Interlayer exchange coupling, crystalline and magnetic structure in Fe/CsCl–FeSi multilayers grown by molecular beam epitaxy

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Crystalline and magnetic structure as well as the interlayer exchange coupling in MBE grown Fe/FeSi multilayers are investigated. From conversion electron Mössbauer spectroscopy and ion beam channeling measurements the spacer FeSi material is found to be stabilized in a crystalline metastable metallic FeSi phase with the CsCl structure. Strong non-oscillatory interlayer exchange coupling is identified with magnetometry and synchrotron Mössbauer reflectometry. From the fits of the time spectrum and the resonant θ–2θ scans a model for the sublayer magnetization of the multilayer is deduced.

Keywords: magnetic films and multilayers

1. Introduction

Since the discovery of the antiferromagnetic (AF) coupling between two Fe layers separated by a Cr layer by Grünberg [1], there has been a great interest in the exchange interaction between ferromagnetic (FM) layers separated by nonmagnetic spacer materials. Oscillatory interlayer exchange coupling in magnetic metallic multilayers has been observed in a wide variety of metallic materials [2]. The orientation of the magnetization of neighboring magnetic layers is pointing parallel or antiparallel depending on the thickness of the spacer material. The period of the oscillatory coupling has been predicted theoretically from both total energy calculations [3] and model calculations based on a RKKY mechanism [4]. These relate the period of the observed oscillations to external spanning vectors of the Fermi surface of the spacer material. This is able to predict both short (2–3 monolayers) and long period of oscillations. While the interlayer coupling is usually oscillating with the spacer layer thickness for metallic spacer layers, other types of coupling have been suggested for nonmetallic spacers.

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Exponential dependence of the coupling strength on the spacer thickness was predicted by Slonczewski [6] for coupling through a tunneling barrier, by Bruno et al. [4] for insulating and semiconducting spacer materials and by Shi et al. [5] for the Kondo insulator ε-FeSi.

The first experiments on interlayer exchange coupling through nonmetallic spacer layer were performed by Toscano et al. on Fe layers separated by amorphous Si deposited at 40 K [7]. In contrast to the case of metallic spacer layers the coupling was found to increase with the temperature. Experiments were further reported by Mattson et al. on Fe/FeSi and Fe/Si multilayers prepared by sputtering [8]. They found suppression of the AF coupling on cooling and reported that the coupling could be restored by illuminating with a laser. A key issue in the above mentioned studies is the knowledge of the electronic structure of the spacer which was claimed to be a semiconducting amorphous Si or an ε-FeSi phase. The failure to detect oscillations in the coupling of sputtered Fe/Si multilayers was attributed to the amorphous structure of the Si for large thickness [9,10]. In contrast, recent experiments by de Vries et al. prove an exponential dependence of the strength of the interlayer coupling in Fe/FeSi/Fe sandwiches grown by solid phase epitaxy in an MBE [11]. This effect was attributed to the presence of an ordered CsCl type $Fe_{0.5}Si_{0.5}$ alloy spacer material. Band structure calculations of the CsCl type FeSi phase show a peak in the density of states just above the Fermi level [12] and this supports the exponential dependence of the strength of the coupling on the spacer layer thickness. Fullerton et al. suggested that magnetization loops of coupled Fe/Si multilayers can be analyzed using a phenomenological approach wich allows for bilinear and biquadratic coupling and found that a strong increase of the biquadratic coupling constant J_2 with decreasing temperatures reproduces the increase in the remanence of the magnetization loops when the temperature is decreased. Several authors have pointed out that the degree of AF alignment and the strength of the coupling are dependent on the position in the multilayer [9,10].

