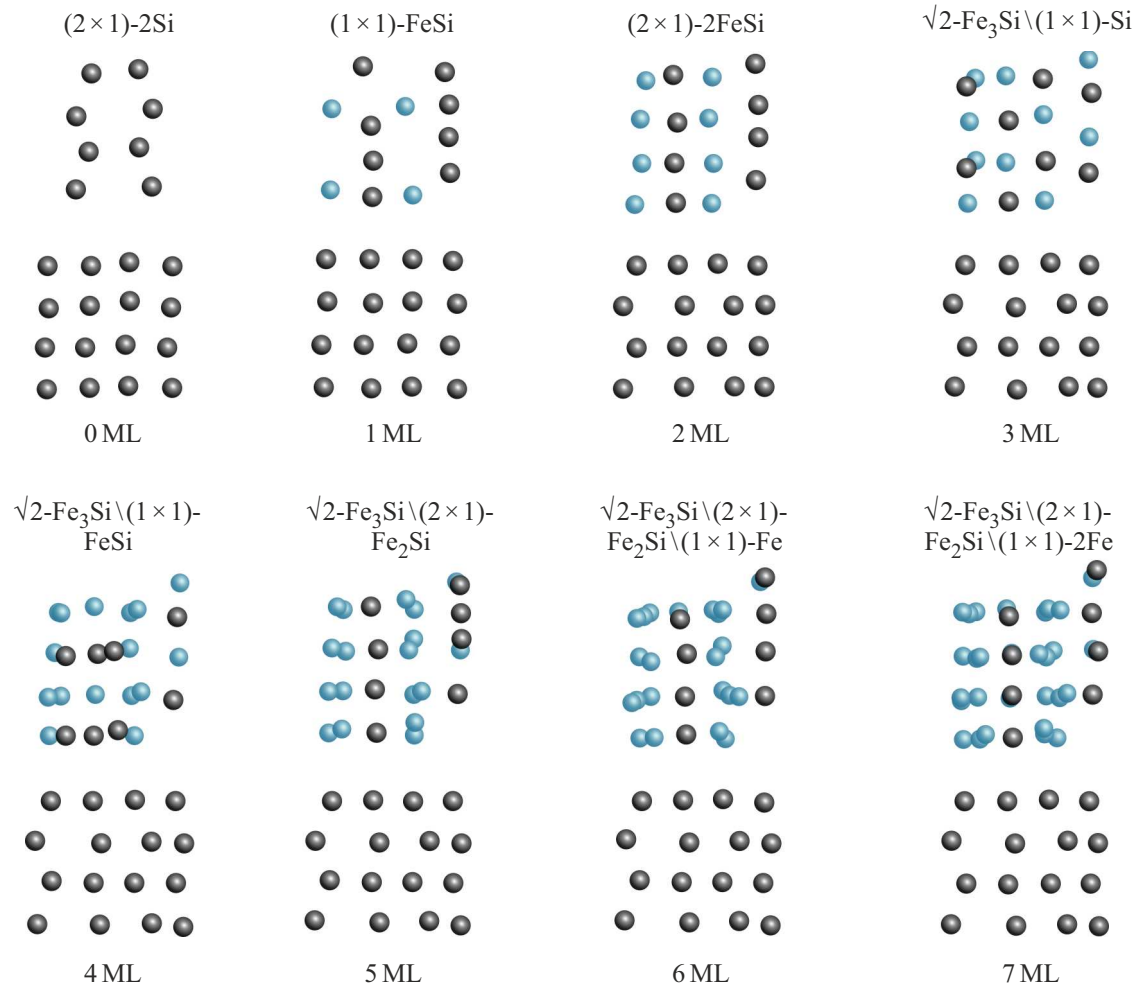

Figure 1. Arrangement of Fe atoms (steel-color balls) and Si (black balls) in SWL, as well as of Si atoms in the lower four layers 4-x of the Si substrate. The number of Fe atoms increases with thickness: 1 ML — 4; 2 ML — 8; 3 ML — 12; 4 ML — 16; 5 ML — 20; 6 ML — 24; 7 ML — 28. Above the image of each SWL there is a symbol of SWL structural type (see text).

using the FHI98PP package [22], the cutoff energy of the set of plane waves was 40 Ry, and the exchange-correlation interaction was taken into account in the generalized gradient approximation. In addition to the atomic coordinates, the total and local densities of states (DoS) associated with individual atomic layers were calculated. The resulting levels (DoS) were „blurred“ using Gaussian function with a half-width of 0.075 eV.

