Electron-energy-loss spectroscopy of Fe thin films on GaAs(001)

J. Yuan, E. Gu, M. Gester, J. A. C. Bland, and L. M. Brown
Cavendish Laboratory, Cambridge CB3 OHE, United Kingdom

An electron-microscopy-based technique of electron-energy-loss spectroscopy (EELS) has been used to characterize electronic and magnetic properties of ultrathin Fe films grown on GaAs(100) surface, as a function of the film thickness. Large-area electron transparent membranes for microscopic analysis are prepared by ion-beam thinning or chemical etching from the substrate side, and the top surface of the ultrathin Fe film is protected by a thin Cr layer. Analysis of the Fe $2p$, Cr $2p$, and O $1s$ absorption spectra confirms that only the Cr layer is oxidized. The local magnetic moments of the ultrathin Fe films are deduced from the "white line" branching ratio in the Fe $2p$ absorption spectra. For Fe films as thin as 150 Å, the magnetic moment is not different from that found in bulk α-Fe. For a 70-Å Fe film, the local magnetic moment is enhanced although the average magnetization is reduced. As doping is suspected to be the cause for the departure from bulk α-Fe properties. In the case where the 50-Å film is polycrystalline and discontinuous, spatially resolved EELS has been used to distinguish small island clusters from large crystalline particles. The large particles are α-Fe crystallites and the islands are probably also heavily affected by As doping.

I. INTRODUCTION

Epitaxially grown Fe thin films on GaAs(100) hold great promise for the integration of magnetic film technology into semiconductor and opto-electronic technologies.[1-3] However, many physical properties of the thin films have a strong thickness dependence and the origins of these are currently poorly understood. For example, the average magnetization per Fe atom starts to decrease from the bulk value for films as thick as 230 Å.[4] To understand the microscopic origin of this behavior, we have to separate the intrinsic physical effects from the effect of defects, impurities, etc., associated with the growth problem. This can be achieved by studying the Fe film with a *localized magnetic probe*. In this article, we carried out such a characterization of thin and ultrathin Fe films by studying element-selective inner-shell ionization using electron-energy-loss spectroscopy (EELS).[5] The EELS measurement is carried out using a scanning transmission electron microscope (STEM), which not only allows us to study uniformly deposited films, but also permits analysis of inhomogeneous films with high spatial resolution. All the Fe films are preserved from oxidation and degradation by encapsulation between the substrate and a top protective layer. This distinguishes us from early studies of transition metal films that are thermally evaporated with poor control for impurity and crystallinity and inevitably contains surface oxide layers. We will be able to show from the Fe $2p$ absorption, which accesses to the final states involving the Fe $3d$ conduction band, that the electronic structure of Fe films grown on the GaAs(100) surface is bulklike at 150 Å but different from the bulk for 70-Å and 50-Å ultrathin films; and that the difference is consistent with As doping.

II. EXPERIMENT

The ultrathin Fe films are deposited on a GaAs(001) substrate inside a UHV chamber with a base pressure better than 5×10^{-9} mbar during the growth. A detailed characterization of the growth process by both reflection high-energy electron diffraction (RHEED) and low-energy electron diffraction (LEED) techniques can be found in Ref. 6. At the end of Fe deposition, the top surface is covered with a thin layer of Cr to prevent the oxidation of Fe films. To produce electron-beam-transparent samples for transmission electron microscopy and transmission electron-energy-loss analysis, the sandwich film is thinned from the substrate side only. This is achieved by either ion-beam sputtering or by chemical etching. The latter is particularly favored since a large uniform thin membrane can be produced using a thin layer (about 0.2 μm thick) of the relatively chemically inert $Ga_{0.7}Al_{0.3}As$ as an "etching stop" layer[6] on top of the GaAs(100) substrate.

EELS is conducted inside a dedicated vacuum generate (VG)-HB501 STEM operating at 100 keV. The transmitted electrons are analyzed by a VG magnetic sector prism, and the spectrum is further magnified by a quadrapole lens system before being collected on a CCD (charge-coupled device)-based parallel detection system.[7] All the spectra have been corrected for the dark current and flat-field response of the CCD camera. The convergence semiangle of the incident electron is about 7 mrad, and the collection semiangle of the spectrometer is about 8 mrad. Under such experimental conditions, inner-shell transitions of interest (O $1s$ at 530 eV, Cr $2p$ at 576 eV, and Fe $2p$ at 706 eV) all obey the dipole-selection rule. The spatial resolution of the focused electron probe is better than 5 Å and the optimal energy resolution of the EELS system is 0.3 eV.