The above discussion shows the need for a method which combines some depth selectivity with the capability of determining the relative magnetization directions of buried layers. Here we have used the recently developed synchrotron Mössbauer reflectometry (SMR) to determine the microscopic magnetic properties of Fe/FeSi multilayers. SMR utilizes resonant scattering of synchrotron radiation for angles of grazing incidence and combines the technique of θ–2θ X-ray diffraction and the measurement of the hyperfine interaction in the form of time domain quantum beats. Just as in polarized neutron reflectometry SMR gives, e.g., information on the alignment of the magnetization of the Fe layers in a magnetic multilayer. It is complementary to classical X-ray and neutron diffraction since it is sensitive to the specific hyperfine parameters of the components of the multilayer. The first experiments of resonant scattering of synchrotron radiation on a nuclear multilayer were performed by Chumakov et al. on ^{57}Fe/Sc/^{56}Fe/Sc [13] and on ^{57}Fe/Cr multilayers by Toellner et al. [14]. In both experiments one observed the possibility to separate the pure nuclear reflection from the electronic reflection of the multilayer structure at the resonant energy of 14.41 keV

which was pointed out to be of interest for monochromatization of synchrotron radiation at the μeV level. In the present work we further explore the role of the structure of the iron silicide spacer material and its temperature dependent electronic properties on the interlayer exchange coupling in Fe/FeSi multilayers. We find that an epitaxial iron silicide with a CsCl structure which is not stable in bulk can be formed during MBE growth of Fe/FeSi multilayers. It is not straightforward to examine the electronic properties of this metastable silicide phase when multilayered with Fe. The Fe layers have much higher conductivity than the silicide and this will mask electronic peculiarities of the silicide material. Therefore, metastable CsCl–FeSi layers were grown epitaxially on Si (111), which allows us to investigate their structural and electronic properties in detail. We will discuss the formation of this cubic Fe silicide phase by codeposition of Fe and Si on a suitable substrate or by annealing of an Fe thin film on Si.

2. Experimental procedure

(111) oriented FeSi films, (001) and (110) oriented Fe/FeSi multilayers were grown by molecular beam epitaxy (MBE) on Si (111), MgO (001) and Zerodur glass. Enriched ^{57}Fe was evaporated from a thermal Knudsen cell at a temperature of 1300°C. ^{57}Fe was incorporated either in the FeSi spacer or in the Fe layers of the multilayer. Natural Fe and Si were evaporated from two electron beam guns which were stabilized with a homemade feedback to a Baltzers mass spectrometer. This is able to codeposit Fe and Si in stoichiometric 1 : 1 ratio with a stability of the evaporation rate <3%.

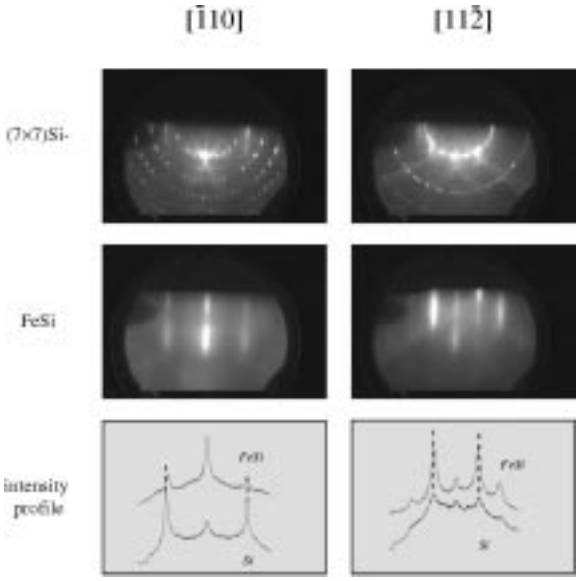

Figure 1. RHEED pattern of (7 × 7) reconstructed Si (111) substrate and 720 Å thick epitaxial CsCl–FeSi films. The FeSi film is relaxed towards its equilibrium lattice parameter (2.77 Å).

The Si substrates were first etched in HF and subsequently annealed in two steps at 350 and 850°C. The remaining native SiO_2 was removed at this temperature by exposing the Si substrate to a low Si flux (0.1 Å/s). A 1000 Å Si buffer layer was then grown at 650°C and annealed at 750°C after growth to improve the smoothness of the surface. Using this procedure the Si surface shows a clear (7×7) reconstruction (see figure 1) and is atomically smooth as evidenced by in situ scanning tunnel microscopy measurements. The MgO (001) and Zerodur glass substrates were washed in isopropanol and annealed to 600°C prior to the growth. The structure of the layers was investigated by reflection high energy electron diffraction and by ion beam channeling. The electrical transport and magnetization measurements were performed in an Oxford Instruments continuous flow cryostat equipped with a vibrating sample magnetometer and a four-point vanderpauw probe.

