

## Formation of Fe<sub>2</sub>Si Wetting Coating on Si (001) 2×1 and Growth of a Stable Fe Nanolayer: AES and EELS Study

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**Abstract.** The structural-phase state of two-dimensional ( $d = 1 - 3$  ML) coatings before and after annealing and that of Fe nanolayers ( $d = 4 - 10$  ML) were investigated on Si (001)2×1 by electron spectroscopy methods of Auger-electrons and energy losses. The room (30 °C) and lowed ( $\leq 1250$  °C) temperatures of the Si (001) substrate and Fe vapor, respectively, were used during Fe deposition. This study showed the following. An ordered two-dimensional 1×1 phase of Fe stable up to 600 °C and then a Fe<sub>2</sub>Si wetting coating stable at 250 °C form near the thickness 1 ML and 3 ML, respectively. Fe deposition on this Fe<sub>2</sub>Si coating leads to the one-after-another formation of the Fe<sub>3</sub>Si, the Si-in-Fe solution, and then a stable up to 250 °C Fe nanofilm with segregated Si.

### 1. Introduction

The growth of ultrathin layers of ferromagnetic metals and their alloys on silicon is critical for the microelectronic integration of magnetic memory and spintronics (see, e.g., reviews [1, 2, 3]). In particular, as predicted by theoretical calculations, the tunnel spin injector on base of a Fe/ Si (001) Schottky barrier can be very effective since its polarization can achieve 100% at low reverse voltage [4]. Moreover, the study of the growth of metal on Si (001) is especially essential since the surface (001) is technologically important in silicon microelectronics.

However, there are only a few works on the initial stages of the Fe growth on single-crystal silicon with using Auger electron spectroscopy (AES) and electron energy loss spectroscopy (EELS) in the literature [5-7]. In most cases, other methods were used for study of this growth (see [8-17]). However, in general, the results of various studies and also their interpretation are in significant contradictions between themselves. Obviously, these contradictions were because of considering only the substrate temperature, and other deposition conditions, such as the type and geometry of source, evaporation rate, vapor temperature and kinetic energy were not considered.

In addition, these investigations as a rule use a primary beam with non-adequate energy for analyzing two-dimensional layers by AES and EELS methods. This not allowed correctly evaluate the growth mechanism, film composition and its phase state at the initial (1-10 ML) stage of growth. The used probing depths for AES and for EELS usually were higher and differed in magnitude between themselves. This did not allow correctly comparing the composition and density of the formed films with the composition and density of the bulk phases in the studied system.

Therefore, after understanding these shortcomings, we studied the growth of Fe on Si (111) and Si (001) under the same growth conditions and used the same and minimum probing depths (3 ML) for AES and EELS [18, 19]. In addition, we lowered the temperature of the vapor to reduce mutual diffusion during Fe growth. These studies allowed to compare the densities of the formed phases with the density of bulk phases and to detect wetting coatings of the metal on silicon, which form in the thickness range 1-3 ML. Moreover, these studies allowed concluding that the wetting coatings play an important role in the formation of the metal-semiconductor interface [20]. In turn, the discovery of the nanophase wetting coating provided us to explain the contradictions that existed in the interpretation of earlier works performed by us and other research groups.

However, the question arises: is it possible to maintain the minimum thickness of this interface and make it more stable when the metal-silicon interface is formed under more equilibrium conditions? To answer this question, we decided that it is necessary to study growth on a more stable silicide-like layer. Obviously, as such a layer, you can use some intermediate metastable silicide-like wetting layer, if we can obtain it by annealing the wetting coating of metal.

Thus, the aim of this work is to grow a Fe layer on Si (001) of a minimum thickness (10 ML) and to use an intermediate silicide wetting coating for that. With this purpose, it needed to study the growth, composition, stability, and morphology of the Fe film on such silicide coating on Si (001).

## 2. Experimental Technique and Methods

Samples were prepared in an ultrahigh-vacuum (UHV) chamber, which was equipped with a two-sample manipulator, a evaporative source of iron, as well as AES-EELS and LEED analyzers (both from “Riber” company). Fe was deposited onto Si(001)2×1 substrate (n-type,  $\rho = 4.5 \text{ Ohm}\times\text{cm}$ ,  $d = 420 \text{ }\mu\text{m}$ ) maintained at a room temperature. Under selected Fe thicknesses of 1 ML, 3 ML and 10 ML, samples annealed at temperatures of 500–600 C, 250 °C and 250 °C, respectively.

