

## Formation of a ferromagnetic silicide at the Fe/Si(100) interface

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The interplay between magnetism and chemistry at the Fe/Si(100) interface has been examined by spin- and angle-resolved photoemission. A ferromagnetically ordered metallic silicide of  $\sim 20$  Å thickness is formed by deposition of Fe on Si at room temperature. This interface layer is ferromagnetic in-plane with a reduced spin polarization in comparison to bulk Fe. Its electronic structure indicates an Fe-rich composition close to  $\text{Fe}_3\text{Si}$ . The Fe/Si and Si/Fe interface are inequivalent with respect to silicide formation and to the resulting magnetic properties. [S0163-1829(97)04142-8]

Metal-semiconductor interfaces are a topic of intensive research due to their potential technological applications in microelectronics.<sup>1</sup> Particularly the Fe/Si interface is of fundamental interest in the development of magnetic, silicon-based heterostructures. Recent interest has been focused on the investigation of the electronic structure of semiconducting Fe silicide films<sup>2-4</sup> due to their possible exploitation in the development of silicon-integrated optoelectronic devices. Lately another dimension has been added to this field of research due to the observation of antiferromagnetic interlayer coupling in Fe/Si multilayers.<sup>5,6</sup> The mechanism of interlayer coupling across a semiconducting spacer layer could be fundamentally different from that observed for ferromagnetic films coupled across nonmagnetic metallic spacer layers. However, it is not yet understood how the formation of iron silicides in the spacer affects the coupling. Recent research results question whether the spacer is semiconducting but rather attribute the antiferromagnetic coupling observed in Fe/Si multilayers to the formation of metallic silicides in the interlayer.<sup>7,8</sup>

In order to better understand the mechanism of the coupling in these multilayers, it is of central importance to elucidate the chemical and magnetic properties of the spacer layer. A number of studies have dealt with the Fe/Si(100) interface at room temperature<sup>9-15</sup> and several of these studies included photoemission measurements.<sup>13-15</sup> Different estimates of the thickness of the reacted layer at the interface have been made ranging from 0 up to  $\sim 30$  Å.<sup>9,11-13,15</sup> Also the chemical composition of the interface layer is a still disputed question. Various silicides like  $\text{FeSi}$ ,<sup>11</sup>  $\text{FeSi}_2$ ,<sup>10,12</sup> and  $\text{Fe}_3\text{Si}$  (Refs. 14 and 15) have been proposed to form at the Fe/Si(100) interface. Up to now very little is known about the correlation between interface chemistry and magnetism. To investigate this correlation we have studied the electronic structure of Fe overlayers on Si(100) by spin- and angle-resolved photoemission.

In this paper we present spin-integrated and spin-resolved photoemission spectra of Fe overlayers deposited both at room temperature (RT) and at 100 K [low temperature (LT)] on Si(100). Further we have studied trilayers consisting of Si/Fe/Si(100). We show that by RT deposition of Fe on Si a

metallic and magnetic iron silicide is formed at the interface. This silicide is  $\sim 20$  Å thick and is ferromagnetically ordered in plane. By depositing the Fe at LT the intermixing between the two interface components is strongly reduced. Moreover we show that the Fe/Si and Si/Fe are inequivalent with respect to the magnetic properties of the reacted interface layers.

The experiment has been performed in an UHV chamber at the TGM 1 and TGM 5 beamline at the storage ring BESSY. The experimental apparatus<sup>16</sup> consists of a 90° spherical electron energy analyzer coupled to a 100 kV Mott detector for spin analysis. The experimental setup is sensitive to the in-plane component of the magnetization. Si(100) wafers were cleaned by cycles of  $\text{Ar}^+$  sputtering and annealing up to 900° C. After this preparation the Si(100) wafers showed the expected sharp ( $2 \times 1$ ) two-domain low-energy electron-diffraction (LEED) pattern and no contamination could be observed in the photoemission spectra. Fe was deposited by electron beam evaporation. Here, one Fe monolayer (ML) is conventionally defined as the atomic density of a single bcc Fe(100) monolayer, which corresponds to  $1.21 \times 10^{15}$  atoms/cm<sup>2</sup>. The evaporation rate was calibrated with a quartz crystal microbalance. Spin- and angle-resolved photoemission spectra were measured at various photon energies between 20 and 50 eV and for Fe thicknesses up to 25 ML. The Fe films have been magnetized remanently in-plane along the spin-sensitive direction of the spin detector.