3. Stabilization and structural properties of metastable CsCl–FeSi in Fe/FeSi multilayers

In the FeSi phase diagram, only two semiconductors appear at room temperature: Si and β-$FeSi_2$, a semiconductor which can be grown epitaxially on both Si (100) and Si (111). From both band structure calculations and experimental band gap determinations one finds that β-$FeSi_2$ has a direct gap of 0.8 eV [16]. The ε-FeSi phase is metallic at ambient temperatures but at low temperatures semiconducting properties (minigap of 0.05 eV) have been reported [17]. Although these materials seem to be appealing to study coupling phenomena, in the thermodynamic equilibrium the bilayer systems Fe/Si, Fe/β-$FeSi_2$ or Fe/ε-FeSi are not stable at ambient temperatures. It seems, therefore, a severe challenge to form a layered system composed of Fe layers separated by one of these semiconductors. In contrast to systems with very little intermixing, the growth of Fe–Si compounds couples alloying and epitaxy effects. In principle, MBE is a very powerful technique to form structures out of thermodynamic equilibrium. As a result, epitaxial growth of Fe–Si compounds has led to the discovery of several metastable silicides. The most relevant phase for the multilayers discussed below is FeSi with the CsCl lattice structure, a metastable compound which was first stabilized on Si (111) up to several tens of nm thickness [18]. The CsCl phase can be prepared with various silicon concentrations (Fe_1Si_{1+x} with $0 < x < 1$). The silicon atoms substitute the Fe atoms and the lattice gradually transforms from a CsCl–FeSi into the CaF_2 type $FeSi_2$ lattice. For Fe concentrations larger than 50% the CsCl–FeSi transforms first into Fe_3Si with DO_3 structure and finally into pure bcc Fe. Cubic CsCl–FeSi films can be stabilized essentially by two distinct methods. If a thin Fe layer is deposited on Si (111) and subsequently annealed, a gradual transformation from Fe with some intermixed interface region to a silicide characterized by a single line Mössbauer component is observed. The single line component has an isomer shift of 0.26 mm/s (all isomer shifts are expressed with respect to α-Fe at room temperature) and is characteristic of CsCl–FeSi. Upon increasing the annealing temperature, this cubic silicide transforms either directly to the semiconducting β-$FeSi_2$ for the thinnest

layers ($d < 15$ Å) studied and to the ε-FeSi phase for thicker layers. The ordering of the CsCl lattice in such annealed Fe/Si (111) films is far from perfect as evidenced by the large linewidth of 0.8 mm/s. CsCl–FeSi films with much better ordering can be obtained by codepositing Fe and Si in a stoichiometric 1 : 1 ratio on a Si (111) substrate. In figure 1 is shown the RHEED pattern of such a 720 Å thick film. The RHEED pattern evidences the epitaxial growth of a (1×1) cubic CsCl film. From the position of the RHEED streaks one can determine that the FeSi film is slightly relaxed to its equilibrium lattice parameters of 2.77 Å. Attempts to grow this FeSi films in a (001) orientation on Si (100) failed. This is probably due to the larger interfacial energy for the epitaxy of CsCl–FeSi on Si (100). On the other hand, this argument is not valid for (001) CsCl–FeSi films on bcc Fe (100) since the CsCl–FeSi film can be seen as a natural continuation of the bcc structure of Fe. Epitaxial growth of CsCl–FeSi on Fe and in FeSi multilayers is thus possible due to the similarity in crystal structure and a small lattice mismatch [19]. The lattice mismatch between Fe ($a = 2.866$ Å) and CsCl–FeSi ($a = 2.77$ Å) is -3% [18].

