Interfacial mixing of ultrathin Cr films grown on an Fe whisker

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(Received 11 September 1995)

$\frac{1}{2}$-ML Cr films grown on an Fe whisker have been studied using angle-resolved Auger electron forward scattering as a function of the substrate temperature at which the Cr was deposited. The angular scans of the peak-to-peak Cr Auger intensity show pronounced peaks due to forward scattering, which indicate significant intermixing of Cr atoms into the second layer for films grown at 100, 180, and 246 °C, and into the third layer for the film grown at 296 °C. Calculations based on a single-scattering theory show that half of the Cr deposited at 296 °C is below the surface. Since previous studies of exchange coupling through Cr films used samples grown at this elevated temperature, the alloying may be related to the earlier finding that the exchange coupling through Cr(001) is much weaker than, and of opposite phase to, that predicted by first-principles calculations.

Ultrathin magnetic metallic structures are studied intensively both to provide insight into the basic aspects of low-dimensional magnetism, and for the development of different materials based on nanostructures. One thrust of this research has been to investigate the magnetic exchange coupling between two ferromagnets separated by a nonferromagnetic film. In this regard, the Fe whisker/Cr/Fe(001) system has played an important role, particularly as the (001) surface of the whisker provides a nearly perfect, atomically smooth template for the epitaxial growth of the Cr layer. Studies using secondary electron microscopy with polarization analysis (SEMPA) and the magneto-optical Kerr effect (MOKE) (Refs. 1 and 2) have revealed that the exchange coupling through the Cr film oscillates as the Cr film thickness is increased. This oscillation has two characteristic wavelengths: 2.11 and 12 ML. Quantitative studies of the exchange coupling have been subsequently performed using Brillouin light scattering (BLS).[3,4] The strength of the exchange coupling through the Cr(001) spacer was found to be extremely sensitive to small deviations in growth conditions, and was reproducible only in those samples which exhibited a nearly perfect layer-by-layer growth. Short-wavelength oscillations in the exchange coupling were confirmed, with the coupling strength $J_{\max}\approx 1$ erg/cm^2. The phase of the short-wavelength component, in agreement with the SEMPA results,[5,6] was ferromagnetic for an even number of Cr ML, and antiferromagnetic for an odd number of Cr layers, for thicknesses between 5 and 13 ML.

The presence of the short-wavelength oscillatory component in the exchange coupling is in agreement with theoretical predictions.[7,9] Bulk Cr has a spin-density wave with a wavelength of 2.11 ML, which should be pinned by the strong antiferromagnetic exchange coupling with Fe at both of the interfaces. However, the phase of the short-wavelength oscillations is predicted to be opposite to that observed. Furthermore, the strength of the exchange coupling obtained from first-principles calculations,[8,9] $J_{\max}\approx 30$ erg/cm^2, is much greater than the experimental results. This represents a significant disagreement between experiment and theory.

These discrepancies may indicate that the detailed formation of the Fe whisker/Cr/Fe sample is more complex than has been acknowledged so far. Layer-by-layer growth of the Cr on the whisker was observed only in a small range of substrate temperatures near 300 °C.[3,4,10] However, the atomically smooth growth may be chemically rough. Interface alloying due to an atomic exchange mechanism has been seen for Fe growth on Ag(001) and Cu(001), even at room temperature.[11,12] As was demonstrated using Mössbauer spectroscopy,[11] the atom exchange mechanism is an asymmetric effect which favors a configuration where the atom type with the lower bulk melting temperature is at the surface. In the whisker/Cr/Fe studies, this will favor Fe at the surface. Furthermore, the growth of the Fe film on top of the Cr was performed at a much lower temperature (30 °C) than the Cr growth on the whisker. This will act to decrease further the interchange of atoms at the second interface. Taken together, these effects might create two inequivalent interfaces, and alter the phase of the overall coupling compared to two equivalent interfaces.

