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Metastable tetragonal structure of $Fe_{100-x}Ga_x$ epitaxial thin films on ZnSe/GaAs(001) substrate

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We investigated by x-ray diffraction the Ga concentration dependences of the structural properties of $Fe_{100-x}Ga_x$ (galfenol) thin films grown on a ZnSe/GaAs(001) substrate, a material known for its high magnetostriction. By molecular beam epitaxy (MBE) we grew a series of (001)-oriented layers without in-plane misorientation, ranging from pure Fe up to $x = 29.4\%$ Ga. We find a strong Ga-induced tetragonal distortion that conserves the pristine Fe in-plane lattice parameters for all Ga compositions. Supported by theoretical predictions [R. Wu, J. Appl. Phys. **91**, 7358 (2002)], we attribute this unusual tetragonal distortion to short-range ordering of Ga-Ga pairs along the [001]-growth direction. The low-temperature and out-of-equilibrium MBE growth regime tends to stabilize a strong deformed tetragonal phase (up to $c/a \sim 1.05$ for $x \sim 29\%$). This tetragonal structure is fully released by postgrowth annealing.

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Galfenol alloys, $Fe_{100-x}Ga_x$, exhibit enhanced magnetostriction approaching 400 ppm when $x = 20\%$ at room temperature (tenfold that of pristine Fe).[1,2] When Ga is introduced into the bcc α-Fe phase, it induces different crystal structures, including chemically disordered bcc-derived A2, ordered phases such as DO_3 (Fe_3Ga), B2 (FeGa), and fcc LI_2 (Fe_3Ga). Intensive studies of the structural and magnetic properties of bulk Fe-Ga alloys has been carried out by many experimental methods, including Mössbauer spectroscopy[3] and neutron or x-ray diffraction.[4,5] It has been found that the size of the magnetostriction in Fe-Ga is very sensitive to Ga concentration,[6] thermal treatment, crystallographic texture, and to chemical ordering.

In this context, recent *ab initio* calculations indicate an intrinsic origin of the magnetostriction enhanced by spin-orbit interactions.[7] A huge enhancement of galfenol's magnetostrictive coefficients at low concentrations is foreseen when Ga atoms are diluted in the pristine bcc Fe structure.[8] On the other hand, when B2-like or DO_3-like Ga clusters are formed into the pristine A2 structure, strong deviations from experimental findings are foreseen.[9] These theoretical findings suggest that Ga pairing is detrimental for magnetostriction at low x values. This seems to be at odds with other models where Ga pairing is the main ingredient of the x dependence of galfenol magnetostriction.[6] It is also important to remind that other models invoke an extrinsic origin of the magnetostriction based on the field-induced rotation DO_3-DO_{22} of nanoprecipitates.[4,10]

Whatever may be the origin of the magnetostriction, Ga ordering, tetragonal distortion, a high degree of texture (preferably $\{100\}$ $\langle 001 \rangle$),[11] and strong Ga-dependent elastic constants are the main required ingredients. The control of these parameters is the necessary condition to perform crucial experiments to determine the correct magnetostriction model.

Epitaxial thin films present the required texture, $\langle 001 \rangle$ out-of-plane orientation, if grown by molecular beam epitaxy (MBE) with a judicious choice of the substrate, i.e., GaAs(001) or ZnSe/GaAs(001).[12] In this Rapid Communication, we report about the epitaxial growth of (001) $Fe_{100-x}Ga_x$ thin films on ZnSe epilayers on GaAs(001) substrate. Results show that the films' galfenol lattice parameter is Ga dependent and that the growth conditions favor very unusual Ga-induced tetragonal distortions compatible with a large softening of the elastic constants observed in magnetostrictive bulk galfenol. We also show that this architecture is unstable against thermal annealing.

