Magnetic proximity effect in thin films of Ni on nonmagnetic metals

J. S. Moodera and R. Meservey
Francis Bitter National Magnet Laboratory, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139
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The effect on the ferromagnetism of very thin films of Ni in contact with the nonferromagnetic metals Al, Au, Cr, and Mn was studied by spin-polarized tunneling measurements. For up to three atomic layers of Ni in contact with Al, the measured spin polarization P of the tunneling electrons was zero, implying that the Ni was not ferromagnetic. This result agreed with our previous result for Ni on Al. On the other hand, for only one atomic layer of Ni in contact with Au, $P \simeq 4\%$; for two atomic layers $P \simeq 17\%$, which was 70% of the thick-film value. Two atomic layers of Ni on Mn or Cr showed very small ($P \simeq 1\%$), but finite, values of polarization. These results are compared with other experimental results and with theory and show generally good agreement.

INTRODUCTION

There has been much recent interest in magnetism of surfaces, thin films, and interfaces. The present experiments are concerned with the situation in which ultrathin films of ferromagnetic Ni are in contact with nonferromagnetic metals. The effect on the ferromagnetism of the Ni that is attributable to the contact with nonferromagnetic metals will be called the magnetic proximity effect. A number of experimental techniques have been used to study this effect with the three-dimensional ferromagnetic metals.

Liebermann and co-workers[1,2] measured the magnetic moment of Fe and Ni electroplated on Cu, Ag, and Au single-crystal substrates. They concluded that the Fe(110) plane, which was presumed to form on the Cu(111) plane, did not show magnetization at room temperature until two atomic layers had been deposited. Ag and Au substrates yielded the same result. Similar results were obtained for Co. For Ni electroplated on Cu, four nonmagnetic layers were found at room temperature and two nonmagnetic layers remained when the magnetization was extrapolated to $T=0$. Walker and co-workers[3] using Mössbauer spectroscopy found no nonmagnetic layer of Fe deposited on Ag(111) which was epitaxially grown on mica. Gradmann[4] measured the magnetization of epitaxial films of Co(111) and $Ni_{0.48}Fe_{0.52}(111)$ on a Cu(111) substrate and found no evidence for a nonmagnetic layer at $T=0$.

To avoid possible contamination problems, Pierce and Siegmann[5] measured the spin polarization of the photoemitted electrons in ultrahigh vacuum from Ni films 0.25 to 2.5 nm thick on Cu substrates and found noticeable polarization even for the thinnest Ni films. Tedrow and Meservey[6] studied the polarization of tunneling electrons from ultrathin Co films on an Al substrate and found no firm evidence of a proximity effect. Bergmann,[7] using the technique of measuring the anomalous Hall effect of cryogenically deposited ultrathin films of Ni on Pb-Bi substrates, found that the Ni did not become ferromagnetic until about three atomic layers were deposited. On the other hand, he found that Fe showed evidence of ferromagnetism at only $\frac{1}{6}$ of an atomic layer. Identical results for Ni and Fe on Al substrates were found by Meservey and co-workers,[8,9] using spin-polarized tunneling. Recently Bergmann[10] has shown that ferromagnetism in Ni is suppressed for the first three atomic layers when deposited on Al, Mg, In, Sn, and Pb (as well as Pb-Bi) substrates, whereas for Cu, Ag, and Au substrates the first atomic layer of Ni showed ferromagnetism. In the case of Fe, these substrates had no effect on the moment which was observed at very small fractional coverages. Rau[11] has recently reported that by using electron-capture spectroscopy he finds no evidence of nonmagnetic layers of Ni(100) layers epitaxially grown on Cu(100). However, he does find that the electron-spin polarization is greatly decreased for thin layers. Apparently one atomic layer shows about 15% of the bulk polarization and the bulk polarization is reached only for layers of about 64 atomic layers (14.2 nm).

