

Reversible electrodeposition of ultrathin magnetic Co films

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Abstract— Ultrapure preparation conditions equivalent to ultrahigh vacuum conditions of 5×10^{-10} mbar allow the reproducible deposition of magnetic films in the monolayer (ML) range from aqueous electrolytic solutions. We used this cost and time efficient technique to prepare ultrathin Co films on Cu(001) substrates. A unique feature of electrodeposition is its ability to dissolve previously deposited layers. The thickness of deposited films can be adjusted in situ by dissolution without damaging the rest of the film. This might be useful in precisely tailoring film properties, for example in magnetic multilayers. In situ magneto-optical Kerr effect (MOKE) measurements are a simple and efficient tool for such a purpose and provide a thickness resolution of better than 0.2 ML. The magnetic properties and anisotropies of the electrodeposited films as derived from our in situ MOKE measurements are mainly determined by their epitaxial growth on Cu(001).

Index terms—Co, electrodeposition, magnetic thin films, ultrathin films

The application of ultrapure preparation conditions equivalent to ultrahigh-vacuum conditions of 5×10^{-10} mbar has been shown to allow the reproducible electrodeposition of ultrathin and in particular magnetic films [1]. This is of importance from the point of view of applications since this deposition technique allows fast film deposition onto large substrates, provides low material consumption, does not require expensive equipment, and is therefore cost effective in comparison to the usual film preparation by molecular beam epitaxy or sputtering. In addition, electrodeposition offers a unique feature compared to other deposition techniques: reversibility. This means that films previously deposited onto a substrate can be fully or even partially removed by a simple potential change of the substrate without modification of the substrate surface. The thickness of films can be exactly tailored to achieve desired physical and particularly magnetic properties. This point seems to be most interesting in view of preparation processes which might automatically prepare films of identical magnetic properties

controlled by appropriate feedback circuits. One example to obtain a measurement signal which may be used as a feedback signal will be shown in this paper: In-situ magneto-optical Kerr effect (MOKE) which allows exact tailoring of magnetic moment and coercivity.

I. EXPERIMENTAL DETAILS

The electrochemical cell for the electrodeposition of ultrathin magnetic films (fig. 1) is made out of quartz glass which does not contaminate the electrolyte by dissolution of constituents into the electrolyte, and which can be cleaned by oxidizing reagents like H_2SO_4 and H_2O_2 [2]. All parts of the electrochemical cell are routinely sterilized in ultrapure water (Milli-Q plus) before each experiment.

The aqueous electrolyte consists of ultrapure water, suprapure grade Na_2SO_4 (0.3 M) and $CoSO_4$ (1 mM). The pH of the electrolytic solution is approximately 5. We do not use other additives to avoid, e.g., surfactant effects or other unknown influences on the growth of the films.

The volume of the electrochemical cell as shown in fig. 1 is approximately 100 ml. Various joints allow the insertion of a Pt counter electrode to achieve current flow to or from the substrate, and insertion of a reference electrode to measure accurately the electrode potential of the substrate. An essential requirement for the reproducible electrodeposition of ultrathin magnetic films is the in situ removal of dissolved oxygen from the electrolyte, mainly for two reasons: to avoid oxidation of the Cu or Co surfaces [3] or electrochemisorption of hydroxid or other oxygen species at the substrate surface [4]. Second, the background currents in the potential range between 0 mV and the onset of the hydrogen evolution from the aqueous electrolyte, which is observed around -650 mV, can be reduced by deaeration to less than $0.5 \mu A/cm^2$ (fig. 2). An estimated part of $0.3 \mu A/cm^2$ of this current is due to the charging current of the electrolytic double layer assuming a capacitance of $30 \mu F/cm^2$ [5]. This allows the determination of the deposited charge from the current-voltage characteristics with a resolution of better than $10 \mu C/cm^2$, corresponding to a thickness resolution of 0.02 ML. The deaeration is achieved by in situ saturation of the electrolyte with 99.999% (5 N) pure N_2 or Ar gas. Ex situ deaeration and subsequent transfer of the electrolyte into the electrochemical cell has been found to be not efficient enough to achieve base currents

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of less than $0.5 \mu\text{A} / \text{cm}^2$ in the current-voltage characteristics. Without deaeration, an additional thickness measurement would have to be applied, which complicates the film preparation. Using the deposition time as a measure of the film thickness would result in large thickness errors particularly of ultrathin films, since nucleation effects in the initial stages of the film growth, which strongly depend on the Co concentration and the deposition potential, result in a non-linear current with time, as reported in detail in ref. [6].