$Fe_{100-x}Ga_x$ thin films were deposited by MBE on a $c(2 \times 2)$ Zn-terminated ZnSe epilayer, a prototype of the low reactive iron/semiconductor interface.[13] Details of the MBE growth of a pseudomorphic 20-nm-thick ZnSe epilayer have been previously reported.[14] Such an epilayer constitutes an efficient chemical barrier to separate galfenol from the substrate.[13] We kept the growth temperature and the alloy film thickness constant for all Ga compositions, i.e., 180 °C and 36 nm, respectively. At the end of the Fe-Ga growth, the samples were transferred from the MBE chamber to UHV-interconnected multichambers, where the film compositions were first analyzed by x-ray photoemission spectroscopy (XPS). At the end, the films were covered by a protective 3-nm gold capping layer. The Ga composition obtained by XPS was confirmed by Rutherford backscattering (RBS) and energy-dispersive x-ray spectrometry (EDX). X-ray diffraction (XRD) experiments were performed using Cu $K\alpha$ radiation in a Philips X'Pert MRD diffractometer. The crystalline phases, in-plane orientation, and lattice parameter of the films were evaluated by XRD [reciprocal space mapping (RSM): $2\theta/\omega$ radial scan versus ω rocking scan]. The results are presented in Figs. 1 and 2.

RSM results are displayed in Fig. 1. The Bragg peaks of the galfenol layers around (002), (202), and (112) for two representative Ga compositions are reported: See Figs. 1(d)–1(f) and 1(g)–1(i) for 15.6% and 29.4% Ga, respectively. Pristine Fe layer XRD data are also plotted in Figs. 1(a)–1(c).

