Structure of sputtered Fe/Si multilayers

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Fe/Si multilayers with thin Si layers have given evidence of both structural coherence over many bilayer distances and magnetic coupling between the Fe layers. The presence of Fe silicides, inferred from several different properties, has been suggested as the origin of these effects. We have done transmission electron-diffraction measurements on Fe/Si samples exhibiting structural coherence and magnetic coupling in an attempt to directly observe these silicides. No evidence of known Fe silicides was found.

INTRODUCTION

By the end of the 1980's the structure of Fe-Si multilayers, Fe/Si, seemed to be well understood. Mossbauer results indicated that an amorphous alloy separated the crystalline Fe and amorphous Si layers. Moreover, Fe layers of less than 20 Å were not crystalline.[1] Polarized neutron results were consistent with an amorphous alloy interface having a 16 Å thickness. These same samples produced cross-sectional TEM images with well-defined and continuous layers.[2] Extended x-ray-absorption fine-structure data for the K shell of Fe indicated a crystalline environment for 30-Å Fe layers and an amorphous environment for 20-Å Fe layers.[3] Magnetization and standard x-ray diffraction (XRD) results for a fixed Si layer thickness and varying Fe layer thicknesses indicated isolated, noninteracting Fe layers. The thickness dependence of the saturation magnetization was consistent with 8–10 Å of each Fe layer being nonmagnetic.[4] Two early 1990's studies reinforced this understanding. Mossbauer, cross-sectional TEM and resistivity studies suggested a more complicated interface and increased its size to about 18 Å.[5] A new polarized neutron-scattering study separated nuclear and magnetic scattering to conclude that the interface contained magnetically dead Fe layers having a thickness of 12.4 Å.[6] The above interface thicknesses are totals: symmetric bilayers would have two interfaces of one-half the above thickness values.

All of the above studies involved relatively thick Si layers, typically 35 Å or greater. Recent studies of Fe-Si systems with thin Si layers have challenged the above understanding. In studying the spin polarization of secondary electron emission from Fe-Si trilayers Toscano *et al.* found evidence for an oscillating magnetic coupling between the Fe layers.[7] They suggest the magnetic coupling is mediated through amorphous, semiconducting Si. In a series of studies on sputtered Fe/Si a group at Argonne found evidence of structural coherence through thin Si layers and documented, using several techniques, an associated magnetic coupling between the Fe layers. They found no evidence of an oscillation in this magnetic coupling.[8] The Argonne group inferred that the structural coherence was caused by Fe silicides. They suggested that the silicides composed nearly 30% of the repeating bilayer unit of a 30 Å Fe/15 Å Si multilayer—a value twice the pure Fe portion of the bilayer unit.

In this paper we report an attempt to directly observe the presence of Fe silicides in sputtered Fe/Si. Our samples have structural and magnetic properties consistent with those of the Argonne group. However, the results of our transmission electron-diffraction (TED) study give no evidence of Fe silicides. Instead, all observed Bragg lines for samples having Si layers ranging from 10 to 30 Å in thickness are consistent with a single bcc structure.

EXPERIMENTAL PROCEDURES

The samples were prepared by dc magnetron sputtering under conditions similar to those used by the Argonne group.[8] The sputtering environment was pure Ar at a pressure of 3 mTorr and a computer controlled substrate plate, holding up to 16 different substrates with associated blocking masks, cycled a given substrate over the targets to achieve the nominal Fe and Si layer thicknesses. The sputtering rates of the targets were determined by quartz crystal thicknesses monitors at the beginning of each preparation run and these rates were remeasured several times during each run. A detailed description for this system has been published.[9] The Fe layers in all samples were nominally 28.7 Å thick, approximately 14 monolayers, while the Si layers varied from 10 to 30 Å. Sapphire, crystalline Si, and NaCl were used as substrates. The total sample thickness on sapphire and Si substrates was about 2000 Å, while the total thickness on NaCl substrates was slightly less than 500 Å. In every preparation sequence, samples with the same nominal thicknesses but different substrates were made sequentially.

Standard reflection x-ray diffraction using a rotating-anode system with a Cu target was done on all samples. Portions of the sapphire and Si substrate samples were used for magnetization measurements in a superconducting quantum interference device magnetometer with a maximum field of 5 T. These measurements were done at a temperature of 5 K for fields applied parallel and perpendicular to the sample. Portions of the samples on NaCl were floated off onto Cu grids and used for TED studies in a field-emission STEM, a VG501. In every

case, TED results from at least three different regions were obtained to confirm the uniformity of the samples.