MOKE measurements are done in situ to avoid unwanted modification or oxidation of the surface of the Co films. Capping layers which may protect the Co films would result in strikingly different magnetic properties as reported recently [7] and as known from evaporated films [8]. Our electrochemical cell is small enough to fit between the pole pieces of an electromagnet which can provide magnetic fields up to 0.5 T at the substrate position. The magnet is rotatable to adjust the magnetic field direction perpendicular and parallel to the film normal for longitudinal and polar MOKE measurements, respectively. The optical setup for the MOKE measurement is easily adapted to our electrochemical cell as described in ref. [2].

Cu(001) crystals were mechanically polished to an orientation accuracy of better than 0.2° . They were then electropolished in 65% H_3PO_4 at +1.8 V versus a carbon electrode and transferred into the electrochemical cell un-

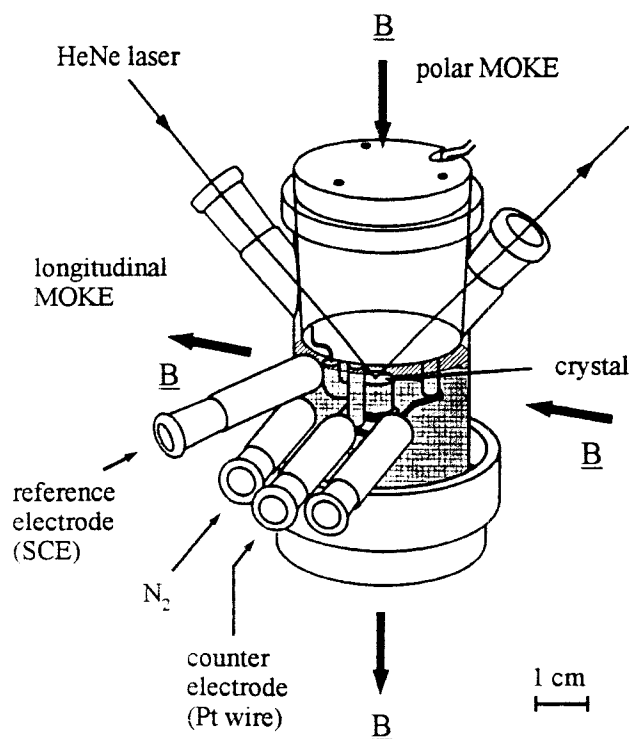
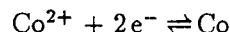


Fig. 1. Electrochemical cell. The angle of incidence of the HeNe-laser beam is 45° with respect to the film normal. The adjustable magnetic field directions are indicated by arrows.

der the protection of a drop of ultrapure water to avoid degeneration of the crystal surface by air.

II. REVERSIBILITY

The reversibility of the electrochemical film deposition can be seen in the current-voltage characteristics, shown in fig. 2 for Co/Cu(001). The electrochemical Nernst potential of the redox-reaction



is approximately -640 mV (for 1mM Co^{2+}) versus the saturated calomel electrode (SCE), to which reference all potentials in this paper refer. Therefore, adjusting the substrate potential higher than the Nernst potential of $\text{Co}^{2+} / \text{Co}$ provides and maintains a clean substrate surface. The metal deposition onto the substrate will only start after lowering the substrate potential below the Nernst potential of $\text{Co}^{2+} / \text{Co}$, seen by the increasing negative current in fig. 2. The deposition of Co is usually done at potentials around -780 mV at a low supersaturation near the thermodynamical equilibrium. A subsequent change of the substrate potential to a higher value than the Nernst potential of $\text{Co}^{2+} / \text{Co}$ will accordingly

