EVIDENCE OF PHASE SEPARATION IN AMORPHOUS Fe_xSi_{1-x} FILMS

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Abstract

Anomalous small-angle x-ray scattering studies of magnetron sputtered Fe_xSi_{1-x} alloys (0.044 \leq x \leq 0.54) have been performed. For films with compositions between 4.4 and 23 at.% Fe, there is a strong, anisotropic small-angle scattering maximum that is highly dependent on x-ray energy near the Fe K-edge. Based on the similarity of these results with those reported for amorphous M-Ge (M=Fe, Mo, W) alloys¹ and on our observations reported here, the Si atoms are most likely distributed homogeneously with the origin of scattering from an inhomogeneous distribution of Fe atoms. Density calculations indicate phase separation into regions of a-Si and an intermetallic close in composition to a-FeSi₂, consistent with the disappearance of this scattering maximum for x \geq 0.34. Analysis of the scattering in terms of correlation functions indicates that the phase separated regions are well-correlated in the film plane and on the order of 6 Å. In the growth direction, however, the regions are poorly correlated and typically 10 Å in size. The metal/insulator transition, which occurs in a composition range in which phase separation is observed, thus apparently results from the percolation of metallic a-FeSi₂ in a-Si and not from a continuous, homogeneous structural transition from an open network to a dense intermetallic structure.

1. Introduction

Amorphous iron silicon (a-Fe_xSi_{1-x}) alloys have been extensively studied for the last several years,^{2,3,4,5,6} but most, if not all, work has assumed that the alloys are homogeneous on the scale of a nanometer or greater. In this report, we address fundamental questions concerning the possibility of phase separation as a function of iron concentration in the a-Fe_xSi_{1-x} alloy.

It is well known that a-Fe_xSi_{1-x} undergoes a metal to insulator (M/I) transition.² As the Fe concentration is raised, the conductivity rises from a negligible value near x \sim 0.2 and increases by

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an order of magnitude by x~0.4, a relatively narrow composition range. Then, over a broader range from x~0.4 to 1.0, the conductivity rises by another order of magnitude. Electron diffraction studies on a-Fe_xSi_{1-x} alloys have tried to correlate changes in the interference function with changes in composition. Two structures have been proposed³ that are consistent with the diffraction studies but each implicitly assumes a homogeneously disordered system: (1) For x<0.2, a continuous random network model. (2) For x>0.2, a progressive evolution to a dense random packing. If the alloys are phase separated, however, similar diffraction results would be obtained from, for example, an increasing fraction of an intermetallic phase that coexists with a-Si.

The transition from a paramagnetic to ferromagnetic alloy at x~0.4 has been reported from Mössbauer and magnetization studies.^{4,5} Similar results from Mössbauer have been reported more recently for Fe implanted Si samples.⁶

All of these studies assume that the films are homogeneous, but the presence of voids and/or phase separation must be considered even if the deposition procedure does not typically allow for large-scale inhomogeneities. If phase separation is present, the resulting microsctructure is typically on a very fine size-scale, which is difficult to image directly with TEM, but has been observed and characterized for a variety of $a-M_xGe_{1-x}$ (M=Mo,W, Fe) alloy films using anomalous small-angle x-ray scattering (ASAXS).^{1,7,8,9} As a consequence, the metallic and magnetic phase transitions may result from the percolation of a metallic or magnetic phase within one that is semiconducting or non-magnetic.

ASAXS allows one to quantitatively measure the degree of inhomogeneity in a sample as well as ascertain the origin of the inhomogeneity. Due to the similarity of amorphous Fe-Si and Fe-Ge alloys in terms of their physical properties,¹⁰ the importance of Fe-Si alloys to industry, and the fundamental physics of the M/I and magnetic phase transitions in thin films, we have pursued the question of chemical homogeneity in a-Fe_xSi_{1-x}.

