Spin Polarization of Ion-Excited Secondary Electrons from Ferromagnets and Its Application for Magnetic Sputter Depth Profiling

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We study the spin polarization of secondary electrons from Fe(110) excited by noble-gas ions from 0.5 to 4 keV energy, covering the range from potential emission to kinetic emission of secondary electrons. We find majority-spin polarization at all energies and for all ion species, but less than with primary electrons from the same sample. There is no magnetically "dead" layer produced, even by heavy sputtering. This leads to the possibility of "magnetic sputter depth profiling" which is demonstrated by sputter profiling through a 50-Å iron oxide layer on iron while the secondary-electron spin polarization is monitored.

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We report on first observations of the spin state of secondary electrons excited by kinetic ions from a ferromagnetic surface. While the spin polarization of electron-excited secondary electrons recently has raised a good deal of attention,[1-3] mainly in the context of the spin-polarized scanning electron microscope for magnetic structure imaging,[4,5] no spin analysis of electrons ejected by ions in potential emission[6] or kinetic emission[7] has been undertaken. The only work remotely related to ours is that of Onellion *et al.*,[8] who directed slow, polarized metastable He atoms onto a Ni surface and observed intensity changes in the secondary-electron spectrum when the atomic polarization was reversed. In the first part of this Letter, we present results of spin-polarized electron emission from ferromagnetic Fe(110), excited by kinetic noble-gas ions. The range of kinetic energies and ion species is such that we cover the whole range from predominantly potential emission to predominantly kinetic emission of secondary electrons. We find substantial spin polarization at all energies and for all ions, and we find the polarization to be of majority type, but less than when using primary electrons of similar energy. In the second part, we demonstrate the application of spin-polarized secondary-electron emission by ion impact with an experiment on "magnetic sputter depth profiling" through a thin iron oxide film on iron. The technique consists of eroding the sample by noble-gas ion bombardment while monitoring the spin polarization of the secondary electrons excited by the same ions. Its potential for simultaneous three-dimensional analysis of chemical composition and magnetic structure is sketched at the end.

The experiments have been carried out with the LEED (low-energy electron diffraction) spin-polarization detector[1] and a differentially pumped ion gun (He^+, Ar^+, and Xe^+ ions, 0.5 to 4 keV energy, and angle of incidence $\simeq 45°$). The secondary electrons were extracted along the surface normal within a cone of $\simeq 10°$ full opening angle. The sample is a Fe(110) single crystal, clamped to a soft iron yoke and magnetized along the [100] direction. The magnetic domain structure was observed *in situ* by means of the magneto-optic Kerr effect. Surface composition and structure are checked by Auger spectroscopy and LEED. The sample temperature was $\simeq 350$ K. Preliminary measurements of the spin-polarization distribution versus kinetic energy of the secondaries showed that the maximum of the polarization generally occurred at very low kinetic energies. Therefore the subsequent polarization data were all taken at 1 to 2 eV energy.

A summary of the data on spin polarization and total secondary-electron yield from the clean Fe(110) surface as functions of ion energy is given in Fig. 1. The main results are the following: (i) There is substantial electron spin polarization at all ion energies and for all ion species. This is an important point, since it proves that the magnetization in the top layers is not destroyed by the ion bombardment. This is most clearly seen at low ion energies for Ar^+ and Xe^+, i.e., in the potential-emission regime. Here the secondary-electron emission is mainly due to Auger neutralization of the incoming ion, which is known to occur several angstroms in front of the surface. The extreme surface sensitivity of ion neutralization spectroscopy[6] is well known, and the sensitivity of Auger deexcitation for the top-layer magnetization has been proven by the work of Onellion *et al.*[8] Thus, if a "magnetically dead layer" were induced by the ion bombardment, the secondary electrons from potential emission would be unpolarized. This is obviously not the case. In spite of substantial damage and erosion (the sputtering yield for 1-keV Xe^+ is around 2 Fe atoms per ion), which destroy the long-range crystalline order (as confirmed by the disappearance of the LEED diffraction pattern), we have to conclude that the magnetic long-range order apparently is preserved.