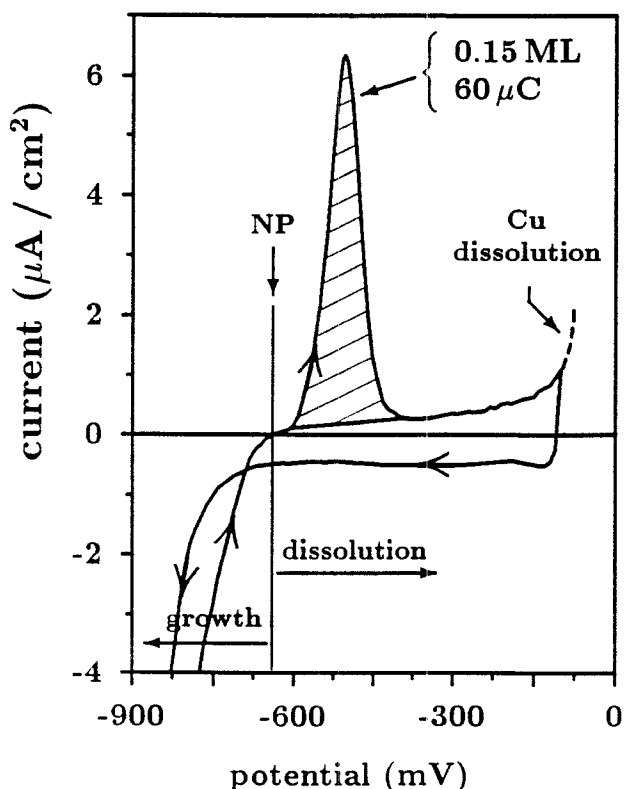


Fig. 2. Current-voltage characteristics of the reversible Co deposition on Cu(001). Growth and dissolution of the films can be controlled by a simple change of the substrate potential to lower or higher than the Nernst potential (NP) of $\text{Co}^{2+} / \text{Co}$. Dissolution of the Cu crystal starts if the potential is adjusted to more than -150 mV. The arrows indicate the cycling direction of the Cu potential (with 10 mV/s).

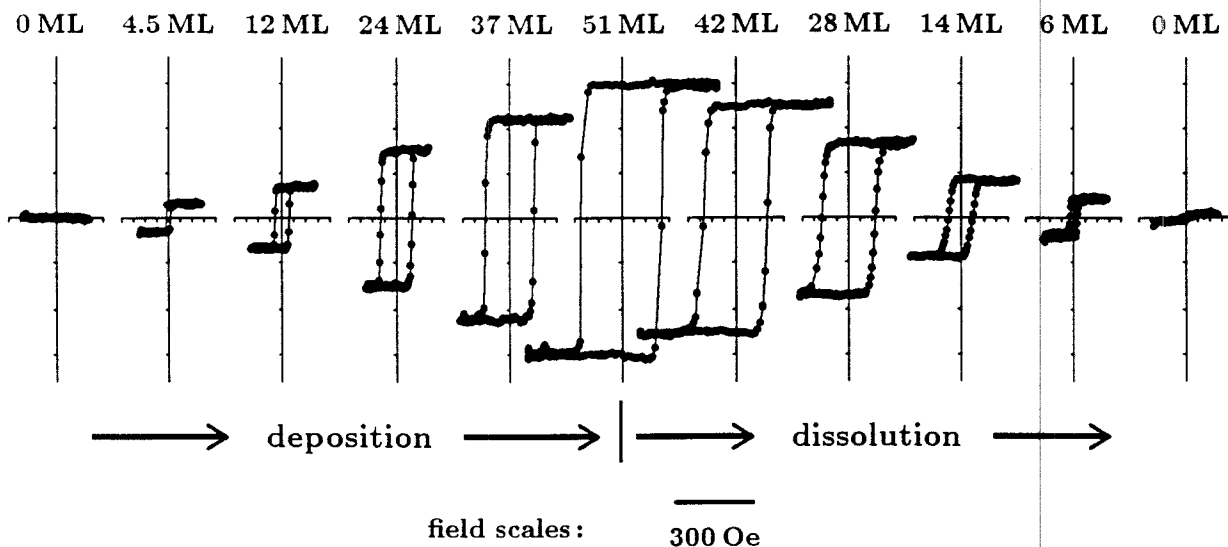


Fig. 3. Sequence of hysteresis loops during deposition and subsequent dissolution of a single Co film ($\underline{E} \parallel [110]$, in $-$ plane; $T = 300\text{ K}$). The vertical axis is the same in all graphs (a.u.).

result in a stripping of Co from the substrate, seen as positive current peak in fig. 2, without damaging the substrate surface, if the potential is kept lower than the Nernst potential of the substrate. According to fig. 2 this potential is approximately -150 mV for the Cu(001) substrate. These considerations hold in principle for all substrates with Nernst potentials higher than the Nernst potential of the film to be deposited.

Na^+ ions of the electrolyte provide conduction in the electrolyte, and remain in the liquid because of their low Nernst potential of -2.5 V , as well as SO_4^{2-} anions, which are known to adsorb at surfaces at potentials higher than approximately $+400\text{ mV}$ [9]. Both potential ranges are far outside the potential range which is of interest for the film deposition, as shown in fig. 2.