3. Results and discussion

Figure 1 shows the location of Fe atoms (steel-colored balls) and Si atoms (black balls) in the SWL (in the upper part of the corresponding fragments) and in the lower 4 layers of the substrate Si(001)-2×1.

At coverage 0 ML the top two monolayers of Si atoms (dimers) are shown. The number of Si monolayers/atoms in the substrate is constant (4/16), and the number of Fe monolayers/atoms in SWL increases with thickness from 1/4 to 7/28. Figure 1 shows the designations of the structural types of the corresponding SWL, taking into account the composition of the layers, their number and type of ordering: „1×1“, „2×1“ and „$\sqrt{2}$“ (where „$\sqrt{2}$“ is a short designation for the structure $(\sqrt{2} \times \sqrt{2})R45°$). These types were identified through detailed examination of the supercell structure, including top, bottom, side, and views at different rotations.

Figure 1 shows that Fe atoms prefer positions in interstices along the direction of Si(001) dimer rows -2×1. Besides, it can be seen that the structural type of SWL changes each time with thickness change. At 1−2 ML is 2D $(1 \times 1)-$FeSi, and after 2 monolayers this is 2D $(\sqrt{2} \times \sqrt{2})R45°-Fe_3Si$. And already in Fe_3Si 2D grow: $(1 \times 1)-$Si ($d = 3$ ML); $(1 \times 1)-$FeSi ($d = 4$ ML) and $(2 \times 1)-Fe_2Si$ ($d = 5$ ML). And then, on $(2 \times 1)-Fe_2Si$, 2D grow: $(1 \times 1)-$Fe ($d = 6-7$ ML). This growth mechanism can be called: „layer-by-layer growth with mixing and stratification“.