III. RESULTS

A. Cr(25 Å)/Fe(150 Å)/GaAs(001) structure

The magnetization measurement of this 150-Å Fe film shows a pronounced fourfold anisotropy.[8] Thin membrane of the sandwich structure is produced by chemical etching. The electron diffraction pattern is consistent with an epitaxial α-Fe film lattice-matched on a GaAs(001) substrate. The composition analysis using the theoretical cross sections[5] for the continum part of the Cr and Fe $2p$ absorption shows that the Fe and Cr concentrations are in the ratio 6.33, close to the expected ratio of 6.10, which is calculated from the

0021-8979/94/75(10)/6501/3/$6.00

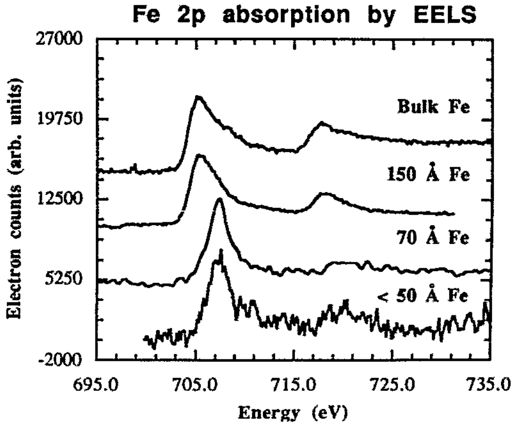

FIG. 1. The Fe $2p$ absorption spectra from ultrathin films of different thickness. The bulk reference spectra is taken from 2000-Å thick particles (see the text for detail).

thickness difference of the two films as measured by quartz microbalance, *in situ*. The thickness of the membrane is estimated from the low-loss spectrum to be about 300–400 Å and is very uniform. An analysis of the Cr $2p$ absorption spectra indicates that at least a part of Cr has been converted into oxides.[9] The Fe $2p$ absorption for the thin film is shown in Fig. 1. It is similar to that for the bulk Fe absorption spectrum shown on the same figure, with the energy of the first peak at 706 eV. There is no sign of Fe oxidation since its white line would appear at much higher energies.[9]

B. Cr(25 Å)/Fe(70 Å)/GaAs(001) structure

The magnetization of this 70-Å Fe film shows a mixture of fourfold and twofold anisotropy.[8] As there is no built-in etching stop on the GaAs substrate, ion-beam thinning was used to produce electron-beam transparent membrane. From electron diffraction analysis, the Fe film growth is again found to be epitaxial. To avoid areas where the GaAs substrate has been completely removed, we deliberately move to areas where the sandwich structure is over 700 Å thick and where signal from the GaAs substrate is unmistakable. With at least about 600 Å of the GaAs substrate still intact, the possibility of ion-beam-induced effects on the thin Fe film is very small. The Fe $2p$ absorption spectrum taken from this thick sample is deconvoluted to remove multiple scattering, and the result is also shown in Fig. 1. It is clear that the 70-Å Fe film is already different from the bulk and 150-Å Fe film. The first peak in the Fe $2p$ absorption spectrum from the 70-Å Fe film has a shoulder at 706 eV where the $2p$ absorption of the bulk Fe has its maximum.

C. Cr(25 Å)/Fe(50 Å)/GaAs(001) structure

This film is slightly different in its fabrication from the above two films. The GaAs wafer containing the etching-stop layer has been thinned to produce a membrane window prior to Fe deposition. The magnetization of the film is found to be isotropic[8] and is associated with the polycrystalline nature of the film, as shown by electron diffraction. In addition, electron microscopy shows that the Fe film is discontinuous and that the grains have two characteristic sizes. The Fe is mostly sparsely distributed in clusters of small islands of the order of 50 Å across. From the analysis of the ionization cross sections, using that of the Cr layer as a standard, the thickness of the Fe islands is deduced to be about 20–30 Å. The Fe $2p$ absorption spectrum from one of these nanometer-sized islands is shown in Fig. 1. It is similar to that of the 70-Å film, except for an additional shoulder at 710 eV. Much less numerous are the large Fe particles with diameters over several thousand angstroms. The energy-loss spectrum from the large particles has been taken as representative of the bulk Fe films and is also presented in Fig. 1 for comparison purpose.

