Experimental probe for thin-film magnetism in $p(1\times1)$ Pd and V on Ag(100)

R. L. Fink, C. A. Ballentine, and J. L. Erskine
Department of Physics, University of Texas, Austin, Texas 78712-1081

Jose A. Araya-Pochet
Escuela de Física, Universidad de Costa Rica, San José, Costa Rica
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We report high-sensitivity experiments utilizing the magneto-optic Kerr effect which probe for ferromagnetism in ultrathin epitaxial films of Pd and V on Ag(100) substrates. Our experiments fail to detect unambiguous manifestations of ferromagnetism in these two thin-film systems.

Recent theoretical[1-4] and experimental[5-8] efforts have addressed an interesting issue: the possible existence of ferromagnetism in thin-film structures of metals that are not ferromagnetic in thier naturally occurring bulk form. Two elements V and Pd have been singled out as particularly attractive candidates for exhibiting ferromagnetism induced by stabilizing a two-dimensional epitaxial film having an expanded lattice constant. Atomic V has a large magnetic moment resulting from spin alignment governed by Hund's rule ($3\mu_B$), and although atomic Pd has no magnetic moment (its ground state is $4d^{10}5s^0$) it is isoelectronic with Ni which is ferromagnetic in its metallic state. Formation of the conduction bands in V and Pd is accompanied by a partial destruction of the atomic character of the d states and other valence levels (hybridization and quenching of orbital momentum) but in both instances the result is a metal which exhibits strong paramagnetic susceptibility.

The ability to stabilize thin epitaxial layers having lower symmetry, reduced atomic coordination, and significantly increased neighbor distances compared with the bulk materials offers the possibility of inducing novel magnetic behavior in thin-film structures.[9] Indeed, first-principles calculations tailored to the structure of surface layers on bulk crystals and epitaxial thin-film structures have predicted a rich variety of new magnetic phenomena.[1-4]

Experiments reported in the present paper address the possibility of induced magnetism in epitaxial films of V and Pd on Ag(100) surfaces. An appreciable amount of experimental and theoretical work on these two systems has already appeared. The first computational studies of V on Ag(100) predicted enhanced magnetic moments and ferromagnetic ordering.[1,2] Corresponding calculations including spin-orbit effects predicted ferromagnetism in free-standing V monolayers (having the Ag lattice constant).[3] In these calculations, the crystalline anisotropy favors spin alignment perpendicular to the film plane, but the shape anisotropy is dominant and forces the spin to lie in the film plane. Subsequent calculations,[4] however, suggest that the ground state of V on Ag(100) is an antiferromagnetic $c(2\times2)$ state.

Four experiments have explored the magnetic properties of V grown on Ag(100). Electron-capture-spectroscopy (ECS) experiments[5] appear to indicate that a $p(1\times1)$ monolayer of V on Ag(100) is ferromagnetic, with in-plane magnetization and a transition temperature of 475 K. The temperature dependence of the magnetization inferred from ECS studies of a five-layer V film on Ag(100) yielded critical behavior in good agreement with the two-dimensional Ising model (experimentally determined exponent $\beta=0.128\pm0.01$). More recently, Moodera and Meservey[6] have used surface impedance measurements to probe the magnetic properties of V layers on Ag as well as on Pb, Al, and Au. Their experiments suggest that 1.5 monolayers of V on all of these metals is ferromagnetic. On Au and Ag the V magnetic moment is comparable to an isolated Fe atom. Inverse photoemission studies of V on Ag(111) have been interpreted to suggest the existence of exchange split d states above E_F.[7] This interpretation of inverse photoemission spectra is certainly consistent with a finite magnetic moment for epitaxial monolayer V films, but does not exclude the possibility that the film is paramagnetic. Spin-polarized photoemission,[8] a more direct and broadly accepted probe of ferromagnetism, has been used to study 1–3 monolayer films of V on Ag(100). These experiments subjected carefully prepared epitaxial films to 30 K temperatures and 18 kOe magnetic fields perpendicular to the film plane while probing for magnetic behavior at a sensitivity that had previously identified magnetism in monolayer Ni films. Although the spin-polarized photoemission experiments probe for magnetism with spin alignment perpendicular to the film plane (and ECS suggests that the moment lies in the plane) the applied fields were sufficient to overcome the shape anisotropy of the films. If the V films were ferromagnetic, a signal should have been detected. No evidence of magnetism was apparent in this particular spin-polarized photoemission study.

