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The effect of substrate on magnetic properties of Co/Cu multilayer nanowire arrays*

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Ordered Co/Cu multilayer nanowire arrays have been fabricated into anodic aluminium oxide templates with Ag and Cu substrate by direct current electrodeposition. This paper studies the morphology, structure and magnetic properties by transmission electron microscopy, selective area electron diffraction, x-ray diffraction, and vibrating sample magnetometer. X-ray diffraction patterns reveal that both as-deposited nanowire arrays films exhibit face-centred cubic structure. Magnetic measurements indicate that the easy magnetization direction of Co/Cu multilayer nanowire arrays films on Ag substrate is perpendicular to the long axis of nanowire, whereas the easy magnetization direction of the sample with Cu substrate is parallel to the long axis of nanowire. The change of easy magnetization direction attributed to different substrates, and the magnetic properties of the nanowire arrays are discussed.

Keywords: multilayer nanowire, Co/Cu, anisotropy
PACC: 8166D, 7550C, 7530G

1. Introduction

Magnetic nano-structured materials, especially magnetic nanowire arrays, have attracted much attention due to their importance in fundamental research and potential technological applications.[1−6] Ordered magnetic nanowire arrays can be obtained by using the anodic aluminium oxide (AAO) templates method due to its convenience and the readiness of the technology.[7−9] Many experimental factors involved in the fabrication procedure, such as voltage, pH value, and temperature of the solution, can affect the structure and anisotropy of magnetic nanowire arrays.[10−16] Besides, multilayer nanowire arrays have been employed in controlling the magnetic properties of nanowire arrays, and the thickness of magnetic metal layer can be changed with different electrodeposition time to adjust their magnetic properties.[17−20]

Recently, extensive experiments have attempted to control the magnetic anisotropy of nanowire arrays.[20,21] In films, it is well known that films grown on different substrates show remarkable difference on the structure, anisotropy, and other properties.[22−25] However, the properties of multilayer nanowire arrays with different substrates have not been studied widely. Metals of Ag and Cu have been widely used in many areas and are abundant on the Earth's surface. In this study, we prepared anodic aluminium oxide (AAO) templates covered with Ag or Cu film as substrate, respectively. Face-centred cubic (FCC) phase Co/Cu multilayer nanowire arrays have been fabricated successfully at room temperature. Different magnetic anisotropies of multilayer nanowire arrays with different substrates were obtained on the same electrodeposition condition.

2. Experimental details

Nanoporous AAO templates were prepared by a two-step anodization process. First, 0.5 mm thickness aluminium foils (99.999%) were annealed in a furnace at 500 °C for 5 hours to eliminate the mechanical stress. The annealed Al foils were degreased and electropolished in a mixed solution of perchloric acid and ethanol. Then the foils were anodized in 25.6 $g{\cdot}l^{-1}$ $H_2C_2O_4$ solution under a constant direct current (DC) voltage of 40 V for 1 hour. The resultant alumina layers were removed by a mixed solution of chromic acid and phosphoric acid. Afterwards, the foils were anodized again by using the same parameters as in the first step. The remaining metal Al was

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etched in saturated $HgCl_2$ solution, and the barrier layer can be removed in 0.5 M H_3PO_4 solution for 5 minutes at 40 °C. Finally, a layer of metal Ag or Cu with the thickness of 200 nm was sputtered on one side of the AAO template serving as the working electrode and substrate.

The electrolyte for the preparation of the Co/Cu multilayer nanowire consists of 0.1 M $CoSO_4{\cdot}7H_2O$, 0.025 M $CuSO_4$ and 30 g·l^{-1} H_3BO_3 solution, and the pH value was adjusted to 2.7 by $NaHCO_3$ to obtain cobalt nanowires with FCC structure.[26] A direct current electrodepositon procedure was carried out under pulses of –1.0 V for 3 s and –0.2 V for 10 s within 200 cycles by a CHI660B electrochemical station at room temperature without stirring.

Scanning electron microscopy (SEM, Hitachi-S4800, Japan) and transmission electron microscopy (TEM, H-600, Japan) were used to investigate the morphology of the AAO template and the Co/Cu multilayer nanowires. The composition and structure of the Co/Cu nanowire arrays were studied by x-ray diffraction (XRD, Cu-1.54056 Å (1 Å=0.1 nm), Philips X'pert, Holland) and selective area electron diffraction (SAED, H-600, Japan). The magnetic properties were measured by using a vibrating sample magnetometer (VSM, Lakeshore 7304, USA) at room temperature.