The development of the photoemission spectra with Fe deposition at room temperature on Si can be described as a sequence of three different stages. Figure 1 shows spin-integrated spectra in normal emission for different amounts of Fe on Si(100). The spectrum of clean Si shows several pronounced peaks. The peak at 1 eV binding energy corresponds to dangling bond surface states.<sup>17</sup> The peaks between 2 and 5 eV are due to direct transitions from bulk states.<sup>18</sup> The LEED pattern, which is observed for clean Si, becomes weaker already with very small amounts of deposited Fe and disappears with 0.5 ML. This suggests that a chemical reaction between the Fe and Si atoms results in a disordered Fe/Si overlayer. Furthermore the LEED pattern does not reappear for large Fe coverages (up to 25 ML). Due to the

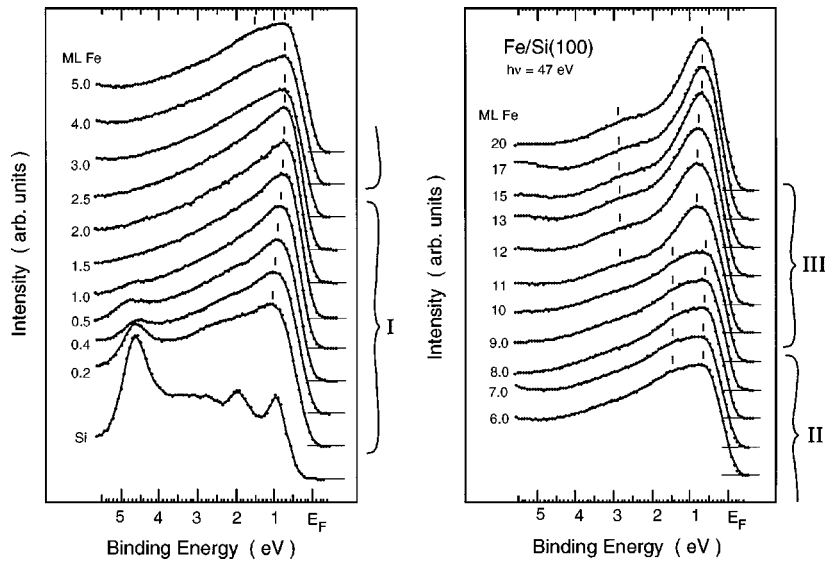


FIG. 1. Angle-resolved photoemission spectra taken at 47 eV photon energy in normal emission for different thicknesses of deposited Fe.

enhanced photoemission cross section of Fe with respect to Si the spectral features are rapidly modified with Fe deposition. Three thickness regions (labeled I–III) are distinguished in the photoemission spectra of Fig. 1 as a function of deposited Fe. Up to 3 ML the spectra exhibit a single Fe-induced structure at about 1 eV binding energy, which shows a weak but continuous shift towards the Fermi level with increasing coverage. The changes of the spectra in region I suggest a nonstoichiometric intermixing of Fe and Si at the interface. Above 1 ML of deposited Fe a photoemission signal is detected at the Fermi level. This implies a nonvanishing density of states at the Fermi energy and indicates that the overlayer is metallic from that point on.

Above 4 ML thickness the peak at 1 eV broadens and a new structure develops at about 1.5 eV binding energy. In the second thickness region between 4 and 10 ML the spectral shape remains stable in dependence of the Fe deposition. This indicates the formation of a silicide phase with a uniform composition over this thickness range. The silicide formation abruptly ends when the nominal Fe thickness reaches 10 ML. The spectral shape changes suddenly, as a strong peak develops close to the Fermi level and a weaker structure at about 3 eV binding energy. The shape of the spin-integrated spectra above 10 ML, in thickness region III, resembles closely that of corresponding bulk bcc Fe(100) spectra.<sup>19</sup>

The measurement of the photoelectron spin polarization provides insight on the magnetic behavior of the system at different stages of the interface formation. We find a correspondence between the development of the electronic structure, described above, and the magnetic ordering as probed by the spin analysis of the photoelectrons. In the first thickness region no polarization is detected by the spin-resolved measurements, indicating a lack of long-range in-plane ferromagnetic order. The transition to the second phase is accompanied by the onset of polarization. The measurement of the spin polarization shows that the onset of the in-plane magnetization occurs at 4 ML and it is followed by a rapid increase between 4 and 5 ML. This is in line with surface magneto-optical Kerr effect (SMOKE) measurements<sup>20</sup> where ferromagnetic order is observed above 5 ML of RT deposited Fe. However, the photoemission results show that

the magnetic signal between 5 and 10 ML does not derive from a film of elemental Fe, but rather from an intermixed interface region.