The magnetic character of Pd surfaces and thin Pd films has not been as extensively investigated as for V. Calculations[10] for bulk predict magnetic ordering upon expanding the lattice by $\sim10\%$, and preliminary experimental results[11] based on ECS experiments have suggested the existence of ferromagnetism at Pd surfaces and in thin epitaxial Pd films grown on Ag(100).

In order to address the important issues and apparent discrepancies between the existing experiments described above, we have carried out high sensitivity experiments which probe for ferromagnetism in epitaxial films of Pd and V on Ag(100) surfaces. Our experiments have failed

to yield unambiguous evidence of ferromagnetism in either system within the sensitivity limits of our experimental technique. This paper documents our observations including film growth, structure analysis, and the range of parameters over which measurements were conducted including an analysis of the sensitivity of our experimental probe for magnetic behavior.

Our Ag(100) single-crystal samples were prepared by spark cutting 2-mm-thick wafers from a 99.995% pure rod after alignment to approximately $\pm 1°$ using x-ray Laue techniques. The 1-cm-diam wafers were mechanically polished using various size abrasive pastes down to 0.05 μm and were cleaned *in situ* using standard methods (sputtering in 5×10^{-5} Torr Ne at 500 eV and 10 μA followed by annealing to 500 °C. Auger analysis of the surface indicated contamination levels of S and C below 1%, and O below 2% prior to and after V film growth. These low-level surface contaminants were not found to affect magnetic behavior of other thin films that clearly exhibited ferromagnetic behavior on Ag(100). We note, however, that Rau *et al.*[5] were able to achieve O contaminations below 1% in their V film growth, and on bulk V surfaces[12] which ECS also shows to be ferromagnetic. It is conceivable, but unlikely, that surface oxygen contamination in the 1–2 % range is sufficient to quench the magnetic moment of V on Ag(100). (Rau *et al.* report a spin-polarization reduction from 30% to 22% on V(100) when 0.06 monolayer of oxygen is on the surface.) The growth of Pd films was slightly cleaner (O contamination below 1%), however, accurate C contamination levels were difficult to monitor because of overlapping Pd and C Auger lines. Low-energy electron diffraction (LEED) analysis of the Ag(100) substrate indicated that the substrate surface was well ordered (low diffuse background) and that the average terrace widths were ~75 Å based on the width of the diffracted LEED beams. This result is consistent with the estimated alignment accuracy of the crystal surface.

We used a substrate temperature for V film growth of approximately 370 K as reported by both Rau *et al.*[5] and Stampanoni *et al.*[8] Time-dependent Auger analysis of V film growth exhibited an exponential decay with no evidence of breaks in slope. In the liquid state, V and Ag are insoluble, but the surface energy of V (2.6 J/m^2) is significantly higher than that of Ag (1.25 J/m^2). This suggests that intermixing at the interface is not likely, but that cluster formation or Ag segregation, rather than layer growth, is favored by equilibrium thermodynamics. The lattice mismatch for V on Ag(100) is 4.2% (expanded V lattice), assuming that V grows on Ag in a $p(1\times1)$ structure with a surface net rotated 45° about the surface normal, similar to Fe on Ag(100). LEED patterns of the first few layers of V on Ag suggest that the growth is pseudomorphic with some dislocations as evidenced by the lower quality of diffraction spots for thicker films. Based on all of the surface structure sensitive information available at this time, it appears that V grows on Ag(100) as uniform layers (for the first 3–4 layers), and does not exhibit significant three dimensional island formation over the coverage range of interest here (below five layers).

Pd films were grown on Ag(100) using substrate temperatures of 180 and 300 K. Clear evidence of interdiffusion and island growth was apparent in films grown at substrate temperatures of 300 K and above or in films which were annealed above 300 K. Time-dependent Auger analysis studies of Pd growth at 180 K and at lower temperatures exhibited exponential decay of Ag signals similar to that observed for V (Fig. 1). The surface energy of Pd (2.1 J/m^2) is also higher than that of Ag again suggesting that cluster formation is thermodynamically favored over layer growth. The lattice mismatch for Pd on Ag should yield a 5% expansion of the Pd lattice when grown as a $p(1\times1)$ layer on Ag(100). LEED patterns for one monolayer of Pd on Ag(100) were of poorer quality than for V on Ag(100); suggesting an appreciable amount of disorder in the film. Nevertheless, a few atomic layers of Pd appear to cover the Ag(100) surface with a reasonably uniform continuous film.