The experimental methods are described in Section 2. In Section 3, we report ASAXS results obtained at the Fe K-edge for several film compositions. Our data indicate that quite anisotropic composition fluctuations originate once small amounts of Fe are incorporated in a-Si. These grow in magnitude with increasing x to an apparent maximum at x=0.16, and then decrease and finally disappear for x=0.34. The observed anisotropic scattering is on the same size and magnitude scale as previously reported for amorphous magnetron-sputtered M-Ge (M-Fe, Mo, W) alloys. Finally, we predict endpoint compositions from the measurements and interpret the phase separation in terms of particle and film growth models using the cylindrical correlation function. Our results indicate a microstructure consistent with particles of composition close to a-FeSi₂(a-Si) embedded in an a-Si (a-FeSi₂) matrix.

2. Experimental Technique

2.a. Sample Preparation

Films of a-Fe_xSi_{1-x} (x = 0.044, 0.096, 0.160, 0.235, 0.345, 0.350, 0.438, 0.537 and 0.538) were prepared by magnetron co-sputtering of elemental Fe (DC) and Si (RF) targets. The substrate table, with the vapor directly deposited on 25 µm kapton, passed several times under each target per monolayer deposited, ensuring macroscopic compositional homogeneity. The base pressure was never greater than 2 10⁻⁶ Torr while the Ar sputtering pressure was kept constant at 2 10⁻³ Torr. The thickness of the samples was typically between 1 and 2.25 µm as checked with an alpha-step profilometer. The iron concentration was determined with an electron microprobe, and

initial characterization and checks for crystallinity determined by a conventional Picker diffractometer.

2.b. ASAXS Experiment

The ASAXS experiment was performed on the eight-pole wiggler end-station 4-2 at the Stanford Synchrotron Radiation Laboratory (SSRL). The basic line consists of a bent cylindrical platinum coated mirror and a double crystal monochromator. Both Si(111) and Si(220) crystals have been used in these experiments, with typical 30% detuning in order to avoid contamination from harmonics. Ionization chambers were placed before and after the sample to measure the transmitted intensity, $I_1(E)=I_0(E)\exp(-\mu(E)t)$, where $\mu(E)$ is the absorption coefficient for x-ray energy E, t the sample thickness, and $I_0(E)$ the intensity of the primary beam. The optimal thickness, one absorption length (i.e. $I_0(E)/I_1(E)-e^1$), was achieved by stacking several kapton-supported films together. The ASAXS spectrum from k= $4\pi \sin\theta/\lambda=0.05$ to 0.67 Å⁻¹, with θ one-half the scattering angle, was collected with a linear position sensitive detector placed at various distances from the sample. The sample-detector distances have been determined by measuring the scattering from polycrystalline cholesterol myristate

Measurements were performed at five energies [200, 50, 30, 20, and 10 eV below the Fe K-edge (7112 eV)]. Due to limits from absorption and to the energy range of the monochromator crystals, Si K-edge (1839 eV) ASAXS was not possible with our apparatus. In general, with such soft x-rays, the x-ray absorption length is so short that ASAXS scans for samples held in transmission are usually not possible.

In order to test for anisotropy, oblique transmission measurements which allow for various orientations of the scattering vector were performed (see Figure 1). By tilting the sample to angle θ_k , the scattering vector rotates out of the sample surface plane (θ_k =90) and begins to align with respect to the sample normal (θ_k =0, the direction of film growth). For these experiments, we recorded radial k scans at 5 different θ_k positions: θ_k =90, 75, 60, 45, and 30.





The data were centered and normalized to the measured transmitted intensity I_1 , corrected for kāpton and air scattering by subtracting the scattering recorded from the kapton under identical experimental conditions, and interpolated to a common k mesh. The kapton subtraction is tricky, and fortunately the well defined kapton maximum at k=0.4Å⁻¹ is distinct from the a-Fe_xSi_{1-x} scattering as well as energy independent. Hence, by using anomalous scattering it is clear what contribution the kapton makes to the overall scattering pattern, but perfect subtraction is not always possible. Conversion to an absolute scale was accomplished by measuring the ASAXS from a lupolen secondary standard¹¹ and multiplying the a-Fe_xSi_{1-x} corrected intensities by a constant dependent on tilt angle and sample, κ_{s,θ_x} :

$$\kappa_{s,\theta_k} = \frac{d\sigma_{lup}}{d\Omega}(k') \cdot \frac{t_{lup}}{I_{lup}(k')} \cdot \frac{\sin\theta_k}{Nt_s},\tag{1}$$

with $d\sigma_{lup}/d\Omega$ the differential cross-section per unit volume of lupolen at some point k', I_{lup} the corrected scattering from the lupolen at k', t_{lup} and $t_s/\sin\theta_k$ the thickness of the lupolen and a-Fe_xSi_{1-x} sample respectively, and N the number of stacked sheets to obtain the optimal thickness.