The chemical composition of the interface phase formed between 5 and 10 ML can be discussed by comparison with the spectra of bulk silicides.<sup>21</sup> The spectra obtained in region II exhibit a strong resemblance with those of  $\text{Fe}_3\text{Si}$ . Photoemission spectra of bulk crystalline<sup>21</sup> as well as those of thick ( $\approx 20$  nm) amorphous and polycrystalline  $\text{Fe}_3\text{Si}$  films<sup>22</sup> display a strong peak close to the Fermi level at about 0.6 eV binding energy and another emission at about 1.4 eV. The spectra show similar features for crystalline and amorphous  $\text{Fe}_3\text{Si}$ , with more pronounced peaks in the crystalline case. The broad photoemission peaks and the absence of a LEED pattern point towards the formation in region II of a phase with an Fe-rich composition close to  $\text{Fe}_3\text{Si}$  and a low degree of crystalline order. A stoichiometry close to  $\text{Fe}_3\text{Si}$  has also been previously assigned by Gallego *et al.*<sup>14</sup> to the reacted phase formed at the Fe/Si(100). Assuming the lattice constant of bulk  $\text{Fe}_3\text{Si}$  the average thickness of this silicide layer can be estimated to be about 20 Å.

Figure 2 shows characteristic spectra of the second thickness region (bottom spectra), measured with spin analysis. The spin-dependent line shape of the spectra reflects the ferromagnetic ordering of the system with an in-plane magnetization component. The spectra differ considerably from those of 25 ML Fe on Si (top spectra). Due to the lack of long-range structural order in the interface silicide the peaks can be expected to correspond to maxima in the density of states. We compare the results to the calculated spin-polarized density of states of  $\text{Fe}_3\text{Si}$ ,<sup>23</sup> which is the only ferromagnetic bulk iron silicide. The majority-spin spectrum displays two broad structures at 0.5–1.5 eV binding energy and at 2–4 eV binding energy. The latter one agrees indeed well with a maximum in the majority-spin density of states of  $\text{Fe}_3\text{Si}$ .<sup>23</sup> Within 2 eV from the Fermi level the theoretical density of states consists of overlapping majority and minority structures, with predominant spin-up states at the Fermi energy, in qualitative agreement with the experimental results. In comparison to the thick Fe layers the integrated minority-spin intensity is increased in the thinner layer

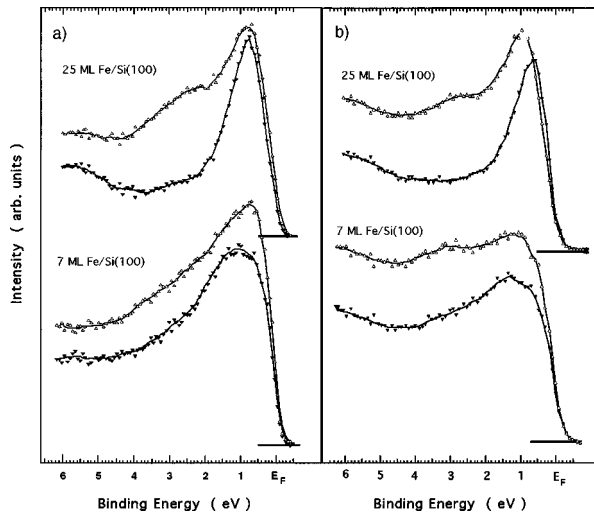


FIG. 2. Spin-resolved photoemission spectra at (a) 47 eV and (b) 21 eV photon energy in normal emission. Black up triangles and white down triangles denote the majority- and minority-spin spectrum, respectively.

