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Conversion electron Mössbauer spectroscopy of epitaxial $Co_2Cr_{0.6}Fe_{0.4}Al$ thin films

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Heusler half-metals are promising for spintronic applications. Epitaxial thin films of the exemplar compound $Co_2Cr_{0.6}Fe_{0.4}Al$ (CCFA) were investigated using conversion electron Mössbauer spectroscopy to clarify the factors influencing the spin polarization. CCFA films were deposited by rf magnetron sputtering on MgO substrates with and without an Fe buffer layer. Annealing improves their crystallographic order, causes the diffusion of Fe atoms from the Fe buffer layer into the CCFA, and favors the Co–Fe disorder. The listed factors are possible reasons for the increase and subsequent reduction of the tunneling magnetoresistance in CCFA thin films observable across the annealing temperature range. © *2008 American Institute of Physics*. [DOI: 10.1063/1.2952760]

The Heusler alloy $Co_2Cr_{0.6}Fe_{0.4}Al$ (CCFA) attracts large interest as a potential half-metallic ferromagnet.[1–6] In this compound a high tunneling magnetoresistance (TMR) is expected as a result of a high spin polarization at the Fermi level. With CCFA as one electrode, 317% TMR effect at 4.2 K was recorded using a MgO barrier.[4]

For the spin polarization the degree of structural disorder of Heusler compounds is an important factor. Many Heusler compounds with the stoichiometric composition X_2YZ (where X and Y are transition metals, and Z denotes an sp element) are ordered in the $L2_1$ structure. The preference of thin CCFA films to grow in the $B2$ structure with disorder on the Y-Z positions is a known fact.[7–9] Calculations predict that $B2$ type of disorder has a minor effect on the spin polarization, whereas disorder on the X sites strongly reduces the spin polarization.[10]

Local disorder as well as crystallographic quality of thin films can be influenced by annealing. The effect of the annealing temperature on the TMR ratio of junctions with CCFA electrodes deposited on Fe buffer layers on MgO substrates was studied in Ref. 11. It was found that the TMR increases abruptly for annealing temperatures above 500 °C. However, a further increase in the annealing temperature above 550 °C results in an equally abrupt reduction in the TMR. Since x-ray and electron beam diffraction indicate an improved crystallographic quality of the CCFA thin films after annealing at 600 °C, the reason for the TMR reduction remains to be clarified. To explain this observation and to get insight into the structural and magnetic properties of epitaxial CCFA thin films, we carried out ^{57}Fe conversion electron Mössbauer spectroscopy (CEMS) and x-ray diffraction studies.

Epitaxial CCFA films with an average thickness of 80 nm were deposited by rf sputtering on MgO(100) substrates with and without 10 nm Fe(100) buffer layer at room temperature.[12,13] Afterward, every sample of both types was annealed at specific temperatures in the temperature range between 450 and 650 °C. Finally, to prevent oxidation, a 4 nm Al cap layer was deposited on the top of CCFA at room temperature. X-ray diffraction revealed a CCFA with a $B2$ type structure.

CEMS spectra of as-deposited samples with an Fe buffer layer show distinguishable subspectra originating from the CCFA and the α-Fe buffer layer [Fig. 1(a)]. The former subspectrum can be described as a broad distribution due to the reduced crystalline quality of the as-deposited CCFA. The average hyperfine magnetic field H_{hf} on Fe atoms in the prephase is 248(1) kOe. Annealing narrows the lines of the