However, the situation is slightly more complicated, because the film deposition at potentials lower than -650 mV is accompanied by the above mentioned simultaneous hydrogen evolution at the substrate. This results in a non-balance of cathodic (integral of negative current during film deposition (fig. 2)) and anodic charges (integral of positive current peak due to the film dissolution (fig. 2)) in the current-voltage characteristics. Whereas the cathodic charge represents the sum of charges due to hydrogen reduction and film deposition, the anodic charge results exclusively from the film dissolution. For this reason we usually take the anodic charge to determine the film thickness. Nevertheless, the cathodic charge can be calibrated with the corresponding anodic charge in several deposition/dissolution cycles.

Thus, by simple adjustment of the substrate potential we can control growth or dissolution of the films. In particular, we can hold the films in a stable condition with respect to their thickness, if we adjust the potential of the substrate in the range between deposition and dissolution

regime at the Nernst potential of Co^{2+}/Co , as indicated in fig. 2 by 'NP'. The stability of films under these conditions for up to one hour has been proven by using MOKE as an independent measure of the film thickness.

The sequence of hysteresis loops in fig. 3 has been taken during the growth and the subsequent dissolution of a single film. It represents the linear thickness dependence of the longitudinal MOKE signal of Co films with the easy magnetization axis in $-$ plane for films thicker than 2 ML [1]. To achieve a constant film thickness during each MOKE measurement in fig. 3, we balanced the growth and the dissolution for approximately 20–30 s by switching the Cu potential to the Nernst potential of Co^{2+}/Co where the film thickness remains constant, as indicated in fig. 2 by 'NP'. The square hysteresis during the deposition suggests a uniform Co film thickness across the measured surface area of approximately 1 mm^2 , whereas the increasing rounding of the hysteresis loops during the dissolution of the film might be caused by a slightly inhomogeneous dissolution across the substrate area, which would result in a thickness distribution and hence the observed rounding of the square hysteresis.

In particular, the Co films can be completely removed from the Cu(001) surface if the substrate potential is adjusted to approximately -300 mV according to the current-voltage characteristics of Co (fig. 2). Correspondingly, the magnetic hysteresis vanishes, as is shown in fig. 3.

Whereas the saturation magnetization increases linearly with the film thickness [1], the increase of the coercivity with the film thickness is not linear because of the complex mechanisms of magnetization reversal in ultrathin films, which are closely related to the microstructural properties of the films. This can be clearly demonstrated by preparing films at different supersaturation and hence

at different deposition current densities. The increase of the coercivity with deposition rate is shown in fig. 4 for films of same thickness (6 ML), deposited at different overpotentials η . The coercivity of the film deposited at a high supersaturation ($\eta = 200$ mV; right curve in fig. 4) is approximately 7 times larger than the coercivity of the film deposited at a low supersaturation ($\eta = 120$ mV; left curve in fig. 4).

III. EPITAXIAL PROPERTIES

Whether electrodeposited Co grows epitaxially on Cu(001) during the simultaneous hydrogen evolution can be answered both by the detection of magneto-crystalline anisotropies and by a direct structural analysis. The in-plane magnetization anisotropy of a 13 ML Co film was investigated by rotating the film about its normal with the optical MOKE setup and magnetic field direction fixed (fig. 5). As is seen with evaporated Co films on Cu(001) [10], we observe a fourfold in-plane anisotropy of the remanence of Co/Cu(001) due to the symmetry of the fcc structure of the Cu substrate, proving the epitaxial growth of Co. The easy axis is in-plane and in the [110] direction, the hard in-plane axis is in the [100] direction. The ratio of the remanence in the [100] and [110] directions is approximately $\sqrt{2}/2$ as theoretically expected.

We independently confirmed the epitaxial growth by in situ surface X-ray diffraction in a special electrochemical thin electrolyte layer cell [11]. These measurements show directly the epitaxial growth of fcc-Co on Cu(001). In particular, we find a pseudomorphic growth regime of Co/Cu(001) which extends up to approximately 14 ML [12].