In order to investigate the mixing at the interface of a Cr film grown on an Fe whisker, the angular distribution of Auger electrons emitted by the Cr atoms was studied. Because of the strong forward scattering of electrons with a kinetic energy of several hundreds of eV, the number of Auger electrons emitted within a small solid angle is markedly peaked when the emission direction lies along the line from the emitting atom to a nearest neighbor or next-nearest-neighbor atom.[13] These forward focusing effects are most pronounced when caused by a single scattering event, that is, when only one atom intervenes between the emitting atom and the detector.[14] The technique is therefore ideally suited to the study of the intermixing of monolayer and submonolayer films with a crystalline substrate. Figure 1(a) demonstrates the qualitative expectation for Cr atoms deposited on the (001) face of bcc Fe. The substrate is rotated by $\phi=45°$ about the normal vector **n**, so that a (110) plane lies in the plane of emission formed by **n** and the detected outgoing Auger electron beam **k**. The rotation axis for θ lies normal to the plane of emission, and θ is measured between **n** and **k**. A Cr atom in the top (vacuum) layer has no atoms intervening between itself and the detector, and should therefore produce an isotropic Auger intensity. A Cr atom in the second layer

should produce a forward scattering peak at $\theta_1=54.7°$, whereas one in the third layer should produce forward scattering peaks along both the normal, $\theta_2=0°$, and along θ_1. This last peak will, however, have a significant contribution from multiple scattering, as two atoms lie between the emitting atom and the detector.[14] A Cr atom in the fourth layer would contribute to the peaks at θ_2 and $\theta_3=25.2°$ through single scattering, and to the peak at θ_1 via multiple scattering.

It is evident that Auger intensity scans in the $\theta=45°$ azimuth will indicate the mixing of Cr into the Fe whisker. There is, however, a complication with the measurement near $\theta=0°$ arising from the forward scattering of the exciting primary beam **q**.[15] In the apparatus used for these experiments, **q** makes a fixed angle of $\psi=54°$ with the emission direction **k**. As can be seen in Fig. 1(b), when $\phi=45°$ and $\theta=0°$, **q** coincides almost precisely with the line connecting a first- and second-layer atom. Under these conditions, the incoming beam undergoes forward scattering for a small range of θ about 0°, and Cr atoms in the second layer experience an increased flux of exciting primary electrons, thus producing proportionately more Auger electrons. This results in an increase in Auger intensity near $\theta=0°$, which may be misinterpreted as due to emission from atoms in deeper layers. The solution to this geometric difficulty is to measure the angular distribution at two azimuthal angles. Measurements at $\phi=45°$ display the peak at $\theta_1=54.7°$ with maximum sensitivity, and measurements at another azimuth ($\phi=34.2°$) which does not meet the forward focusing condition for the incoming beam, give an unambiguous measure of any peak at normal emission.

Fe whiskers are small samples. A typical whisker is a rectangular bar about $100\times100\times10000$ μm^3, with its long axis oriented in the [001] direction, and displaying (001) facets. For this study an uncommon ''blade''-shaped whisker was selected which had a 10-mm length, a 500-μm width, and a thickness of about 100 μm. The sample was mounted on an polycrystalline Mo holder using a spring clip. The cleaned blade face produced an excellent RHEED pattern consisting of pointlike diffracted beams without appreciable streaking. The Auger spectra were recorded using a PHI 10-360 180° hemispherical analyzer configured to give an estimated resolution of $\pm2°$ and 500-μm diameter. The spatial resolution was checked by measuring the Auger signals of the Fe and the Mo holder as the sample was translated. The Fe(702 eV)/Mo(186 eV) peak-to-peak Auger ratio changed by more than two orders of magnitude across the edge of the sample, and the Fe signal showed a clear central plateau region. It was concluded that by positioning near the center of the whisker, the Auger signal from Cr deposited on the Mo holder would constitute $\leqslant1\%$ of the Auger signal from an equivalent thickness of Cr on the Fe whisker. The Fe measurements were collected simultaneously with the Cr measurements for all of the samples, and were found to be highly reproducible. Typical peak-to-peak Fe(702 eV) Auger data are shown in Fig. 2(a), and reveal features at the expected angles. The relative sizes of these features are difficult to interpret qualitatively because of the important effects of multiple scattering in the thick Fe sample. Figure 2(b) presents measurements of the peak-to-peak Cr(529 eV) Auger signal from a nominal 1-ML film on the Mo sample holder.