An important feature of the observed scattering, independent of tilt angle, is the apparent $1/k^4$ fall-off in intensity with increasing scattering vector at large k (typically k>0.5 Å⁻¹). This is a region in reciprocal space where interparticle interference effects are less important while scattering from particle surfaces dominate. The $1/k^4$ power-law is the characteristic Porod law of smooth interfaces and has been used to remove the constant, incoherent sample scattering (e.g. fluorescence, resonant Raman scatter). We have thus fit A+B/k⁴ to the large-k regions and subtracted A from the data presented here, which allows us to present the coherent scattering of interest. For more details of data normalization, absolute scale and subtraction of fluorescence, see Regan.⁹

2.c. Atomic Scattering Factors

In order to analyze the anomalous scattering data, it was necessary to determine the values of the real and imaginary part of the atomic scattering factor, f'(E) and f''(E). X-ray absorption measurements at the Fe K-edge were performed on the wiggler side stations 4-1 and 4-3 at SSRL. The atomic scattering factors were extracted by using the optical theorem and Kramers-Kronig relations.¹²

3. ASAXS Results

3.a. Small-Angle Scattering Results

To our knowledge, no SAXS studies have been undertaken before on this system, so we will present in detail the scattering results. Figure 2 shows the SAXS spectra obtained at 6912 eV from the a-Fe_xSi_{1-x} alloys for a variety of concentrations at normal incidence (i.e. $\theta_k=90^\circ$). At low k, in the vicinity of the beamstop, and near the kapton scattering maximum at 0.45 Å⁻¹ imperfect subtraction of the background scattering is evident. The first data point corresponds to k-0.05 Å⁻¹.

A broad intensity maximum appears in the measured small-angle region for 0 < x < 0.34while no effect is present for $x \ge 0.34$. There is some scattering from the 34 at.% Fe sample, which is located in a different region of k, and very close to a kapton scattering maximum at $k=0.05\text{Å}^{-1}$. It has been difficult to isolate the coherent scattering for this sample from that of the kapton since it is extremely weak. Since the kapton scattering is strongly anisotropic,¹³ it is possible that the sheets of a-Fe_xSi_{1-x} are phased differently than the subtraction kapton sample, and hence we are just observing a poor subtraction of the kapton scattering. This subtraction problem is not observed for any of the other samples. The signal-to-noise ratio between kapton and sample is not sufficient for us to draw any definitive conclusions about the 34 at.% Fe sample, and future studies plan to investigate this composition with kapton-free samples.





For a-Si we do not observe any appreciable SAXS over this k-range, and with the addition of Fe up to x<0.34, the scattered intensity develops a maximum at nonzero k, k_{max} . This implies that some degree of density fluctuation is present in the alloy with average spatial correlations of some characteristic distance, typically given as $\sim 2\pi/k_{max}$. At normal incidence there is a continuous shift of the SAXS to smaller angles: k_{max} decreases for increasing Fe concentration (from 0.36 Å⁻¹ to 0.27 Å⁻¹). The maximum intensity at k_{max} first increases from 4.4 to 16 at.% Fe, begins to decrease as x is further raised to 23.5 at.% Fe, and finally disappears by 34-44 at.% Fe. As a whole, these results imply that the maximum degree of inhomogeneity occurs for the 16 at.% Fe sample, with the length scale increasing monotonically with the addition of Fe.

