Ferromagnetism and growth of Ru monolayers on C(0001) substrates

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The magnetic and growth properties of Ru monolayers on C(0001) are studied using spin-polarized secondary electron emission and Auger electron spectroscopy (AES). Using AES, we find that the initial growth of Ru on C(0001) occurs *laterally* until the first monolayer is completed. One monolayer-thin Ru film shows ferromagnetic order below a surface Curie temperature of approximately 250 K. The in-plane magnetization saturates in small applied fields of a few tenths of an Oe. This is the first observation of spontaneous, long-ranged, two-dimensional ferromagnetic order in an ultrathin film composed of a 4*d* transition metal.

Recent advances, both experimentally and theoretically, enable us to explore the possibility of inducing spontaneous, two-dimensional, long-ranged ferromagnetic order in elements that are paramagnetic in their bulk form. Interesting candidates are the paramagnetic 3*d*, 4*d*, and 5*d* transition metals.[1–6]

One way to address this interesting issue is to grow such a metal epitaxially on an adequate nonmagnetic substrate. Ferromagnetic order in such ultrathin films may be induced by the reduced coordination number and hence reduced interatomic hybridization, band structure effects due to the restriction to two dimensions and, compared to the bulk paramagnetic solid, an increased lattice constant imposed by pseudomorphic film growth.

As to ultrathin films of the 4*d*-transition metals, recent studies[2–10] have focused on Ru and Rh monolayers (ML) deposited on Ag(100) and Au(100) substrates. Theoretical works indicate that these systems should possess a ferromagnetic ground state.[2–6] Recent experiments for Rh on Ag(100) and on Au(100), however, failed to find any evidence for spontaneous, long-ranged ferromagnetic order,[13,14] or were inconclusive.[15] There is experimental evidence that an explanation for the discrepancies between theory and experiment can be found in the structural properties of the films deposited on these substrates: Schmitz *et al.*[16] propose that the equilibrium structure of Rh on Ag(001) is actually that of a sandwich with an Ag monolayer atop. Mulhollan *et al.*[14] find evidence for diffusion of Rh into the Ag matrix. Other authors do not rule out islanding.[13,14] These effects are indeed likely to prevent spontaneous, long-ranged ferromagnetic order.

Therefore we decided upon a different substrate and selected graphite C(0001) for the following reasons: similar to the noble metals, there is hardly a band overlap with the 4*d*-transition metals due to the low density of states near the Fermi level, which should prevent strong hybridization with the 4*d* bands. Moreover, the graphite (0001)-surface is known to be very flat, possessing only few steps and nearly no defects. This should considerably suppress interdiffusion. As film material we selected Ru, which has a hexagonal bulk lattice structure with an in-plane nearest neighbor distance which is almost twice that of graphite. Despite the difference in the surface free energy, epitaxial or pseudomorphic growth of metastable Ru with a lattice slightly stretched (5%) compared to the bulk should be favored.[11,12]

To study the growth and magnetic properties, we used Auger electron spectroscopy (AES) and spin polarized secondary electron emission (SPSEE). For many metal-on-metal systems, it was already shown, that AES is a very suitable technique to distinguish between various types of initial growth modes (lateral growth, islanding, intermixing).[19] We recorded the Auger intensity of the substrate and that of the adsorbate line as function of coverage or deposition time. The lateral growth and the completion of a ML is evident from the *linear* increase in the signal and the abrupt change in slope in both plots.

In SPSEE, an unpolarized electron beam of energy of a few keV is used to induce the emission of secondary electrons from the sample. The electron spin polarization (ESP) of the emitted secondary electrons is a direct measure of the surface magnetization. For SPSEE, we use an einzellens system with a 90° cylindrical energy analyzer connected to a 20 keV Mott polarimeter.