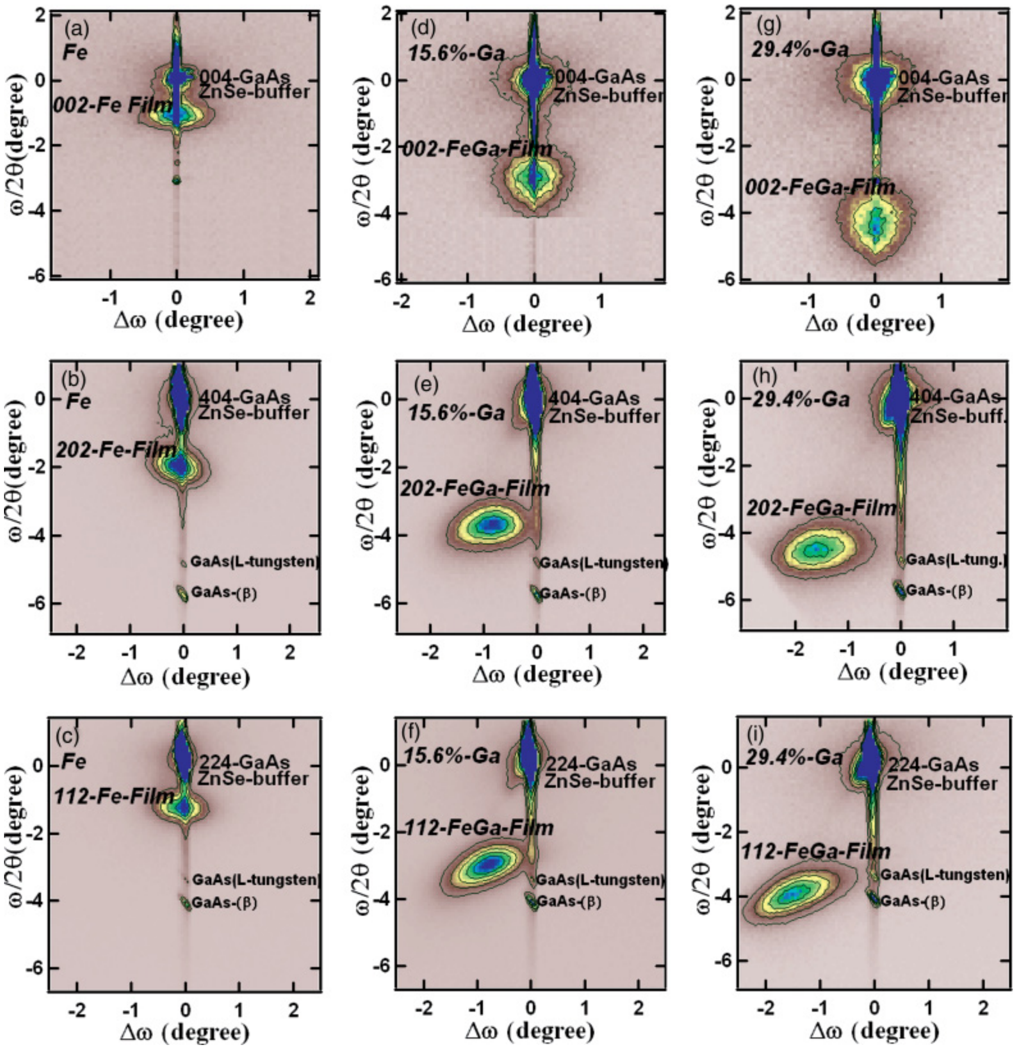

FIG. 1. (Color online) Reciprocal space mapping around the (002), (202), and (112) Bragg reflection of Fe film (a)–(c), two representative alloys film with 15.6% (d)–(f) and 29.4% Ga (g)–(h), and the associated reflections of the ZnSe/GaAs (001) substrate. The axes of $2\omega/\theta$ and $\Delta\omega$ are centered on the GaAs substrate.

Throughout this Rapid Communication, Fe-Ga diffraction peaks are indexed by adopting the bcc A2 pristine structure as a reference. We notice that the 20-nm-thick ZnSe buffers are completely strained by the substrate.[14] Figures 1(a)–1(c) attest to the high epitaxial quality of the Fe film that is (001) oriented. It very important to notice that the 36-nm-thick Fe films are fully relaxed in the bcc structure [no shift was observed along the ω axis for (202) and (112) reflections in Figs. 1(b) and 1(c)]. This is coherent with previous extended x-ray-absorption fine structure (EXAFS) experiments that indicate a full relaxation for few-nanometer-thick films.[15] The galfenol thin films will relax even faster since the lattice mismatch increases from 1.4% (pure iron) to 3.08% at $x = 29.4\%$. The $Fe_{100-x}Ga_x$ films are (001) oriented with in-plane axes parallel to those of the substrate, as attested to by reflection high-energy electron diffraction measurements and confirmed by x-ray ϕ-scan measurements (not shown).

A first inspection of the (002) peak positions of galfenol thin films [Figs. 1(d) and 1(g)] reveals that the Ga substitution induces dramatic modifications: The large 2θ shift of the peak accompanied by a huge broadening testifies to structural irregularities along the $\langle 001\rangle$ directions. As reported in Fig. 3, at approximately $x = 20\%$ the out-of-plane film lattice parameters are found to be close to $d = 0.296$ nm (full triangle-up symbols), significantly larger than the bulk values of $Fe_{80}Ga_{20}$ ($d_{\mathrm{bulk}} = 0.29$ nm, open square symbols from Ref. 3). Even more impressive is the deviation at $x = 29.4\%$ with $d = 0.302$ nm, to be compared with $d_{\mathrm{bulk}} = 0.292$ nm. Similar shifts and broadening of the (002) peaks were reported by other authors for MBE-grown Fe-Ga films on GaAs substrates without a ZnSe epilayer. The increase of the lattice parameter was not discussed, instead, the deviation of the (002) peak, up to 0.308 nm, was associated with an overestimation of the Ga content, up to 50%.[12]

Even more surprising are the Ga-induced deformations deduced from the (202) and (112) peaks, as reported in Figs. 1(e)–1(f) and 1(h) and 1(i), respectively. At each Ga content, a single diffraction peak was found, shifted along the $\Delta\omega$ direction. These results clearly indicate that the Fe-Ga film structure is tetragonally deformed. Quantitatively, in order