On the theoretical side, there has been much activity. Cox, Tahir-Kheli, and Elliott[12] gave an explanation of the early Bergmann[10] results on Ni and Fe. In their model the principal dependence on the magnetization depends on both the degree of hybridization occurring at the interface and the band occupancy of the magnetic film. Their model also agrees with the spin-polarized tunneling results[9] with Co in which the magnetization was at most slightly depressed by the Al substrate. More recently Tersoff and Falicov[13,14] have calculated the effect on the electronic properties of Ni films one to five atomic layers thick on Cu(100) and Cu(111). They concluded that a monolayer of Ni(100) is substantially magnetic on a Cu(100) substrate, whereas for a monolayer of Ni(111) on Cu(111) the magnetization is completely or very nearly suppressed. A fully self-consistent calculation by Wang, Freeman, and Krakauer[15] of a monolayer of Ni on Cu(100) is consistent with the above result for the (100) face in which the moment is reduced to 60% of its bulk value. The validity of these calculations has been questioned by Kleinman[16] and replied to by Tersoff and Falicov.[17] Tateno and co-workers[18] have calculated the spin polarization of Ni overlayers on Al(100) and concluded that the polarization of the first monolayer should be

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severely depressed but still finite. The conclusions of Tersoff and Falicov[17] are as follows: (1) *sp-d* hybridization coupling is the crucial physical effect suppressing the magnetization; (2) one monolayer is extremely sensitive to the coupling strength; (3) the substrate effect should be limited to approximately two layers even for strong coupling.

MEASUREMENT

The technique used to study the proximity effect in Ni in contact with various metals was substantially as described previously.[6,19,20] Al films 4.2 nm thick were deposited on liquid-nitrogen-cooled glass substrates and then warmed to room temperature. The films were then oxidized in a glow discharge of pure O_2 for about 1 min at a pressure of 10 Pa to form an Al_2O_3 tunnel barrier. The substrate was cooled again to liquid-nitrogen temperature to suppress agglomeration during the Ni deposition.[9] Then the ultrathin cross strips of Ni were deposited from a well-outgassed alumina-coated tungsten basket. The Ni thickness was controlled by a rotating sector disk, which allowed five different thicknesses of film to be deposited in one evaporation.[21] Through the same cross-strips mask, a 50-nm-thick film of the nonferromagnetic metal M (M=Al, Au, Cr or Mn) was deposited to complete the tunnel junction. The substrate was then warmed to room temperature, removed from the vacuum system, leads connected, and then mounted in the cryostat for measurements. To study the spin polarization of the Ni films, the junctions were cooled to about 0.45 K in a ^{3}He cryostat. Upon applying a magnetic field of a few teslas (generally 3.3 T), Al quasiparticle states show Zeeman splitting and the electrons tunneling from/to the Ni film show polarization depending on the degree of ferromagnetism exhibited by the Ni film.[20] The tunneling conductance was measured for junctions with different Ni film thicknesses and the electron-spin polarization was calculated with a first-order correction for spin-orbit scattering in the Al film.[19]

Measurements were made with thin Ni films backed with Al about 50 nm thick. Figure 1 shows the results for Ni thicknesses from 0.2 to 9 nm. For Ni films less than 0.65 nm, which is about 2.9 atomic layers, the polarization $P=0$. For thicker Ni films the value of P increased and reached about 80% of its bulk value at about 2.6 nm, or 12 atomic layers. Here the average thickness of an atomic layer a was taken to be $\delta=[\text{atomic weight}/(\text{Avogadro's number})(\text{bulk density})]^{1/3}$, which for Ni=0.22 nm. Since the true density of such thin films is not known, the bulk density was used and the value of δ can only be considered as an approximate nominal value. The error in the value of δ is partly compensated for because the bulk density is also used with the quartz-crystal thickness gauge.

Very different behavior was found for thin Ni films when backed by Au. Figure 2 shows P as a function of Ni thickness for Au and Al and also points for Cr and Mn. A single atomic layer of Ni shows significant polarization and two layers give $P=0.70P_\infty$. The difference in convergence toward P_∞ for Au and Al backing films is very striking. The single measurements obtained for Ni with Mn and Cr backing films show some polarization at about two atomic layers, but very much less than Au. These metals appear to have a critical onset thickness intermediate between Au and Al.

DISCUSSION

It should be noted that the value of P_∞ for these measurements is about 24%, whereas in early measurements the value ranged between 6 and 13%.[9,19] This change resulted from a change in the barrier-preparation technique. In early experiments the thin Al counterelectrodes were oxidized in humid air. It is known by inelastic tunneling that this method of oxidation leads to OH ions in the Al_2O_3 barriers. The present method of using a glow discharge in pure oxygen avoids most of this OH-ion contamination and the values of P_∞ are about 24% and much less variable. The value of $P_\infty=25\%$ was given by Rogers,[22] who also used an oxygen glow discharge to make barriers for spin-polarized tunneling measurements of Ni. It appears that the smaller absolute values of P obtained in early measurements of Ni were caused by contamination of the Ni surface in contact with the tunnel-