As the orientation of the scattering vector changes with respect to the film plane, a strong anisotropy appears that is similar for all strongly scattering samples. As the scattering vector rotates out of the sample surface plane and begins to align with the direction of film growth, the SAXS maximum decreases markedly in amplitude and shifts inward to smaller magnitude of scattering vector. This can be seen, for example, in the 9.6 at.% Fe sample displayed in Figure 3. k_{max} changes from 0.31 Å⁻¹ to 0.23 Å⁻¹ by positioning the scattering vector from an "in plane"



Figure 3. Oblique transmission results for 9.6 at.% Fe alloy measured at 6912 eV.

orientation (θ_k =90°) to one that it is θ_k =30° from normal incidence. These results are similar to those reported for Fe-Ge and Mo-Ge and have been explained with cylindrical correlation functions and various particles models.⁹ A later section addresses the interpretation of these data in more detail.

3.b. Anomalous Scattering Results

As the x-ray energy approaches the Fe K-edge from below, so that $f_{Fe}(E)$ becomes increasingly negative with $f'_{Fe}(E)$ essentially constant, the SAXS intensity, particularly near the maximum, decreases markedly. This occurs for all samples 0<x<0.34, and is shown in Figure 4 for a representative, the 9.6 at.% Fe sample. These results indicate that the Fe atoms are inhomogeneously distributed in the films.

- Similar results¹ have also been obtained at the metal edge of sputtered M-Ge alloys (M=Fe, Mo, W). The Ge K-edge ASAXS for these alloys show little change in the SAXS with energy, indicating that the Ge atoms are relatively homogeneously distributed, leading to a model of a-Ge coexisting with a Ge-rich intermetallic of similar Ge number density.



Figure 4. Anomalous scattering results for the 9.6 at.% Fe film at four energies below the Fe K-edge (7112 eV).

Since, as noted earlier, it is not possible to perform ASAXS at the Si K-edge, we cannot determine the degree of Si homogeneity in these films nor compare it to that of the Fe.¹⁴ An inhomogeneous distribution of Fe atoms could arise, for example, from phase separation or defects like voids. Considering the composition dependence of the Fe-Si SAXS and analogous results¹ from the M-Ge alloys, it appears likely that there is significant chemical inhomogeneity in the Fe-Si system as well. The SAXS originates with the addition of Fe to a-Si, is greatest near the midpoint between a-Si and a-FeSi₂ (~16 at.% Fe), and finally disappears once x>0.34.

4. Discussion

In this Section, we discuss the real-space interpretation of the small-angle scattering. The magnitude of scattering and further characterization of the inhomogeneity are addressed in terms of general two-phase and specific microstructural models.

4.a. General Two-Phase Model

Since ASAXS is first observed with the addition of Fe to a-Si and there exists a Porod law behavior, it seems reasonable to assume that phase separation exists, where one endpoint is a-Si and the other is an intermetallic a-Fe_ySi_{1-y}, with fairly well defined and abrupt phase boundaries between the two. For this two-phase model, the mean-square fluctuation in electron density, $\langle n^2 \rangle$ can be analytically written as

$$\langle \eta^2 \rangle = c(1-c) \left| n_{Fe_ySi_{-y}}^{Fe} f_{Fe} + \left(n_{Fe_ySi_{-y}}^{Si} - n_{Si}^{Si} \right) f_{Si} \right|^2$$
 (2)

with the volume fraction of Fe_ySi_{1-y} denoted by c, the number density of Fe in Fe_ySi_{1-y} by $n_{Fe_ySi_{1-y}}^{Fe}$, and similarly for the number density of Si in each of the two phases.

 $\langle \eta^2 \rangle$ is directly proportional to the integrated intensity. The method used here for integrating the anisotropic scattering to arrive at $\langle \eta^2 \rangle$ is described in the Appendix. The values of $\langle \eta^2 \rangle$ obtained by integrating the data at 6912 eV are shown as a function of the Fe composition for several samples in Figure 5.



Figure 5. Mean-square fluctuation of electron density $\langle \eta^2 \rangle$ versus iron concentration x measured at 6912 eV. Full line corresponds to the best fit of the data to Eq. 4.