RESULTS AND DISCUSSION

Low-angle XRD data confirmed the layered structure. For the larger total thickness samples no less than three peaks occurred and many samples had five or six peaks. The largest number of low-angle peaks observed for a single sample was eight. For the thinner samples on NaCl only two low-angle peaks were observed but these peaks were consistent with the locations of the corresponding peaks on samples having identical nominal layer thicknesses but larger total thickness. Using the low-angle peaks to determine the bilayer distance Λ produced values substantially lower than the nominal values. Figure 1(a) depicts the variation of Λ as a function of nominal thickness of the Si layer. This result is consistent with the findings of the Argonne group.[8] Additional confirmation that actual bilayer thicknesses are less than their nominal values is provided by the Kiessig fringes observed for our samples on NaCl substrates. Kiessig fringes are caused by interference between rays reflected from the front and back surfaces of the multilayer. The presence of these fringes indicates the layers are smooth

and the locations of the nodes (or maxima) provide a measure of the total thickness of the multilayer film. The results for nominal and actual total sample thicknesses were consistent with the differences found for nominal and actual bilayer values.

XRD data at higher angles revealed only a single Bragg line. For samples with very thin Si layers the higher angle XRD data gave a narrow Bragg line near the location expected for the $\langle 110 \rangle$ line of Fe with very weak satellites on its lower edge. The narrowness of this line is generally offered as evidence that structural coherence exists over more than a single bilayer distance. For thicker Si layers this line broadened and gave a coherence distance comparable to that of a single Fe layer thickness. No satellites were observed. The full width of half maximum (FWHM) results for the Bragg line reported in terms of coherence length are given in Fig. 1(b). Once again, these results are consistent with the findings of the Argonne group[8]—with the proviso that they appear to have obtained coherence for a slightly larger Si nominal thickness than we did.

The magnetization behavior of our samples is also consistent with results reported by the Argonne group.[8] First, all of our samples have a saturation magnetization that is 70% of the saturation for a comparable amount of bulk Fe. Second, our samples exhibit a coupling between the Fe layers for the thinner Si layers. In our samples this coupling is evident in both the large parallel fields needed to achieve saturation and in the value of field in excess of the demagnetizing field required to achieve saturation with a perpendicular geometry.

Selected area electron-diffraction patterns indicated the samples were polycrystalline and line scans through these patterns were used to obtain quantitative data. Focusing variations in an electron microscope make it difficult to obtain absolute values for lattice parameters. Thus, we chose a 450 Å Fe film as our standard for bcc structure and used the ratios of its line locations to the $\langle 110 \rangle$ line location to calibrate the angular response function at several fixed camera length settings. The line scan for the 28.7 Å Fe/10 Å Si sample is given in Fig. 2. The ratios in this line scan are identical to those of the pure Fe scan with one major exception: the $\langle 400 \rangle$ line is observed in this scan and it was not observed for pure Fe. The line scans for all the other Fe/Si samples were consistent with a single bcc structure. No evidence for the presence of any Fe silicide was found.

