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Surface magneto-optic Kerr-effect probe for magnetization in monolayer $p(1\times1)$ Rh on Ag(100)

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A magneto-optic Kerr-effect study of monolayer Rh on Ag(100) was undertaken to test recent predictions of 4*d* ferromagnetism. For temperatures down to 40 K, no evidence of ferromagnetic order was observed. Possible explanations for the absence of long-range spin ordering are presented.

Bulk single-crystalline elemental ferromagnetism is confined to the 3*d* transition metals and the rare earths. The application of negative pressure to certain 4*d* paramagnetic materials can lead to a bulk transition in which ferromagnetic ordering provides the lowest-energy stable state.[1] By depositing such materials epitaxially onto crystalline substrates with lattice constants greater than the bulk paramagnetic metal, it is possible to exert such a negative pressure and in principle to achieve a ferromagnetic state. Extrapolation to systems of epitaxial ultrathin films is not straightforward; hybridization effects between the substrate and the film which compete with an increased ratio of electron-electron interaction to bandwidth can displace the ferromagnetic state away from the equilibrium configuration.[2] Recent advances in the predictive power of total-energy ground-state calculations of ultrathin film systems has helped to spur interest in this area.

Early predictions favored V on Ag(100) as a candidate for ferromagnetic ordering in ultrathin films formed from a normally paramagnetic 3*d* metal.[3] An electron capture spectroscopy experiment seemed to indicate that ferromagnetism was present in a $p(1\times1)$ V overlayer.[4] Subsequent experiments, however, suggest that long-range ferromagnetic order does not exist in such a V film.[5,6] Theoretical predictions are now in line with these latter experiments.[7] Current *ab initio* and pseudopotential calculations now point to the 4*d* metals Rh (isoelectronic with Co) and Ru (isoelectronic with Fe) as possessing stable ferromagnetic states when epitaxed onto Ag(100) or Au(100).[8,9] Ideal pseudomorphic growth would yield an areal expansion of $\sim$7% over that of the bulk lattice in the case of Rh. This expansion is significantly smaller than the 14% necessary for a weak transition to ferromagnetism in bulk Rh (Ref. 1) and suggests that the lower coordination at the surface is a critical ingredient of the ferromagnetic state. These predictions have motivated us to undertake the search for 4*d* ferromagnetism in ultrathin $p(1\times1)$ Rh on Ag(100) films.

It is worth noting that a 4*s* core-level splitting as measured by angle-resolved photoemission[10] does not necessarily provide a unique test for the existence of ferromagnetism. A comprehensive study of various crystalline and amorphous alloys has shown that there is poor correlation between 3*s* core-level splitting and magnetic moments.[11] In fact, the Pauli paramagnet WFe_2 exhibits a 3*s* core splitting equal in magnitude to that of ferromagnetic Fe. While the situation for the 4*d* metals is not as well known, any 4*s* splitting should not be taken as an indicator of a local magnetic moment without corroborating evidence.

Several techniques do exist, however, which are capable of proving the existence of long-range ferromagnetic order. Few of them, however, are as versatile and as sensitive as the surface magneto-optic Kerr effect (SMOKE) apparatus in obtaining hysteresis measurements. An outline of the machine has appeared previously;[6,12] the presence of magnetization manifests itself as an ellipticity or a rotation in an initially linearly polarized monochromatic light beam reflected from the surface or film in question. Hysteresis loops (when they exist) can be acquired in a few minutes with a magnetic field sequentially applied both parallel and perpendicular to the film plane.

The Rh films were grown on spark-cut single-crystal Ag(100) substrates which were aligned to better than $\pm0.5°$ using an x-ray Laue camera. The Ag crystals were cleaned by sputtering with 500-eV Ne ions followed by anneals to 645 K. Substrate ordering was established by the existence of a sharp low-energy electron diffraction (LEED) pattern while sample cleanliness was monitored with Auger electron spectroscopy (AES). A liquid-nitrogen-cooled electron-beam evaporator was used to deposit the Rh overlayers. After 12 h of degassing the evaporator, the films as deposited, after experimentation, had oxygen contamination levels below 1.0%. Film thickness was determined using a quartz-crystal microbalance with the sensitivity geometrically enhanced by a factor of 10. Absolute thicknesses were obtained by cross calibrating with 2+ monolayer (ML) Fe-Ag(100) films which exhibit a well-characterized transition perpendicular to the in-plane easy axis.[13]