The FeySi_{1-y} endpoint composition can be determined by fitting $\langle \eta^2 \rangle$ to Eq. 2, where the volume fraction of the Fe-rich phase is defined by the overall film composition and the relevant number densities

$$c = \frac{x \, n_{Si}^{Si}}{(1-x)n_{Fe_{y}Si_{1-y}}^{Fe} + x(n_{Si}^{Si} - n_{Fe_{y}Si_{1-y}}^{Si})},$$
(3)

and with n_{Si}^{Si} , $n_{Fe_ySi_{1-y}}^{Fe}$ and $n_{Fe_ySi_{1-y}}^{Si}$ as fitted parameters. Our fits give nearly identical values for n_{Si}^{Si} and $n_{Fe_ySi_{1-y}}^{Si}$ indicating that the Si number density in Fe_ySi_{1-y} is nearly the same as in a-Si.

With this simplification, Eq. 2 becomes

$$\left\langle \eta^{2} \right\rangle = \frac{x}{1-x} \left(1 - \frac{x}{1-x} \frac{n_{\tilde{S}}}{n_{Fe}} \right) n_{Fe} n_{Si} \left| f_{Fe} \left(E \right) \right|^{2}, \tag{4}$$

with n_{Fe} the Fe number density in Fe_ySi_{1-y} and n_{Si} the Si number density (same in both phases). Fitting Eq. 4 to the results presented in Figure 5, we find $n_{Fe} = 0.0227$ at./Å³ and $n_{Si} = 0.0558$ at./Å³. The predicted intermetallic endpoint composition $[y=n_{Fe}/(n_{Fe}+n_{Si})]$ is thus 0.29, within the homogeneity limits of the c-FeSi₂ found in the equilibrium phase diagram. High temperature α -FeSi₂ has homogeneity limits from 30 to 27.6 at.% Fe, whereas the low temperature intermetallic β -FeSi₂ contains 31.1 at.% Fe.¹⁵ Since, however, the value of n_{Si} that was fit is greater than that from c-Si, we have tried other fitting procedures to test the sensitivity of our results.

An alternative approach is to calculate the endpoint composition for each particular alloy. For fixed values of n_{Si} , the only unknown is n_{Fe} . For n_{Si} identical to c-Si (0.05 at./Å³), endpoints range from 30.3 to 33.5 at.% Fe .With n_{Si} equal to that of a-Si (0.0475 at./Å³), endpoints range from 30.3 to 35.4 at.% Fe (see Table 1). These results are also consistent with phase separation into a-Si and an intermetallic close in stoichiometry to a-FeSi₂.

sample (at.% Fe)	$2\pi/k_{max}$ $\theta_x=90^{\circ}$ (Å)	$\langle \eta^2 \rangle$ (e/Å ³) ²	y ₁ c-Si (at.% Fe)	y ₂ a-Si (at.% Fe)	voids (%)
4.4	17.6	0.02368	33.4	32.7	4.3
9.6	19.5	0.05498	33.5	35.4	8.2
16.0	19.7	0.06558	31.8	32.6	7.4
23.5	23.5	0.04840	30.1	30.7	4.1

Table 1.

1. Relationship between Fe-Si composition, characteristic "in-plane" wavelength $2\pi/k_{max}$, mean-square fluctuation of electron density $\langle \eta^2 \rangle$ at 6912 eV, computed endpoint compositions for two Si number density assumptions (c-Si and a-Si), and the volume fraction of voids that would be consistent with $\langle \eta^2 \rangle$.

For 0 < x < 0.33, the Fe-Si equilibrium phase diagram shows no solid solubility, with separation into c-Si and c-FeSi₂. The number density of Si in c-Si and c-FeSi₂ is only marginally different, by only ~5-10% (see Table 2). This appears similar to what we observe in the vapor-deposited amorphous state. ASAXS shows Fe atoms inhomogeneously distributed up to ~34 at.% Fe. From the analysis of $\langle \eta^2 \rangle$, we find the Si number density in the Fe_ySi_{1-y} to be similar to that of a-Si, with the predicted endpoint phase a-FeSi₂.