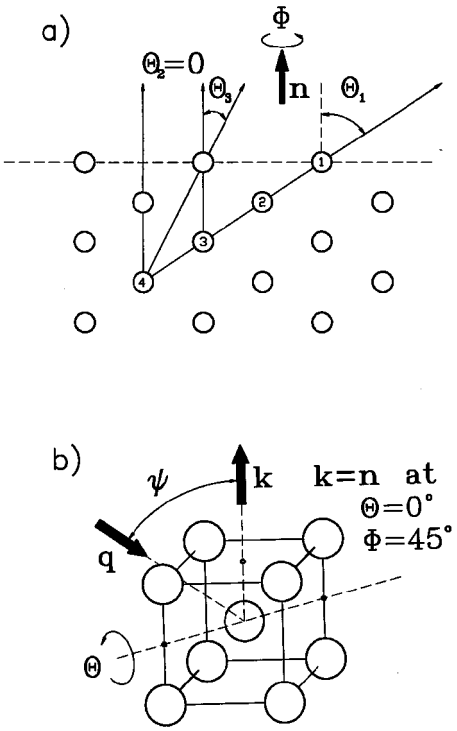

FIG. 1. The experimental geometry. (a) The plane of emission includes the surface normal **n** and the direction at which Auger electrons are detected. When $\phi=45°$, this is a (110) plane of the whisker. The axis of θ rotation lies normal to the page, and $\theta_1-\theta_3$ are emission angles where forward scattering increases the emission from atoms in the top four atomic layers. (b) The bcc structure of the whisker is shown in perspective. The incident primary electron beam **q** makes a fixed angle ψ with the emission direction **k**.

These data demonstrate the crystalline origin of the intensity variations in Fig. 2(a), and also characterize the angular profile of the measurement technique.

Having demonstrated the ability to perform Auger forward-scattering measurements on an Fe whisker, a series of $\frac{1}{2}$ -ML Cr films were grown on the whisker at different temperatures, and the angular dependence of the Fe and Cr Auger lines were measured for each. The $\frac{1}{2}$-ML coverage was chosen to minimize the occurrence of Cr deposition on Cr. The Cr growth was monitored using a RHEED primary beam scattered at the second anti-Bragg condition for the substrate. Cr growth was stopped when the specular beam intensity first reached a minimum, and a picture of the RHEED pattern was recorded. Four growth temperatures were investigated: 100, 180, 246, and 296 °C. These temperatures span the range where the RHEED oscillations for layer growth show a strongly damped, sinusoidal oscillation characteristic of rough growth (100 °C), to where the oscillations have a sharply peaked, parabolic shape characteristic of very smooth layer-by-layer growth (296 °C). It is important to note that at all the above substrate temperatures the first RHEED intensity oscillation shows a large and sharply cusped peak, indicating that the first ML of Cr is smooth with negligible pileup of the Cr atoms. The RHEED patterns at $\frac{1}{2}$ ML for the sample growths showed long streaks in the scattering direction, because of the high density of atomic steps at this coverage. There was clear lateral splitting of the streak for 100 and 180 °C growths, indicating a mean separation of the nucleation centers for the growth of approximately 100 and 200 Å, respectively. This is in agreement

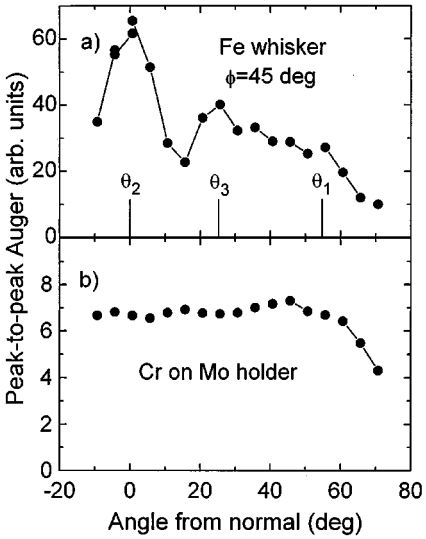

FIG. 2. (a) Peak-to-peak Fe(702 eV) Auger intensity as a function of θ for the whisker. The angles $\theta_1-\theta_3$ are those indicated in 1(a). (b) Peak-to-peak Cr(529 eV) Auger intensity as a function of θ for about 1 ML Cr on the Mo holder.