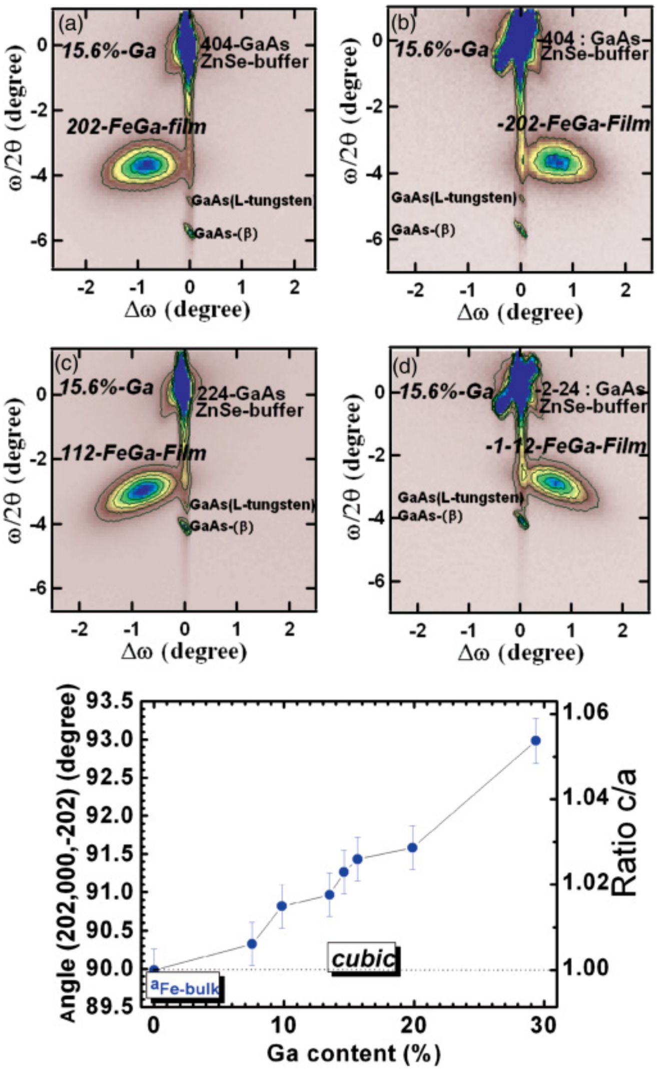

FIG. 2. (Color online) Area scans around the asymmetric (202) and (−202) (a),(b); (112) and (−1 − 12) (c),(d) Bragg peaks of an alloy film with 15.6% Ga; (e) variation in the angle [202,000, − 202] and the ratio of $c/a = \tan[202,000, -202]$ (full circles) of the alloy film as a function of the Ga content.

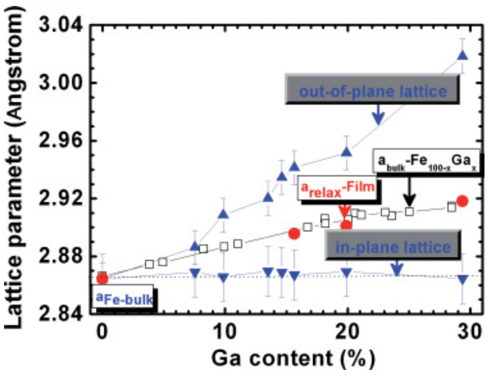

FIG. 3. (Color online) Out-of-plane (up triangles), in-plane (down triangles), and the relaxed lattice parameters (full circles) of the films vs the Ga content, as compared with the bulk lattice parameters (open squares) from Ref. 3.

