Long-range order in thin epitaxial Fe_3Si films grown on GaAs(001)

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As-grown thin epitaxial Fe_3Si films fabricated by molecular beam epitaxy on GaAs(001) are studied by grazing incidence x-ray diffraction. The long-range order parameters of the films of different stoichiometry are determined by measuring fundamental and superlattice crystal truncation rods and comparing them to simulations in dynamical approximation. Two order parameters, associated with the degree of migration of Si atoms into different Fe sublattices, are obtained. A residual intermixing of the sublattices is found, even near complete stoichiometry. The relative positions of the Fe_3Si and GaAs lattices are determined. Fe atoms in Fe_3Si are located at the positions of the Ga atoms in GaAs, with an additional shift of 0.1 ± 0.04 Å of the tetragonally distorted Fe_3Si lattice normal to the interface.

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I. INTRODUCTION

The combination of magnetic and semiconducting materials opens up new pathways in the development of semiconductor devices utilizing the spin of the carriers.[1] From the viewpoint of such spintronic device structures, it is highly desirable to explore epitaxial ferromagnet/semiconductor heterostructures that possess a rather perfect interface[2] structure as well as high thermal stability. Fe_3Si on GaAs is a promising candidate for spintronics applications.[3–5] It can be grown by molecular beam epitaxy at GaAs substrate temperatures near 200 °C.[6] The Curie temperature of Fe_3Si is as high as 840 °C.[7] Spin injection at room temperature has been already demonstrated.[8] The lattice misfit between stoichiometric Fe_3Si and GaAs is very low.[6] The interface between Fe_3Si and GaAs is found to be smooth and of good structural perfection: Fe_3Si on GaAs can be grown without misfit dislocations at the heterointerface.

Fe_3Si has the face-centered cubic $D0_3$ structure.[9,10] This structure (see Fig. 1) can be considered as four interpenetrating fcc sublattices A, B, C, and D with origins at A(0, 0, 0), B(0.25, 0.25, 0.25), C(0.5, 0.5, 0.5), and D(0.75, 0.75, 0.75). In the ordered Fe_3Si crystal, Fe atoms occupy the three sublattices A, B, and C, while Si atoms fill the sublattice D. Bulk Fe_3Si crystals acquire a long-range order of the sublattices after an annealing in vacuum at 600 °C for about two hours.[11] The ordered alloy can be regarded as a magnetic Heusler alloy $Fe(B)Fe(A,C)_2Si(D)$ with the two distinct Fe sites (A,C) and (B).[10,12] The order in Heusler alloys[13] has a significant influence on their electric and magnetic properties: the magnetic moments of the Fe atoms at the positions Fe(A,C) linearly depend on the number of nearest Fe neighbors.[14,15] Thus, the magnetic properties can be tuned: some of the local Fe magnetic moments are almost as large as in pure bcc iron, while others are reduced due to the presence of Si. Moreover, the introduction of small amounts of transition metal impurities into the Fe_3Si matrix opens up new possibilities[11,16] to tune the magnetic properties. Impurities to the left of Fe in the periodic table prefer the Fe(B) site with eight first-neighbor Fe atoms. Those beneath and to the right of Fe in the periodic table enter the Fe(A, C) site with four Fe and four Si atoms as nearest neighbors. A highly ordered and stoichiometric Fe_3Si matrix is the starting point for most experiments with bulk Fe_3Si.

In as-grown thin epitaxial films of Fe_3Si on GaAs, the lattice mismatch and the long-range order depend on the stoichiometry. Significant changes of the saturation magnetization and the resistivity with film stoichiometry have been observed.[17] While the saturation magnetization changes almost linearly with composition and the coercive field remains unchanged over a wide range of compositions, a clear minimum of the resistivity R_S near stoichiometric conditions is found. It has been suspected that the minimum is due to alloy scattering, which is smallest for an ordered crystal structure, but detection of the degree of the order has been lacking. Moreover, an additional contribution to the planar Hall effect was recently found, which reflects magnetic in-