Without Si-specific information, the possibility that Si is inhomogeneously distributed cannot be completely excluded. Voids could lead to similar values of $\langle \eta^2 \rangle$. However, there appears to be no logical model of voids that we can find that might explain the variation of $\langle \eta^2 \rangle$ with composition. With the additional similarity of the Fe-Si alloys to the M-Ge films, we think it is highly unlikely and improbable that voids are the source of the inhomogeneity. For completeness,

Material	n (atoms/Å ³)	n _{Fe} (atoms/Å ³)	n _{Si} (atoms/Å ³)
Si	0.050	0.0	0.050
FeSi ₂	0.795-0.797	0.0265-0.0266	0.0530-0.0532
FeSi	0.0868-0.0890	0.0434-0.0445	0.0434-0.0445

we have also calculated the volume fraction of voids (<10%) that must be present in order to lead to such $\langle \eta^2 \rangle$; the results are listed in Table 1.



4.b. Microstructure

Three different approaches have been developed to interpret the anisotropic scattering. Cylindrical correlation functions (CCFs), inhomogeneous particle models, and close-packed homogeneous particle models have been utilized to arrive at a plausible real-space interpretation of the phase separation.⁹ As these approaches lead to the same physical model, we present the CCFs here.

The electron density pair correlation function, $\gamma(\vec{x}) = \langle \rho(\vec{x}_0) \rho(\vec{x} + \vec{x}_0) \rangle$, is proportional to

the Fourier transform of $d\sigma/d\Omega$. Since the films are grown in one direction, with in-plane isotropy, $\gamma(\vec{x})$ has a cylindrical symmetry. The appropriate correlation function is then the cylindrically symmetric pair correlation function, or CCF, which has been calculated with a spherical harmonics approach.¹⁶

The CCF for the 9.6 at.% Fe sample is shown in Figure 6, with a two-dimensional plot, and Figure 7 shows the CCF along different radial directions of the correlation vector \bar{x} . $\gamma(\bar{x})$ is large and positive at small x, which arises from well-defined regions of similar electron density and is considered to be from a particle of particular dimensions. For the CCFs that we have obtained, the particles are elongated by ~50% in the growth direction (~10 Å) relative to the inplane directions (~6 Å). The average particle sizes are obtained from the CCF by arbitrarily assigning the radii as those values for which $\gamma(\bar{x})=0$ has decreased by 90%. A truly columnar film growth model is thus inappropriate.

For the 9.6 at.% Fe sample, the a-FeSi₂ phase occupies less than one-half volume fraction of the film, so we can consider the particle to consist of FeSi₂. Then, the negative portion of $\gamma(\vec{x})$, which surrounds the intraparticle correlations, is a result of a region deficient in Fe. The depletion regions are quite evident for in-plane correlations, but are difficult to discern in the growth direction. In addition, secondary maxima in $\gamma(\vec{x})$ indicate that the particles are well-correlated in-plane with little correlation in the growth direction.



Figure 6. Mesh plot of the CCF, $\gamma(\vec{x})$, for the 9.6 % at. Fe sample (6912 eV), in units of $(e^{-1}/\dot{A}^{3})^{2}$. Mesh lines are spaced 3 Å by 3 Å.



Figure 7. CCF as in Figure 6, but plotted along different radial directions, θ_x . Plot offset and truncated at small x in order to better observe the oscillations.

5. Summary and Conclusions

We have used anomalous small-angle x-ray scattering to address the possibility of phase separation in sputtered amorphous alloys of iron and silicon. No scattering intensity was detected from samples with an iron concentration higher than 34 at.% of Fe nor for a-Si, while a strong peak was recorded for all samples of composition between 4.4 and 23.5 at.% Fe. Thus, this low-x region is phase separated with an endpoint in the $0.30 \le x \le 0.33$ region.

By recording the oblique transmission SAXS spectra, we have shown that the films structure is quite anisotropic, depending significantly on the direction of film growth. The scattered intensity markedly decreases as the x-ray energy approaches the iron K-edge from below, indicating Fe inhomogeneity. This behavior, together with our analysis of the mean-square fluctuation of electron density, indicates that the scattering is most likely from a fine-size scale phase separation of a dispersion of particles with composition close to a-FeSi₂ (a-Si) in a-Si (FeSi₂).