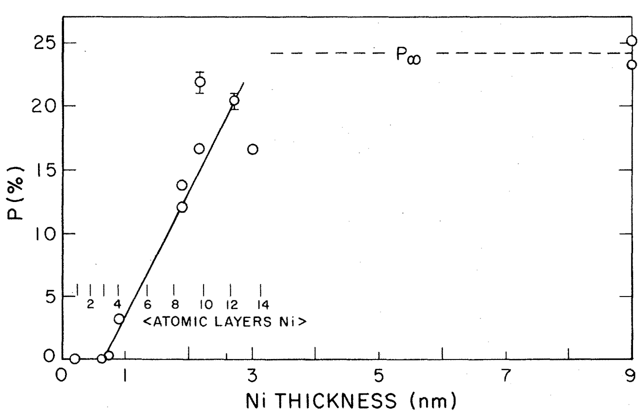

FIG. 1. Measured electron-spin polarization P for Ni of various thicknesses in contact with Al. The points are for different junctions and the error bars show the range in P in different measurements of a given junction when it exceeded the size of the data points.

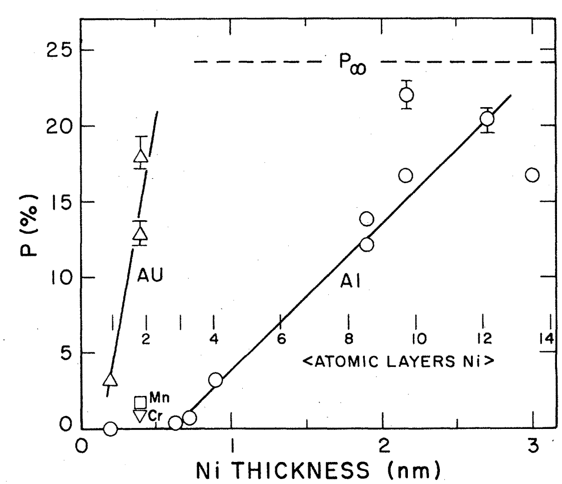

FIG. 2. Measured electron-spin polarization P for Ni of various thicknesses in contact with Al, Au, Mn, and Cr.

barrier material rather than because of spin scattering in the tunneling process. This conclusion is based on the fact that the change in technique of barrier preparation did not affect the value of $P_\infty = 44\%$ obtained for Fe. In spite of the large difference in absolute value of P_∞, the minimum thickness for which P became finite agrees with the earlier proximity-effect measurements of Ni films with an Al backing. In addition, the slow convergence of P to P_∞ for greater thicknesses of Ni is similar to previous results in which $P = 0.80P_\infty$ at a Ni thickness of 10 atomic layers.[9]

The present results with Al and Au agree with the results of Bergmann[10] using the anomalous Hall-effect technique. The results are consistent with the following interpretation. Polyvalent metals such as Al, Pb, Sn, etc., suppress the magnetic interaction in Ni so that the first 2—3 layers of Ni are nonmagnetic. On the other hand, monovalent metals such as Au, Ag, and Cu have much less or no effect in suppressing the magnetic interaction of Ni. As previously shown by spin-polarized tunneling and the anomalous Hall-effect measurements, Fe is not affected by the backing metal. The value of P in Co appears to be somewhat suppressed by Al, but not nearly as much as Ni.

These results on the minimum onset thickness for P in Ni for Al, Au, Mn, and Cr fit very well with the theoretical picture as detailed by Tersoff and Falicov.[14] The basic mechanism of hybridization of *s-p* electrons of the backing metal with *d* electrons in the ferromagnet as suggested by these authors and by Cox *et al.*[12] appears to be satisfactory. It was suggested by Tersoff and Falicov[14] that the operative mechanism which suppresses the ferromagnetism in Ni films on nonmagnetic metal substrates is substantially the same as that which suppresses impurity magnetism in a nonmagnetic host and that which determines the magnetism in alloys of Ni. Figure 3 shows some experimental data in Ni alloys to illustrate this trend. The suppression of the magnetic moment increases

