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Initial stages of the growth of Fe on Si(111)7×7

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We present a multitechnique (scanning tunneling microscopy, photoelectron spectroscopy, and ion scattering spectroscopy) approach to study the formation of the Fe/Si(111) interface at room temperature. The first-deposited Fe atoms react with the surface, displacing Si atoms from their positions. The result is an amorphous layer with composition and density of states close to those of FeSi. On top of this reacted layer, crystallites of Fe with interdiffused Si grow. Upon further Fe deposition, the crystallite composition evolves to pure Fe.

Metal/silicon interfaces are a topic attracting sustained attention for many years. An atomistic view of the processes occurring during the deposition of metal atoms on semiconducting substrates is an important step towards basic understanding of the properties of these technologically vital systems. The complexity of processes taking place during formation of these, usually reactive, interfaces has defied our complete understanding, in spite of the tremendous effort carried out to study them with a host of experimental techniques.[1] For silicide-forming systems, such as Fe/Si, a detailed characterization of the interface is crucial because the phases spontaneously formed there may act as a precursor for epitaxy. In favorable cases they may provide a buffer layer for epitaxial silicide films. This is the reason behind the success obtained in growing highly perfect $CoSi_2$ or $NiSi_2$ films even at room temperature.[2] On the other hand, the initial formation of an unfavorable phase, e.g., Pd_2Si at the Pd/Si interface, can hinder the growth of the desired phase (PdSi, in that case).[3] Recently, the different iron silicides have received great attention due to their potential applications (infrared detectors, optoelectronic devices).[4–10] Due to this interest, the formation of the Fe/Si(111) interface at room temperature has also been investigated. The nature of the interface has been the subject of an intense controversy. It has been alternatively reported that it is a nonreactive interface resulting in layer-by-layer growth of pure Fe,[4] or that thin layers of β-$FeSi_2$,[5] FeSi,[6,7] or $FeSi_2$ (Ref. 8) are spontaneously formed at the surface. In all cases, growth of pure Fe has been observed for a large enough deposited thickness. In these works mainly a single experimental technique was used to study the interface. We describe in the following a multitechnique characterization of the interface formation and growth of Fe on Si(111), in which scanning tunneling microscopy (STM) has been combined with low-energy electron diffraction (LEED), ultraviolet photoelectron spectroscopy (UPS), and ion scattering spectroscopy (ISS). The aim of this work is to use such a combination of techniques in order to clarify the actual properties of the interface. The experiments were carried out in two separate vacuum chambers. The first one includes STM, Auger electron spectroscopy (AES), and LEED facilities, while the second one allows us to perform x-ray photoelectron spectroscopy (XPS), UPS, AES, and ISS measurements. The samples were phosphorus-doped (10^{19} cm^{-3}) Si(111) wafers. They were cleaned either by heating inside the UHV chamber followed by deposition of Si at 600 °C or by Ar^+ sputtering and annealing. The resulting surface was characterized by a 7×7 LEED pattern of outstanding quality; STM images showed the 7×7 reconstruction extending over terraces ~1000 Å wide separated by straight steps 3.14 Å high. UPS spectra displayed well-defined features corresponding to the surface states. Fe was deposited on Si(111)7×7 from a resistively heated high-purity filament at a rate of ~2 Å/min. The sample was held at room temperature (RT) during evaporation. The Fe coverage on the sample, given in Å, was determined from an absolute calibration of the Fe 2*p* and Si 2*p* XPS intensity.[9,10] In order to transform thickness in Å into equivalent monolayers of Fe(111), one must have in mind that Fe(111) layers with a density of 7.07×10^{14} atoms/cm^2 are separated by 0.83 Å. The accuracy of the coverage is ±10%, except for the ultralow coverage regime (≤ 0.2 Å), where the Fe coverage was estimated by counting atoms with the STM and measuring carefully the evaporation time. Since these methods are subject to significant errors, the accuracy in this range is only ±50%.