3. Results and discussion

Figure 1 shows the morphology of the AAO template and the Co/Cu multilayer nanowire after

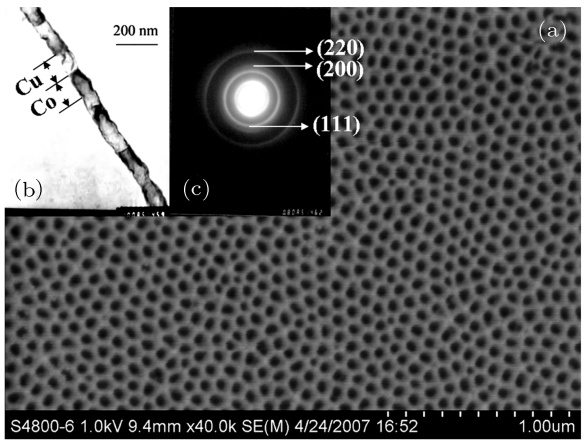


Fig.1. (a) The SEM image of AAO template, (b) the TEM micrograph, and (c) the SAED pattern of the Co/Cu multilayer nanowire with the diameter of 50 nm after removing the alumina.

removing the AAO template and metal substrate. As can be seen from Fig.1(a), the average pore diameter of the AAO template is about 50 nm. Figure 1(b) demonstrates that the nanowire in AAO template with Ag substrate are of layered structure, and the diameter of nanowire is about 50 nm, which agrees well with the SEM result. Figure 1(c) shows the ratio of the square radii of diffraction rings is 3:4:8, which indicates that the nanowire is of FCC structure. This corresponds with three typical diffraction rings of (111), (200) and (220), respectively.

Figure 2 shows the XRD patterns of the Co/Cu multilayer nanowire arrays without removing the AAO template. Figures 2(a) and 2(b) correspond to the results of the samples with Ag and Cu substrate, respectively. The Cu substrate has been removed by HNO_3 solution. Both nanowires and substrates exhibit especial diffraction peaks corresponding to the FCC structure and this result also agrees well with the former report with similar experimental condition.[26] Three diffraction peaks corresponding to (111), (200) and (220) of FCC Co appear at 2θ angles of 44.23, 51.53 and 75.87 degree in Fig.2(a), while a single diffraction peak corresponding to the (111) reflection of FCC Co almost disappear in Fig.2(b). The peak height corresponding to the FCC Co on the Ag substrate is higher than that of the FCC Co on Cu substrate in addition. Thus, the growth process of nanowire arrays may be influenced by the utilization of different metals as the substrate.

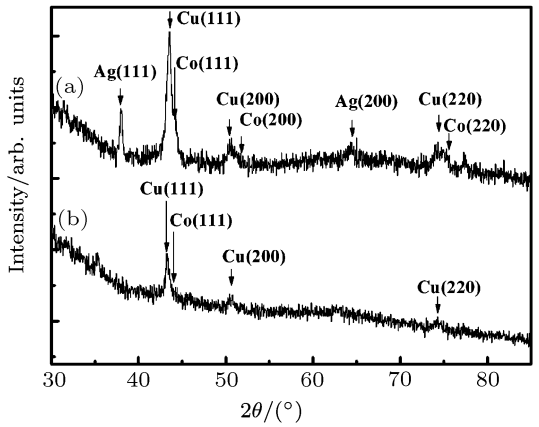


Fig.2. The XRD patterns of the Co/Cu multilayer nanowire arrays films with Ag substrate (a), Cu substrate (b) without removing the alumina.

Room-temperature hysteresis loops of Co/Cu multilayer nanowire arrays with Ag or Cu substrate are demonstrated in Fig.3. The applied field is parallel (out of plane) or perpendicular (in plane) to the long axis of the nanowires, respectively. Figure 3(a) shows that the easy magnetization direction of the nanowire array with Ag substrate is perpendicular