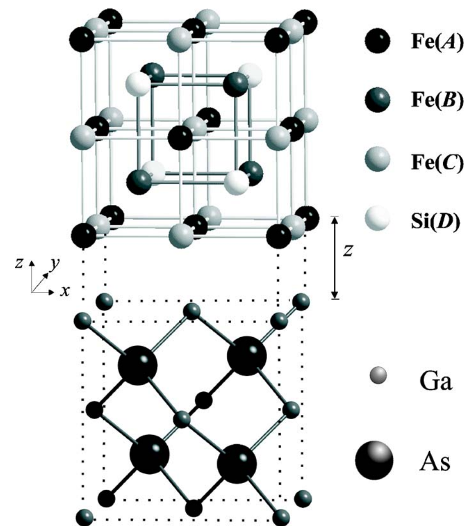

FIG. 1. (Color online) Schematic view of the $D0_3$ unit cell of Fe_3Si grown epitaxially on GaAs. The A and C sites are equivalent and are occupied by Fe. The B sites are also occupied by Fe, whereas the D sites are occupied by Si. In the epitaxial system, the first layer of Fe atoms is located at the positions of the Ga atoms in the GaAs lattice. The vertical shift z is enlarged for clarity. The choice of the radii of the atoms is arbitrary.

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TABLE I. Structural parameters and the low temperature resistivities of the samples under investigation.

Sample	Si cell temperature (°C)	Si content in Fe_3Si (%)	Layer thickness (nm)	Misfit (%)	Order parameters α to Fe (B)	Order parameters β to Fe (A, C)	Relaxation z Å	Resistivity (μΩ cm)
1	1395	25.5	32.6	−0.06	0	0.3	0.14	23
2	1390	22.5	28.4	0.15	0.25	0.28	0.06	50
3	1375	16.5	28.2	0.62	0.25	0.5	0.08	103

teractions with reduced crystal symmetry for certain Fe sublattices in ordered Fe_3Si on GaAs.[18]

Our aim in the present work is the determination of long range order in thin Fe_3Si films by grazing incidence x-ray diffraction (GID) measurements. We use the same measurements for a precise determination of position of the Fe_3Si unit cell with respect to the GaAs substrate. We utilize the method of grazing incidence diffraction that is ideally suited for thin film investigation, since it gives access even to those reflections that cannot be measured by conventional diffraction methods.

II. EXPERIMENTAL

The Fe_3Si films were grown by solid source molecular beam epitaxy (MBE). The GaAs(001) templates were prepared in a separate III-V growth chamber using standard GaAs growth techniques. The sample was then transferred into an As-free chamber through UHV for the Fe_3Si deposition. The Fe_3Si layers were grown[6] on the As-rich GaAs surface at 200 °C with a growth rate of 24 nm h^{-1}. The Si cell temperature was varied in order to obtain different degrees of stoichiometry of the films. The Si content of the film was obtained[6] from the position of the Fe_3Si layer peak on the x-ray diffraction curve. For the present study, we have chosen three samples with different Si contents; see Table I. Samples 1 and 2 are nearly stoichiometric, sample 1 with a small Si surplus, sample 2 with a slight Fe excess. Sample 3 is clearly nonstoichiometric.

The x-ray measurements were performed at the wiggler beamline U125/2 KMC (PHARAO) at the storage ring BESSY in Berlin, Germany. A double crystal Si(111) monochromator was used. The energy of the radiation was 10 keV. A six-circle x-ray diffractometer[19] was used for grazing incidence diffraction measurements. The incidence angle was 1.2°. The acceptance angle of the detector was 0.1° perpendicular to the surface and 1° (open slits) parallel to the surface. Additional conventional coplanar x-ray diffraction measurements were made using a Panalytical X-Pert system with Ge (220) hybrid monochromator and CuKα_1 radiation.

III. THEORY

The stoichiometric compound Fe_3Si possesses three types of reflections. Fundamental reflections, which are not influenced by disorder, are given by $H+K+L=4n$, where n is an integer and (HKL) are the Miller indices of the diffracting net planes. The structure amplitude of these reflections is

$$F_0 = 4(f_{\mathrm{Si}} + 3f_{\mathrm{Fe}}), \tag{1}$$

where f_{Si} and f_{Fe} are the atomic scattering factors of the respective elements.

The disorder is described by two order parameters α and β, which are fractions of Si atoms occupying the Fe(B) and Fe(A,C) sites, respectively. There are two distinct types of superlattice reflections.[9] Reflections with odd H,K,L are sensitive to both types of disorder, the structure amplitude being

$$F_1 = 4i(1 - 2\alpha - \beta)(f_{\mathrm{Si}} - f_{\mathrm{Fe}}). \tag{2}$$

Reflections given by $H+K+L=2n$ (where n is an integer) are sensitive to disorder in the Fe(A,C) sublattice,

$$F_2 = -4(1 - 2\beta)(f_{\mathrm{Si}} - f_{\mathrm{Fe}}). \tag{3}$$

In order to obtain the order parameters α and β, we measure diffraction curves of all three types of reflections and fit them by dynamical diffraction calculations. They are obtained for each sample by a simultaneous fit of the diffracted intensities of all the measured Fe_3Si peaks. The epitaxial layers themselves are thin enough and their diffraction peaks can be well fitted in the kinematical approximation. However, we want to fit simultaneously the layer and the substrate peaks, the latter serving as an internal reference to obtain the absolute values of the structure amplitudes (1)–(3). The dynamical calculation automatically solves this problem.