to determine the c/a ratio, we have measured the angles between [202,000,−202] by an asymmetric {202} rocking curve [see Figs. 2(a) and 2(b)]. In order to visualize the tetragonal distortion, the c/a values are plotted [Fig. 2(e)] as a function of the Ga concentration: The c/a ratio varies continuously from the Fe cubic film up to 1.055 for $x = 29.4\%$. These results were double checked by measuring the angle between [112,000,−1−12] by an asymmetric {112} rocking curve [see Figs. 2(c) and 2(d)] which attests to the fact that the in-plane square symmetry is preserved. For all the probed Ga compositions, galfenol films are tetragonally distorted along the c axis (the growth direction). The in-plane lattice parameters of the Fe-Ga films were extracted from RSM measurements of (002) reflections coupled to c/a ratios. We report the out-of-plane and in-plane lattice parameters in Fig. 3 as a function of the Ga content. Surprisingly, the in-plane lattice parameter remains almost constant with Ga content. Its value is very close to pure bcc Fe and is much larger than the substrate's lattice parameter, i.e., $a_{\rm GaAs}/2 = 0.2826$ nm.

Let us assume that the thin-film elastic constants remain equal to the bulk ones reported in Table 1 of Ref. 16. We calculate the Ga dependence of lattice parameters of galfenol relaxed to the cubic structure. These relaxed lattice parameters can be calculated in the following way:

$$a_{\rm rel} = (2c_{12}a_{\text{in-plane}} + c_{11}a_{\text{out-of-plane}})/(c_{11} + 2c_{12}), \qquad (1)$$

where c_{11} and c_{12} are the bulk elastic constants. The important finding is that these relaxed values (filled circles in Fig. 3) lie on the bulk lattice parameters curve (open squares in Fig. 3). This indicates that the huge tetragonal deformation of epitaxied galfenol is compatible with the dramatic linear decrease of the shear elastic constant $c = (c_{11} - c_{12})/2$ observed in iron-gallium solid solutions.[16,17] In particular, Ga additions up to 27.2% caused a large increase in c_{12} and smaller modifications in c_{11}.[16]

Our discussion starts from the evidence that the origin of this phenomenon is not due to substrate-induced residual strain (epitaxy scenario) for the following reasons: (i) Galfenol films are too thick to be constrained by the substrate, as discussed above in the text. (ii) The lattice mismatch with the substrate increases dramatically with the Ga content since the bulk unit-cell lattice parameters are 0.2866 and 0.2916 nm for $x = 0\%$ and 29.4% Ga, respectively. Since the measured in-plane parameters do not depend on the Ga content, an epitaxy scenario would imply that residual strain increases with the lattice mismatch, which is in contrast with relaxation mechanisms of the usual epitaxy.

The scenario we propose takes inspiration from the theoretical work performed by Wu and his collaborators.[7,9] By *ab initio* calculations the authors have shown that the B2 structure experiences a tetragonal distortion. Calculated c/c_0 total energy dependence indicates that c/c_0 variations of 4% (as observed experimentally for 25% Ga) strongly lower the total energy of ~100 meV for the unit cell.[9] Similarly, B2-like Ga clusters embedded in an A2 matrix stretch to a tetragonal structure, even at low Ga concentrations ($x \sim 3\%$).[9] Equilibrium lattice constants obtained by these calculations are in very good agreement with our experimental findings: Despite the huge c-parameter variation induced by the Ga concentration (c increases by 2% when Ga varies from ∼3 to 11.7%), the in-plane lattice parameters increase by only 0.2%.

We put forward the hypothesis that during low-temperature (180 °C) MBE growth of epitaxied FeGa thin films, because of the low mobility of adatoms on the growth front, Ga pairing is favored along the [001] direction. This is coherent with an experimental finding by Ruffoni *et al.*[18] and induces the tetragonal distortion that is clearly detected at $x \sim 10\%$. This could be attributed to the local short-range ordering onset of Ga pairs that increases the c/a ratio. This structural deformation is accompanied by a broadening of (002) fundamental Bragg peaks. At $x = 15\%$, we observe the presence of a weak peak located at the (001) superlattice reflections (not shown), forbidden for the A2 structure, but compatible with DO_3 or B2 short-range-ordered phases. The presence of DO_3 phase transformation is excluded by the absence of the DO_3-characteristic [113] reflection (noted in the fcc structure with a double bcc unit cell). This confirms our scenario of nonrandom solute Ga pairs leading to the early development of the B2-like phase probably at less than 10% of Ga content. These findings are coherent with computer modeling of structural transformations by Boisse *et al.*,[19] indicating that the B2 tetragonal deformation is favored when the DO_3 phase is absent in bulk galfenol. In other words, the in-plane invariance and the out-of-plane stretching of the lattice is the genuine response to Ga-induced B2-like clusters embedded in an A2 matrix.