As substrate, we use highly oriented, pyrolytic graphite (HOPG) ($8\times15\times1$ mm^3) with a standard distribution of the *c* axes $\sigma=0.2°$ and randomly oriented *a* axes. The HOPG sample is cleaved in air. No further *in situ* treatment is necessary, because the extremely low gas adsorption efficiency guarantees a clean surface for ample time. The sample is mounted on a manipulator between the pole caps of an electromagnet and can be cooled to liquid nitrogen temperatures. The temperature is monitored using a copper-constantan thermocouple. Ru (purity 99.95%) is evaporated using electron beam evaporation (evaporation rate: 0.03 ML/min). The film thickness is monitored by using a quartz microbalance. AES is performed using a cylindrical mirror analyzer (CMA). During the magnetic measurements, the residual gas pressure amounted to $\approx3\times10^{-10}$ mbar; during the evaporation, it increased to $\approx8\times10^{-10}$ mbar.

The growth of Ru on C(0001) was studied by measuring peak-to-peak heights of differentiated Auger lines versus deposition time. In Fig. 1, dN/dE vs E Auger spectra of the clean and the Ru covered graphite surface are given. The graphite spectrum shows one peak at 272 eV. The Ru spectrum is more complicated with nearly symmetric peaks at

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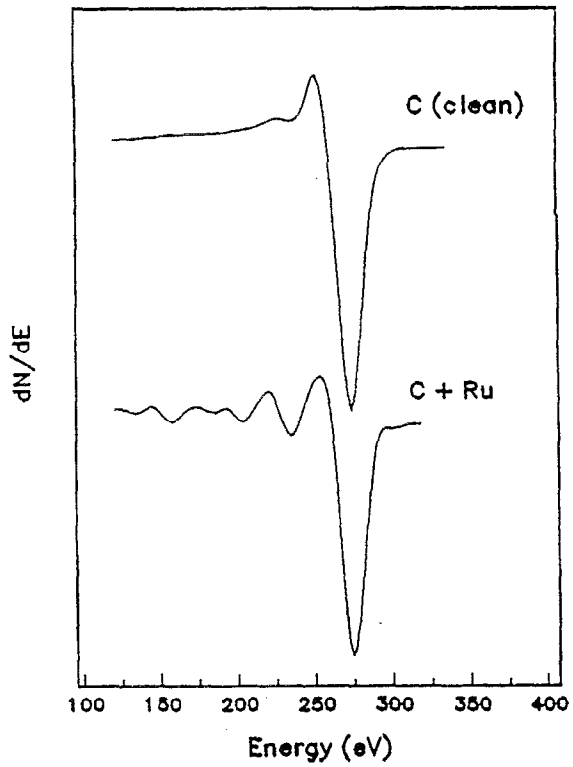

FIG. 1. Differentiated Auger spectra for the clean and Ru covered C(0001) surface.

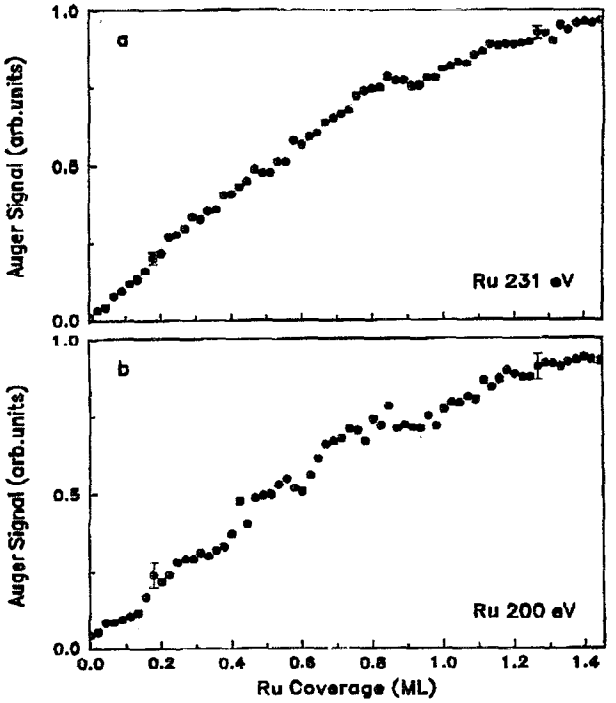

FIG. 2. Auger peak-to-peak height vs Ru coverage on C(0001) of the (a) Ru 231 eV and (b) Ru 200 eV line. The coverage is referred to the atomic density of the bulk Ru(0001) plane.