to the long axis of the nanowire, which is significantly different from the results of the continuing magnetic nanowire arrays.[5] This is attributed to the special structure of the multilayer nanowire array. Demagnetization factors are different for the samples with different geometries, thus magnetic shape anisotropy can be adjusted by varying the shape and microstructure of the samples. For example, the magnetic moment can be forced lying parallel to the plane in the thin magnetic film, while the magnetic moment can be aligned easily along the long axis of wire in the magnetic nanowire. For FCC Co, the shape anisotropy energy density $\pi M_s^2 = 6.0 \times 10^6$ erg·cm^{-3} (1 erg=10^{-7} J) for the ideal infinite nanowire is larger than the magnetocrystalline anisotropy energy density $k_1 = -6.3 \times 10^5$ erg·cm^{-3},[27] so an easy axis anisotropy dominated by a large aspect ratio (length/diameter ratio) can be found in pure FCC Co nanowire arrays. In our study, the aspect ratio of a magnetic Co single-layer is only about 1.5:1 as shown in Fig.1(b), and this will lead to a large decrease of the shape anisotropy field in comparison with the ideal infinite nanowire. On the other hand, the thickness of the Cu spacer layer between the magnetic Co layer is more than 50 nm, thus magnetic dipole-dipole interactions between the magnetic layers can also lead to further decrease of the shape anisotropy field along the long axis of nanowire. As a result, the magnetic anisotropy may change from easy axis anisotropy along the long axis of nanowire to an easy plane anisotropy in the plane of film, and this can be ascribed to the different microstructure of the multilayer nanowire arrays and ordinary continuous magnetic nanowire arrays. A similar hysteresis loop with in-plane anisotropy was also found in Ref.[17]. The existence of diffraction peaks corresponding to (111), (200) and (220) shown in Fig.2 suggests relatively random orientations of the Co crystal grains in the sample with Ag substrate, therefore the magnetocrystalline anisotropy may give average contribution to total effective anisotropy of the sample. Figure 3(b) shows that the easy axis of multilayer nanowire arrays on Cu substrate is parallel to the long axis of nanowire, and it is completely different from the results of the former sample on the Ag substrate. One possible reason is that only a single diffraction peak corresponding to (111), which is the magnetocrystalline easy axis of FCC Co,[28] was found in this sample with Cu substrate shown in Fig.2, thus the easy axis of magnetocrystalline anisotropy is paralleled to the long axis of the nanowire. As mentioned above, the shape anisotropy of the Co segment, whose aspect ratio is 1.5:1, is smaller than ideal infinite nanowire. Therefore, the cooperation of the magnetocrystalline anisotropy and smaller shape anisotropy results in the total effective anisotropy along the long axis of nanowire. In our study, the only difference between the deposition templates is the metal substrate which covers them. It is worthwhile to note that the cell parameters of FCC Ag, FCC Cu and FCC Co are 4.086 Å, 3.615 Å and 3.544 Å (1 Å=0.1 nm), respectively, thus the change of magnetic properties may relate to the lattice constant of the substrate. The FCC Co crystal grains may grow confusedly on Ag substrate because the cell parameters of Ag is larger than that of FCC Co, coincided with the main diffraction peaks of Co in Fig.2(a). On the other hand, the FCC Co crystal grains may have a more regular growth on Cu substrate because the cell parameter of Cu is comparable to that of FCC Co. In summary, the growth process

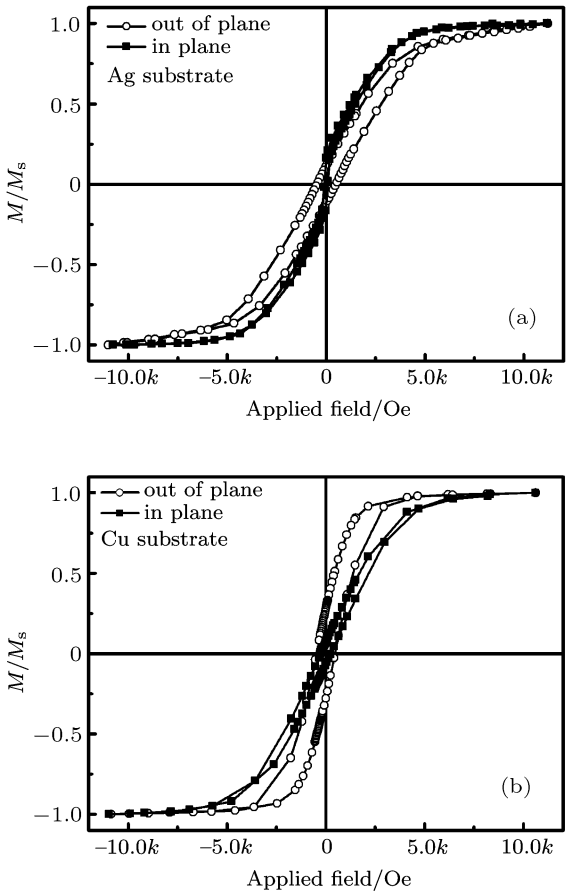


Fig.3. Room-temperature hysteresis loops of the Co/Cu multilayer nanowire arrays films with (a) Ag substrate, (b) Cu substrate (1 Oe=80 A·cm^{-1}).

of Co layer is different on the substrate with different lattice constant, and different magnetic anisotropy can

be aroused on different substrates.