which can be related to the reduced Fe magnetic moment of the silicide. In region III the total polarization of the spectra increases. Figure 2 shows that the spin-resolved spectra of 25 ML deposited Fe are strongly polarized. They show a broad majority-spin peak around 2.7 eV binding energy and a sharper peak close to the Fermi level. Further a minority-spin emission is observed at about 0.6 eV binding energy. The high binding-energy majority peak and the minority peak close to the Fermi level can be identified as a pair of exchange split states, resulting in an exchange splitting equal to 2.1 eV which corresponds to the bulk bcc Fe value. The spin-resolved spectra resemble markedly those characteristic of bcc Fe(100),<sup>19</sup> suggesting a preferential orientation of the Fe crystallites.

The reactivity of the Fe/Si interface is modified at reduced temperature as a result of kinetics. In fact, lower temperature deposition can be exploited to produce compositionally

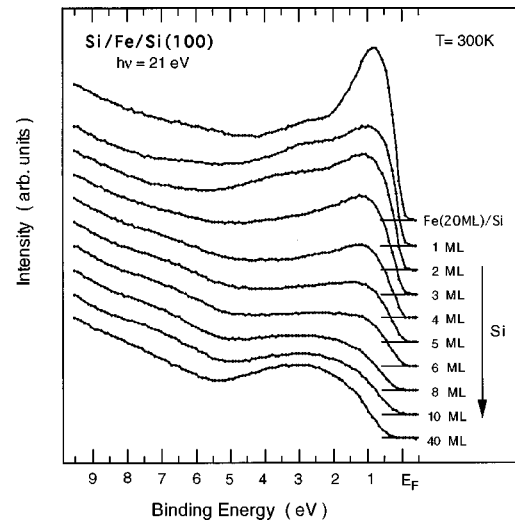


FIG. 4. Angle-resolved photoemission spectra taken at 47 eV photon energy in normal emission for different thicknesses of Si depositions on thick Fe on Si(100).

sharper interfaces between the two elements. Figure 3 shows the comparison between Fe deposited on Si at room temperature and at 100 K, measured with 21 eV photon energy. The RT spectra exhibit a similar thickness dependence as in Fig. 1. The peaks at about 1.2 and at 3.2 eV binding energy for Fe thicknesses between 4 and 10 ML correspond to the reacted ferromagnetic phase discussed above. Above 10 ML the spectra develop abruptly an intense peak close to the Fermi level and a second peak at about 2.8 eV binding energy, as for bulk bcc Fe. The right panel of Fig. 3 shows the corresponding spectra for low-temperature Fe deposition. In contrast to the room-temperature results, the spectral shape changes continuously with increasing amount of Fe, indicating that a compositionally defined Fe-Si phase is not formed at LT. The spectra change gradually with Fe thickness as a peak develops close to the Fermi level. Spin-polarization measurements on the LT deposited films show no in-plane

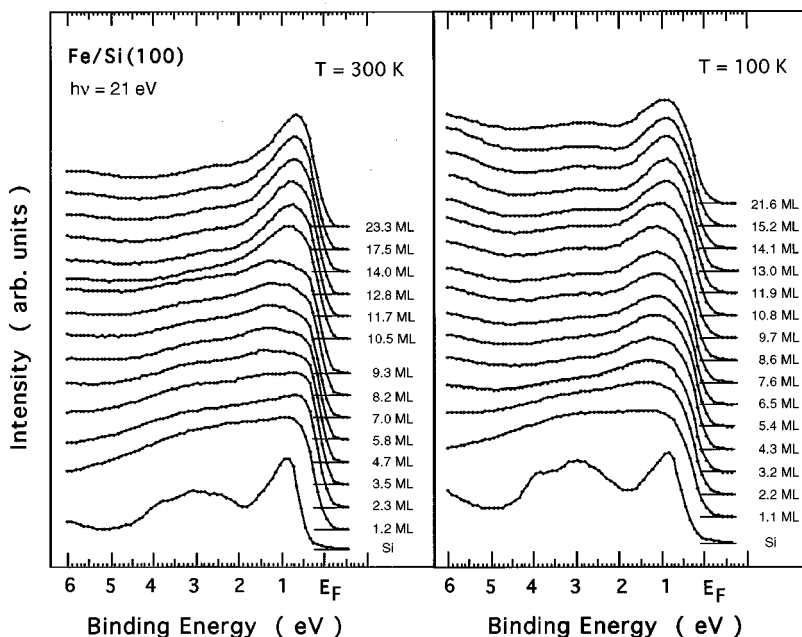


FIG. 3. Angle-resolved photoemission spectra at 21 eV photon energy in normal emission for different thicknesses of Fe overlayers evaporated at room temperature (left panel) and at 100 K (right panel) on Si(100).