273, 231, 200, and 160 eV.[20] The most prominent Ru peak at 273 eV overlaps with the graphite peak, therefore, we used the smaller Ru peaks as adsorbate Auger signal. A quantitative analysis of the substrate Auger signal was already the subject of several studies.[21]

In Fig. 2(a), the peak-to-peak heights of the Ru 231 eV Auger line is shown. The x-axis scale is converted from deposition time to coverage, using the quartz reading, calibrated by a geometrical factor. We refer the coverage to the atomic density of the (0001) plane in bulk Ru and assume the sticking coefficient to be one. The Auger signal increases linearly up to a coverage of nearly 1 ML, where a breakpoint occurs. For higher coverages, the Auger signal increases further and reveals a smaller slope. These results are confirmed by the Ru 200 eV Auger signal [Fig. 2(b)], although the data points show a little more scattering due to the smaller signal.

The linear increase of the Auger signal shows that Ru grows laterally until the graphite surface is homogeneously covered, and the first Ru ML completed. From our data, it is unlikely that Ru continues to grow in a layer-by-layer mode (Frank–van der Merwe). Our findings point to a Stranski–Krastanov growth mode (three-dimensional islands on top of a ML) for the following reasons: The (average) slope ratio between the data beyond and below the breakpoint is 0.42, which is smaller than the value 0.70 calculated for layer-by-layer growth using an inelastic mean free path $\lambda=0.82$ nm for 231 eV electrons and a thickness $d=0.214$ nm for one Ru layer.

In Fig. 3(a), we show the peak-to-peak heights of the composite C 272 eV+Ru 273 eV Auger signal. The signal decreases linearly until a sharp breakpoint occurs at nearly 1 ML. These findings are even clearer, when we take only the graphite contribution of the composite Auger line [Fig. 3(b)]. The substrate signal then shows the qualitative behavior as expected for lateral growth and confirms the findings from the adsorbate signal.

To summarize, we find that Ru grows laterally on the graphite surface until the first ML is completed. Beyond the first ML, the data indicate that Ru begins to form three-dimensional islands, i.e., Ru seems to grow on C(0001) in a Stranski–Krastanov mode. These findings are corroborated by our scanning tunneling microscopy measurements, showing in the range of submonolayer coverage lateral growth of Ru.[17]

Next, we report on the magnetic properties of Ru ML films. Initially, we measured the ESP as function of small applied fields up two 2 Oe which were reversed in order to calibrate for instrumental asymmetries. From the magnetization curves, we find that saturation is reached at field strengths of a few tenths of an Oe.

For more refined checks on the effect of instrumental asymmetries on the measured ESP, we used the nonmagnetic surface of the graphite crystal and performed the same procedure as for the Ru films. We find that the small applied fields have no effect on the measured ESP.

The results of the SPSEE experiment are shown in Fig.