A detailed description of our Kerr effect spectrometer is presented in a recent publication[13] along with an analysis of the sensitivity of the polarimeter. We use a 1 mW He-Ne laser source and detect changes in intensity ΔI that result from reversing the magnetization of the film which is placed between crossed polarizers (Fig. 2). The substrate can be masked during film growth, and our system contains two molecular-beam epitaxy sources. These features permit either growing a film on one-half of the substrate, leaving the other half clean as a nonmagnetic reference surface, or growing two films of different material on the same surface. These films may then be studied sequentially under identical experimental conditions.

The intensity of transmitted light as a function of analyzer angle γ is given by the well-known Malus law $I = I_0 \sin^2\gamma + I_r$, where I_0 is the light intensity reflected from the sample, and I_r is the residual intensity resulting

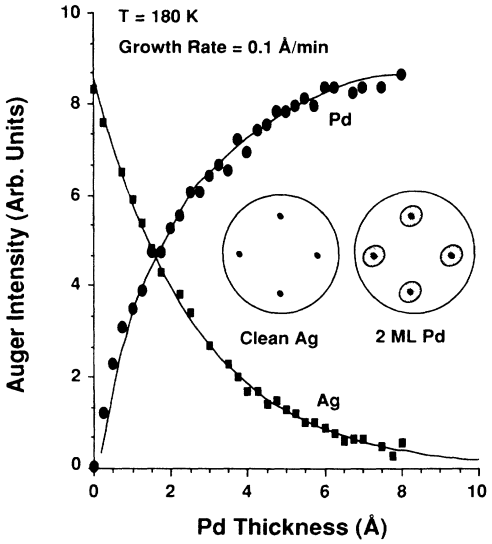

FIG. 1. Surface analysis of Pd film growth on Ag(100): Substrate and overlayer Auger signals as a function of overlayer thickness (determined by a mass microbalance ~5 cm from the evaporation source). Inset figure provides an indication of the LEED pattern quality prior to (2-mm-diam spots, 65 V) and after film growth (10-mm-diam spots, 75 V).

from the finite extinction ratio of the polarizers and depolarization effects resulting from scattering from the sample surface and window birefringence. (Slight window birefringence effects are eliminated by the compensator.) The contrast due to the magneto-optical effect defined by $C=\Delta I/I_0$, where ΔI is produced by a small Kerr effect rotation ϕ, is given by

$$C=\frac{\gamma/\gamma_m}{1+(\gamma/\gamma_m)^2}\frac{2\phi}{\sqrt{\epsilon}},$$

where γ and ϕ are assumed small, γ_m is the angle that yields maximum contrast, and $\epsilon=I_r/I_0$ is the extinction ratio of the system. In our experiments, $4\epsilon \gg \phi^2$, and the maximum contrast occurs at $\gamma_m=\sqrt{\epsilon}$. In other words, the extinction ratio is an important figure of merit for a single beam polarimeter. We typically operate our polarimeter at $\gamma \sim 4\sqrt{\epsilon}$. Under normal operating conditions, we have found that the signal-to-noise ratio of our Kerr effect measurements is basically limited by the intensity I_0, i.e., the ultimate sensitivity is limited by statistical error associated with the number of photons/sec from the 1 mW laser when the signal averaging is carried out for about 1 or 2 min.

Our Kerr effect spectrometer is capable of probing magnetism in thin film structures at temperatures below 40 K, and in magnetic fields of up to 2800 Oe applied either in the plane of the film or perpendicular to it. The polarimeter can measure the magnetic hysteresis loop for a monolayer Ni film (Fig. 3) which yields Kerr rotations of the order of 1 sec of arc, with a signal-to-noise ratio of 5 in approximately 2/min. If we assume that the Kerr effect signals scale generally with the size of the magnetic moment per atom, we estimate that the sensitivity is sufficient to detect ferromagnetism in a monolayer film having a magnetic moment greater than $0.05\mu_B$ per atom. This sensitivity estimate must be qualified because the strength of optical dipole matrix elements and of spin-orbit coupling in the magnetic bands are material dependent and also affect the strength of magneto-optical effects. Spin-orbit effects in the $3d$ metals (V, Fe, and Ni) should be comparable; in Pd, a $4d$ metal (higher Z) the effects should be stronger. However, our measurements on thin films of Fe and Ni (Refs. 13–15) generally indicate that the Kerr effect signals are proportional to the film thickness, and the magnetic moment per atom.