We demonstrate first that Fe/Si interface formed upon RT deposition is reactive. Figure 1(a) shows an STM image after deposition of 0.04 Å of Fe. Most of the surface displays an unperturbed 7×7 reconstruction. Additionally, bumps appear on the surface [indicated by an arrow in Fig. 1(a)] with an apparent height corresponding to 1.3 Å above the Si adatoms and arranged in randomly distributed clusters of ~7 protrusions. Their density increases with Fe coverage. The bumps could be attributed to Fe atoms on the surface, but we will assign them in the following to Si atoms of the first bilayer, displaced by Fe during the intermixing reaction, and ejected to the surface. ISS data supporting this assignment will be shown below. The ejected Si atoms are mobile enough to coalesce in small clusters almost identical in size and shape to those resulting from room-temperature evaporation of Si on Si(111).[11] A similar sequence of events (Si displacement from the subsurface, ejection, and regrowth on the surface) has been observed during the initial oxidation of Si(100).[12] Thus, this sequence might be common to the formation of reactive interfaces. In fact, during both thermal oxidation of silicon[13] and silicide formation[14] the formation of Si interstitials has been reported, injected in the *bulk* of the Si crystals by the chemical reaction. In complete analogy, reactions taking place in the subsurface region would produce Si adatoms *at* the external surface, such as those viewed here by the STM.

Further Fe deposition up to ~0.5 Å of Fe causes the disappearance of the 7×7 LEED pattern, with only the 1×1 spots visible over a high background. A characteristic STM image of this surface is reproduced in Fig. 1(b). The clusters of protrusions now cover the substrate surface, forming an amorphous, continuous overlayer. Evaporation of 4 Å of Fe [Fig. 1(c)] results in the appearance of three-dimensional (3D) crystallites, mostly of triangular or hexagonal shape, on top of this amorphous, reacted overlayer. The crystallites are ~30 Å high and ~80–90 Å wide. At this stage of deposition they cover ~10% of the surface. Finally, at ~8–10 Å, the crystallites coalesce and cover the surface (not shown). In conclusion, the STM results indicate that the Fe/Si interface is reactive at RT. Growth of 3D crystallites occurs on top of the reacted interface.

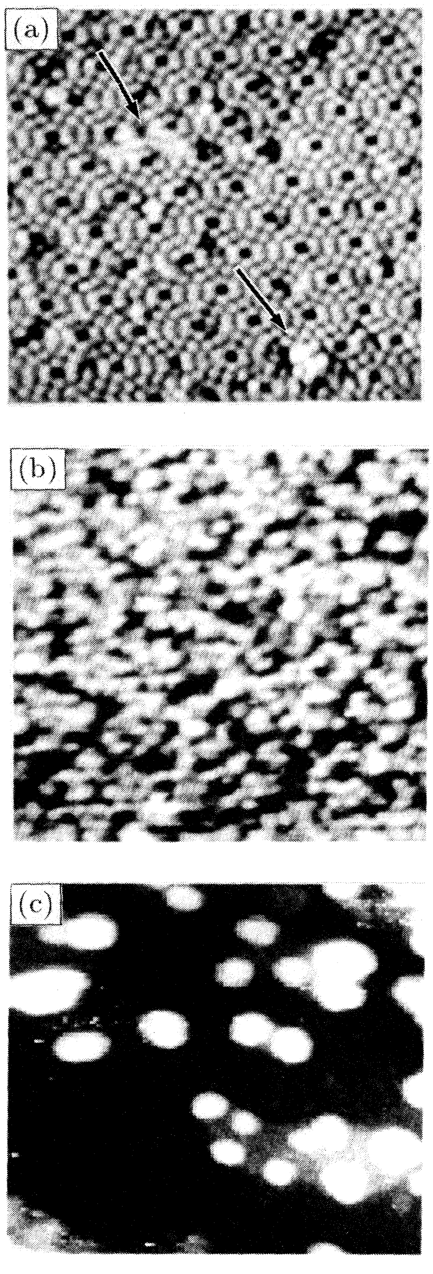

FIG. 1. STM topographs recorded after deposition of different amounts of Fe on Si(111) at room temperature: (a) 0.04 Å; (b) 0.5 Å, (c) 4 Å. Images (a) and (b) are 200×200 Å^2 and were recorded with $V_t=1.95$ V and $I_t=0.5$ nA. Image (c) is 1026×1175 Å^2, and was recorded with $V_t=2.10$ V and $I_t=0.8$ nA.

