Electrically-controlled resistance and magnetoresistance in a SiO₂-Co film

Xiaoli Li^{a,c,*}, Yanchun Li^{a,c}, Yana Shi^{a,c}, Fanfan Du^{a,c}, Yuhao Bai^{b,c}, Zhiyong Quan^{a,c},

Xiaohong Xu^{a,c,*}

Abstract

A SiO₂-Co film with a Pt bottom electrode and an Au top electrode was deposited by magnetron sputtering at room temperature. The sample exhibits bipolar resistive switching properties. Both oxygen vacancies and Co nanoparticles in the SiO₂-Co film contribute to resistive switching properties and the formation of conducting filaments. The sample, at high and low resistance states, exhibits magnetoresistance at 300 K and 10 K, respectively; this may be due to spin-dependent tunneling between Co particles through the SiO₂ barriers. Thus, the combination of resistive switching and magnetoresistance in a simple Pt/SiO₂-Co/Au structure leads to the formation of multiple resistance states, which is promising for future applications of multiple-state non-volatile storage.

Keywords: magnetron sputtering; resistive switching; magnetoresistance

1. Introduction

Information storage and communication technology require solutions for further miniaturization, low power consumption, and multi-functionality, which rely on the development of new materials and novel device concepts [1]. Many studies have extensively investigated magnetoresistance (MR) in heterogeneous structures [2-5] and resistive switching (RS) behavior in various semiconducting or insulating materials [6,7]; this has been primarily for information storage applications. Determining RS and MR in a system can increase the data storage density [1]. In our previous study, we designed an electrode/ZnO/ZnO-Co/electrode device, in which the storage layer was a combination of a nanostructured ZnO-Co layer and a ZnO layer, in order to observe the RS and MR of the device [8]. It is well-known that SiO₂ is a common material in standard complementary metal-oxide semiconductor (CMOS) processes, and it is insulating. In the present work, we selected a single nanostructured SiO₂-Co layer as a storage material and found that its RS and MR properties can be simultaneously achieved.

2. Experimental

A SiO₂-Co film was deposited on a Si(100)/SiO₂/Ti/Pt substrate by magnetron sputtering at room temperature (RT). The SiO₂-Co film was designated as [Co(0.6 nm)/SiO₂(0.6 nm)]₆₀, and was prepared by sequentially depositing 0.6-nm-thick Co layers and 0.6-nm-thick SiO₂ layers for 60 periods. The details of the film growth are similar to those discussed in previous studies [8-9]. Circular Au top electrodes (TEs) with a diameter of 500 μm and a thickness of 40 nm were deposited through a metal shadow mask onto the SiO₂-Co film by magnetron sputtering. The Pt layer of the Si/SiO₂/Ti/Pt substrate was used as the bottom electrode (BE). The current–voltage

(I - V) characteristics of the Pt/SiO₂-Co/Au sample were evaluated in a two-probe configuration. During measurements, all the voltages were applied to the TEs, and BEs were kept grounded. The structure of the sample was identified by transmission electron microscopy (TEM). The magnetic field dependence of MR at 300 K and 10 K and the temperature dependence of the resistance in the SiO₂-Co sample were assessed using a physical properties measurement system. The magnetic properties of the SiO₂-Co sample, including the magnetic hysteresis loops at 300 K and 10 K and the zero-field-cooled and field-cooled magnetizations in the range from 2 K to 300 K in 100 Oe, were measured using a superconducting quantum interference device magnetometer with a magnetic field applied in the plane of the film.

3. Results and discussion

Fig. 1 (a) shows the cross-sectional TEM image of the Pt/SiO₂-Co/Au sample. The SiO₂-Co layer exhibits a granular structure with a non-uniform particle-size distribution. This can be seen from the zero-field-cooled magnetization data discussed later [Fig. 4(a)]. The high-resolution TEM image of the SiO₂-Co layer, Fig. 1 (b), and the corresponding fast Fourier transform (FFT) image, Fig. 1 (c), reveal no clear SiO₂ or Co lattice fringes. Thus, in the present work, an amorphous Co dispersed SiO₂ film is formed.