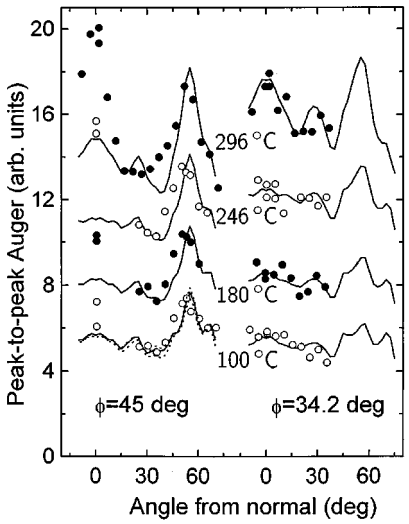

FIG. 3. Cr(529 eV) Auger intensity as a function of θ for $\frac{1}{2}$-ML Cr films grown at the indicated temperatures, for two values of azimuthal rotation. The lines are fitted using single-scattering theory as described in the text. The dotted lines show the variation in the fit in one case, when the layer abundances are varied by ± 0.04.

with the findings of STM studies of this system.[10] At 246 and 296 °C the lateral splitting was no longer evident, the streaking became progressively less pronounced, and the patterns were very similar to those described in earlier studies.[3,4]

The angular dependence of the Cr peak-to-peak Auger signal is plotted in Fig. 3. The data for each successive temperature have been offset by an additional three units along the y axis for clarity. All measurements were made at or close to room temperature. Integrating over θ, the average Cr/Fe Auger ratio is a factor of 1.3 times greater than that expected for $\frac{1}{2}$-ML Cr on semi-infinite Fe (Ref. 16)—this small discrepancy is likely due to the fact that the angular scan is along a direction where the Cr Auger intensity is concentrated more effectively by single-scattering events than the Fe intensity is concentrated by multiple scattering. Ignoring for the moment the solid lines, a number of qualitative results are immediately evident. The data for $\phi=45°$ on the left side of the figure show a clear peak in Auger intensity near 54.7°, indicating that a significant number of Cr atoms lie in the second layer or deeper in these $\frac{1}{2}$-ML films. Furthermore, the size of this peak relative to the intensity at $\theta\approx 38°$ increases monotonically with increasing growth temperature, showing that more Cr atoms are moving below the top layer. At all growth temperatures, the data point at $\theta=0°$ also shows a greater intensity than at $\theta\approx 38°$. This is primarily due to forward scattering of the primary beam onto the Cr atoms below the surface. This is evident because (a) the peak is absent at the lower growth temperatures for the data at $\phi=34.2°$, where the primary beam effect is absent, and (b) because the peaks at $\theta=54.7°$ and 0° increase in tandem. The data on the right side of Fig. 3 show a peak at normal emission due to forward scattering once the growth temperature reaches 296 °C, and it is evident that this $\frac{1}{2}$-ML Cr film has significant mixing into the third layer of the Fe substrate.