IV. DISCUSSION

The properties of electrodeposited films are similar to the properties of evaporated ultrathin films, if they are electrodeposited under conditions equivalent to ultrahigh-vacuum conditions of 5×10^{-10} mbar. 'Magnetic dead' layers, as reported years ago for electrode-

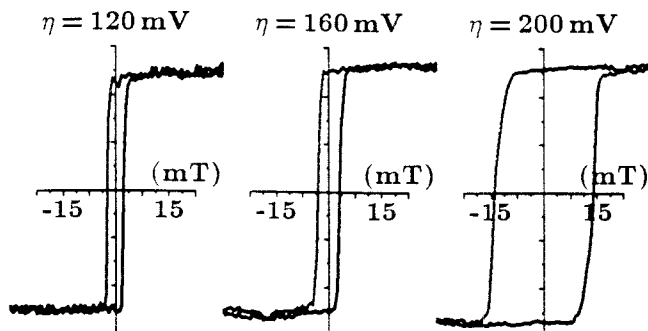


Fig. 4. Enhancement of the coercivity caused by deposition at high overpotentials η . Vertical scales are the same for all graphs (a.u.). The film thickness is 6 ML (\underline{B} || [110], in-plane; T = 300 K).

posited ultrathin films [13], are not unique to the electrodeposition technique, but rather to unclean preparation conditions. The films even grow epitaxially in the fcc structure on Cu(001) as shown in fig. 5. If done under these clean conditions, the electrodeposition technique is easier, less expensive, and therefore more attractive for film preparation than the typically utilized evaporation or sputtering techniques.

The electrodeposition of ultrathin magnetic Co films, as demonstrated in this paper, can be easily extended to the deposition of other magnetic materials as we have shown for Fe in ref. [14].

The demonstrated in situ MOKE measurements are one example of the variety of optical measurements which can be, similarly to MOKE, adapted to an electrochemical cell in a simple way. The stability of the films near the Nernst potential allows the in situ application particularly of those analytical techniques which require long measurement times.

In general, MOKE can be performed simultaneously with the growth or dissolution of films; however this results in non-closed hysteresis loops due to the variation of the film thickness at the beginning and at the end of the MOKE measurement. In cases which require only a certain value of the magnetic moment of the sample it is not necessary to measure the complete hysteresis loop: It would be enough to monitor simply the saturation magnetization at a defined magnetic field value.

The properties of electrodeposited films are of interest in fundamental research, since the electrodeposition in contrast to evaporation and sputtering techniques, is done near thermodynamical equilibrium. The properties of electrodeposited magnetic thin films are so far poorly known. For example, we observe a progressive nucleation

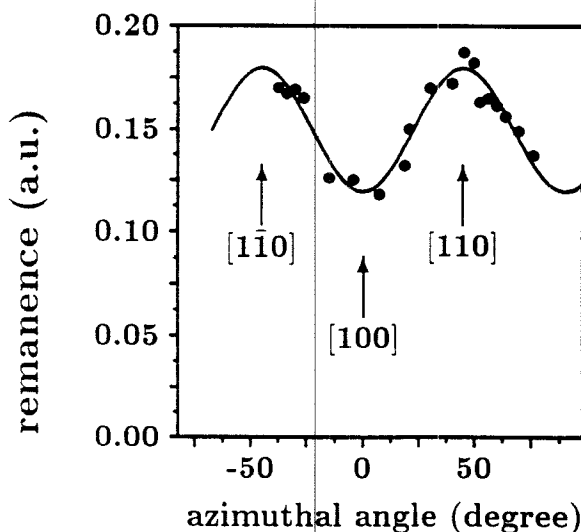


Fig. 5. In-plane magnetization anisotropy of 13 ML Co on Cu(001) showing the epitaxial growth of the electrodeposited films (T = 300 K). The azimuthal angle is measured with respect to the hard [100] direction.

behaviour [15] of Co on Cu(001) [6] in agreement with a variety of investigations of the electrochemical nucleation of Cu [16] or Ni [17], whereas very recently an instantaneous nucleation of Co on Au has been reported during Co deposition using high deposition currents [7].

The wide adjustable range of the deposition parameters as, e.g., the supersaturation, allows a wide variation or tailoring of magnetic properties, which has been shown by the enhancement of the coercivity caused by a simple increase of the supersaturation (or current density) during deposition (fig. 4). This also shows that adequate descriptions of experimental details must necessarily contain considerable information on the deposition conditions.

The reversibility of deposition demonstrated in fig. 3 is unique to electrodeposition. It allows a fine tuning of magnetic properties of ultrathin films by simply stopping the deposition or starting the dissolution (as shown in fig. 2) to achieve the desired properties. This opens interesting prospects for the preparation of ultrathin films with tailored properties in view of potential applications as magnetoresistive sensors, in the storage technology, or in complex multilayered systems.

Reversibility may also be very useful in the study of thickness dependent structural transitions in ultrathin magnetic films since it provides an opportunity to study these effects while the film thickness decreases without damaging the remaining film.

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