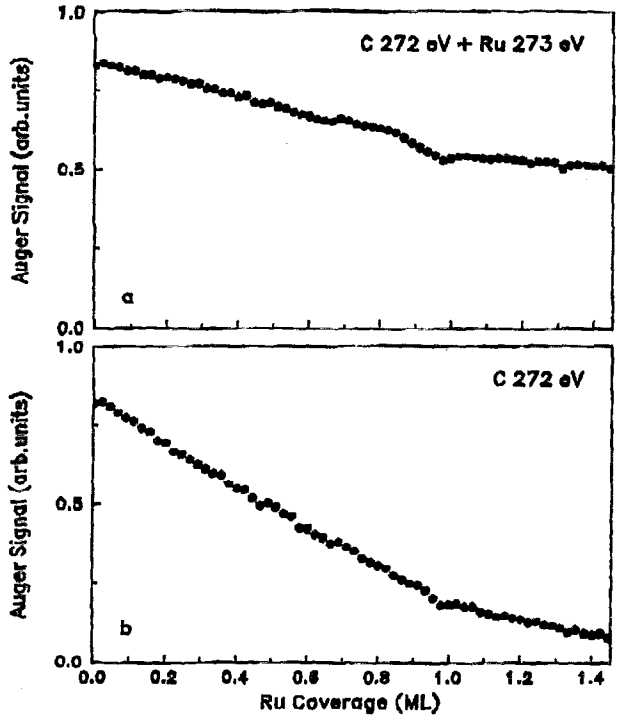

FIG. 3. Auger peak-to-peak height vs Ru coverage on C(0001) of (a) the composite C 272 eV+Ru 273 eV line, and (b) the C 272 eV line only. (b) is obtained from the composite signal in (a) by subtracting the Ru 231 eV Auger intensity multiplied by a factor of 2.35.[13] The coverage is referred to the atomic density of the bulk Ru(0001) plane. Statistical errors are contained withint the symbol size.

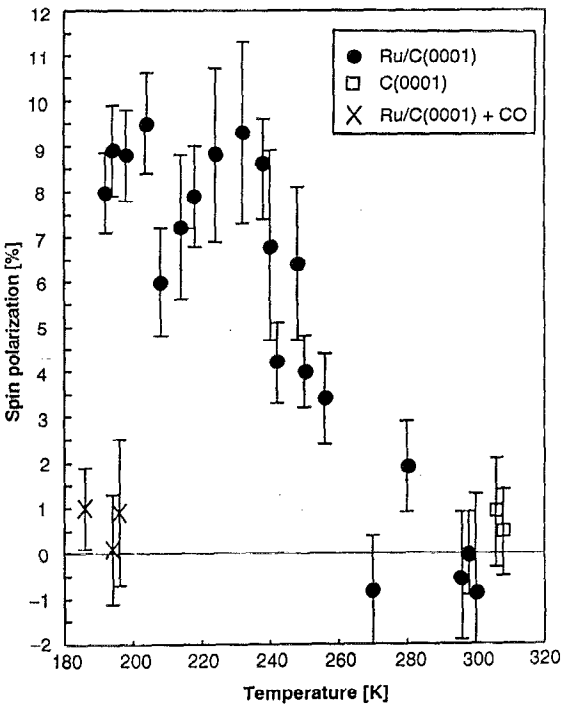

FIG. 4. ESP of 3 eV electrons as function of temperature for a ML-thin Ru film on C(0001) (solid circles), for the clean C(0001) surface (open squares), and for the CO covered Ru ML film on C(0001) (crosses).

4. Solid circles represent the ESP of a Ru ML film as function of temperature T. The low temperature value of the ESP is between +8% and +9%, i.e., the film is indeed ferromagnetic. The positive sign indicates a predominance of electrons with magnetic moment oriented parallel to the applied magnetizing field. With increasing temperature, the ESP drops to zero within a narrow temperature range. This behavior of the ESP is completely reversible. It is not the intent of the present publication to evaluate the critical exponent of the two-dimensional (2D) phase transition near the surface Curie temperature T_{Cs}, which is located at around 250 K.

We performed additional SPSEE measurements on adsorbate covered Ru ML films. At 300 K, we exposed the clean Ru film to 10 L of CO, which is the saturation coverage of CO at the clean Ru/C(0001) surface. From Fig. 4 (crosses), it can be directly seen that chemisorption of CO results in zero ESP within the experimental errors which is identical to the result we obtain for the clean graphite surface (see Fig. 4, open squares).

In conclusion, we have demonstrated that Ru can be grown laterally on a HOPG C(0001) surface until the first ML is completed. We find that the deposited Ru ML film is ferromagnetic below a surface Curie temperature $T_{Cs} \approx 250$ K. This is the first observation of 2D ferromagnetism of a 4*d* element.

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