The observation of significant inhomogeneity for $x \le 0.33$ is not disputed by complementary measurements. Mössbauer studies on these samples¹⁷ detect only the presence of one phase. As the Mössbauer technique is only able to detect those phases that contain the probe (⁵⁷Fe), the result is consistent with phase separation into two distinct phases, one a-Si (not seen) and the other an Fe-Si intermetallic. A noticeable change in the composition dependence of the isomer shift occurs at some concentration between the x=0.23 and x=0.34 compositions studied here, indicating a change in the microstructure, in agreement with the present results and other Mössbauer studies previously reported in amorphous Fe-Si samples prepared by co-evaporation of the elements⁴ and by Fe implantation⁶ in Si.

The origin of the anisotropy is explained with the CCFs, which show depletion regions and interparticle correlations in the film plane but which are far less evident in the growth direction. These observations have been noted previously for the amorphous M-Ge alloys. They are consistent with a physical picture in which phase separation occurs at the film surface by laterally depleting a local area of, for example, Fe atoms, defining intraparticle and interparticle correlations in the film plane. Fluctuations in the growth process then lead to little correlation between the location of new particles in the emerging film and those which already exist and are buried by a few atomic layers of vapor-deposited material.

The metal-insulator transition in amorphous Fe-Si is likely to be related to the anisotropic microstructure we have reported. Electron tunneling and hopping phenomena are probably strongly influenced by the depletion regions, which also lead to unique percolation paths for the metallic phase. Conversely, we have not observed phase separation for sputtered films with concentrations greater than 34 at.% Fe. The magnetic transition (~40 at.% Fe), then, occurs considerably differently from the metal-insulator transition, since it does not progress through the percolation of a magnetic phase on a fine-size scale.

Since the c-FeSi₂ intermetallic compound can form in at least four phases, an important problem is to understand the short-range order in the a-FeSi₂ phase and compare it to its crystalline counterparts. The c-FeSi₂ intermetallic compound has been observed in a stable orthorhombic

(β -FeSi₂) phase, which exhibits an insulator/metal transition to tetragonal α -FeSi₂ with an increase

in temperature. Metastable phases γ -FeSi₂ (fluorite structure) and/or cubic-FeSi₂ (CsCl structure) have also been recorded. Analysis of extended x-ray absorption fine structure data which were collected in the course of this work may help resolve this question.¹⁸

An additional area of interest is to utilize the phase separated amorphous Fe-Si films to synthesize related metastable phases which have potential applications in Si technology. A controlled crystallization of the amorphous phase could lead to, for example, metastable phases γ -FeSi₂ and/or cubic-FeSi₂ recently obtained by epitaxial growth on Si(111).¹⁹

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Appendix

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To calculate the mean-square fluctuation of electron density, $\langle \eta^2 \rangle$, commonly known as the invariant or integrated intensity, the scattering results must be integrated over the radial and polar angle components of \vec{k} . With an azimuthal symmetry:

$$\left\langle \eta^2 \right\rangle = \frac{1}{(2\pi)^3 r_e^2} \int \frac{d\sigma(\bar{k})}{d\Omega} d^3k = \frac{1}{(2\pi)^2 r_e^2} \int_0^{\pi} Q(\theta_k) \sin(\theta_k) d\theta_k \,, \tag{A1}$$

with re the classical radius of the electron and the integrated radial intensity, $Q(\theta_k)$, given by

$$Q(\theta_k) = \frac{1}{2}k_1^3 \frac{d\sigma(k_1)}{d\Omega} + \int_{k_1}^{k_2} \frac{d\sigma(k,\theta_k)}{d\Omega} k^2 dk + \frac{k_p}{k_2}.$$
 (A2)

 $Q(\theta_k)$ is determined by considering three different contributions: for $0 < k < k_1$ and k_1 the value of the first reliable data point, the integral is evaluated with a triangular approximation; the second term is the numerical integration of the intensity from k_1 to k_2 , with k_2 a value for which the scattered intensity obeys the Porod law; the final term is the analytic expression with a Porod law integrand. The integral over θ_k in Eq. (A2) is performed using the Simpson rule for 7 points (five data points and the value of Q(15) obtained from the best fit of $Q(\theta_k) \sin(\theta_k)$ against θ_k -Q(0) is not needed due to the $\sin(\theta_k)$ in the integrand).

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Footnotes

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