Figs. 2(a-b) show the I - V curves of the SiO₂-Co film. A current compliance of 10 mA was applied to prevent the dielectric breakdown of the sample. The voltages were swept in two modes, namely 0→positive→0→negative→0, and 0→negative→0→positive→0, as denoted in Figs. 2(a) and (b), respectively. The sample exhibits bipolar RS properties in the two sweeping-voltage modes. Generally, an electro-forming process is required in electrode/oxide/electrode structures in order to

generate an initial conducting path throughout the oxide matrix that is absent in the virgin devices [10]. With the pre-formed conduction path, the sample can be reversibly set and reset between a high resistance state and a low resistance state [10]. No electro-forming process is required in our work. Moreover, the setting and resetting voltages, V_{set} and V_{reset} , respectively, are similar for the two modes. The V_{set} and V_{reset} values may be related to the type of electrode material and the roughness of the interface between the SiO_2 -Co layer and TE or BE [10]. The similar values of V_{set} and V_{reset} in the present work may be due to the dispersal of Co particles in the SiO_2 -Co matrix on account of the high concentration of Co (approximately 50 vol. %). The Co particles serve as conduction channel precursors that significantly facilitate the electro-forming process and dominate RS behavior. Choi et al. [11] have also obtained promising RS properties due to Pt particles serving as precursors of conduction channel in a SiO_2 -Pt composite system.

The MR properties of the SiO_2 -Co film after setting/resetting to the low resistance state (LRS)/the high resistance state (HRS) were measured at 300 K and 10 K, as shown in Figs. 3(a–d). The film, at LRS and HRS, exhibits MR effect at 300 K and 10 K, respectively. Milner et al. [2,3] investigated the magnetotransport properties of SiO_2 -Co granular films with various Co concentrations. They found that Co grains in the SiO_2 -Co films, at low Co concentrations, are isolated from each other, that the resistance–temperature coefficient of the films are negative, and that their electric transport properties are a result of intergranular tunneling [2,3]. In our work, the negative resistance–temperature coefficients of the sample at HRS and LRS [Fig. 3(e) and its inset] imply that the MR may be mainly due to tunneling transport between Co granules by the SiO_2 barrier. The MR ratio at LRS is lower than that at HRS at both 300 K and 10 K. The migration of oxygen ions in the SiO_2 -Co sample to

the anode during setting process induces the accumulation of oxygen vacancies. As the SiO_2 barrier at LRS becomes oxygen deficient, its conductivity increases, thus reducing the MR ratio of the SiO_2 -Co film [8]. Moreover, the MR ratio at 300 K is lower than that at 10 K for the sample at HRS and LRS. A similar temperature dependence of the MR ratio has also been observed in SiO_2 -Co, ZnO-Co, and Fe- Al_2O_3 granular films [5, 12-13].

Apart from different MR ratios at 300 K and 10 K, the shapes of the MR curves are quite different. At 300 K, the magnetic field dependence of MR shows a sharp and non-hysteretic curve. However, at 10 K, the sample adopts a “butterfly-loop-shaped” curve. These findings suggest that the magnetic properties may change from superparamagnetic at 300 K to ferromagnetic at 10 K [5]. Fig. 4(a) shows the zero-field-cooled and field-cooled magnetizations of the as-deposited Pt/ SiO_2 -Co/Au sample. At low temperatures, a large bifurcation is observed between the zero-field-cooled and field-cooled magnetizations; this pattern is normally exhibited by superparamagnetic particles [14]. The blocking temperature is 65 K. Hence, Co particles in the SiO_2 -Co granular film exhibit superparamagnetism and ferromagnetism at 300 K and 10 K, respectively, as demonstrated by the hysteresis loops shown in Fig. 4(b). The coercivity of the sample is 0 and 1503 Oe at 300 K and 10 K, respectively. The broad peak in the zero-field-cooled magnetization curve, Fig. 4(a), is a further indication of the non-uniform particle-size distribution, Fig. 1(a). The possibility of modulating the magnetic properties of the film at HRS/LRS will be investigated in future work.

4. Conclusion

A nanostructured SiO_2 -Co film was grown by magnetron sputtering. Bipolar RS

properties were observed in the sample for two sweeping-voltage modes. The sample, at high and low resistance states, exhibits MR behavior at 300 K and 10 K, respectively. It may be mainly due to the spin-dependent tunneling transport between Co particles. The MR ratio at LRS is lower than that at HRS. The MR ratio at 300 K is lower than that at 10 K for the sample at two resistance states. The different shapes of the MR curves at 300 K and 10 K are related to the superparamagnetism and ferromagnetism of the sample at 300 K and 10 K, respectively. Thus, the tunable resistances and magnetoresistance ratios of the SiO₂-Co system have promising applications in multibit non-volatile data storage.