IV. DISCUSSION

In a one-electron picture, the inner-shell transition should give information about a symmetry-projected, empty density of states localized on the excited atoms, and the result can be compared with the bandstructure calculation. In the case of Fe $2p$ absorption, it probes the empty density of states of the conduction band with the $3d$, and to a less extent $4s$ character. However, strong coupling between the partially filled d band and the remaining inner-shell p electrons produce a significant distortion to the empty density of state. The spectra are dominated by two "white-line" structures separated by 12.5 eV, approximately the energy difference between the Fe $2p_{1/2}$ and $2p_{3/2}$ core levels. Information about the electronic structure of the Fe film can still be assessed in these cases. For example, the density of the conduction electrons controls the lifetime of the core hole states, hence the width of the core level transition. In bulk metal Fe (see Fig. 1), the width of the white line is quite large (3.5 eV), reflecting a large conduction electron density around Fe. It is reduced to less than 2.1 eV for the 70-Å and 50-Å films, indicating a large reduction in the density of the conduction electron. Because of this reduction in the width, the multiplet structures in the white lines becomes visible for the spectra from these two films. These are due to resonant transition from the $2p^6 3d^n$ initial states into $2p^5 3d^{n+1}$ final states, and are sensitive to the d-level occupancy of the Fe atom. Comparison of line shape of l_3 peak with an atomic multiplet calculation[10] suggests that the average d-level occupancy (n) in the 70-Å film is 6, assuming the crystal-field effect is unimportant.

Because of the spin-orbit coupling, the branching ratio of the white lines arising from transitions from the two sublevels of the Fe $2p$ state (defined as $I_3(2p_{3/2})/[I_2(2p_{1/2})+I_3(2p_{3/2})]$) deviates from the statistical values $\frac{2}{3}$ (Ref. 11) and depends on the specific configuration of the partially filled $3d$ levels.[9] Although a first-principle calculation of these effects is still not feasible for the time being, an empirical relationship has been found between the local magnetic moment per Fe atom (which depends on the $3d$ configuration of the Fe) and the branching ratio of the Fe $2p$ absorption.[12] The branching ratio of Fe $2p$ absorption from the bulk and 150-Å Fe is found to be 0.74 ($I_3/I_2=2.9$), in agreement with that reported from the literature.[12,13] The corresponding branching ratio for the 70-Å Fe film is 0.83 ($I_3/I_2=5$). This indicates an enhanced magnetic moment per atom according to the empirical relationship of Kurata and Tanaka.[12] To translate local magnetic moments into volume magnetization, we need to consider the nature of local magnetic ordering. The branching ratio of the thinner film ("50 Å") film is not available due to poor statistics of the spectrum.

The cause for the departure from the bulk Fe signal in the thin and ultrathin films is not clear. The effect of low dimensionality is unlikely in this particular case as the Fe $2p$ absorption spectra of a two monolayer and a four monolayer film on Cu(100) substrate, obtained using *in situ* x-ray absorption,[13] is similar to that found for bulk Fe and the 150-Å film. A more likely cause maybe due to the atomic diffusion across the boundary. The Cr/Fe bilayer has been studied extensively in terms of ultrathin film, and multilayer fabrication and interdiffusion is generally not a problem. Contamination of the Fe film by more diffusive As species has been found in earlier deposition experiments,[4,14,15] and the formation of antiferromagnetically coupled Fe_2As microcrystallites has been speculated as a possible reason for the drop of the average magnetization per atom in thin film.[4] There are some evidence for As contamination of Fe film from *in situ* Auger spectroscopy; however, there is no electron diffraction evidence for Fe_2As microcrystalline particles in the films we have examined. On the other hand, the As-doped α-Fe is also possible in the equilibrium phase diagram of the Fe-As binary system[16] and cannot be dismissed purely from our plan-view electron microscopy and EELS results. We may speculate on the electronic structure of the As-doped Fe film. Crudely speaking, the more electronegetive As atom will be an electron acceptor and reduces the d-level occupancy in the Fe atom. This is consistent with the reduced branch ratio and decrease in the line width of the white lines in the Fe $2p$ absorption spectra from the 70- and 50-Å films. According to the empirical relationship between branch ratio and the local magnetic moment per atom, the magnetic moment per atom for the As-induced α-Fe film may actually increase (from 2.5 to 6 μ_B). This finding may not necessary be in conflict with the decrease in the average magnetization per atom, as the relationship between the two are not necessary in tandem particularly for an itinerant ferromagnetic Fe sample, since the local ordering of the atomic moments is also important and may also be affected by As doping.

