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A flexible giant magnetoresistance sensor prepared completely by electrochemical synthesis

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A flexible giant magnetoresistance (GMR) film was prepared completely by electrochemical synthesis; the composite film has potential in applications as flexible magnetic recording heads, actuators and sensors *etc.*

Since the discovery of GMR of antiferromagenetically coupled Fe/Cr multilayers in 1988,[1,2] interest in magnetic metallic multilayers has been greatly stimulated. Apart from the intrinsic interest of the physics involved, many researches have been stimulated by the possibility of the incorporating GMR films in magnetic field sensors for magnetic data recording.[3] Usually, metal/metal multilayers and superlattices for GMR experiments are prepared by vacuum deposition techniques such as sputtering and molecular beam epitaxy (MBE),[4,5] however, the vacuum deposition techniques are relatively complex and expensive. Recently, non-vacuum processes have been used to prepare multilayered GMR materials, among them, electrodeposition is one of the widely used methods.[3] Compared with MBE and sputtering techniques, the advantages of electrodeposition over vacuum-based techniques include the high deposition rates, the simplicity of the experimental setup and its low cost. Additionally, the technique of electrodeposition also removes the high heat resistance restriction of the substrate and the preparation can be carried out at room temperature.[3,6–8] Among the reported studies, electrodes typically used for electrodeposition are normally metallic substrates, such as GaAs (001), Cu and conducting silicon, and the multilayered GMR materials are directly electrodeposited on the surface of the electrode. However, the multilayers electrodeposited on the electrode surface are very thin (normally a few nanometers), of course, and cannot be completely peeled off from the surface of the substrate. So, the prepared GMR materials can only be used together with the substrates. Since most of metallic substrates used are rigid and heavy (such as metals and conducting silicon), sometimes this drawback retards the practical application of GMR multilayers.

To overcome this drawback, polymers have been used to replace metals. Compared with inorganic materials, polymers are light-weight and flexible, and these significant advantages endue polymers for the application of flexible GMR sensors. Piraux *et. al.*[9] prepared a GMR material by electrodeposition of Co/Cu multilayers into nanometer-sized pores of a polycarbonate membrane template. Since the polycarbonate membrane is an insulator, and it could not be used as an electrode directly, before the electrodeposition of GMR multilayers could take place, evaporation of a thin Au film on the surface of the membrane was necessary. Parkin[10] successfully prepared a flexible GMR sensor by sputtering of an exchange biased sandwich (EBS) material on organic films, and this allowed the possibility of preparing flexible magnetoresistance heads. However, Parkin's method still did not overcome the disadvantages of the sputtering, and the organic substrates used in this method must be very stable at higher temperatures.

During the last two decades, conducting polymers have been extensively studied due to their exclusive physical properties,[11] such as light-weight, flexible and with tremendous potential for future scientific and technological development in electronic applications. Usually, conducting polymer films can be easily prepared by electrochemical synthesis, and some of them have been widely used to modify electrodes,[12] and some high-quality films can be peeled off electrodes and be used directly in applications.[13] In this work, a conducting polymer film was used as the substrate for the preparation of a flexible GMR sensor.

The electrodeposition method is applicable only to a conductive substrate, and the key issue in the preparation is to choose a conducting polymer film which is very stable at a negative potential during the electrodeposition process. Among the conducting polymer materials investigated, heavily doped polypyrrole (PPy) film (especially when *m*-sulfobenzoic acid was used as the dopant) exhibited good stability and high conductivity, in the order of 10^2 S cm^{-1} in air, at elevated temperatures, especially in the reductive agent (such as NH_3OH), and a negative potential.[14,15] Thus, we chose the doped PPy film as a conductive substrate and on which GMR multilayers were electrodeposited.

Electrochemical studies and polymerization were performed in a one-compartment three-electrode cell with the use of a PARC M273 potentiostat under the control of a computer. Stainless steel sheets (1.5×2 cm^2) were employed as the working and counter electrodes, which were polished with abrasive paper (1200 mesh) and diamond paste (1.5 μm), and then cleaned in an ultrasonic acetone bath before use. The electrolyte was 0.1 M toluene-*p*-sulfonate solution containing 0.1 M freshly distilled pyrrole. The galvanostatic method was used for electrochemical polymerization of PPy at a current density of 1 mA cm^{-2}, and the thickness of the deposited films was controlled by the electric charge passed during film growth (the thickness of the PPy film prepared at a current density of 1 mA cm^{-2} for 1 h was about 10 μm which was estimated by comparison with samples grown earlier). Then the working electrode, covered with PPy film, was washed well with distilled water and acetone before electrodeposition of multilayered GMR films. To electrodeposit Co/Cu multilayers, a Pt sheet and saturated calomel electrode were employed as counter and reference electrodes respectively. A pulsed electrodeposition technique was used to electrodeposite Co/Cu multilayers, the electrolyte contained both Cu^{2+} (1×10^{-3} M) and Co^{2+} (2×10^{-1} M) and 0.1 M acetic sodium was added as buffering agent. Deposition potentials of Cu and Co were −0.4 V and −0.9 V respectively. The thickness of each metal layer was given by the product of the thickness of the nominal metal and the current efficiencies (estimated by comparison with samples grown earlier). All electrochemical experiments were performed in an atmosphere of purified nitrogen at room temperature. Dynamic mechanical properties of the film were measured by a dynamic viscoelastometer Rheovibron DDVII-EA at a