This lack of evidence for the presence of Fe silicides is illustrated graphically in Fig. 2. The expected locations of Bragg lines for several known silicides are given in the lower portion of Fig. 2. Tables of bulk sample data and the angular response function at the camera length of the scan were used in locating these lines. With the exception of the suessite form of Fe_3Si, whose three Bragg lines could coincide with the bcc lines, the line scan data exclude the presence of known Fe silicides. Fe_3Si has known Mossbauer features and the Fe/Si Mossbauer results did not suggest its presence.[8] The Argonne group suggest the Fe silicide might have a CsCl structure with a lattice parameter near 2.72 Å.[8] The initial three lines of this structure should produce two lines that surround the
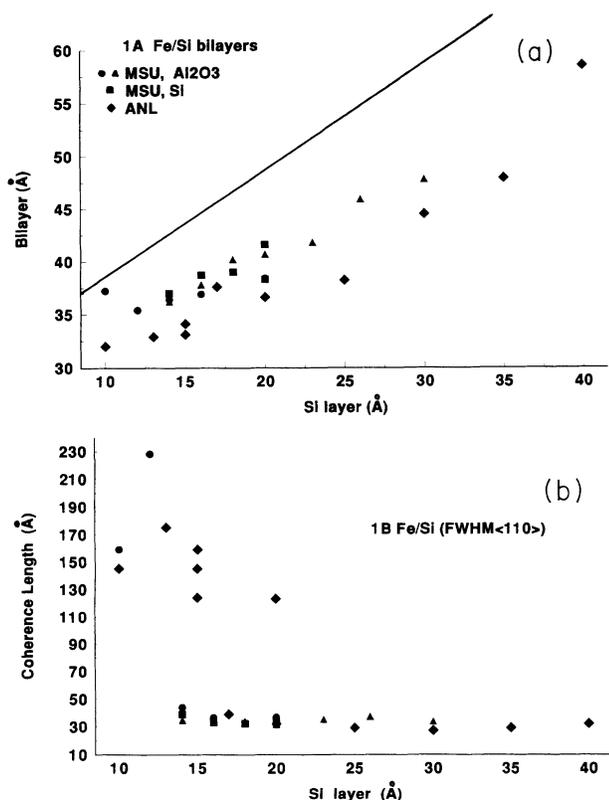
FIG. 1. Lengths for Fe/Si samples as a function of nominal thickness of the Si layer. (a) gives the bilayer thickness and (b) gives the coherence length determined from the FWHM of the Bragg line. Data reported by the Argonne group (Ref. 8), with 1.3 Å subtracted from their bilayer thicknesses to give 28.7 Å of Fe, are included in the figures. The solid line in (a) represents nominal bilayer values.
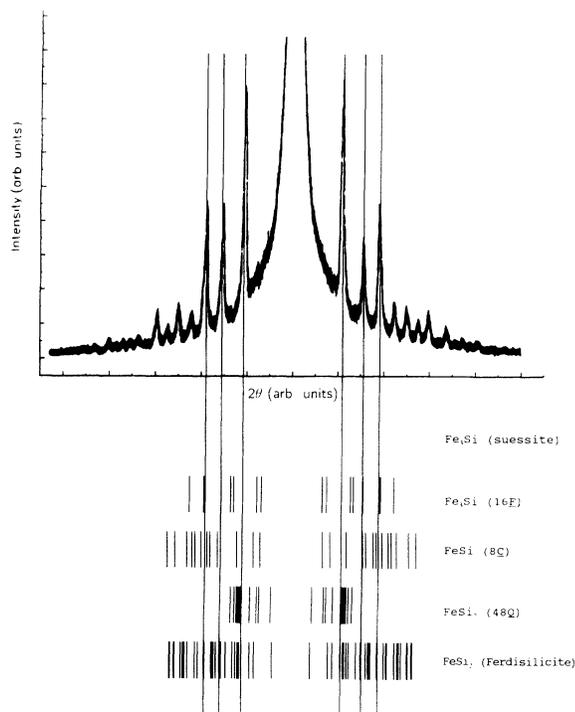
FIG. 2. Scan of transmission electron-diffraction pattern from Fe 28.7 Å/Si 10 Å sample. Locations of Bragg lines from several known Fe silicides are given below the scan and the three Fe_3Si (suessite) lines are extended throughout the figure to identify the common reference for 2 θ values.

bcc $\langle 110 \rangle$ in a manner similar to that shown for the $(Fe_3Si)16F$ structure. No such lines are seen. Figure 3 is line scan data for a V/Ag multilayer sample taken with the same camera length used for the Fe/Si samples. The locations of the expected fcc Ag lines and bcc V lines, also given in Fig. 3, have differences comparable to those between the bcc lines and expected silicide lines in Fig. 2. Effects caused by the presence of numerous lines are evident in Fig. 3. Therefore, the lack of evidence for Fe sili-
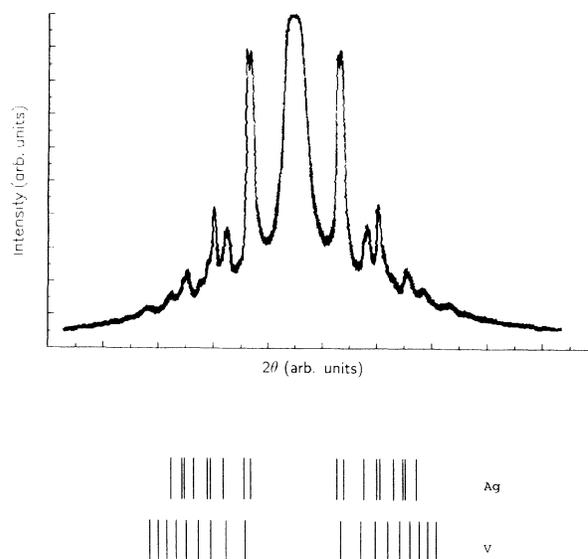
FIG. 3. Scan of transmission electron-diffraction pattern for a Ag/V sample. Locations of Bragg lines for bulk fcc Ag and bcc V are given below the scan.