These conclusions can be made more quantitative using single-scattering calculations of Cr Auger electron forward scattering. These calculations used the computer program SSC created by Friedman and Fadley[17] for single elastic scattering from an array of atoms. The scattering events are treated using scattering phase shifts generated by the computer program FEFF-3 written by Rehr, Albers, and Mustre de Leon.[18] Single-scattering calculations should be entirely adequate for these studies because (i) the absence of a peak at $\theta=25.2°$ suggests that there is little Cr in the fourth layer or deeper; (ii) in emission from the top three layers, there is only one chainlike alignment of atoms where multiple scattering will be important; and (iii) this single chain alignment is for emission at $\theta=54.7°$ by atoms in the third layer, and previous investigations into the effect of multiple scattering have shown how an approximate compensation can be made. The compensation is based on calculations of the forward scattering along the close-packed direction of the 3d metal Cu,[14] where the nearest-neighbor distance and scattering phase shifts at the energy of the Auger electrons are very close to those of bcc Fe. The calculations for Cu show that the effect of multiple scattering along such a chain is to reduce the contribution of the third-layer atoms to 60% of the contribution calculated in the single-scattering approximation. Detailed results for emission from Cr in bcc Fe when $\phi=45°$ show that scaling the contribution to the peak at $\theta=57.4°$ from a third-layer atom by 0.60 makes it very nearly equal to that calculated for a second-layer atom—that is, second- and third-layer atoms are indistinguishable along this emission direction. The data at $\phi=45°$ are therefore fit to a linear combination of angular distributions calculated for the first- and second-layer atoms, giving a measure of the relative Cr abundance at the surface and deeper. For the data at $\phi=34.2°$, $\theta=0°$, there is no ambiguity due to multiple scattering, but the calculated angular profiles for both first- and second-layer atoms are flat and indistinguishable—neither shows forward scattering. These data are therefore fit to a linear combination of the angular distributions for a top-layer and third-layer atom, giving a measure of the relative abundances in the third layer and above the third layer. Combining these estimates gives the relative abundances in

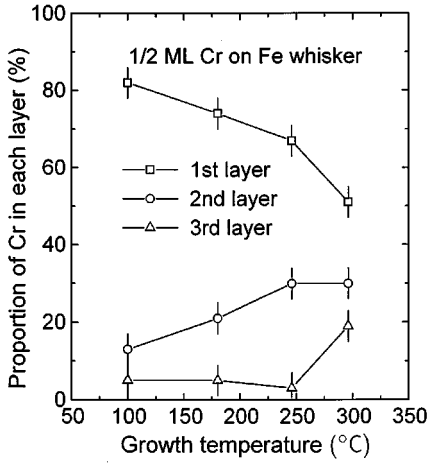

FIG. 4. The relative abundances of Cr in the top three layers, as found from the fit to the data shown in Fig. 3. The finding of a threshold level of Cr in the third layer at the three lowest temperatures is not believed to be significant.

all three layers, and results in the calculated solid lines in Fig. 3. An estimate of the uncertainty in the relative abundances is ± 0.04. This magnitude of change generates the fits shown by the dotted lines for the data at 100 °C, $\phi = 45°$. The fitted relative abundances are shown in Fig. 4 as a function of the growth temperature of the film. This plot clearly shows the diffusion of the Cr into the Fe whisker as the temperature increases. Significant movement of Cr into the third layer is first seen for growth at 296 °C. Although inclusion of a small contribution from the third layer is indicated by the fit at lower temperatures, it does not vary systematically with temperature, and is close to the estimated fitting error. At and below 246 °C, the mixing is likely confined to the top two layers. At 296 °C, roughly half the Cr is in the second and third layers. Evidently, smooth film growth is accompanied by strong intermixing of Cr and Fe at the interface, and noticeable intermixing occurs even at 100 °C.

The present data do not address directly the question of mixing in a thicker film, but there is evidence that mixing beyond the third layer will not be important. An 11-ML Cr film was prepared, and Auger electron spectroscopy at normal emission showed that the Fe substrate was covered very well. The Fe signal was diminished by a factor of 8.8 compared to that of a clean whisker. Assuming that intermixing occurs only near the interface, this decrease was due to two effects: the attenuation by the Cr on top of the Fe (a factor[16] of 3.7), and the removal of the forward-scattering peak for normal emission [Fig. 2(a) shows a factor of 2.5]. This yields an overall reduction of 9.3 times, in approximate agreement with the measurement.