The second result is that (ii) the spin polarization is of

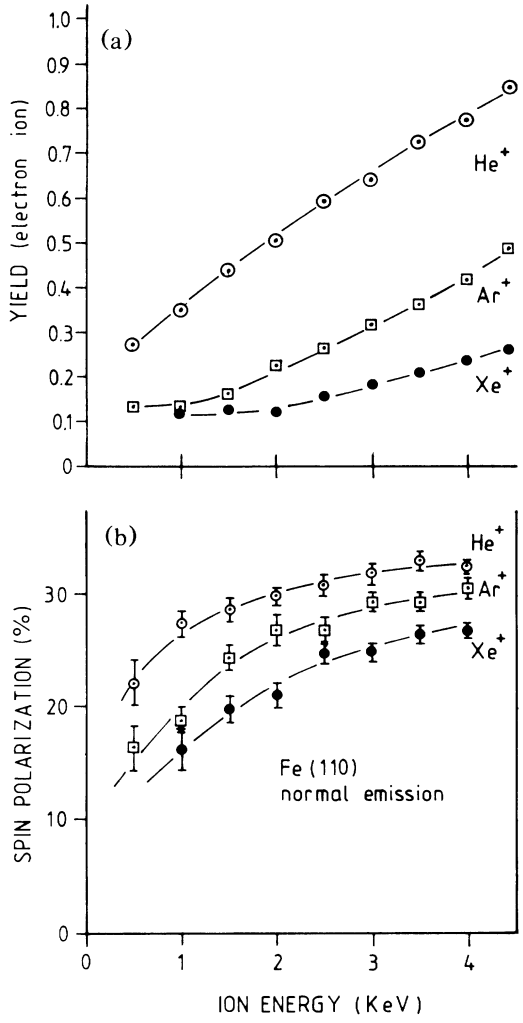

FIG. 1. Secondary-electron emission from clean Fe(110) as a function of primary ion energy for various ion species. (a) The total secondary-electron yield showing the transition from the potential-emission regime (plateaus for Ar^+ and Xe^+) to the kinetic-emission regime at high energy. (b) Spin polarization of secondary electrons of 1–2-eV kinetic energy emitted along the surface normal. The error bars indicate the 1σ statistical error. The lines are drawn to guide the eye and have no physical significance.

majority type at all energies, and that the polarization vector is aligned antiparallel to the magnetization vector. At least in the potential-emission regime the majority-spin polarization is not quite a trivial result, since the net spin density *in front of the surface* is not necessarily majority type (=positive), but may be negative as well,[9] depending on the surface. For example, in one-electron capture spectroscopy, which is thought to probe the average net spin density a few angstroms above the surface,[10] for ferromagnetic Co and Ni, opposite spin-polarization signs were found on different faces.[10] For Fe(110) $P=(13\pm2)\%$ was observed. The Auger neutralization process, however, is a two-electron process, in which some convolution of (spin-resolved) layer-dependent densities of states (DOS) is involved. It is not entirely clear whether a cross convolution between the top-layer DOS and a local DOS at the position of the ion at the time of neutralization[11] gives a better description of the experimental intensity distribution than the self-convolution of a local DOS somewhere intermediate between the surface and the ion.[6] Most likely such a convolution will tend to reduce the spin polarization from the value to be expected from a self-convolution of the *bulk* DOS. Such a process is involved in L_3VV Auger electron emission from Fe, for which a spin polarization of +30% was found.[12] In fact, we observe a substantially lower polarization of +15% to +20% in the potential-emission regime for Ar^+ and Xe^+. We believe that these values are even somewhat enhanced by a contribution related to kinetic electron emission, to be discussed next.