Methods of Si substrate cleaning and iron deposition were previously described in [19]. We deposited each Fe layer by evaporation of a thin Fe film on Ta ribbon by numerous short flashes at Ta ribbon temperature of 1250 °C. In turn, a thin Fe films onto the Ta ribbon deposited by Fe evaporation (within several minutes) from a W spiral wrapped around a piece of Fe wire and heated to 1550 °C. The deposition rate of iron was calibrated using quartz microbalances. That made it possible roughly estimating the film thickness. More precisely, the thickness of the Fe films was determined from the dependence of the amplitude of the Fe and Si Auger peaks on the film thickness using the iterative procedure: selection of growth model — thickness estimation — correction of the growth model — selection of new growth model — thickness estimation — correction of the growth model — etc. After deposition and annealing, Auger electron and electron energy loss spectra were obtained.

The film composition was calculated by the ratio of the amplitudes of the Fe and Si AES peaks. Under this, we considered the ratio of the LMM and  $L_{23}VV$  Auger peaks of pure Fe and pure Si, respectively ( $I_{\text{Fe}}/I_{\text{Si}} \sim 0.7$ ). To determine the changes in the electron density in the interface bonds and the energy structure of the valence electronic states in the film, the fine structure of the  $L_{23}VV$ -Si peak in AES and the shift of the interband peak in EELS were used. The position of the EELS plasmon peaks was used to estimate the electron and atomic density in the film. For AES and EELS spectra, the energy of the primary electrons was set at 300 eV, which was ensured the minimum and equal probing depth (about 3 ML).

## 3. Results and Discussion

**AES.** Figure 1 shows the AES dependence on the thickness for Fe films on Si (001). In fig. 1, the difference  $E_4 - E_2$  in the AES spectra corresponds to the plasmon loss energy in the electron clouds of Si - Si and Si - Fe interatomic bonds near the interface Si atoms of the substrate and the film. Therefore, a change of the energy position of the Auger peak  $E_2$  and the  $E_4 - E_2$  energy difference in Figure 1 show a change in the electron density and bonds in interface and film with increasing thickness. Moreover, the electron density depends on the atomic density. Consequently, the change in  $E_4 - E_2$  is ultimately caused by a change in the atomic density of Si interface layer and film.

As it is seen from Figure 1, the difference  $E_4 - E_2$  at 2, 4 and 10 ML increases up to 19.4, 22.1 and 23 eV, respectively. Considering the plasmon losses for the bulk phases in the Fe – Si system [5– 7, 21, 22] and the film composition obtained from the ratio of the amplitudes of Auger peaks, we made the conclusion that our data show the formation of a non-bulk Fe phase with a reduced

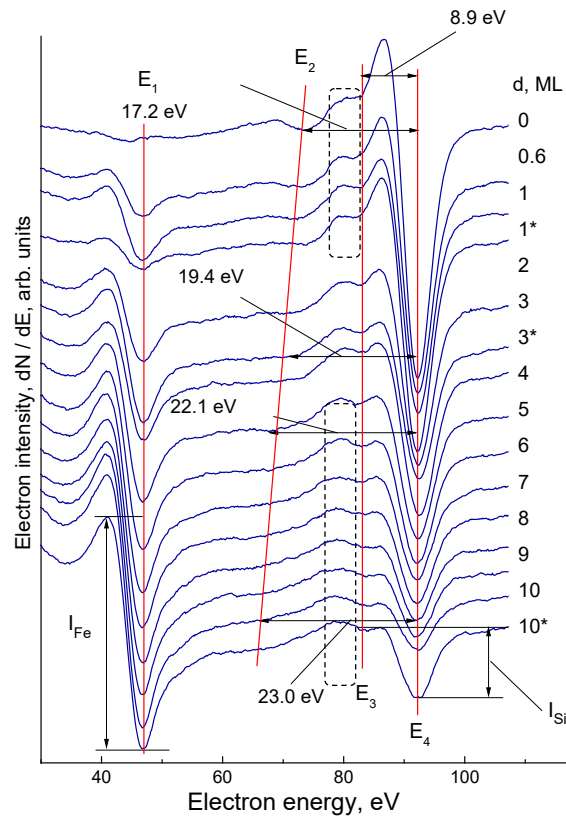


Figure 1 - AES of Fe films on Si (001) of various thicknesses. The solid lines are guides for the eyes approximately following to the position of the peaks (E).  $E_1$  is the position of the Fe LMM Auger peak,  $E_2$  and  $E_3$  are the positions of the plasmon and interband satellites of the Si  $L_{23}VV$  Auger peak,  $E_4$  is the main Si  $L_{23}VV$  Auger peak. By an asterisk is noted a coating after annealing.

electron density (or the non-bulk near-interface Si phase with an increased electron density), the bulk  $Fe_3Si$  silicide and the Fe bulk phase, respectively.