The dynamical diffraction theory for layer structures is well established, and we use the well-known algorithm described in Ref. 20 and references therein. One point of the dynamical calculations needs a special discussion. The scattering properties of each layer are described by the Fourier components of the polarizability $\chi_{\mathbf{H}}$. In the computer programs for the analysis of x-ray diffraction experiments available so far, the coefficients $\chi_{\mathbf{H}}$ are considered as eigenproperties of each layer. That means that the origin of the unit cell to calculate $\chi_{\mathbf{H}}$ is chosen independently for each layer, usually according to the symmetry of the respective layer. The phase factor $\exp(i\mathbf{H}\cdot\mathbf{R})$ that arises if the origin is shifted by a real-space distance $\mathbf{R}$ is not taken into consideration. Such a phase factor does not appear if all epitaxial layers have a similar structure (an AlAs/GaAs superlattice would be a simple example). However, if the structures are different, the relative positions of the unit cells are not known in advance and an additional phase factor in the polarizability of one layer with respect to another may appear.

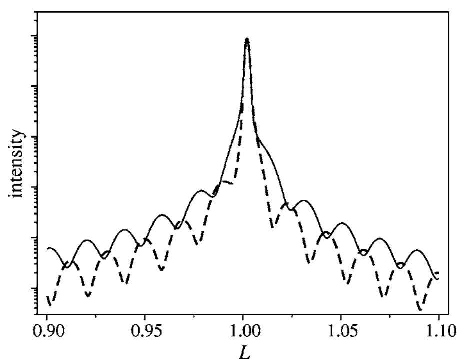

FIG. 2. Calculated CTRs at the 111 reflection from a stoichiometric fully ordered Fe_3Si layer (30 nm thick) on GaAs(001) for the lattice registry shown in Fig. 1 (full line) and for the case of the Fe_3Si structure shifted by 1/2 of the unit cell in the (100) direction (broken line).

The problem is resolved by choosing a common origin for all structures. This is a commonplace in surface diffraction,[21,22] but not taken into consideration in practical dynamical diffraction calculations. Figure 2 shows the influence of the relative shift of the crystal lattices on the diffraction curves. We compare a crystal truncation rod (CTR) scan at the 111 reflection calculated for relative positions of the Fe_3Si and GaAs lattices shown in Fig. 1 with the same scan for the case when the Fe_3Si lattice is shifted by 1/2 of the unit cell in the interfacial plane. The corresponding shift of the layer thickness oscillations is obvious. Thus, we have included the relative positions of the layer and the substrate crystal lattices in the fits to obtain the registry of the layer on the substrate. The z component (normal to the interface) of the shift is a relaxation at the interface. A similar analysis is commonly performed in x-ray surface structure studies to obtain the registry of a reconstructed layer with respect to the bulk structure, but has not been applied to studies of epitaxial layers so far.

IV. RESULTS

Figure 3 combines CTR scans performed on sample 1 at different bulk reflections. The width of the GaAs substrate peak is limited by the resolution of the experimental setup. The Fe_3Si layer peak is broadened due to the small thickness of the layer, and evidencing periodic side maxima thanks to the high quality of its top and bottom interfaces (see Table I). The layer peak is fairly close to the substrate peak, indicating that the sample is nearly stoichiometric. The 004 and 022 reflections are not sensitive to disorder. The 002 and 222 reflections are influenced by disorder in the Fe(A,C) sublattice, see Eq. (3), and the 111, 311, and 113 reflections are sensitive to disorder in both sublattices Fe(B) and Fe(A,C), as given by Eq. (2). A well-pronounced Fe_3Si layer reflection in all these scans indicates a high degree of long-range structural order in the layer.