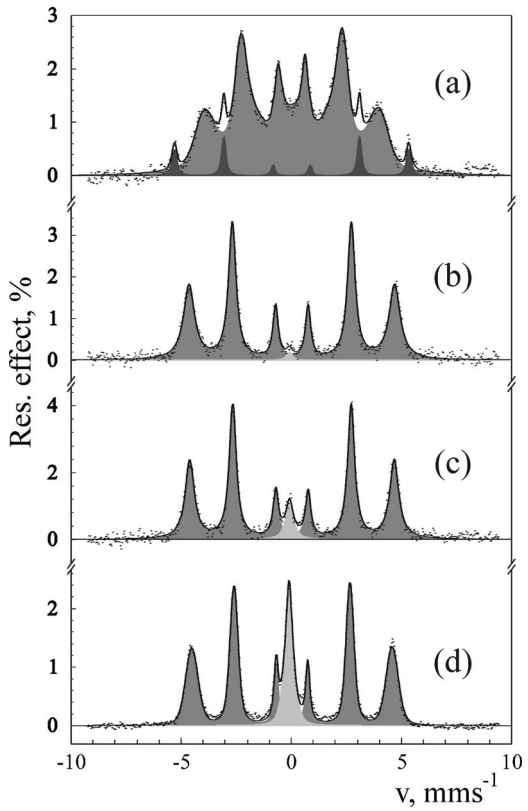

FIG. 1. ^{57}Fe CEMS spectra of 100 nm CCFA thin films (gray) deposited on MgO substrates with a 10 nm α-Fe buffer layer (dark gray) (a) without annealing; spectra of 100 nm CCFA thin films (gray) deposited on MgO substrates without a buffer layer annealed at (b) 450 °C, (c) 550 °C, and (d) 600 °C. The central peak (light gray) corresponds to Fe atoms occupying Co sites.

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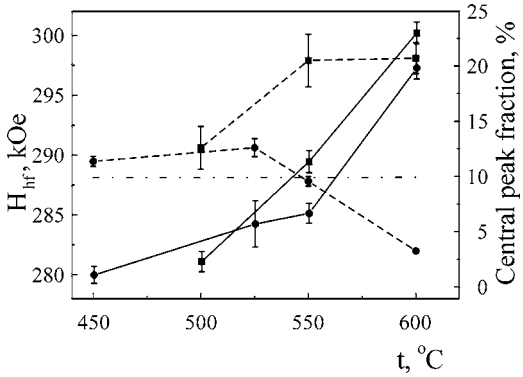

FIG. 2. Hyperfine magnetic fields (dashed lines) on Fe sites and central peak fraction (solid lines) in CCFA thin films as a function of the annealing temperature. The dot-dashed line corresponds to the CCFA target material. Filled circles and squares relate to samples without and with a buffer layer, respectively. The lines are guides for the eye.

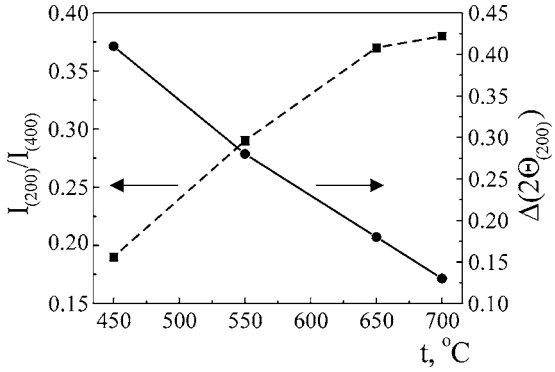

FIG. 3. Intensity ratio $I_{(200)}/I_{(400)}$ (dashed line) and width Δ of the x-ray diffraction (200)-peak (solid line) vs annealing temperature. The CCFA thin films are deposited on MgO substrates without a buffer layer. The lines are guides for the eye.

CCFA sextet spectrum and leads to an increase in H_{hf} up to the typical value of bulk samples of ≅ 290 kOe. Figures 1(b)–1(d) present the spectra of thin films without Fe buffer after annealing at 450, 550, and 600 °C, respectively. Spectra of samples with a buffer layer have broader lines and look similar, except for the presence of an α-Fe subspectrum. Its intensity diminishes and the H_{hf} is reduced with an increase in the annealing temperature. The subspectrum of a buffer layer disappears with annealing above 600 °C. This result indicates a diffusion of Fe from the buffer layer into the CCFA thin film (in agreement with Ref. 13), and apparently the related diffusion of Cr atoms from the CCFA thin film into the Fe buffer layer also occurs. From the relative intensity of the Mössbauer lines follows that the orientation of the magnetic moment of both types of films is in plane.

Experimental values of isomer shifts (δ) of CCFA sextets are close to 0.10(3) mm s^{-1}. The increase in the annealing temperature causes the appearance of a central quasiparamagnetic peak with δ=−0.10(3) mm s^{-1} in the Mössbauer spectra of both types of samples [Figs. 1(b)–1(d)]. The fraction of this peak increases with the annealing temperature for both types of samples (Fig. 2). For samples with and without Fe buffer a pronounced rise in the central peak intensity is observed above 500 and 550 °C, respectively.