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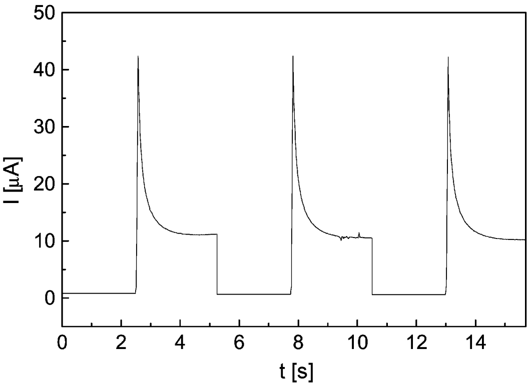

Fig. 1 Current-time transient curve for the electrodeposition of Cu/Co multilayer films.

frequency of 110 Hz. The resistance was measured using standard four-probe d.c. current techniques with the in-plane magnetic fields.

Since the deposition potential of Cu was much less negative than that of Co, deposits obtained at −0.4 V were almost pure Cu layers while deposits at −0.9 V were predominantly Co layers (Fig. 1) with some traces of Cu (about 5–5.3 atom%, as determined by X-ray photoelectron spectroscopy (XPS)). Following the above described sample preparation procedure, a free-standing GMR conducting polymer composite film has been successfully prepared completely by electrochemical synthesis. The GMR composite film can be easily peeled off from the surface of the electrode for further characterization. The magnetoresistance properties were measured with in-plane magnetic fields, and the results of 2 nm Co-rich and 3 nm Cu multilayers are presented in Fig. 2. It can be clearly seen that the MR ratio of the material we prepared amounts to about 4% at room temperature.

However, the GMR value in this work is lower than that of which be deposited on metallic electrodes.[3,6] There are several possible reasons for this low value: firstly, the amount of copper in the cobalt layer is relatively high compared with reported literature values.[16,17] The high amount of copper in the cobalt layer decreased the available ferromagnetic mass of cobalt and decreased the GMR ratio.[16] The electrodeposition of Cu/Co multilayers has been researched thoroughly,[16,18] and it was reported that the more negative the potential applied to deposit the cobalt the lower the amount of copper in the cobalt layer.[16] However, in order to keep the high conductivity of the PPy film here, we did not apply a more negative potential to deposit the cobalt. Secondly, from the results of scanning electron microscopy (SEM), we can clearly see that the surface of the PPy film (facing the solution) is quite rough, and the thicker the film, the rougher the surface. Since the surface of the PPy film is not as smooth as carefully polished copper or a single crystalline substrate, and is even rougher than ITO glass, the interfaces between the GMR multilayers deposited on the film will not be as sharp and as regular as on carefully polished metallic electrodes.[16] Thirdly, both the rough surface and the relatively low conductivity of the PPy film will cause non-uniformity in the conductivity of the electrode surface, which may result in the non-uniformity of the thickness of multilayers. We assume all the facts mentioned above will decrease the GMR value.

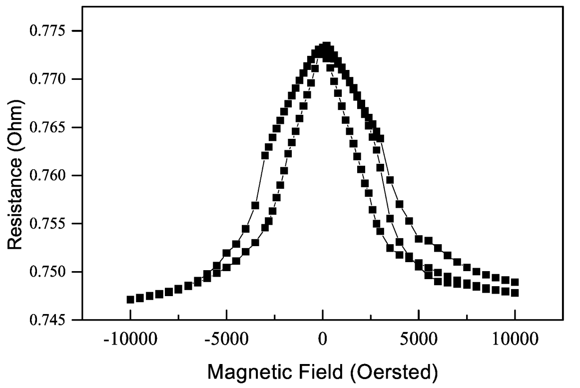

Fig. 2 Resistance *versus* in-plane magnetic field curves at room temperature for electrodeposited (30 repeats) Co (2 nm)/Cu (3 nm) on conductive polypyrrole film (thickness 5 μm).

The quality of this free-standing GMR composite film has been characterized thoroughly. The multilayered film is very flexible and can be cut like a metal sheet by a knife or a pair of scissors into various shapes. The tensile strength is measured to be 36.7 MPa at a stretching rate of 5 cm min^{-1}; this value is only a little lower than that reported for pure PPy films.[19] At −20 °C, the real modulus of this composite film is 1.09×10^{11} dyne cm^{-2} and the loss modulus is 1.92×10^{10} dyne cm^{-2}. These two moduli were almost unchanged when the test temperature increased from −20 °C to 50 °C implying that the composite film can be reliably used between this temperature region. Moreover, the moduli of the composite film are almost the same as those of the pure PPy film, indicating the ultrathin multilayered Co/Cu films do not have much influence on the mechanical properties of the conductive polymer substrate.

In this preliminary work, we have described a simple method for the preparation of a flexible GMR polymer composite film completely by electrochemical synthesis. The GMR value of the sensor is still low, however, compared with conventional inorganic substrates; the conducting polymer composite film is light and flexible and can be easily made into any shapes. Like traditional GMR materials, the flexible GMR polymer composite film prepared by this method should have a wide range of applications such as flexible magnetic recording head, actuators and sensors. Further investigations on the applications of these GMR conductive polymer composite films are now in progress in our laboratory.

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