In order to determine the best conditions for epitaxy, Rh was deposited with the substrate held at temperatures ranging from 610 to 130 K. Rh deposited at the highest temperature was not detectable with AES. Apparently, at this temperature Rh easily diffuses into the Ag matrix. This is not surprising since Rh forms low-concentration alloys with Ag.[14] Films deposited at 320 K did not form a well-ordered system. LEED patterns were highly streaked, with the principle broadening occurring along a line connecting the first-order beams through the specular beam. This disorder may be evidence of severe islanding, since it is not energetically favorable for Rh to wet the Ag surface. However, it is most likely caused by the related phenomenon of substitutional mixing at the Rh-Ag interface. It has been shown that room-temperature growth of

Rh on Ag can result in a free-floating Ag monolayer atop the Rh film.[15] Several films were deposited at $T=130$ K as an attempt to suppress any such intermixing by decreasing the mobility of the adatoms.

The clean Ag(100) surface had an average island size of ~80 Å as determined from LEED spot profiles. The films deposited at low temperature yielded a low background $p(1\times1)$ LEED pattern with spots diameters nearly twice that of those from the substrate. These films were subsequently annealed to 180, 273, and 373 K between data-acquisition runs in an attempt to increase the local order while still inhibiting interdiffusion. Additional LEED studies of the low-temperature epitaxy of Rh on Ag(100) are currently underway.

SMOKE measurements were undertaken on films grown under all conditions except for the highest-temperature deposition. Prior to measurement, all films were cooled to either 130 or 40 K depending on the probe arm to which the substrate was attached. Films at both temperatures yielded qualitatively similar results. Magnetic fields up to 2 kOe were applied to probe for magnetization both perpendicular (along ⟨001⟩) and parallel (along ⟨110⟩) to the film plane. Previous studies in this laboratory have shown that fields of this magnitude are sufficient to yield a clear signal from ultrathin ferromagnetic films *regardless* of the easy axis.[13]

The signal from a typical measurement appears in Fig. 1. The slight deviation from linearity is due to eddy currents in the substrate. A hysteresis loop from a 2 ML film of $p(1\times1)$ Fe on Ag grown on the same substrate immediately after removing the Rh film appears in the figure for contrast. The signal size from the Fe film gives us a direct measure of the sensitivity of the SMOKE technique because previous results suggest that the size of the SMOKE signal generally scales with magnetic moment.[12,13] After correcting for run-dependent factors such as varying extinction, we can extract a limit on the size of the magnetic moment of the Rh atoms. Knowing that the signals from both layers of the Fe add linearly,[16] and assuming an upper bound on the magnetic moment of the Fe in the 2 ML film to be $2.96\mu_B$,[17] we place an upper limit on the Rh moment of $0.08\mu_B$. This is nearly an order of magnitude smaller than the predicted values of $1.09\mu_B$ and $0.62\mu_B$ per Rh atom.[8,9] In essence, the Rh films were not seen to be ferromagnetic. A simplifying assumption in this estimate is that the optical dipole matrix elements and the spin-orbit coupling which govern the strength of the SMOKE signal are approximately the same for the two materials. Clearly, Rh, with $Z=45$, has a larger spin-orbit coupling (strength of spin orbit $\sim Z^4$) than Fe which would boost its relative signal size.

One possibility for the absence of the signal is the presence of a diffuse interface between the Rh film and Ag substrate or, in the case of room-temperature growth, the burial of the Rh film by 1 ML of Ag. In the latter case, we expect an Ag overlayer may have a catastrophic effect on the existence of magnetism in the Rh film. Hybridization between Rh and Ag is weak at best and is unlikely (if one believes the calculations) to quench the ferromagnetism.[8] Experimentally, we know that noble-metal overlayers have little detrimental effect on the presence of ferromagnetism in ultrathin films of the 3*d* transition metals.[18,19] However, as in the case of V,[3] an Ag overlayer would increase the coordination of the Rh ML and subsequently widen the electronic bandwidth. This would move the Rh film away from satisfying the Stoner criterion for ferromagnetism.