4. Conclusions

The Co/Cu multilayer nanowire arrays grown on the substrate of Ag and Cu have been fabricated into the AAO templates by direct current electrodeposition. The morphology, structure and magnetic properties have been studied by TEM, SAED, XRD, and vibrating sample magnetometer, respectively. The XRD and SAED results show that both samples are FCC structure. Magnetization hysteresis loops indicate that the easy magnetization direction changes from perpendicular direction to parallel direction along the long axis of nanowire, as the substrates are Ag and Cu, respectively. The reason for the changes of easy axis may be attributed to the competition between the smaller shape anisotropy field and the magnetocrystalline anisotropy of FCC Co segment.

References

[1] Xia Y N, Yang P D, Sun Y G, Wu Y Y, Mayers B, Gates B, Yin Y D, Kim F and Yan H Q 2003 *Adv. Mater.* **15** 353

[2] Rao C N R, Deepak P L, Gundiah G and Govindaraj A 2003 *Progress in Solid State Chemistry* **31** 5

[3] Zhang J, Jones G A, Shen T H, Donnelly S E and Li G H 2007 *J. Appl. Phys.* **101** 054310

[4] Grimsditch M, Jaccard Y and Schuller K 1998 *Phys. Rev.* B **58** 11539

[5] Zhang X Y, Wen G H, Chan Y F, Zheng R K, Zhang X X and Wang N 2003 *Appl. Phys. Lett.* **83** 3341

[6] Chen Z Y, Zhan Q F, Xue D S, Li F S, Zhou X Z, Kunkel H and Williams G 2002 *J. Phys.: Condens. Matter* **14** 613

[7] Sellmyer D J, Zheng M and Skomski R 2001 *J. Phys.: Condens. Matter* **13** 433

[8] Wang J B, Zhou X Z, Liu Q F, Xue D S, Li F S, Li B, Kunkel H P and Williams G 2004 *Nanotechnology* **15** 485

[9] Gao T R, Chen Z Y, Peng Y and Li F S 2002 *Chin. Phys.* **11** 1307

[10] Li Y B, Zheng M J and Ma L 2007 *Appl. Phys. Lett.* **91** 073109

[11] Lee W, Ji R, Ross C A, Gosele U and Nielsch K 2006 *Small* **2** 798

[12] Lee W, Ji R, Gosele U and Nielsch K 2006 *Nature Materials* **5** 741

[13] Masuda H, Yamada H, Satoh M, Asoh H, Nakao M and Tamamura T 1997 *Appl. Phys. Lett.* **71** 2770

[14] Hu N H, Chen H Y, Yu S Y, Chen J L, Wu G H, Meng F B, Qu J P, Li Y X, Zhu H and Xiao J Q 2005 *J. Magn. Magn. Mater.* **295** 257

[15] Darques M, Encinas A, Vila L and Piraux L 2004 *J. Phys.* D: *Appl. Phys.* **37** 1411

[16] Pan H, Liu B H, Yi J B, Poh C, Lim S H, Ding J, Feng Y P, Huan C H A and Lin J Y 2005 *J. Phys. Chem.* B **109** 3094

[17] Tang X T, Wang G C and Shima M 2006 *J. Appl. Phys.* **99** 033906

[18] Zhang M, Nozaki Y and Matsuyama K 2005 *IEEE Transactions on Magnetics* **41** 2583

[19] Cho J U, Liu Q X, Min J H, Ko S P and Kim Y K 2006 *J. Magn. Magn. Mater.* **304** e213

[20] Tang X T, Wang G C and Shima M 2007 *J. Magn. Magn. Mater.* **309** 188

[21] Chaure N B, Stamenov P, Rhen F M F and Coey J M D 2005 *J. Magn. Magn. Mater.* **290–291** 1210

[22] Gerlach A, Sellner S, Schreiber F, Koch N and Zegenhagen J 2007 *Phys. Rev.* B **75** 045401

[23] Ranjbar Z and Moradian S 2005 *Progess in Organic Coatings* **54** 292

[24] York S M and Leibsle F M 2001 *Phys. Rev.* B **61** 033411

[25] Min J H, Cho J U, Kim Y K, Wu J H, Ko Y D and Chug J S 2006 *J. Appl. Phys.* **99** 08Q501

[26] Li F S, Wang T, Ren L Y and Sun J R 2004 *J. Phys.: Condens. Matter* **16** 8053

[27] Cho J U, Min J H, Ko S P, Soh J Y, Kim Y K, Wu J H and Choi S H 2006 *J. Appl. Phys.* **99** 08C909

[28] Chang C A 1991 *Appl. Phys. Lett.* **58** 1745