In figure 2 are shown the CEMS measurements of three Fe(26 Å)/^{57}FeSi(15Å) multilayers which were grown simultaneously onto three different substrates, viz. MgO (001), Si (111) and Zerodur glass. One clearly notices a single line Mössbauer

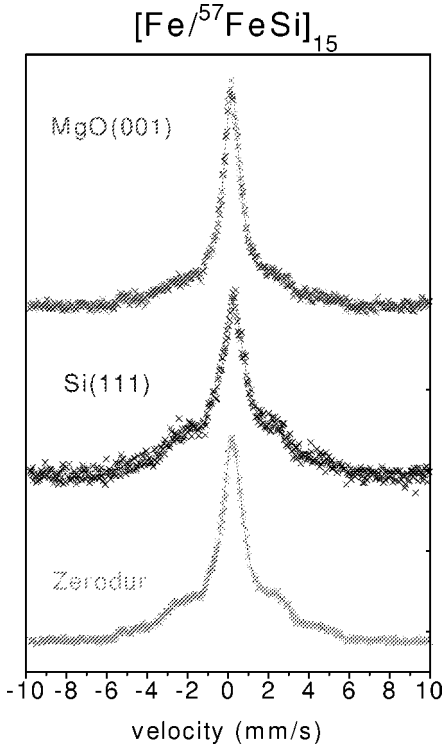

Figure 2. CEMS spectra of ^{57}Fe/FeSi multilayers on MgO (001), Si (111) and Zerodur. The single line component indicates that the spacer silicide stabilizes in the CsCl structure.

component with isomer shift equal to 0.26 mm/s which proves that the silicide phase which forms in a variety of Fe/FeSi multilayers is not the stable ε-FeSi which is characterized by a quadrupole doublet (0.5 mm/s) with the same isomer shift. The linewidth of the CsCl–FeSi phase is larger than expected for a perfectly ordered CsCl–FeSi structure. This can have two origins: first, we have previously shown that strain can increase the linewidth of epitaxially grown CsCl–FeSi films and, second, the deviation of the perfect ordering due, e.g., to off stoichiometry, as observed during the annealing of thin Fe films on Si can also lead to broader line. The last explanation is most probable since the linewidth is the narrowest for the Fe/FeSi multilayers grown on MgO (001). These layers have the best crystalline quality as seen, e.g., by ion beam channeling measurements [20]. It is remarkable that the silicide spacer for the samples grown on Zerodur glass also stabilizes in the metastable CsCl structure. Somehow the presence of (110) textured Fe as a buffer between the Zerodur glass and the silicide film is sufficient to stabilize the CsCl structure.

4. Magnetization and resistivity measurements

The temperature dependence of the resistivity is fitted with a Bloch–Grüneisen relation to which a Kondo term with an $\ln T$ dependence is added. We have previously shown that the single line component of such CsCl–FeSi films can show strong broadening at temperatures below this resistivity minimum. Both observations seem to indicate that CsCl–FeSi films behave intrinsically as a Kondo lattice system but further measurements of the magnetic susceptibility are necessary to draw some conclusions. It is not clear from the present measurements how the position of the resistivity minimum is affected by the thickness of the spacer nor by the presence of neighboring Fe layers but, in principle, in the regime where the resistance shows an $\ln T$ behavior, an inverse temperature dependence of the strength of the interlayer exchange coupling

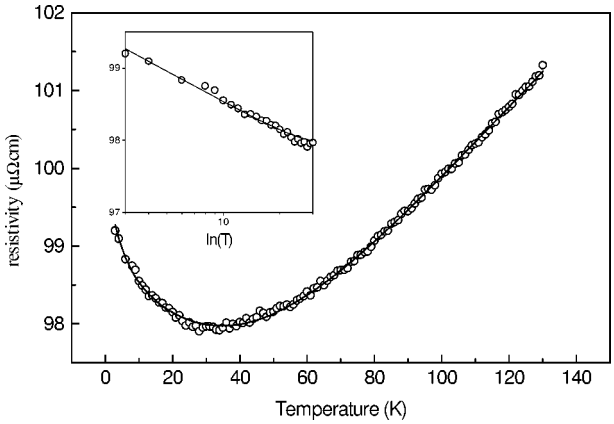

Figure 3. Temperature dependence of the resistivity of CsCl–FeSi. It is characteristic for a metal. The inset shows an $\ln T$ behavior below 30 K.