All measured curves were fitted simultaneously by the dynamical diffraction calculations. We obtain the order parameters α and β from the relative intensities of the layer peaks (with the substrate peak serving as an internal reference), the layer thickness from the oscillation period and the registry of the lattices from the phase of the oscillations. The order parameters are found to be $\alpha=0$ and $\beta=0.3$ (see Table I) with an accuracy of ±0.05. Thus, the as-grown Fe_3Si layer of sample 1 is not fully ordered, although it is nearly stoichiometric. Approximately 30% of Si has left its sublattice D and exchanged with the Fe(A,C) atoms. The Si atoms did not exchange with Fe(B) atoms. This is an unexpected result, since in Fe_3Si powder samples an excess of Si was found to replace the Fe(B) sites.[9–11]

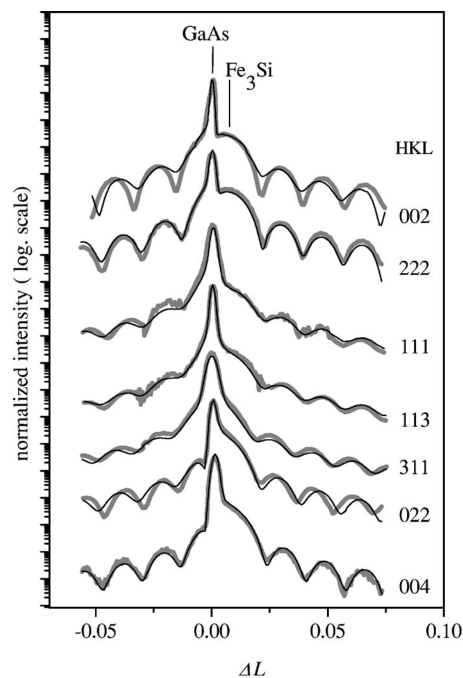

FIG. 3. Measured (thicker gray lines) and fitted (fine black lines) CTRs of sample 1 near different reciprocal lattice points. The fits of all curves are performed simultaneously with one and the same set of parameters. The sample is nearly stoichiometric with a slight surplus of Si and exhibits an ordered structure with some disorder due to the migration of Si atoms into the Fe(A,C) sublattice. The coordinate L along the CTRs has its origin at the respective GaAs peak.

From the positions of the intensity oscillations, we find that the Fe_3Si and GaAs lattices are positioned with respect to each other, as shown schematically in Fig. 1, i.e., the Fe(A) atoms at the positions of Ga atoms. The Fe_3Si unit cell is found to be shifted up vertically along z by 0.14Å with respect to the GaAs unit cell. No signatures of an interface reconstruction are found.

Figure 4 shows the CTR scans of sample 2. The Fe_3Si film of sample 2 contains 22.55% Si, i.e., it is nearly stoichiometric with a small deficit of Si. The fundamental 022 and 004 reflections are similar to those of sample 1, as expected. A large amplitude of the thickness oscillations in the 002 reflection and weak contrast in the 111 reflection indicates that the disorder mainly involves the order parameter α. The simultaneous fit of all experimental curves gives $\alpha=0.25$ and $\beta=0.28$ with an accuracy of ±0.05. Thus, sample 2 still shows some long-range order with considerable disorder. In this case about 25% of the Si atoms migrate into the

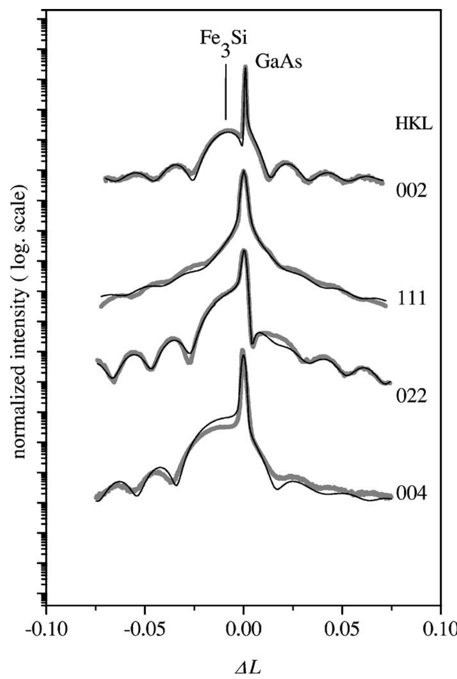

FIG. 4. Measured (thicker gray lines) and fitted (fine black lines) CTRs of sample 2 near different reciprocal lattice points. The sample is nearly stoichiometric with a slight excess of Fe. Long-range order is found as well. In contrast to sample 1, the misfit is of opposite sign, and the Si atoms migrate to all the Fe sublattices.