Another important result is that the tetragonal configuration is unstable against thermal annealing. Figures 4(a)–4(d) display the (002) and (202) mapping of the alloy film at 15.6% of Ga before and after UHV postgrowth annealing at 300 °C (the ZnSe buffer layer is stable at these temperatures[20]). Still, only one Bragg peak of the alloy film is detected. The peak position shifts toward lower 2θ values, the linewidth narrows, and $\Delta\omega$-shift lowers. Thermal annealing reduces the tetragonal distortion in the as-grown film approximately by a factor of 4. Annealed sample parameters merge to the bulk values of galfenol. Our interpretation is that thermal annealing induces a rearrangement of Ga pairs along the ⟨100⟩ directions and/or single atoms diluted in the A2 matrix, breaking the strongly anisotropic configuration discussed above, but we cannot be conclusive about the Ga distribution at low concentrations ($x < 10\%$) due to the x-ray diffraction sensitivity.

In summary, a structural analysis indicates that the lattice parameter of FeGa epilayers on ZnSe/GaAs(001) substrates are strongly dependent on the Ga content. We detected a huge Ga-induced tetragonal distortion that is compatible with the well-known elastic constant softening observed in bulk galfenol. In particular, despite the important out-of-plane lattice parameter expansion, the in-plane parameter is not affected by the Ga content. We attribute this unusual behavior to the short-range ordering of Ga pairs along the [001]-growth direction. This strong anisotropic architecture is probably favored by out-of-equilibrium MBE growth (low temperature) and evolves into a cubic bulk like picture after thermal annealing.

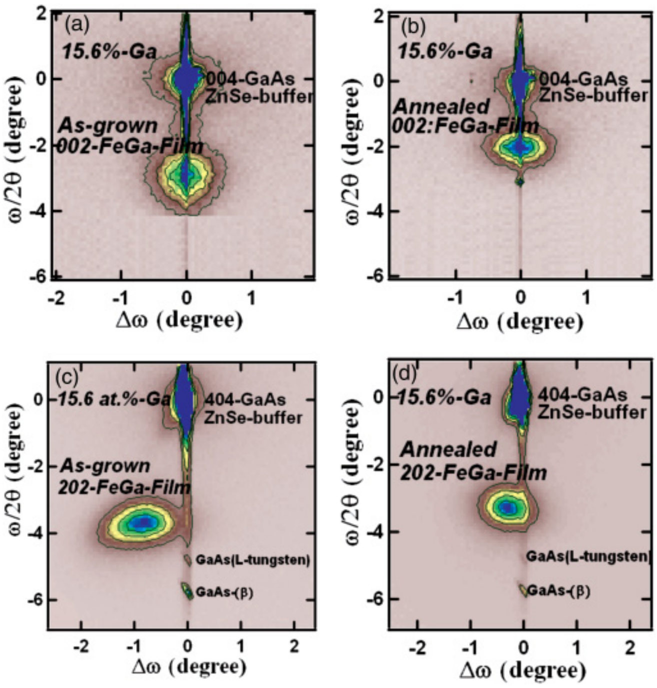

FIG. 4. (Color online) Area scans around the (002) and (202) Bragg peaks of an alloy film at 15.6% Ga content for (a),(c) as-grown and after postannealing at 300°C (b),(d).

These results show that highly oriented FeGa thin films epitaxied on (001) semiconductor substrates grown by MBE are an optimal playground to correlate magnetostrictive properties to their internal atomic architecture and electronic properties. A direct comparison of the magnetostriction properties of galfenol films before and after thermal annealing will give an insight into the origin of the extraordinary high magnetostriction coefficient of galfenol.

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