Site assignment of Fe atoms in Mössbauer spectra is based on the composition of their local surrounding in the *B*2 structure. A magnetic sextet [Figs. 1(b)–1(d)] can be attributed to Fe atoms in *Y* positions with a first coordination sphere comprising eight Co atoms. The central peak stems from Fe in a nonmagnetic surrounding. The Co site possesses such a surrounding consisting of eight units with an average composition of $Cr_{0.6}Fe_{0.4}Al$. Consequently, one has to conclude that the central peak with δ=−0.10(3) mm s^{-1} should be assigned to Fe substituting Co atoms in the *B*2 structure of CCFA. The presence of Cr atoms on nearest neighbor sites leads to a negative isomer shift, which tends to a value of −0.154 mm s^{-1} for Fe in a Cr matrix.[14] The spectra of films with and without Fe buffer layer annealed at 450 °C indicate almost no Fe on Co sites [Fig. 1(b)]. Annealing at 550 °C increases the degree of the antisite Co–Fe disorder [Fig. 1(c)]. The fractions of Fe on Co site in Mössbauer spectra of films with and without Fe buffer layer treated at 600 °C are close to 20% (Fig. 2). From CEMS experiment follows that 1% and 4% of Fe atoms occupy Co sites after annealing of a thin film without an Fe buffer layer at 550 and 600 °C, respectively.

The hyperfine magnetic fields on Fe sites in CCFA thin films as a function of the annealing temperature are presented in Fig. 2. For samples without Fe buffer layer H_{hf} decreases with increasing annealing temperature above 525 °C, presumably because of the enhancement of a Co–Fe disorder. For samples with an Fe buffer layer, a diffusion of Fe atoms from the buffer layer into CCFA causes an increase in H_{hf}. Above 550 °C, H_{hf} does not rise anymore due to the above mentioned Co–Fe disorder process.

A complete disorder on all sites (*A*2 structure) should result in the disappearance of the (200) x-ray diffraction peak of CCFA. Measurements of the intensity ratios of the (200) and (400) diffraction peaks allow the quantification of the degree of disorder on the *X* site of the Heusler structure. Our samples clearly show an increasing scattering intensity ratio of $I_{(200)}/I_{(400)}$ with increasing annealing temperature, which saturates above 650 °C (Fig. 3). This observation corresponds to a monotonous increase in crystallographic order on the Co site of CCFA and is in seeming disagreement with the Mössbauer experiment. However, the sensitivity of x-ray diffraction depends strongly on the difference of the number of electrons of the contributing atoms. Since this difference amounts only to one electron for Fe and Co, possible Co–Fe disorder is invisible for x-ray diffraction. Continuous structure improvement due to annealing also follows from the analysis of the width of the specular x-ray peaks (Θ/2Θ-scans) using the Debye–Scherrer formula. With increasing annealing temperature, the peaks become narrower with a minimum width Δ of the (200)-peak of 0.13° (Fig. 3). This minimum width corresponds to a correlation length of ≈66 nm, which is a substantial fraction of the thicknesses of the films under study.

X-ray and CEMS studies demonstrate that annealing of CCFA thin films (i) monotonously improves their crystallographic order in the temperature range of 450–700 °C, (ii) causes the diffusion of Fe atoms from the α-Fe buffer layer into the CCFA, changing its composition, and (iii) favors the antisite Co–Fe disorder. Additionally, scanning tunneling microscopy investigations show an improved surface morphology. The process of structure evolution of CCFA during annealing has a continuous character; therefore the Fe content and disorder effects could be the main factors determining the TMR maximum in thin film with Fe buffer after anneal-

ing at 550 °C. The enrichment of CCFA with Fe diffusing from the buffer layer modifies the structure of the electronic bands and shifts the Fermi level across the gap in the minority of states due to doping with electrons. The location of the Fermi level relative to the gap affects the spin polarization. The above listed factors [(i)–(iii)] are possible reasons of an increase and a subsequent reduction in the TMR of CCFA thin films with Fe buffer layer observable across the 450–600 °C annealing temperature range.[11] Apparently, the antisite Co–Fe disorder caused by annealing could be considered as the main universal factor influencing the magnetoresistive properties of CCFA thin films.

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