In conclusion, interfacial alloying of Cr grown on an Fe whisker is significant. For films grown at 296 °C, where excellent layer-by-layer growth of Cr is found, about half of the first ML of Cr is below the surface layer, but the mixing is likely confined to three layers. Theoretical calculations for Fe/Cr superlattices which have interfaces formed by 2 ML of an ordered alloy [Fe\Fe(75%)-Cr(25%); Cr(75%)-Fe(25%)\Cr] (Ref. 8) predict that the strength of the exchange coupling across the Fe\Cr interface is greatly reduced, and that the Cr in the alloyed atomic layer closest to the pure Fe is antiferromagnetically coupled to it. Alloying changes the number of atomic layers containing Cr by one, and the phase of the coupling, if plotted against equivalent ML of deposited Cr, becomes reversed compared to an abrupt interface. The level of interface alloying found at the Fe whisker/Cr interface is comparable to that used in these calculations, and therefore could be responsible for the measured phase of the short-wavelength oscillations in Fe whisker/Cr/Fe samples. Quantitative BLS and MOKE studies show that the interface mixing very strongly affects the strength of the bilinear exchange coupling.[19] Studies are under way to find out whether the degree of the interface mixing can be limited to the point that the measured phase of the short-wavelength oscillations are reversed and brought into agreement with first-principles calculations.

We are grateful to C. S. Fadley for providing the computer program SSC and to C. M. Schneider for help in implementing it. This work was performed with the financial support of the Natural Sciences and Research Council of Canada.

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[1] J. Unguris *et al.*, Phys. Rev. Lett. **67**, 140 (1991); **69**, 1125 (1992).

[2] S. T. Purcell *et al.*, Phys. Rev. Lett. **67**, 903 (1991).

[3] B. Heinrich *et al.*, in *Magnetic Ultrathin Films: Multilayers and Surfaces/Interfaces and Characterization*, edited by B. T. Jonker *et al.*, MRS Symposia Proceedings No. 313 (Materials Research Society, Pittsburgh, 1993), p. 119.

[4] B. Heinrich and J. F. Cochran, Adv. Phys. **42**, 523 (1993).

[5] J. Unguris *et al.*, in *Magnetism and Structure in Systems of Reduced Dimension*, Vol. 39 of *NATO Advanced Study Institute, Series B: Physics*, edited by R. F. C. Farrow, B. Dieny, M. Donath, A. Fert, and B. D. Hermsmeir (Plenum, New York, 1993), p. 101.

[6] B. Heinrich *et al.*, in *Magnetism and Structure in Systems of Reduced Dimension* (Ref. 5), p. 175.

[7] D. Stoeffler and F. Gautier, in *Magnetism and Structure in Systems of Reduced Dimension* (Ref. 5), p. 411.

[8] D. Stoeffler and F. Gautier, Phys. Rev. B **44**, 10 389 (1991).

[9] M. van Schilfgaarde and F. Herman, Phys. Rev. Lett. **71**, 1923 (1993).

[10] J. A. Stroscio *et al.*, J. Vac. Sci. Technol. B **12**, 1789 (1994).

[11] P. J. Schurer *et al.*, Phys. Rev. B **51**, 2506 (1995).

[12] D. D. Chamblis *et al.*, J. Vac. Sci. Technol. A **10**, 1993 (1991).

[13] W. F. Egelhoff, Jr. in *Ultrathin Magnetic Structures I*, edited by J. A. C. Bland and B. Heinrich (Springer, Berlin, 1994).

[14] A. P. Kaduwalla *et al.*, J. Electron Spectrosc. Relat. Phenom. **57**, 223 (1991).

[15] S. Chambers, Adv. Phys. **40**, 357 (1991).

[16] For Fe, the inelastic mean-free path is 12 Å. *Practical Surface Analysis*, 2nd ed., edited by D. Briggs and M. P. Seah (Wiley, New York, 1990), p. 209.

[17] D. J. Friedman and C. S. Fadley, J. Electron Spectrosc. Relat. Phenom. **51**, 689 (1990).

[18] J. J. Rehr *et al.*, Physica B **158**, 417 (1989).

[19] B. Heinrich *et al.* (unpublished) and (unpublished).