In order to determine the chemical identity of the atoms at the surface as the interface is formed, low-energy ISS was performed during the Fe deposition. In ISS a surface containing atoms of mass M is bombarded with a beam of ions of mass M_0 and energy E_0 and the energy distribution of the ions scattered into a scattering angle θ is analyzed. For a given scattering geometry the peak positions (E/E_0) are characteristic of the surface-atom mass, and thus can be used to identify the elements present at the surface. The backscattered ion energy spectra displayed in Fig. 2 have been measured using a beam of He$^+$ of 550 eV at scattering angle of 130°. The spectrum of clean Si(111)7×7 shows a peak at the energy ratio ($E/E_0=0.62$), corresponding to the mass of atomic Si. Furthermore, in these conditions (primary ion energy and scattering angle) the experiment is 95% sensitive to the 7×7 reconstructed layer of Si adatoms with an areal density of 1.9×10^{14} atoms/cm^2.[15]

Evaporation of 2 Å of Fe at room temperature (slightly above the completion of the flat, reacted overlayer according to STM) produces a spectrum with an additional peak at $E/E_0=0.79$, which corresponds to the mass of atomic Fe. Notice, however, that the intensity of the Si peak has *not* changed.

Ion scattering signals are directly proportional to the effective surface density times the ion survival probability.[15] In order to quantify the ISS spectra in terms of surface concentrations, the Fe versus Si cross section for He$^+$ neutralization must be determined under our experimental conditions. This was done in the following way. A 12.2-Å-thick polycrystalline film of Fe was deposited at RT on Si(111) and its ISS intensity measured. As shown in Fig. 2, no significant signal from Si is detected under these conditions. Further Fe deposition did not increase the ISS signal. Thus we conclude that the intensity of Fe for a coverage of 12.2 Å corresponds to a completely covered sample. This ISS signal can be assumed to reflect an atomic density of $n_s=1.2\times10^{15}$ atoms/cm^2, i.e., the average of the low-index surfaces of bcc Fe, since the film is polycrystalline. Shadowing effects and partial preferential orientation of the crystallites may modify this number by a factor of the order of 2. As noted above, the scattered signal from clean Si comes from the adatoms with a density of 1.9×10^{14} atoms/cm^2. Using this calibration, the areas under the Si and Fe peaks derived from the data can be converted into relative surface densities.

They have been plotted in the inset of Fig. 2 as a function of the deposited Fe coverage (derived from XPS data). The most relevant information obtained from this plot is the negligible decrease in the Si signal during the early stages of Fe evaporation, in spite of the high sensitivity of ISS. Therefore the bumps shown in Fig. 1 on *top* of Si(111)7×7 are probably Si atoms. Up to 4.1 Å of Fe, when 3D crystallites begin to be seen in STM images, the density of Si atoms visible to the He^+ beam does not change, while the Fe signal increases to 40% of its saturation value. This indicates that Si adatoms are probably at the outer surface of the first 3D crystallites. The fact that with 2 Å of Fe deposited only 10% of the deposited Fe atoms (1.8×10^{14} atoms/cm^2) are detected at the outer surface indicates that the remaining Fe atoms must have been buried in the Si surface below the adatom level. This provides direct experimental evidence of a reactive interface formation. Deposition of 4 and 6 Å of Fe increases the number of Fe atoms detected by ISS at the external surface and decreases the Si signal as the crystallites cover the surface. For ~8 Å, the film surface is almost pure Fe. We conclude from these data that during the early stages of deposition at RT Fe does not grow uniformly on the Si(111) surface, but rather diffuses below the Si surface up to 2 Å and then forms 3D crystallites. The surface composition of the crystallites becomes richer in Fe as the deposition proceeds.

The reaction at the interface during Fe evaporation at RT has been confirmed by UPS, which provides us with the identification of the reacted interface composition. Selected UPS spectra taken during Fe deposition on Si(111) are reproduced in Fig. 3. Clean Si(111)7×7 is characterized by surface states at 0.2 eV (adatoms), 0.8 eV (rest atoms), and 1.8 eV (backbonds) binding energy.[16] The adatom dangling-bond surface state is partially occupied giving rise to the metallic character of the surface.