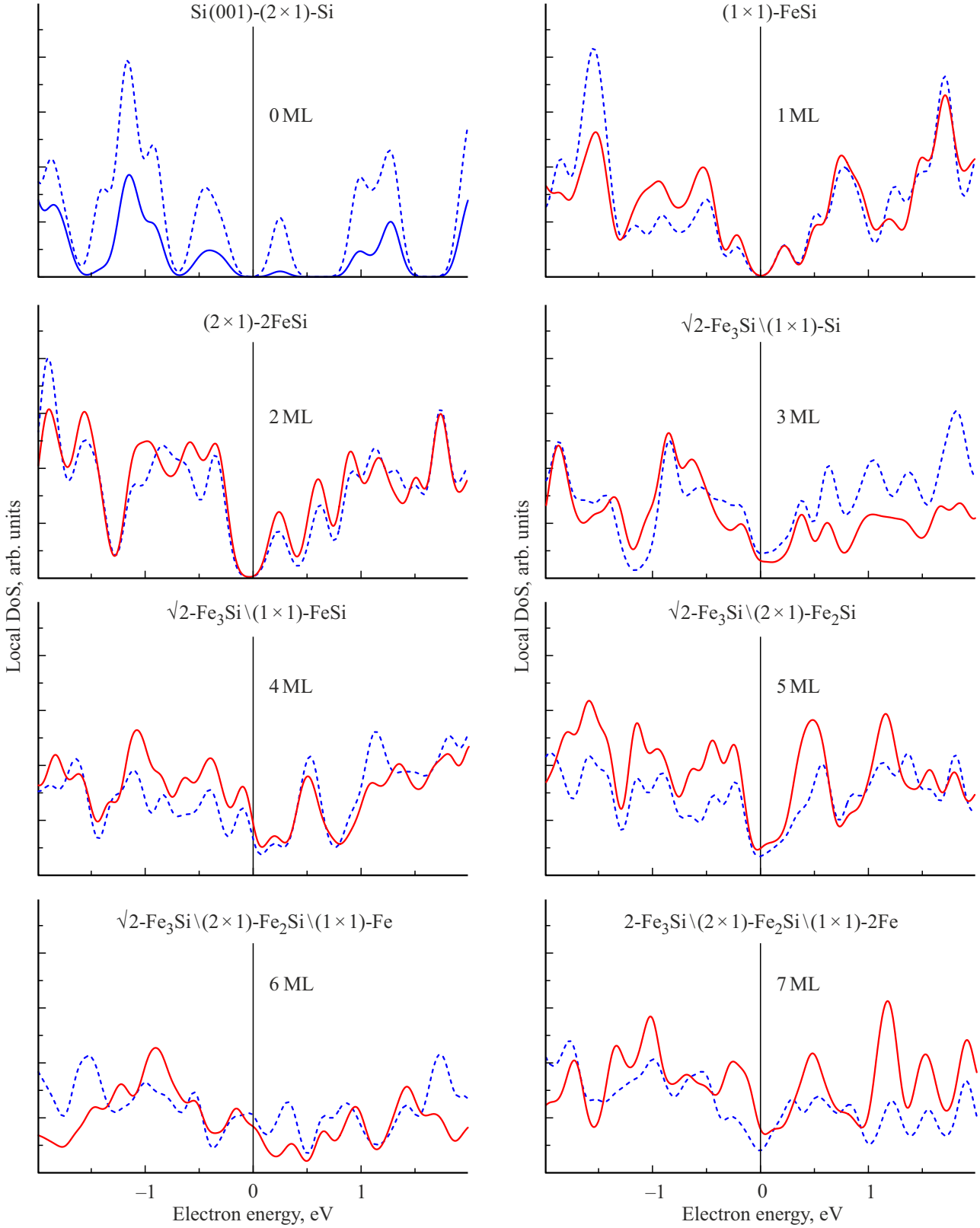

Figure 2. Dependences of local DoS in SWL (red curves) and in the substrate (blue dotted line) on the energy of electronic states and the number of monolayers of deposited Fe (different structures of SWL). Local DoS in SWL corresponds to its upper layer, and in the substrate Si —its 4th layer from bottom.

Figure 1 also shows a structural transformation of the lower rows of the substrate (not affected by mixing with Fe) into a lattice with hexagonal packing and packing faults. This happened already at 2 ML, when a two-monolayer 2D phase of composition Fe−Si was formed.

Figure 2 shows the dependence of the local electronic structure of SWL on the amount of ML of deposited Fe for the upper SWL atoms (dashed curves, red) and the upper (dimers) and fourth from the bottom layer of substrate atoms (dashed and, accordingly, solid curves; blue). First of all, the similarity of the DoS of the upper layers of the substrate and SWL (regardless of SWL thickness) with DoS in the bulk of the substrate is obvious. This is due to the structural similarity between SWL and the substrate (Figure 1). At the same time, during Fe growth a change in the shape of DoS bands is observed, which is obviously associated with the rehybridization — hybridization of Si and Fe states during the growth of various 2D structures Fe−Si.

On the other hand, at one ML and thicknesses greater than 1 ML the electronic structure behaved differently. This is explained by the effects of the evolution of the electronic structure of transition *d*-metals at low coverage [23]. This is: 1) the effect of narrowing/expanding of *d*-band of metal, due to decrease/increase in the coordination of atoms and, accordingly, less/more overlap of their electronic shells and 2) the effect of moving away/approaching of *d*-band towards the Fermi level with increasing/decreasing of reactivity of the coating, in particular, due to change in the proportion of reactants (in this case, metal and silicon).

Similar effects are obviously observed in our experiments. At single ML the DoS bands narrowed and approached the Fermi level due to the fact that the dimers were destroyed, the Si−Si bond in them was replaced by Fe−Si bond, and Si atoms located (see Figure 1) as in the bulk of the substrate — with decrease in their coordination (overlapping of their electron shells). At the same time, the charge balance reduced the reactivity of the coating. At larger thicknesses the bands expanded with thickness increasing and moved away from the Fermi level, due to a) Fe SWL enrichment, b) increased coordination of atoms, and c) increased reactivity of the coating. Besides, after the 1st ML the substrate changed its atomic packing into a hexagonal one with packing faults. In general, at ML, all this led to the leveling and disappearance of the band gap near the Fermi level.

Note that in the literature there are papers relating the epitaxy of bulk phases of Fe on Si(001), including on silicide interlayers: for example, papers [24–27]. But SWL Fe is a low-dimensional phase, has thickness of several monolayers, and SWL Fe growth is carried out under freezing conditions [14–17]. The use of SWL Fe for two-dimensional template at Fe epitaxy on Si(001) still remains to be studied.

4. Conclusion

Features of the atomic structure of SWL during Fe growth on Si(001) were found: 1) SWL stratification according to the composition of two-dimensional layers and their structural type, 2) enrichment of growing SWL in Fe with intermediate stage of surface segregation of two-dimensional Si, 3) more dense arrangement of Fe atoms in SWL than in pure Si substrate, 4) Fe arrangement in SWL in atomic rows parallel to the dimerization direction of Si(001) surface, 5) similarity of SWL structure to the substrate structure and 6) hexagonal packing type with faults of Si substrates after 1st ML. Features of the electronic structure of SWL were also identified: 1) expansion, after 1st ML, of hybrid bands Fe and Si with their overlap at the Fermi level and their center removal from this level and 2) disappearance, at 2−3-x monolayers of the band gap near the Fermi level.

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Conflict of interest

The authors declare that they have no conflict of interest.

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