V. SUMMARY

Thin Fe films grown on GaAs(100) surface have been examined by electron-microscopy-based high-energy EELS. Special sandwich structure has been produced to prevent the oxidation of the ultrathin Fe film at ambient atmosphere. This allows, for the first time, observation of the electron-energy-loss spectrum of Fe metal films not tainted by the surface oxide. For the 150-Å film, the Fe $L_{2,3}$ absorption edge is similar in shape to that obtained from the bulk. But the spectrum from the 70-Å Fe film is very different. The local magnetic moment deduced from the branching ratio of the Fe $2p$ spectrum from the 70-Å Fe film is higher than that from the bulk. For the 50-Å film examined, the magnetization behavior is isotropic because the film is polycrystalline. The film is also discontinuous and has two distinct grain sizes. The electronic structure of the small Fe islands (about 50 Å across) is similar to that of the 70-Å Fe film. The larger grains have diameters of the order of thousand angstroms and bulklike properties. The exact nature of the electronic structure of the deposited Fe films are still under investigation. It is suspected that the changes are partially caused by the proximity of the interface and the related As diffusion across the boundary, which can induce both doping as well as alloying.

[1] J. M. Florczak and E. D. Dahlberg, Phys. Rev. B **44**, 9338 (1991).
[2] G. A. Prinz and J. J. Krebs, Appl. Phys. Lett. **39**, 397 (1981).
[3] K. T. Riggs, E. D. Dahlberg, and G. A. Prinz, J. Magn. Magn. Mat. **73**, 46 (1988).
[4] J. J. Krebs, B. T. Jonker, and G. A. Prinz, J. Appl. Phys. **61**, 2596 (1987).
[5] R. F. Egerton, *Electron Energy Loss Spectroscopy in the Electron Microscope* (Plenum, New York, 1986).
[6] E. Gu, C. Daboo, J. A. C. Bland, M. Gester, A. J. R. Ives, L. M. Brown, and J. N. Chapman, J. Magn. Magn. Mater. **126**, 180 (1993).
[7] D. McMullan, J. M. Rodenburg, Y. Murooka, and A. J. McGibbon, Inst. Phys. Conf. Ser. **98**, 55 (1989).
[8] C. Daboo, R. J. Hicken, D. E. P. Eley, M. Gester, S. J. Gray, A. J. R. Ives, and J. A. C. Bland (these proceedings).
[9] R. D. Leapman, L. A. Grunes, and P. Fejes, Phys. Rev. B **26**, 614 (1982).
[10] G. van der Laan and I. W. Kirkman, J. Phys. Conden. Mat. **4**, 4189 (1992).
[11] R. D. Leapman and L. A. Grunes, Phys. Rev. Lett. **45**, 397 (1980).
[12] H. Kurata and N. Tanaka, Microsc. Microanal. Microstruct. **2**, 183 (1991).
[13] J. G. Tobin, G. D. Waddill, and D. P. Pappas, Phys. Rev. Lett. **68**, 3642 (1992).
[14] J. R. Waldrop and R. W. Grant, Appl. Phys. Lett. **34**, 630 (1979).
[15] S. A. Chambers, F. Xu, H. W. Chen, S. B. Vitomirov, S. B. Anderson, and J. H. Weaver, Phys. Rev. B **34**, 6605 (1986).
[16] F. A. Shunk, *Constitution of Binary Alloys*, 2nd suppl. (McGraw-Hill, New York, 1969).