Indeed, on the one hand, the value of  $E_4 - E_2$  at 2 ML is much lower than the plasmon energy in bulk phases with the composition of Fe, FeSi, or even  $FeSi_2$  (see [5–7, 21, 22]). On the other hand, value of  $E_4 - E_2$  for  $d = 2$  ML is higher than the plasmon energy in Si (001). Since the amplitude of the loss peak from Si is usually much larger than the amplitude of the loss peak from Fe, it can be assumed that the interface layer of the Si substrate (not the Fe film) makes the main contribution to the value of  $E_4 - E_2$ . Then we can calculate the density change in the interface Si layer. Considering the well-known formula for plasmon energy [23], the  $E_4 - E_2$  difference increase (up to value of 19.4 eV) gives to the density increase of the Si interface layer by about 6%. Such a compaction of the interface Si layer extends beyond the limits of elastic deformation and can be associated with its local (within a certain depth) transition into some high-pressure phase with a denser lattice. The existence of such a phase is possible due to an ordered network of stacking faults, similar to how it occurs during  $7 \times 7$  reconstruction of the Si surface. A further increase in the  $E_4 - E_2$  value at 4–6 ML (see Figure 1) shows the transition from the loose-unbulk phase of Fe with negative strain to the bulk phase of  $Fe_3Si$  and then to bulk Fe (23 eV at 10 ML).

As for the difference  $E_4 - E_3$  at 4–6 ML, it obviously belongs to segregated Si. Actually, the positive part amplitude of the peak  $E_3$  is larger the positive part of the main peak  $E_4$  (that highlighted by the dashed region in the lower part of Figure 1). This is in contrast with the magnitude of positive part of the peak, in the case Si and pure Fe on Si (that highlighted by the dashed region at the top of Figure 1). And, moreover, peak  $E_3$  at a thickness of 4 - 10 ML - is shifted in energy at a thickness of 0 - 1 ML and its ratio to main peak (in amplitude) remains unchanged regardless of an increase in the thickness of the Fe film.

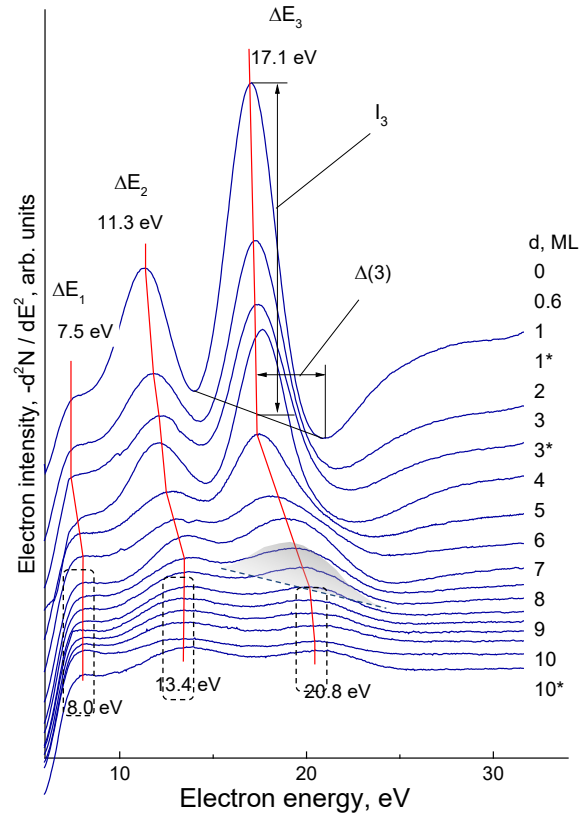


Figure 2 - EELS spectra of Fe films on Si (001) of various thicknesses. The solid lines serve as a guide for the eyes monitoring the position of the peaks in EELS ( $\Delta E$ ).  $\Delta E_1$  is the position of the peak of interband loss, while  $\Delta E_2$  and  $\Delta E_3$  are the positions of the peak of excitation losses of surface and bulk plasmons. By an asterisk is noted a coating after annealing.