Our third main result is that (iii) the spin polarization rises monotonically with increasing ion energy, being higher for the lighter ion at a given energy [Fig. 1(b)]. Comparison with Fig. 1(a) shows that the spin polarization is higher the larger the total secondary-electron yield—saturation apparently is not reached within our range of energies. This behavior resembles that found in electron-excited secondary-electron emission.[13,14] With increasing ion energy, electron emission via the Auger neutralization process decreases and kinetic electron emission increases, first exponentially, then linearly with energy.[15] This is partly due to direct excitation of valence-band electrons in projectile-electron collisions, partly to electron promotion during interpenetration of electron shells in close projectile-target atom collisions.[16,17] With increasing ion energy, the penetration of the projectile into the solid, the energy transfer into the electronic system per unit path length, and the average energy of the excited electrons all increase. [The projected range for 4-keV He^+ is around 100 Å, for Xe^+ (4 keV) about 20 Å in our geometry.] Thus, more electrons are generated within the escape depth of the secondary electrons with increasing ion energy. This explains the rise of the secondary-electron yield but not the increase of spin polarization. However, if the data of Fig. 1 are used to plot the spin polarization versus total secondary-electron yield (not shown), a clear correlation between electron yield and spin polarization is obtained for the kinetic-emission regime, largely independent of the ion species. This correlation resembles that found with primary electrons[13,14] and suggests the same mechanism to be operative. It is the excitation of Stoner pairs (electron-hole pairs with opposite spin character) via exchange-scattering processes.[18,19] These lead to an apparent "spin-flip" of scattered electrons, accompanied by some energy loss (equal to the energy of the Stoner excitation). Together with a higher overall scattering probability for minority electrons,[20] this leads to an enhance-

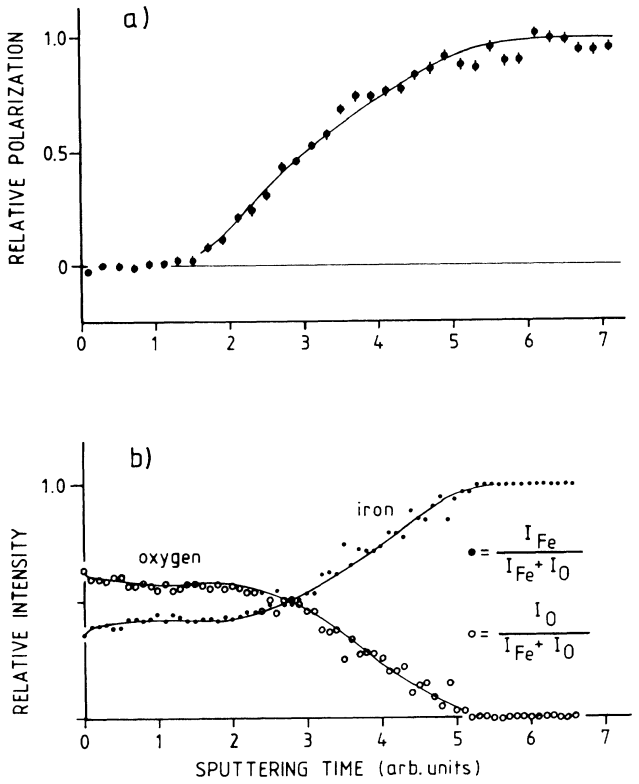

FIG. 2. "Magnetic sputter depth profiling" of a thin iron oxide layer on Fe(110). (a) The relative spin polarization of the ion-excited secondary electrons as a function of sputter time. (b) Normalized peak-to-peak intensities of *KLL* oxygen and *LMM* iron Auger lines vs sputter time. Note the increase of spin polarization with decreasing oxygen signal, indicating the sputter removal of the nonmagnetic FeO top layer.

ment of the spin polarization of very slow secondaries. In addition, those electrons excited at large depths have a higher probability to undergo spin-flip scattering before they escape into vacuum than electrons from the first layer. Thus, with increasing ion energy, i.e., larger penetration, the polarization of the low-energy secondary electrons increases. With primary electrons, the polarization saturates at primary energies beyond those where the maximum of the total yield occurs.[13] In the present measurements, a saturation of the yield is not reached and neither is that of the polarization.