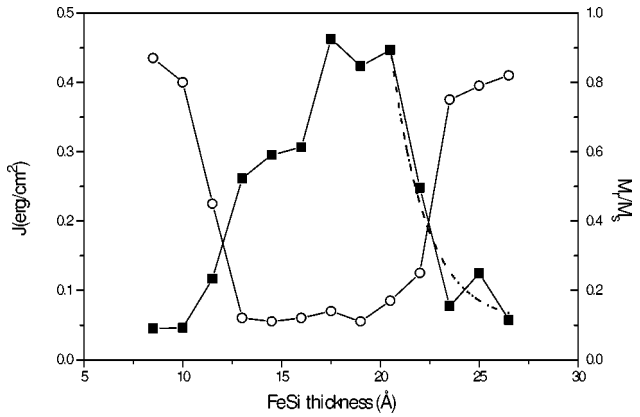

Figure 4. Bilinear coupling constant J (solid squares) and M_r/M_s (open circles) as a function of the spacer thickness t_{FeSi} for Fe/FeSi multilayers grown epitaxially on Si (111).

as predicted for semiconducting and insulating spacer materials cannot be excluded. For Fe/FeSi multilayer grown on Si (111) the strength of the interlayer coupling was determined from the saturation field. Very strong bilinear coupling is observed with a maximum of about 0.45 erg/cm^2 (see figure 4; the bilinear coupling constant J was evaluated with the provision of a vanishing biquadratic coupling). The rapid decay of the strength of the coupling is fitted with an exponential thickness dependence for silicide thickness larger than 20 Å (dotted line in figure 4) [11]:

$$J \sim \exp(-t_{FeSi}/\lambda_s).$$

This results in a value for the length of the exponential decay equal to 1.77 Å.

5. Synchrotron Mössbauer reflectometry

Grazing incidence prompt and delayed time integral θ–2θ X-ray diffraction measurements in a Bragg–Brentano setup and time spectra at angles where delayed intensity could be detected were measured at various temperatures on a [^{57}Fe(25.5 Å)/Fe(15.7 Å)]$_{10}$ multilayer grown on Zerodur glass at the ID18 nuclear resonance beamline of the ESRF [15] using the 14.413 keV ($\lambda = 0.860$ Å) resonant radiation of ^{57}Fe. Both time integral and time differential SMR measurements were performed to confirm the AF alignment of the Fe layers. The prompt and delayed time integral reflectivity of the multilayer is shown in figure 5 for various polarizing fields ($0 < B_{ext} < 0.95$ T) applied perpendicular to the scattering plane.

In the delayed reflectivity a Bragg reflection is observed at 6.28 mrad which corresponds to a periodicity twice that of the multilayer and results from the AF alignment of the Fe layers. The AF Bragg reflection gradually decreases with increasing external field which indicates the increase of the FM component of the Fe layers when their magnetization is rotating towards the direction of the external magnetic field. In a weak

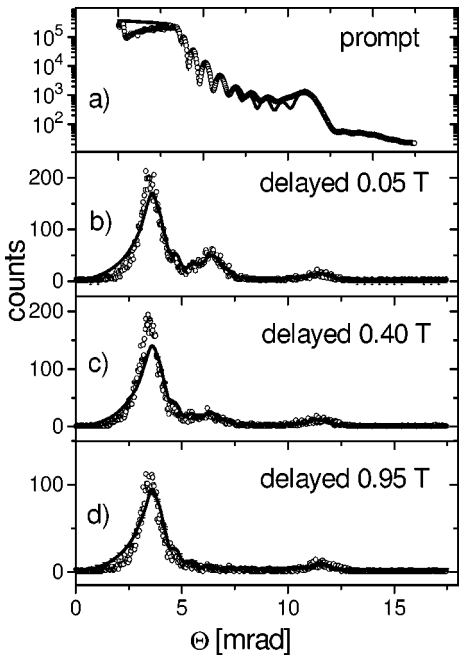

Figure 5. Prompt (a) and time integral (10–300 ns) delayed Θ–2Θ reflectivity scans of Zerodur/[^{57}Fe/FeSi]$_{10}$ multilayer in various external magnetic fields (b)–(d). The fit curves represent the model layer and magnetic structure described in the text.