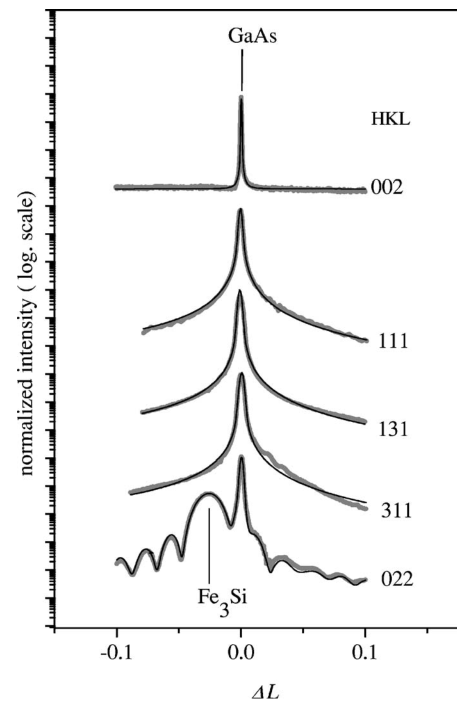

FIG. 5. Measured (thicker gray lines) and fitted (fine black lines) CTRs of sample 3 near different reciprocal lattice points. The sample is nonstoichiometric and exhibits a highly disordered structure.

Fe(B) sublattice, whereas 28% of the Si atoms migrate into the Fe(A,C) sublattices.

Figure 5 shows analogous scans of sample 3. The film contains only 16.5% Si, i.e., it is highly nonstoichiometric. The fundamental reflection 022 shows the layer peak with the adjacent thickness oscillations. All the measured superlattice reflections (002, 111, 131, and 311) of the layer vanish and only the GaAs substrate peaks remain. The fits to the experimental curves give α=0.25 and β=0.5, i.e., a complete intermixing of Fe and Si in the sublattices. The film does not show any long-range order.

Thus, the long-range order in Fe_3Si epitaxial layers strongly depends on their stoichiometry. Near stoichiometry the layers are ordered. It is important to note that the almost complete long-range order is observed without additional thermal treatment, which is usually required for the preparation of bulk samples. The slight remaining disorder may be due to the relatively low growth temperature, which has been chosen to avoid the possible intermixing of Fe and/or Si with Ga and/or As at the ferromagnet/semiconductor interface. Figure 6 illustrates the resistivity R_S of several Fe_3Si films measured at 77 K as a function of the composition. The parameter x is the deviation from stoichiometric composition. Samples investigated in the present work by grazing incidence diffraction are marked by full circles. The ordered Fe_3Si films (samples 1 and 2) have a lower resistivity R_S than the fully disordered film (see also Table I). Sample 1, which exhibits the highest order, has the smallest R_S, indicating that the alloy scattering is indeed an important factor.

V. SUMMARY

In conclusion, we analyzed MBE-grown Fe_3Si films on GaAs using grazing incidence x-ray diffraction. We characterized the relative positions of the film and the substrate lattices as well as the long-range order in films with different stoichiometry. The Fe(A) atoms are positioned above the Ga atoms, as shown in Fig. 1. The Fe_3Si lattice is shifted with

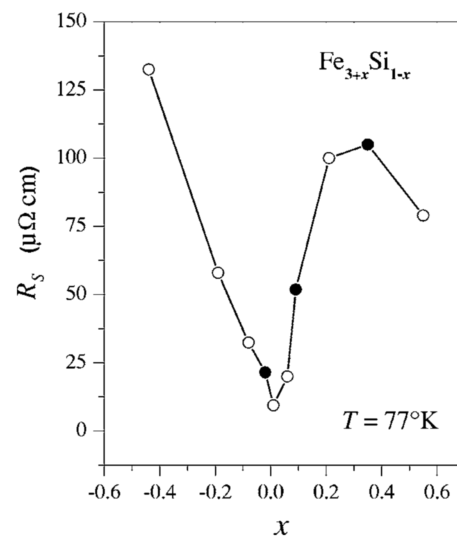

FIG. 6. Resistivity R_S of several Fe_3Si films measured at 77 K as a function of the deviation x from stoichiometric composition. The three samples investigated by grazing incidence diffraction are marked by full circles.

respect to the GaAs lattice by 0.1 ± 0.04 Å normal to and away from the interface. Long-range order is observed in the nearly stoichiometric as-grown films without additional thermal treatment, which seems to be required for the preparation of bulk samples. A slight deficit of Fe in the epitaxial Fe_3Si layer leads to the intermixing of Si and Fe from the Fe(A,C) sites. A small excess of Fe gives rise to the intermixing of Si and Fe on all the Fe sublattices. Better long-range order in the Fe_3Si films leads to lower resistivity R_S.

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