In the following we apply our above findings to establish and demonstrate the technique of "magnetic sputter depth profiling." The basic idea is to erode a layer system by sputtering while simultaneously monitoring the spin polarization of the secondary electrons generated by the same ion beam. This requires little more than a (differentially pumped) ion gun and a simple spin-polarized detector, such as shown in Ref. 1 (Fig. 3.1), though the present experiments have been done with a more elaborate apparatus (at the expense of intensity). The feasibility of this approach is demonstrated in Fig. 2, with sputtering through an iron oxide film thermally grown on iron. It was produced by heating the Fe(110) sample in dry oxygen (1×10^{-6} Torr) at 300 °C for 3 h. After a short flash to 400 °C, LEED showed a hexagonal, somewhat streaky pattern, which is characteristic of an FeO layer.[21,22] The thickness of the layer is about 50 Å.[22,23] The sputtering was done with 4-keV Ar^+ at an angle of incidence of 45°. The spin polarization of the ion-excited secondary electrons as a function of sputter time is shown in Fig. 2(a). The polarization rises from near zero at the surface[24] to the stationary polarization found on clean Fe(110) for the same bombardment conditions [see Fig. 1(b)]. Auger spectra were taken at regular time intervals and the normalized peak-to-peak amplitudes are plotted in Fig. 2(b). It is seen that the rise of the spin-polarization signal occurs simultaneously with the rise of the iron Auger signal and the decay of the oxygen signal. Thus, the sputter removal of the nonmagnetic FeO layer is clearly seen in the spin-polarization signal.

Magnetic sputter depth profiling clearly is a destructive technique, subject to artifacts introduced by the ion bombardment. Many of these artifacts are known and can (partly) be avoided, which has made sputter profiling a universal tool. We need to explore to what extent the magnetic information might be subject to artifacts, but the present first result looks promising. The depth resolution will essentially be determined by atomic mixing in the collision cascade.[25] In general, low energy and heavy projectile will be preferred from this point of view. In the present case there is an additional bonus from working in the potential-emission regime with its pronounced surface sensitivity. At higher ion energies and large penetration depth, the magnetic depth of information coincides with the escape depth of the secondary electrons, mainly generated via kinetic emission. The escape depth, to be taken in the sense of a transport decay length,[26] not directly related to the inelastic mean free path, is of order 5 to 15 Å in metals[27,28] and is thus smaller than or comparable to the projected range of the projectiles if kinetic emission plays a significant role. Thus, the depth resolution can, within limits, be adjusted to the profile to be studied.

It is tempting to speculate about combining this technique with existing sputter depth profiling apparatus, since modern spin-polarization detectors have become rather small and convenient.[1,2] It seems particularly attractive to combine this technique with sputtered neutral mass spectroscopy,[29] since an electrostatic extraction field for the secondaries does not affect the neutral sputtered atoms, and since sputtered neutral mass spectroscopy provides quantitative analysis of the elemental and chemical composition to be correlated with magnetic properties. The superior sensitivity of secondary-ion–mass spectroscopy might be exploited also with suitable extraction optics for positive ions and electrons. With

the use of scanning-type ion microprobes, there are very good prospects to perform two-dimensional or three-dimensional magnetic structure analysis in combination with compositional analysis. With noble-gas ions, one has the option of imaging magnetic surface structure quasistatically (by using He^+: high secondary-electron emission and low sputtering yield) or to perform in-depth analysis using heavier ions. This may be done with a lateral resolution on the micron scale. Possibly the use of liquid-metal ion sources will allow a three-dimensional correlation of magnetic properties with material composition on the resolution level of 50 nm.[30]

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