Deposition of 0.6 Å of Fe produces a spectrum (Fig. 3) almost identical to the one of FeSi,[10] except for a noticeably smaller density of states at E_F. This similarity suggests that the amorphous, reacted layer formed spontaneously at RT (and visualized by STM) has a composition and density of states close to FeSi. For coverages of 2.8 Å, where crystallites appears on top of the amorphous layer, the UPS spectrum is again metallic, as indicated by emission at E_F. Simultaneously, peaks at 0.5, 1.3, and 2.6 eV appear in the spectrum. Peak positions and separations are very close to those of pure Fe (see Fig. 3 for 60 Å) although the line shape is different. Si is also detected at the surface by ISS. On this basis, the UPS spectrum for 2.8 Å can be assigned to crystallites of Fe (with Si interdiffused) grown on top of the reacted FeSi-like layer. The presence of Si in the crystallites and on their surface

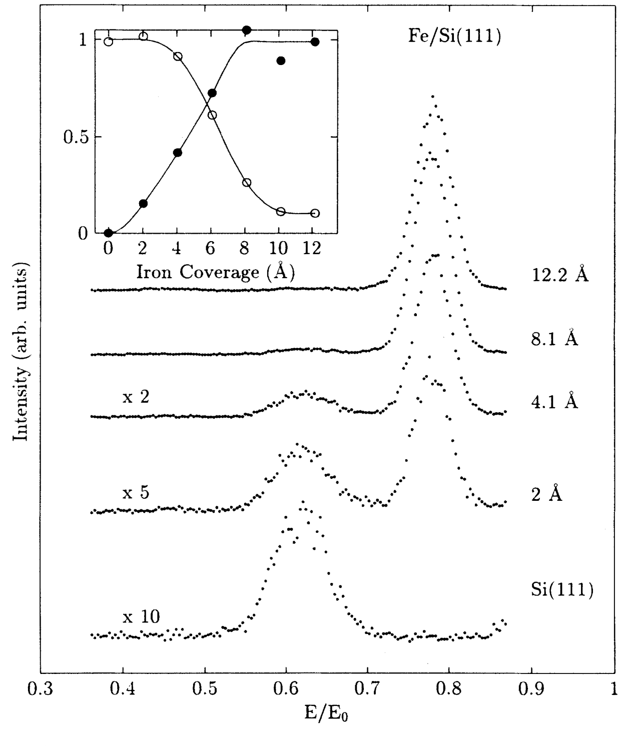

FIG. 2. Low-energy ion scattering spectra recorded during Fe deposition on Si(111) at room temperature. The beam of He^+ (550 eV kinetic energy) impinges on the surface at $\theta\simeq50°$ from the surface normal with a current density of 3×10^{-6} A/cm^2 and the scattered ions are collected normal to the surface, i.e., the scattering angle is 130°. Notice the change in the vertical scale due to the larger cross section of Fe as compared to Si. The inset shows the relative area of Si (open circles) and Fe (black circles) ion scattering peaks. The initial Si area represents 1.9×10^{14} atoms/cm^2, while the final Fe area corresponds to 1.2×10^{15} atoms/cm^2.

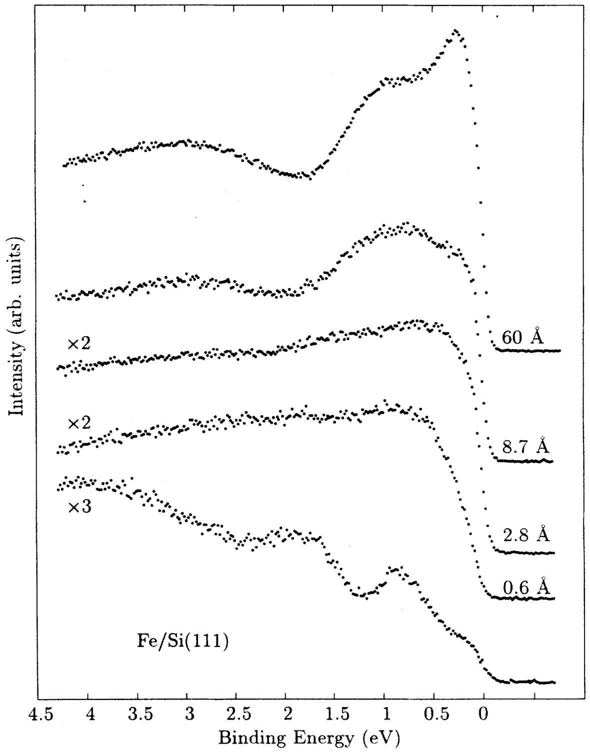

FIG. 3. Angle-integrated UPS spectra. From bottom to top: clean Si(111)7×7 and after deposition of 0.6, 2.8, 8.7, and > 60 Å of Fe at room temperature. The photon energy is 21.2 eV.