cides in the present Fe/Si data is not an artifact of insufficient resolution.

Table I summarizes the Bragg lines observed in TED line scans of our Fe/Si samples. We conclude our discussion of structure in Fe/Si by discussing several features in this table. First, the fact that 14 Bragg lines in pure Fe and at least that many Bragg lines in the Fe/Si samples having a large coherence length are consistent with bcc structure indicates the dominant portion of the bilayer unit is Fe and/or a Fe-Si alloy with a bcc structure. Second, the presence of $\langle 400 \rangle$ and $\langle 521 \rangle$ lines in some of the Fe/Si samples but not in the pure Fe sample may be interpreted as evidence that alloying has occurred.

TABLE I. Bragg lines observed in Fe/Si samples. The lines are identified by their Miller indices, X denotes the nominal thickness of the Si layer, and Y indicates the line was observed, while N indicates the line was not observed.

| $\langle h,k,l \rangle$ | 28.7 Å Fe/X Å Si | | | | | | | | |
	$x = 0$	10	12	14	16	18	23	26	30
$\langle 110 \rangle$	Y	Y	Y	Y	Y	Y	Y	Y	Y
$\langle 200 \rangle$	Y	Y	Y	Y	Y	Y	Y	Y	Y
$\langle 211 \rangle$	Y	Y	Y	Y	Y	Y	Y	Y	Y
$\langle 220 \rangle$	Y	Y	Y	Y	Y	Y	Y	Y	Y
$\langle 310 \rangle$	Y	Y	Y	Y	Y	Y	Y	Y	Y
$\langle 222 \rangle$	Y	Y	Y	Y	Y	Y	Y	Y	Y
$\langle 321 \rangle$	Y	Y	Y	Y	Y	Y	Y	Y	Y
$\langle 400 \rangle$	N	Y	Y	Y	Y	Y	N	N	N
$\langle 411;330 \rangle$	Y	Y	Y	Y	Y	Y	Y	Y	Y
$\langle 420 \rangle$	Y	Y	Y	Y	Y	Y	N	N	N
$\langle 332 \rangle$	Y	Y	Y	Y	N	Y	N	N	N
$\langle 422 \rangle$	Y	Y	Y	Y	N	N	N	N	N
$\langle 510;431 \rangle$	Y	Y	Y	Y	N	N	N	N	N
$\langle 521 \rangle$	N	N	Y	Y	N	N	N	N	N

Third, the disappearance of higher Bragg lines in samples with larger nominal thicknesses, i.e., the lower right-hand corner of Table I, need not be a real change in structure. In all samples these lines are weak. Figure 1(b) documents that the crystalline portion of the bilayer unit decreases as the nominal Si thickness increases and thus the signals from these weak lines might simply be reduced to the noise level.

The data of the present study provide definitive evidence that known Fe silicides are not present in the Fe/Si bilayer. This result has profound implications for any attempt to infer the presence of silicides from other properties. Regrettably, this result is not equivalent to proving that no Fe silicides are present. A number of recent studies involving growth of Fe-Si films on Si have found that unusual, metastable structures can be formed in the thickness range involved in present study. Moreover, metallic or semiconducting behavior varies with the structure.[10,11] A better understanding of the full range of such structures and their possible presence in thin, sputtered (or evaporated) Fe/Si samples is needed before the behavior of Fe/Si can be fully understood.

CONCLUSIONS

Sputtered Fe/Si samples having structural and magnetic properties consistent with those reported by the Argonne group[8] have been studied by transmission electron diffraction in an attempt to observe directly the presence of Fe silicides in the bilayer unit. No evidence of known Fe silicides was observed.

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