Acknowledgments

This work was supported by the National Science Foundation of China (Grant Nos. 61306109, 61434002, 51571136, 11611540333), Shanxi Province Foundations (Grant Nos. 2014–044 and [2014]779).

Reference

- [1]K. Zhang, Y.L. Cao, Y.W. Fang, Q. Li, J. Zhang, C.G. Duan, S.S. Yan, Y.F. Tian, R. Huang, R.K. Zheng, S.S. Kang, Y.X. Chen, G.L. Liu, L.M. Mei, *Nanoscale* 7 (2015) 6334–6339.
- [2]A. Milner, A. Gerber, B. Groisman, M. Karpovsky, A. Gladkikh, *Phys. Rev. Lett.* 76 (1996) 475-478.
- [3]A. Gerber, A. Milner, B. Groisman, M. Karpovsky, A. Gladkikh, A. Sulpice, *Phys. Rev. B* 55 (1997) 6446-6452.
- [4]S. Sankar, A.E. Berkowitz, D.J. Smith, *Appl. Phys. Lett.* 73 (1998) 535-537.
- [5]S. Honda, Y. Yamamoto, *J. Appl. Phys.* 93 (2003) 7936-7938.

- [6]X.J. Zhu, J. Shang, R.W. Li, Front. Mater. Sci. 6 (2012) 183-206.
- [7]F. Pan, S. Gao, C. Chen, C. Song, F. Zeng, Mater. Sci. Eng. R 83 (2014) 1-59.
- [8]X.L. Li, J. Juan, Y.C. Li, Y.H. Bai, J. Li, Y.N. Shi, L.F. Wang, X.H. Xu, Sci. Rep. 6 (2016) 31934(1-8).
- [9]X.L. Li, Z.Y. Quan, X.H. Xu, H.S. Wu, G.A. Gehring, IEEE T. Magn. 44 (2008) 2684-2687.
- [10]W.H. Xue, W. Xiao, J. Shang, X.X. Chen, X.J. Zhu, L. Pan, H.W. Tan, W.B. Zhang, Z.H. Ji, G. Liu, X.H. Xu, J. Ding, R.W. Li, Nanotechnol. 25 (2014) 425204(1-8).
- [11]B.J. Choi, A.C. Torrezan, K.J. Norris, F. Miao, J.P. Strachan, M.X. Zhang, D.A. A. Ohlberg, N.P. Kobayashi, J.J. Yang, R.S. Williams, Nano Lett. 13 (2013) 3213-3217.
- [12]Z.Y. Quan, X.H. Xu, X.L. Li, Q. Feng, G.A. Gehring, J. Appl. Phys. 108 (2010) 103912(1-5).
- [13]T. Zhu, Y.J. Wang, Phys. Rev. B 60 (1999) 11918-11921.
- [14]N. Jedrecy, H.J. von Bardeleben, D. Demaille, Phys. Rev. B 80 (2009) 205204.

Figure captions:

Fig. 1. TEM analysis of the Pt/SiO₂-Co/Au sample. (a) Cross-sectional TEM image; (b) high-resolution TEM image of the SiO₂-Co layer; (c) the corresponding fast Fourier transform image.

Fig. 2. (Color online) I - V characteristics of the SiO₂-Co sample subjected to (a) positive and (b) negative setting voltages shown on a semi-logarithmic scale. The arrows indicate the sweeping directions.

Fig. 3. (Color online) Field dependence of the MR ratio of the SiO₂-Co sample at HRS (a) and LRS (b) at 300 K; field dependence of the MR ratio of the sample at HRS (c) and LRS (d) at 10 K; (e) and its inset show the temperature-dependent resistance of the sample at HRS and LRS, respectively.

Fig. 4. (Color online) (a) Temperature dependence of the zero-field-cooled and field-cooled magnetizations for the as-deposited SiO₂-Co sample; (b) hysteresis loops for the SiO₂-Co sample at 300 K and 10 K.

Fig 1(a-c)

Fig 2(a-b)

Fig 3(a-e)

Fig 4(a-b)