In situ magnetic characterization of ultrathin Ni electrodeposits

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There is a growing technological interest in applying electrodeposition methods to the synthesis of magnetic multilayer films and nanometer-range structures for data storage and retrieval applications. Even with the increasing technological applicability of electrodeposition for production of multi-component materials, there is still much to be learned about the ways thin deposits of a single ferromagnetic element (such as Co, Fe, or Ni) form and perform. Thus, *in situ* (in solution) property studies of single-component magnetic layers are of both fundamental and applied importance.

Using a custom electrochemical cell, we employ the magneto-optical Kerr effect to monitor the magnetic responses of ultrathin magnetic films on single-crystal substrates. In this study, we present the first magnetic investigations of ultrathin Ni films electrodeposited on Ag(111) and Ag(100) single crystal substrates, with ferromagnetic responses observed for coverages of 4–15 effective ML. These findings are compared with our studies of Ni/Au(111), and in the context of recent electrodeposition literature as well as a lone UHV study of Ni/Ag(111).[1-4] These magnetic data are also correlated with information obtained from *in situ* scanning tunneling microscopy (STM) studies.

Both $\mathrm{Ni}/\mathrm{Au}(111)$ and $\mathrm{Ni}/\mathrm{Ag}(111)$ show a large inplane magnetization component. Additionally, deposits on both substrates show a trend of increasing coercivity with increasing deposit thickness for Ni/Au(111) (Figure 1) which is consistent with data reported recently for Ni on (111)-textured Au films deposited from a similar electrolyte.[3] We suggest that these increases in coercivity are a result of increasing deposit roughness with coverage, as described by Zhao *et al.* for ultrathin Co films on Cu(001).[5] For Ni/Ag(111) deposited at high overpotentials, there is fast growth of three-dimensional clusters initially, followed by lateral growth at a slower rate which leaves deep holes between merging islands.[6] Ni/Au(111) deposits become rougher, after their initial layer-by-layer growth, due to increased Ni-on-Ni nucleation with increasing coverage.[7]

Despite the differences in the modes of Ni growth on Au(111) and Ag(111) substrates, the similarity in the magnetic responses indicates that both films are of comparable quality and roughness, with no substantial substrate or growth mode influence for films above 4 ML. Magnetic studies on thinner films, especially those approaching the sub-monolayer range, would likely present a better opportunity for discerning more subtle deposit-substrate interactions. In particular, the growth mode differences between Ni/Au(111) and Ni/Ag(111) discussed here are most prominent for coverages below 3 ML, which is thinner than any of the films measured in this study. An inevitable difficulty in pursuing such a study at room temperature would be the thickness dependence of the Curie temperature. For example, 5 ML of Ni on Cu(111), prepared under UHV conditions, has a Curie temperature near 300K, less than half of its normal bulk value.[8] Thus, investigations on thinner films will likely require magnetic measurements below room temperature. Temperature dependent studies are impractical for our *in situ* electrochemical methods in aqueous electrolyte, so such investigations will require *ex situ* magnetic characterization.

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Figure 1. Ferromagnetic response of Ni deposits with different effective coverages grown on Ag(111). Different deposit thicknesses were obtained by varying deposition time (at $-1.00 V_{SCE}$ in the absence of a magnetic field). Hysteresis loops were recorded at $-0.66 V_{SCE}$, at which potential the deposit displays no substantial growth or decay. Data were averaged over 2–8 consecutive scans and then corrected for diamagnetic contributions from the aqueous electrolyte and silica window. Effective coverages were measured using stripping voltammetry methods, with an error estimate of $\pm 0.2 \text{ ML}$.