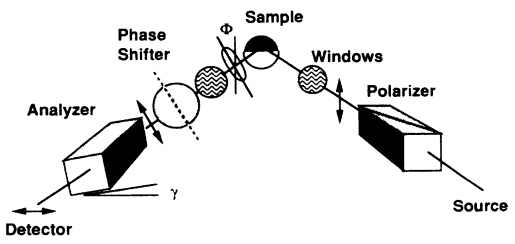

FIG. 2. Optical elements of the Kerr effect polarimeter, and parameters required to characterize the signal-to-noise ratio. The angle γ represents the analyzer offset from a crossed position; the angle ϕ is the Kerr rotation. The extinction ratio of the polarizers is $\sim 10^6$; under typical experimental conditions (windows and sample surface in the optical system) the extinction ratio is $\sim 10^5$.

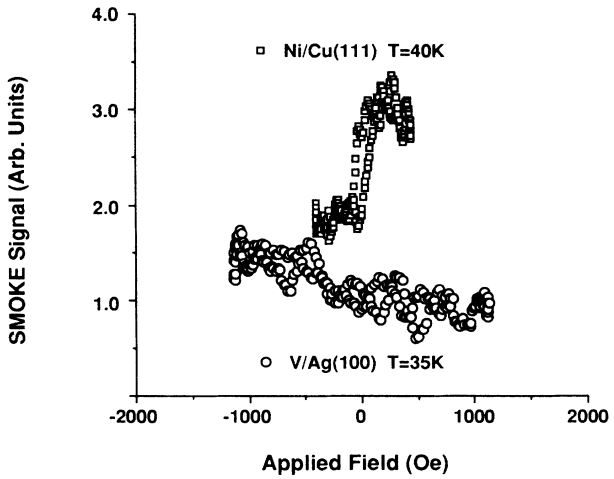

FIG. 3. Surface magneto-optical Kerr effect signals from Ni and V monolayers. Upper curve, typical hysteresis loop obtained from a $p(1\times1)$Ni monolayer film on Cu(111). Lower curve, attempt to measure hysteresis loop from a $p(1\times1)$V monolayer on Ag(100). There was no essential difference between the results shown in the figure for a V covered surface and for a clean silver surface.

Figure 4 displays a typical result of a series of experiments that we conducted in which the magneto-optical response of V and Fe films grown on the same Ag(100) crystal were studied as a function of temperature, applied field strength and direction, and laser wavelength. For temperatures above 40 K, and applied fields below 2800 Oe, either in the film plane or perpendicular to it, no Kerr effect signals were observed for the V films. Similar experiments were conducted for Pd on Ag(100). In no case was a definitive manifestation of ferromagnetism (hysteresis loop) observed.

The magneto-optic Kerr effect is a differential effect which is a consequence of the asymmetry in the absorption of left and right circularly polarized light. The asymmetry results from the combined effects of spin-orbit coupling and a net spin polarization in ferromagnetic materials. It is possible for null Kerr effect signals to result at specific photon energies even when the material being probed is ferromagnetic. In order to reduce the possibility of judging a film to be nonmagnetic based on an accidental Kerr effect null, we carried out all experiments using two photon energies ($\lambda=637.8$ and 543.3 nm). In all cases studied, either null results (V and Pd) or good hysteresis loops (Fe and Ni) were obtained from the thin films.

Our Auger and LEED analysis of the V and Pd films do not constitute an accurate structure determination. However, we have explored the film properties (with LEED, Auger analysis, and Kerr effect measurements) and have determined the temperature range over which films of 1–3 monolayer (ML) appear to be uniform and stable. Under conditions which do not cause temperature-dependent changes in Auger or LEED results ($T<350$ K for V; $T<300$ K for Pd), the films appear to be continuous rather than being composed of three-dimensional clusters. (No LEED patterns were observed which suggested the presence of clusters having

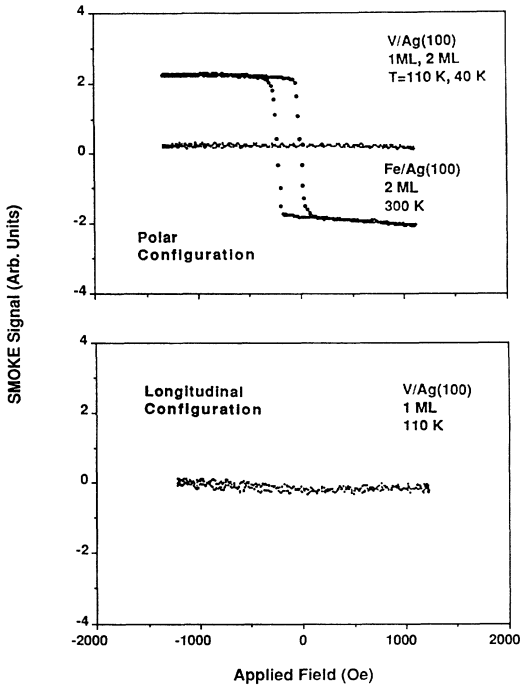

FIG. 4. Direct comparison of Kerr effect polarimeter results for a Ag(100) crystal having a 2 ML $p(1\times1)$Fe film on one-half, and a $p(1\times1)$1 ML V film on the other half. The upper figure displays hysteresis loops for magnetic fields applied perpendicular of the film surface [showing that the easy axis of the 2 ML Fe film on Ag(100) is perpendicular]. The upper and lower figures show no evidence of a hysteresis loop for the V film.