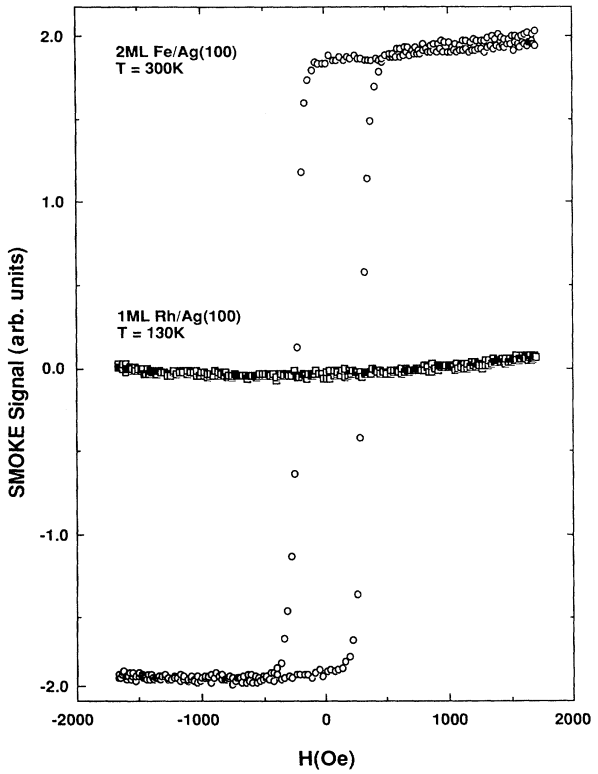

FIG. 1. SMOKE measurements of 2 ML $p(1\times1)$ Fe on Ag(100) at $T=300$ K and 1 ML $p(1\times1)$ Rh on Ag(100) at $T=130$ K. Both sets of data were acquired with $H\|\langle001\rangle$ (perpendicular mode). Data acquired at 40 K and/or in the longitudinal mode ($H\|\langle110\rangle$) are not significantly different.

Dilution of the Rh below the percolation threshold by intermixing with the Ag matrix constitutes a second possibility for suppressing ferromagnetic order. We tested for this eventuality by depositing ~15% more Rh than is necessary to complete one monolayer with no subsequent change in the SMOKE signal. The lack of a ferromagnetic signal probably has little bearing on the film quality. It is well documented that Fe films of reduced epitaxial quality via sputter-damaged or poorly prepared substrates still exhibit ferromagnetic behavior, although with increased coercivities.[20]

This returns us to the question of the reliability of the overlayer calculations. Are we just seeing the V on Ag(100) scenario played out again? When we look at the calculations in detail, some questions directly relating to their applicability immediately arise. Eriksson, Albers, and Boring do not include the possibility of interlayer relaxation into their calculation.[8] In fact, they make a homoepitaxial approximation, i.e., that the Rh goes down with an interlayer spacing of bulk Ag and they discuss

only the effects of a top-layer expansion. A $p(1\times1)$ ML of Fe on W(110), however, which is another strained system ($\sim$10% in that case), relaxes toward the W substrate in a sort of volume conservation effect.[21] Perhaps similar effects occur in the Rh-Ag(100) system. This may be sufficient to drive the equilibrium state toward a paramagnetic or antiferromagnetic state since the minimum responsible for the ferromagnetic ordering in the calculation is only 2.4 mRy deep. The calculation of Zhu, Bylander, and Kleinman is for Rh on Au(100) and is not strictly applicable to our case, although they also make an arbitrary static assignment for the interlattice spacing.[9] Furthermore, neither group addresses the realistic growth characteristics of this system since they omit a calculation of the effects of an overlayer on the Rh film.

In conclusion, we have utilized the sensitive technique of SMOKE to test some recent theoretical predictions concerning the existence of 4*d* ferromagnetism in ML films of Rh on Ag(100). While we do not feel that the results are completely conclusive, as the system requires additional structural analysis for very-low-temperature growth, it is likely that ferromagnetism does not exist in the Rh monolayer film epitaxed onto Ag(100), at least not with a moment larger than $0.08\mu_B$ per Rh atom. The presence of the Ag overlayer upon Rh deposition is a clear roadblock to testing the current predictions for 4*d* ML systems and it is our hope that future calculations will be undertaken with this problem in mind.

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