is consistent with the high (9%) solubility of Si in bulk Fe at RT. Furthermore, the spectrum of Fig. 3 (2.8 Å) is identical to the one observed during RT evaporation of the same amount of Fe on Si(100).[10] In that case, an average Fe_3Si composition for the reacted layer plus crystallites was determined quantitatively by AES.[17] Fe crystallites with Si interdiffused are detected by UPS only in a narrow coverage regime (from ~2.4 to ~4 Å). Figure 3 also reproduces UPS spectra for thicker Fe films. The composition of the crystallites evolves from Fe (9% Si) to metallic Fe according to the measured UPS and ISS spectra for coverages above 8 Å. At coverages of Fe larger than 60 Å (deposited at higher rates, ~10 Å/min), a characteristic spectrum (see Fig. 3) with peaks at 0.2, 1, and 3 eV is detected. This latter is indistinguishable from the one of bcc Fe(111) recorded at normal emission,[18] which is indicative of a preferential orientation of the crystallites. Nevertheless, in these conditions no LEED pattern was observed indicating that the crystallites must be smaller than ~100 Å. Thus, the growth of Fe on Si(111) at high evaporation rates leads eventually to the formation of small bcc crystallites of Fe oriented in the (111) direction. This finding illustrates the importance of kinetic effects in the morphology of the film grown by vapor deposition. In fact, epitaxial growth of 3D crystallites of Fe(111) on Si(111) has been observed with reflection high-energy electron diffraction.[19] For much thicker (~0.3 μm) films the preferential alignment of the columnar grains has been confirmed by x-ray diffraction.[20]

We have presented direct experimental evidence proving that the formation of the Fe/Si interface at RT occurs via intermixing of Fe and Si, with Si being ejected to the outer surface. The amorphous, reacted interface has a composition and a density of states close to FeSi, in agreement with reports of FeSi formation,[6,7] but opposite to recent claims of direct β-$FeSi_2$,[5] or $FeSi_2$ (Ref. 8) during evaporation of Fe on Si(111) at RT. On top of this reacted layer, growth of 3D islands of metallic Fe with Si interdiffused occurs. This is consistent with the high solubility of Si in Fe (about 9%) at room temperature. Somewhat surprisingly, the growth of small crystallites of epitaxial Fe(111) seems to take place at very large coverages and high deposition rates.

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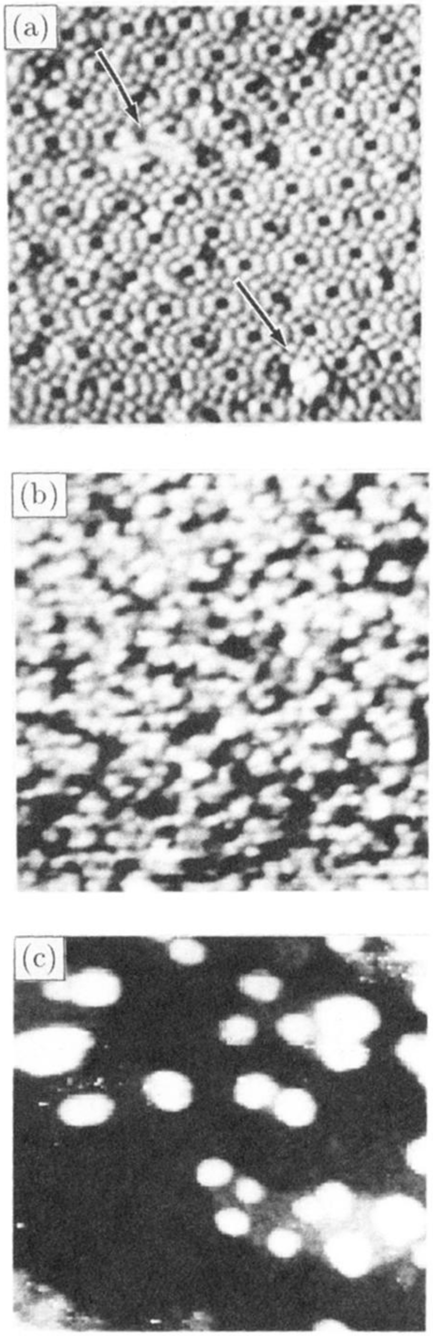

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