Electric field modifications on the coercive force for electrochemical etched Co/Pt(111) films

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A B S T R A C T

The electrochemical etching process for Co/Pt(111) removes the surface atoms ended with a smooth surface and less surface defects due to the appearance of chloride anions. During the electrochemical etching process for Co/Pt(111), the squareness of the hysteresis loop remains nearly unity. The coercive force of Co/Pt(111) after electrochemical etching treatments is slightly enhanced while the electric field control of the coercive force with larger responses is demonstrated. The potential range for magnetic measurements is chosen between −400 and −600 mV to avoid the influences of the possible deposition/etching of the films. Within this potential window, the electric field control of the magnetic properties is manageable. Variations of the coercive force between 0.31 and 0.38 kOe are reproducible for electrochemical etched Co/Pt(111) under conditions of repeatedly electric potential at −500 and −400 mV. The easiness for operation, thickness control of magnetic films, and electric field modification of coercive force in an electrolyte condition show great advantages for further applications in spintronics.

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1. Introduction

Electrodeposition is a practical method used in coating technology for decades while recently its new applications and related mechanisms receive great attentions [1–11]. For instance, electrodeposition for films in nanometer thickness are widely used in solar cells [2,3,9], super capacitors [3], and magnetic switches [4,7,10]. For the fabrication of semiconductor devices, wet etching processes play an important role. Patterned substrate was prepared by etching with Zn powder and HCl diluted in deionized water for further electrodeposition of PbO used as highly efficient planar perovskite solar cells [2]. The transferring of a graphene layer on multilayer h-BN film can be easily achieved by etching process to get a high carrier mobility around 24,000 $cm^2V^{-1}s^{-1}$ [9]. On the other hand, an magnetic switch by electric field induced magnetism was firstly reported in ionic liquid for FePt and FePd films with thickness around nanometer range [10]. In the following years, great efforts have been devoted to the investigations of electric field induced magnetism in ionic liquid such as coercive force switching [7], control of magnetic moment [12] and domain wall motion speed controlling [13]. All of these reports show great potential applications in spintronic devices. In this paper, electrodeposition and electrochemical etching are used to prepare Co/Pt(111) with desired thicknesses in the nanometer range. For Co/Pt(111), the electrochemical etching process might remove the surface atoms ended with a smooth surface and less surface defects due to the appearance of chloride anions. For the electrochemical etched films, the electric field control of the coercive force is demonstrated.

2. Experimental

The platinum crystal was oriented within 0.5° of the [111] direction checked by x-ray diffraction. Before loaded into the electrochemical cell, the surface was mechanically polished with alumina powder with diameter down to 0.05 μm and then annealed by a hydrogen torch. The details of the process for preparing Pt electrode were already reported [14–16]. All solutions were prepared with high purity chemicals (HCl and $CoCl_2$) and ultra-pure water (>18 MΩ cm). To get rid of oxygen contamination, the solutions were purged with high purity argon for 1 h before the experiments. The EC cell for magneto-optical Kerr effect (MOKE) measurements was developed and built in our group [17,18]. A Pt wire and an Ag wire were used as a counter electrode (CE) and a reference electrode (RE), respectively. The standard three-electrode setup was controlled by a home built potentiostat [17–20]. After the deposition of magnetic overlayers at a negative potential, the potential is changed to a more positive value for MOKE measurements [17,18]. The potential window for the MOKE measurements is chosen where no transport of Co to or from the surface occurs. A He–Ne laser with a wavelength of 632.8 nm was used as the light source for the MOKE measurements. The Kerr signals were detected by a photodiode and recorded by a computer-controlled multimeter as a function of magnetic field to generate the hysteresis loops. The thickness of the electrodeposited films was determined by way of the stripping method [17,21]. After waiting for a certain time at a suitable potential for Co deposition, we

performed the linear potential scan in a positive potential direction to strip off the Co film. The Co thickness was determined from the measure of the charge under the anodic peak, using the equivalence charge-to-thickness 2.36 mC/cm^2 per nanometer of Co accounting for a surface atom density 1.85×10^{15} cm^{-2} for Co(0001) [17,21].

3. Results and discussion

Fig. 1 shows the cyclic voltammograms (CV) of Pt(111) in a pure supporting electrolyte of 5 mM HCl and 60 mM KCl (black curve), and in the presence of 2 mM CoCl$_2$ (red curve) taken with a scan rate of 10 mV s^{-1}. In the pure supporting electrolyte, the potential range is setting to be between 0 and -950 mV. The broad and irreversible peak at -400 mV (peak A) arises from reduction of proton ($2H^+ + 2e^- \rightarrow H_2$), followed by an increase of cathodic current (peak B) due to reduction of water ($2H_2O + 2e^- \rightarrow H_2 + 2OH^-$) [16,22]. After adding 2 mM CoCl$_2$ and changing the turning point of CV measurements to -1050 mV, the appearances of the peaks A' and B' are similar while the peak B' is extended to lower potential due to the change of the chemical environment by the Co additive. In addition, a peak pair of C' and D' occurs. The cathodic peak C' around -790 mV is related to the reduction of Co^{2+} while the anionic peak D' around -190 mV is associated to the strip off of the Co deposit [16,22]. According to the results of CV, the electric potentials for Co depositions, electrochemical etching processes and MOKE measurements are determined. They are summarized in Table 1. For electrodeposition of Co on Pt(111), the suitable electric potentials are between -700 and -900 mV. For electrochemical etching processes, the electric potential range is between -100 and -300 mV. For MOKE measurements, we choose the potential range between -400 and -600 mV to avoid the influences of the possible deposition/etching of the films. Hysteresis loops with high squareness, which are indications of high quality films, are observed in this potential range for Co/Pt(111).