the bulk lattice parameter). In addition, corresponding thickness dependent LEED and Auger analysis of Fe and Ni layers grown on Ag(100) (Ref. 14) and Cu(100) (Ref. 15) exhibited very similar behavior, and these films were all found to be ferromagnetic.

Our experiments clearly disagree with the interpretation of electron capture results which report ferromagnetic behavior for V films 1–7 monolayer thick, with in-plane saturation magnetization in applied fields of 600 Oe and Curie temperatures of ~475 K. Our experiments are consistent with the null results obtained by spin-polarized photoemission and achieved higher detection sensitivity.

Summarizing our conclusions for $p(1\times1)$ V on Ag(100), we have found that good quality pseudomorphic films of several monolayers thickness can be grown at substrate temperatures of 370 K. No evidence of ferromagnetism was observed in polar and longitudinal Kerr effect studies of these films for applied fields up to 2800 Oe and temperatures down to 40 K. We looked for, but observed no evidenced of, elastic exchange scattering from an antiferromagnetic lattice that should have appeared as a weak $c(2\times2)$ LEED pattern. However, the sensitivity of this probe of antiferromagnetic order has not been established, and the null result cannot be cited as evidence of the absence of antiferromagnetic order. Tight-binding approximation analysis of the transition-metal series by Heine and Samson[16] accounts for the tendency of V, Cr, and Mn to be antiferromagnetic and Fe, Co, and Ni to be ferromagnetic. This general behavior taken with the calculations of Blugel *et al.*[4] and the predominance of experimental evidence suggest that $p(1\times1)$V on Ag(100) is antiferromagnetic.

In the case Pd on Ag(100), the quality of the $p(1\times1)$ structure at 1 monolayer is not as good as for V, but the Pd films clearly grow as continuous layers rather than clusters. Bulk Pd is predicted to be ferromagnetic at an expanded lattice, and based on this result, it could be regarded as surprising that a $p(1\times1)$ Pd monolayer on Ag(100) is not magnetic. Thin film calculations for Pd on Ag(100) are in progress. Preliminary results[17] predict that an unsupported Pd film with the Ag lattice constant is ferromagnetic, and that $p(1\times1)$ Pd on Ag is nonmagnetic. Based on these new calculations and the unreported ECS results for Pd, it is possible that Pd films on Ag(100) are ferromagnetic, and that the spin-polarized photoemission and Kerr effect studies conducted to date have not achieved sufficient sensitivity to detect the ferromagnetic behavior.

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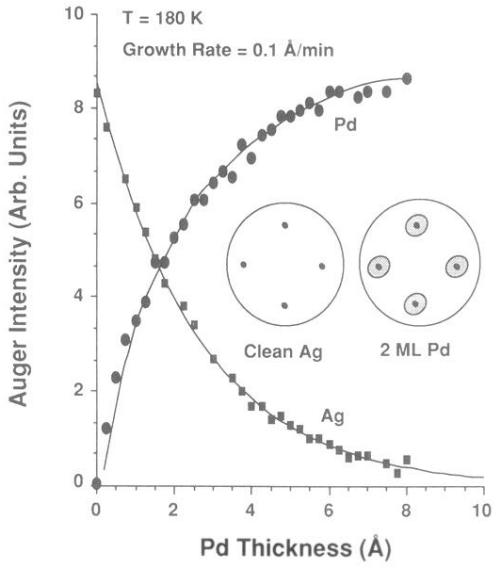

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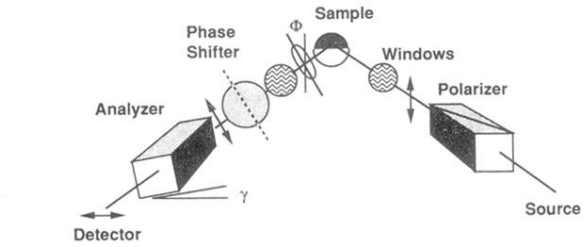

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