**EELS.** Figure 2 shows the dependence of EELS-spectra on the Fe film thickness. The figure shows an increase in the energy  $\Delta E_1$  (to 8.0 eV) after 3 ML. It corresponds to the transitions into the bulk Fe – Si phases considering the PES data for bulk Fe – Si phases (see [14, 15]). This transition coincides with the data of Figure 1. Nevertheless, the thickness for changes in the loss energies surface ( $\Delta E_2$ ) and bulk ( $\Delta E_3$ ) plasmon peaks in Figure 2 does not correspond to the aforementioned phase transition. In the range of 4–10 ML, the values  $\Delta E_2$  and  $\Delta E_3$  show the formation of another bulk phase, namely  $\text{FeSi}_2$ . This AES-EELS data mismatch is explained by the overlay of plasmon losses of film and segregated Si in EELS due to wider form of peaks. Peaks from segregated Si are superimposed on peaks from bulk phases,  $\text{Fe}_3\text{Si}$  and Fe, suppress them and lower the observed values of  $\Delta E_2$  and  $\Delta E_3$ . As for the amplitude of the peaks of  $\Delta E_2$  and  $\Delta E_3$ , it rapidly decreased with increasing thickness to 3 ML (see Figure 2). This is due to the bigger peak amplitude in Si (001) and in coherent two-dimensional Fe phases regarding the amplitude of the peaks of the bulk  $\text{Fe}_3\text{Si}$  and Fe. In addition, small peaks can be formed due to amorphous state of film (like in the case amorphous silicon on single-crystal silicon [24]). Concurrently, the stabilization of small amplitude of these peaks in the range of 4–10 ML is associated not only with the formation of an amorphous structure, but also with the formation of a thin layer of segregated Si on the surface.

We note that the transition from a coherent state of film to an amorphous one (at 2–4 ML) must be gone inevitably through the stage of formation of a nanophased and nanostructured state of the film and the upper layer of the substrate, respectively. Therefore, the decrease in the amplitude of the peaks  $\Delta E_2$  and  $\Delta E_3$  in the range of 2–4 ML can be explained by this process.

The nanophase nature of the film in the range of 2–4 ML is confirmed by the fact that the peak width of the bulk plasmon loss  $\Delta E_3$  (which was highlighted by dimming up to the peak base – see dashed line) reaches a maximum at a thickness near 3 ML. Simultaneously, lesser value in the peak half-width at a thickness of 1–2 ML is more likely connected with nanostructured interface Si layer. Obviously, the film is compacted during all these phase transitions. Moreover, due to the

compaction during transition from Fe<sub>2</sub>Si to Fe<sub>3</sub>Si, excess silicon is formed, which is released (segregates) on the film surface and the grain boundaries of the film.

Based on the above analysis, the following model for the growth of Fe on Si (001) can be formulated. Initially, iron chemically adsorbs in the form of coherent atomic surface structures at a thickness of 0-1 ML. Then, a two-dimensional coating of Fe grows in a pseudo-layer way at 1-2 ML. With this, an extended layer incommensurate with substrate forms in the form of wetting layer. Its formation cause stacking faults in the near-interface silicon layer and transition of this layer into a high-pressure phase. In addition, an agglomeration occurs, and the wetting coating acquires a nanophase structure about 3 ML. Annealing causes a mixing and the formation of a wetting coating of the composition Fe<sub>2</sub>Si. In this case, the high-pressure phase Si transfers to another type layer of nanostructured Si. However, the following mixing of Fe and Fe<sub>2</sub>Si occurs at 4 ML. As a result, a stable Fe<sub>3</sub>Si phase forms and an excess of Si releases on its surface. After that, Fe islands with Si dissolved in it nucleate and grow. As a result, a transition from Fe<sub>3</sub>Si to Fe occurs at 4-10 ML. As the thickness of Fe increases, the solubility of Si in Fe decreases due to increase of film density and Si segregates on the surface of Fe. Under this, Si segregation provides a thermodynamically more stable bulk state of the metal film on silicon [25] and, thus, Fe layer stabilizes.

## Summary

Changes in the composition of Fe coating on Si (001), their relative density, uniformity and electronic structure have been studied during growth at lowered and room temperatures of Fe vapor and Si substrate, respectively, and after annealing coatings with thickness  $\leq 3$  ML. The formation of Fe two-dimensional ordered phase and Fe<sub>2</sub>Si wetting layer has been found at the thickness 1 ML and 3 ML, respectively. In addition, a structural-phase modification of the Si substrate interface layer was shown under Fe<sub>2</sub>Si wetting layer. Transitions from the Fe<sub>2</sub>Si wetting layer of to the Fe<sub>3</sub>Si bulk phase, then to a Si-in-Fe solution and then to a Fe nanolayer with segregated Si have been detected. Stability of this Fe nanolayer up to 250 °C has been shown.

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