external field of 50 mT the magnetization of the Fe layers in an AF coupled multilayer is expected to align perpendicular to the external field and in pairs antiparallel to each other. Time differential SMR spectra, especially those measured at electronically forbidden reflexes turn out to be very sensitive to the alignment of sublayer magnetizations. To evaluate the prompt reflectivity, delayed reflectivity and time spectra at grazing incidence, the program EFFINO [21] based on an optical approach by Deák et al. [22] was utilized. Each nonresonant layer is characterized by its layer thickness as well as real and imaginary part of the complex (electronic) index of refraction. Nuclear resonant layers are further described by p_{hf} hyperfine parameters per non-equivalent nuclear resonant sites in the layer. In general, $p_{\mathrm{hf}} = 12$, for the zero field gradient case of ^{57}Fe/FeSi, $p_{\mathrm{hf}} = 7$ per site (f-factor, isomer shift, spectral width, magnitude and polar angles of magnetic hyperfine field). The total intensity, the background, an additive time shift and an effective interface/surface roughness parameter of the multilayer were also fitted. The polarization of the incident synchrotron radiation was assumed to be 100%. From the fits of the time spectra taken at various angles of incident radiation (a detailed analysis is of the SMR time spectra as function of external field will be published elsewhere [23]) and fits of the delayed θ–2θ profiles a model structure (see figure 6) for the magnetization of the Fe layers is derived. A surprising feature of this model structure is the massive (62°) misalignment of the top AF layers with respect to the expected orientation perpendicular to the external magnetic field. In fact, within

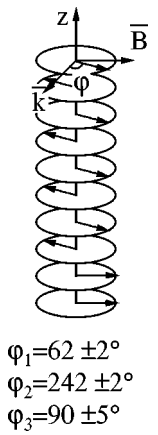

Figure 6. Magnetic structure of a Zerodur/[^{57}Fe/FeSi]$_{10}$ multilayer in an external field of $B = 50$ mT. φ_1, φ_2 and φ_3 are the AF sublayer magnetization directions of the 8 top Fe layers and the FM sublayer magnetizations of the 2 bottom Fe layers, respectively.

this scheme the two Fe layers close to the interface are found to be FM coupled while the 8 top Fe layers are AF coupled. This is probably due to the roughness of the first Fe layer which results in the formation of pinholes in the first FeSi spacer layer. Magnetooptical Kerr effect measurements on Fe/FeSi/Fe trilayers grown on MgO (001) at room temperature (not shown) also indicate an FM arrangement of the Fe layers. For trilayers grown at 150°C AF coupling can be observed. A higher growth temperature results in a smoother Fe buffer layers and allows AF coupling from the very first layers of the multilayer structure. Similar observation was made previously by Chaiken et al. [10]. Upon cooling in a small external field to 16 K a strong increase in the FM contribution to the coupling was observed. This results in a strong reduction of the intensity of the AF Bragg peak in the SMR θ–2θ-scans. A detailed analysis [23] of the time spectra, however, seems to indicate that a small AF component is still present at 16 K.

6. Conclusions

In this work we have shown using CEMS that metastable CsCl–FeSi films can be stabilized in thin film form on Si and in Fe/FeSi multilayers. The temperature dependence of the resistivity of CsCl–FeSi films indicates that it is a metal. At low temperature a shallow minimum with a ln(T) behavior, suggestive of a Kondo lattice behavior, is observed. The sensitivity of SMR time spectra and delayed reflectivity curves to the AF coupling of a [^{57}Fe(25.5 Å)/FeSi(15.7 Å)]$_{10}$ multilayer grown on Zerodur were utilized to establish a model where the coupling parameters depend on the position in the multilayer. Due to roughness the first two Fe layers are FM coupled while the top 8 Fe layers are AF coupled.

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