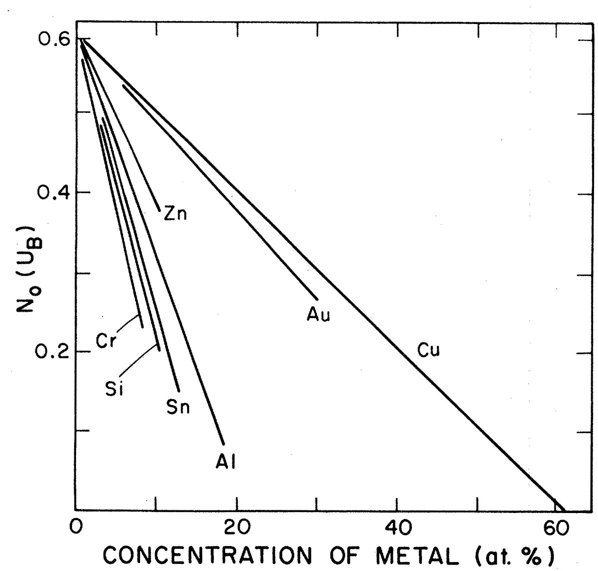

FIG. 3. Magnetic moment per atom N_0 in Bohr magnetons for various alloys of Ni as a function of the (at.%) of the other metal.

only slowly with Au, Ag, and Cu; the suppression is much more rapid with polyvalent metals. In spin-polarized tunneling experiments the ferromagnetic films were deposited at liquid-nitrogen temperature and then immediately covered with a normal-metal film. The Al films are known from previous electron microscope observations to be polycrystalline with a crystallite size of the order of the film thickness[23] and the same is probably true for the other normal-metal films. For the very thin ferromagnetic films there is no direct information about their structure, but it is presumed that they are composed of very small and disordered microcrystallites.[24,25] Thus the experimentally measured proximity effect does not depend on the details of crystal structure. The theoretical calculations mentioned above apply to a coherent crystal structure. However, the general picture in which they are based probably applies qualitatively to disordered films.

A difference between the theory and the measurements of P for Ni films with an Al backing is in the convergence of P to P_∞ as the Ni film is made thicker. Tersoff and Falicov[13,14] predict a suppression of the polarization only for two atomic layers, whereas the spin-polarization measurements show noticeable suppression of P for at least 10 atomic layers. One possible explanation is that the Ni films coalesce into clumps and so it takes over 10 atomic layers of Ni before the layer has no holes in it. However, this explanation is unsatisfactory because the clumping effect in Ni is not expected to be larger than that of Fe for which P_∞ is being approached at two atomic layers. In addition, there is no such slow convergence for Ni when backed with Au. Another possibility is that the Al, when evaporated onto the disordered Ni film, actually diffuses a considerable distance into the Ni film and thus causes the partial suppression of the magnetism of the interface layer of the Ni. From the present experiments it is not possible to distinguish between this explanation of the slow convergence of P and a more fundamental one involving longer-range interactions. However, there are strong arguments against diffusion playing a dominant role. Weaver and Hill[26] have studied the diffusion of Al when deposited on Ni films and have shown that after annealing at 300 °C for some hours AlNi could be detected by x rays. No alloy formation could be detected at a temperature of 200 °C or lower. From their data we can estimate the diffusion constant D to be 10^{-28} cm^2/sec at 300 K so that the time to diffuse 1 Å at room temperature is 10^{12} sec. Using standard data from Smithells[27] we obtain even longer times.[24] The fact that the diffusion coefficients of Ni and Co are very similar[27,28] makes their different magnetic behavior difficult to explain by a diffusion model. The fact that Bergmann's results with an *in situ* measurement at liquid-helium temperature agree with ours in which the tunnel junctions remain at room temperature for an hour are strong evidence that diffusion is not a dominant factor. One might suspect that a chemical interaction between the Al_2O_3 tunnel barrier and the ferromagnetic film would suppress the ferromagnetism of the Ni. Indeed an interaction with Al_2O_3 has been observed with inelastic tunneling[29] for a top electrode of Au or Cu, although the observed interaction was less when the electrode was deposited on a liquid-nitrogen-cooled substrate as in the present experiments. We have not made inelastic tunneling measurements on our junctions. One reason for believing that these effects are not important in the present experiments is that such an interaction with the Al_2O_3 should (contrary to observation) depress the spin polarization of thick Ni films as well as thin ones, since tunneling senses only the surface of the Ni. Also the agreement with Bergmann's results, in which there is no insulating layer, contradicts this hypothesis. The calculations of Tateno and co-workers[18] of Ni on Al(100), which shows less depression of the Ni moment than that measured on disordered films, may not be directly applicable to our Ni films in contact with disordered Al films.

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