Magnetic properties of the as-deposited Co/Pt(111) and electrochemical etched Co/Pt(111) with the same Co thickness (t_{Co}) are investigated using MOKE technique. Fig. 2 shows the hysteresis loops for as-deposited and electrochemical etched Co/Pt(111) ($t_{Co} = 12.5$ nm) at electric potential $E = -500$ mV in both the longitudinal and polar configurations. The etched sample is obtained from initially 17 nm after the electrochemical etching process to 12.5 nm. In the polar configuration, no hysteresis is detected. This shows that the easy axes of magnetization for the as-deposited and electrochemical etched films are both in the surface plane. In the longitudinal configuration, the saturated Kerr intensities are the same due to the same thicknesses of the ferromagnetic layers in both films. The coercive force (H_C) for the electrochemical etched Co/Pt(111) is slightly larger than that of the as-deposited Co/Pt(111). From the literatures, the origins of the coercive

Table 1
The electric potentials for electrodeposition, MOKE measurements and electrochemical etching. The maximum potentials E_{max}, peak potentials E_{peak}, and minimum potentials E_{min} for each process are determined from the CV measurements.

Electric potential	E_{max} (mV)	E_{peak} (mV)	E_{min} (mV)
Co deposition	-700	-790	-900
MOKE measurements	-400	–	-600
Electrochemical etching	-100	-190	-300

force are imperfections and magnetocrystalline anisotropy that give rise to the hysteresis of magnetic materials [23,24]. The enhancement of the coercive force shows that some defects are introduced on the surface layers of the electrochemical etched Co/Pt(111) as compared to the as-deposited sample. We may define $(H_C)_0$ as the coercive force for as-deposited films and $(H_C)'$ as the coercive force after the electrochemical etching process. From Fig. 2a, the increasing ratio of the coercive force

$$\Delta H_C/(H_C)_0 \equiv [(H_C)' - (H_C)_0]/(H_C)_0 \qquad (1)$$

can be calculated to be 4.76%.

By reduction of the ferromagnetic layer to a desired thickness, it is also possible to use ion sputtering method [25,26]. In the sputtering process, high energy ions to remove the surface atoms not only cause imperfections but also break the crystalline of the magnetic film [26,27]. From previous report [25,26], it is common that the H_C is enhanced due to the increasing surface roughness. As an example for Fe$_7$Co$_3$(16 nm)/Ta(15 nm), the increasing ratio of the coercive forces $\Delta H_C/(H_C)_0$ after ion sputtering treatments is as large as 13.2% [25]. This value is obviously
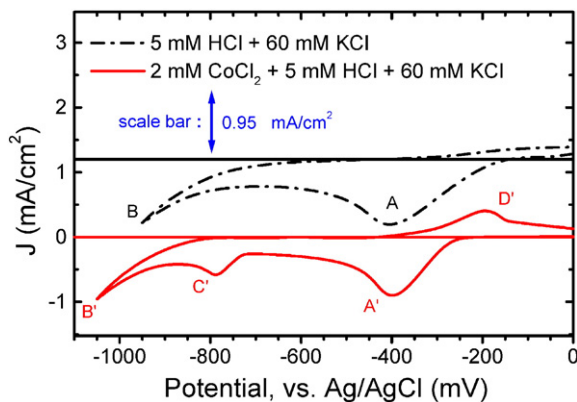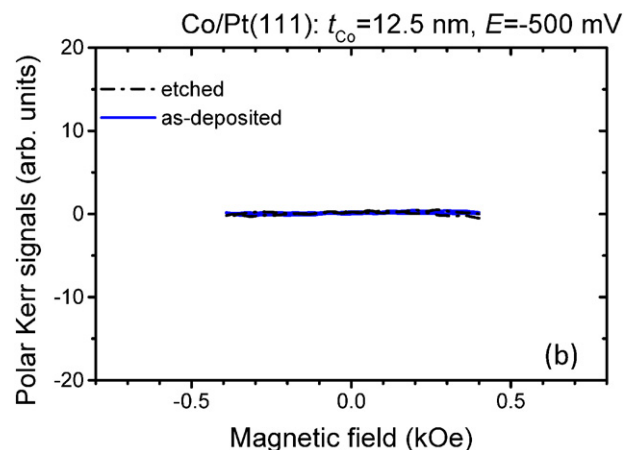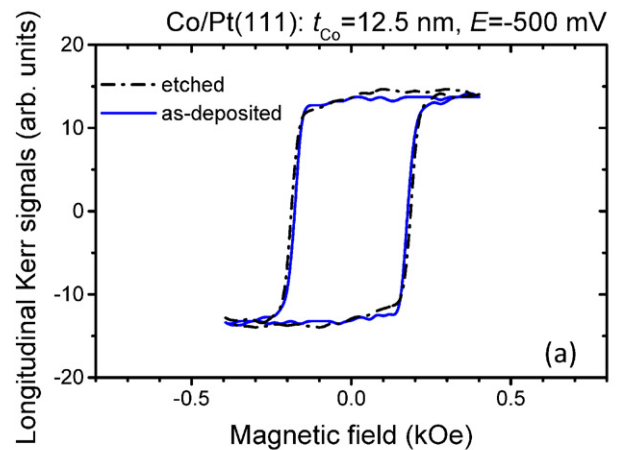

Fig. 2. Hysteresis loops for as-deposited and electrochemical etched Co/Pt(111) at electric potential $E = -500$ mV in the (a) longitudinal and (b) polar configurations.

Fig. 1. Cyclic voltammograms of Pt(111) in supporting electrolyte of 5 mM HCl + 60 mM KCl (black) and in Co-containing electrolyte of 2 mM CoCl$_2$ + 5 mM HCl + 60 mM KCl (red), dE/dt = 10 mV s^{-1}.