magnetization at 3 ML in agreement with results obtained by Nazir *et al.*<sup>20</sup> With 7 ML deposited Fe the Fe/Si interface is found to be ferromagnetic in-plane. The spin-resolved spectra and the integrated polarization of 7 and 20 ML Fe on Si(100) are rather similar for the LT deposited layers. The intermixing between the two elements appears to be, as expected, reduced at LT and the formation of a well-defined silicide phase does not take place. It is interesting to note that the spectra of 10–20 ML Fe deposited at low temperature are however different from the corresponding ones for RT deposition. Small changes in the spectra occur for LT deposition also for Fe thicknesses beyond 20 ML, whereas in RT-deposited Fe there is no indication for significant Si interdiffusion above 10 ML. We attribute these spectroscopic observations to structural rather than to chemical differences of the thicker overlayers, possibly due to a different degree of crystalline order.

We have also examined the electronic structure of the interface formed by deposition of Si on Fe, to obtain complementary information relevant to Fe-Si multilayer systems. In order to study the Si/Fe interface we have prepared trilayers consisting of Si films of variable thickness on a thick Fe layer on Si(100). Figure 4 shows spin-integrated photoemission spectra for different thicknesses of Si overlayers evaporated at room temperature. The top spectrum corresponds to a 20 ML thick polycrystalline Fe film on Si. The spectra for increasing Si deposition on Fe are shown from top to bottom. With up to 6 ML of deposited Si, the spectra change continuously with increasing Si thickness. The peak at 1 eV diminishes and shifts to higher binding energy and additional weak structures appear at binding energies below 3 eV. These states cannot be attributed to the Fe underneath. They indicate instead new chemical bonding states. The change from a metallic to an insulating character of the surface is suggested by the disappearance of the photoemission signal at the Fermi energy with about 4 ML of deposited Si. Above 8 ML the spectra exhibit only minor changes with further Si

deposition. They resemble strongly the spectrum of bulk amorphous Si, with two broad emission peaks centered around 3 and 7 eV in correspondence to maxima in the Si density of states.<sup>24</sup> A comparison of these data to photoemission spectra of amorphous  $\text{Fe}_x\text{Si}_{1-x}$  films of varying composition<sup>22</sup> shows strong similarities in the spectral shape. Amorphous Fe-Si films display a broad emission peak close to the Fermi level which shifts towards higher binding energy with increasing Si content. An emission peak between 3 and 4 eV binding energy is typical for the Fe-rich silicides. The comparison indicates that a number of compositionally different Fe-Si phases are sequentially formed by deposition of Si on Fe. With increasing Si deposition the composition of the interface silicide becomes richer in Si. The spin polarization over the valence-band region decreases with Si deposition. The polarization of the spectra is already reduced by half with 2 ML Si, by one third with 4 ML. Above 10 ML no polarization is detected within a 2% accuracy. Below 10 ML Si the spectral shape of the polarization curve remains similar to that of the thick Fe film. We thus attribute the measured polarization from the Si-covered system to the attenuated emission from the Fe underlayer, rather than to the formation of ferromagnetically ordered Fe-Si phases. The results point out that the reaction at Fe/Si and Si/Fe interfaces produce intermixed phases which differ with respect to both chemical and magnetic properties.

In conclusion, the interplay between magnetic properties and interface chemistry of the Fe/Si system has been examined by spin- and angle-resolved photoemission. RT deposition of Fe on Si(100) forms a ferromagnetically ordered silicide layer. The silicide formation is strongly reduced at 100 K. Si deposition on Fe results in a number of compositionally different intermixed phases, for which no indication of ferromagnetism could be detected. The magnetism of interface silicides has to be considered in the design of exchange-coupled Fe/Si heterostructures and of integrated metal-semiconductor devices.

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