Microstructural stability of NiO-containing spin valves annealed at room temperature*

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Abstract Microstructure of NiO-containing Co/Cu/Co spin valves (CCC-SV) annealed at room temperature for nearly four years has been studied by synchrotron radiation X-ray diffraction. With the annealing time expanding, the thickness of each sub-layer remains nearly unchanged while the interface roughness varies obviously compared with that of samples without annealing. The roughness at the interface of NiO/Co decreases with the annealing time increasing for both of the samples with NiO layer on the top (TSV) and under the bottom (BSV) of CCC-SV. On the other hand, the roughness at Co/Cu interface increases with the annealing time expanding for BSV while it decreases for TSV. These results indicate that the structure of TSV is more stable than that of BSV.

Key words interface roughness, X-ray reflectivity, spin valves

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1 Introduction

Magnetic multilayers of magnetoresistance (MR) materials have recently attracted great interest for their important scientific meaning and extensive applications[1—3], such as magnetic random access memories (MRAM), as well as in recording media. However, it is difficult to accurately control the effect of microstructures on the performance. It is necessary to study in detail the microstructure of magnetic multilayer in order to further increase the storage density, speed and stability of the memory. Spin valves using antiferromagnetic layer (AFM) as the pinning layer have become more and more applicable because they exhibit relatively low saturation field and comparatively large MR[4—9]. Spin valves using oxide AFM materials, such as NiO, as the pinning layer have been recently extensively studied because NiO AFM layer not only acts as the pinning layer but also reflects the spin electrons resulting in the increase of MR value.

In our previous papers[10—13], the microstructures and the transport properties of the spin valves containing NiO layer have been studied in detail[10—12]. The results indicate that the higher MR value is ascribed to the more flat NiO/Co interface for NiO-containing Co/Cu/Co spin valves, and the enhanced MR values are obtained by improving the roughness of the NiO/Co interface through annealing at high temperature. The MR of spin valves decreases abruptly when the annealing temperature is higher than 250 ℃ for the blocking effect, and reaches zero at about 300 ℃.

It is a pity that there is still a lack of systematic study on the time-dependent behavior of microstructures for spin valves annealed at room temperature for a long term by now. In the present paper, samples of the spin valves in our previous study were placed in air at room temperature for about four years to study the time dependence of the microstructures. Results show that the structure of spin valve with NiO on the top of Co/Cu/Co (TSV) is more stable than that with NiO under the bottom of Co/Cu/Co (BSV).

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Therefore, TSV is more suitable for application.

2 Experimental details

Samples in the present paper were all deposited on Si wafers with an amorphous silicon oxide overlayer, having Ta as the buffer and cap layers, by magnetron sputtering at room temperature[13]. Details of the sputtering conditions can be found in our previous studies[11—13]. The bottom and top spin valves have the following configurations: Si/Ta (50Å)/NiO(400Å)/Co(50Å)/Cu(20Å)/Co(50Å)/Ta (50Å) and Si/Ta(50Å)/Co(50Å)/Cu(20Å)/Co(50Å) /NiO(200Å)/Ta(50Å) respectively. Samples were naturally exposed in air at room temperature for about four years.

The grazing incident X-ray reflectivity (XRR) was measured at the Diffraction/Scattering Station of the Beijing Synchrotron Radiation Facility to characterize the microstructures of the samples with different annealing time. The wavelength of X-ray is 1.54056Å. The XRR was scanned with a step size of 0.01° over the angular range of 0—10°. The individual layer thickness, the average roughness at every interface and the average density of individual layer are obtained by the simulation of XRR curves by using Bede REFS MERCURY. The error bars for each fitted parameters are limited within 5% of the corresponding values.

3 Results and discussions

Figure 1 shows the XRR curves and the best-fit simulation ones of BSV and TSV after annealing in air at room temperature (RT) for 0, 1000, and 1360 days, respectively. As seen from Fig. 1, the experimental and the fitting curves are very close, which shows that the theoretical parameters are reliable. The theoretical models used to simulate the XRR curves of BSV and TSV without annealing are given in Table 1 and 2, respectively. There are two extra oxide layers of SiO_2 and Ta_2O_5 on the surface of Si substrate and the Ta cape layer, respectively, because oxide layers always exist on the surface of substrates and films when exposed in air. It must be noted that, with the annealing time expanding, the thickness and the density of each sublayer are almost unchanged when the experimental error was considered. Therefore, the primary designed structure of spin valve was not destroyed when samples were placed in air at RT

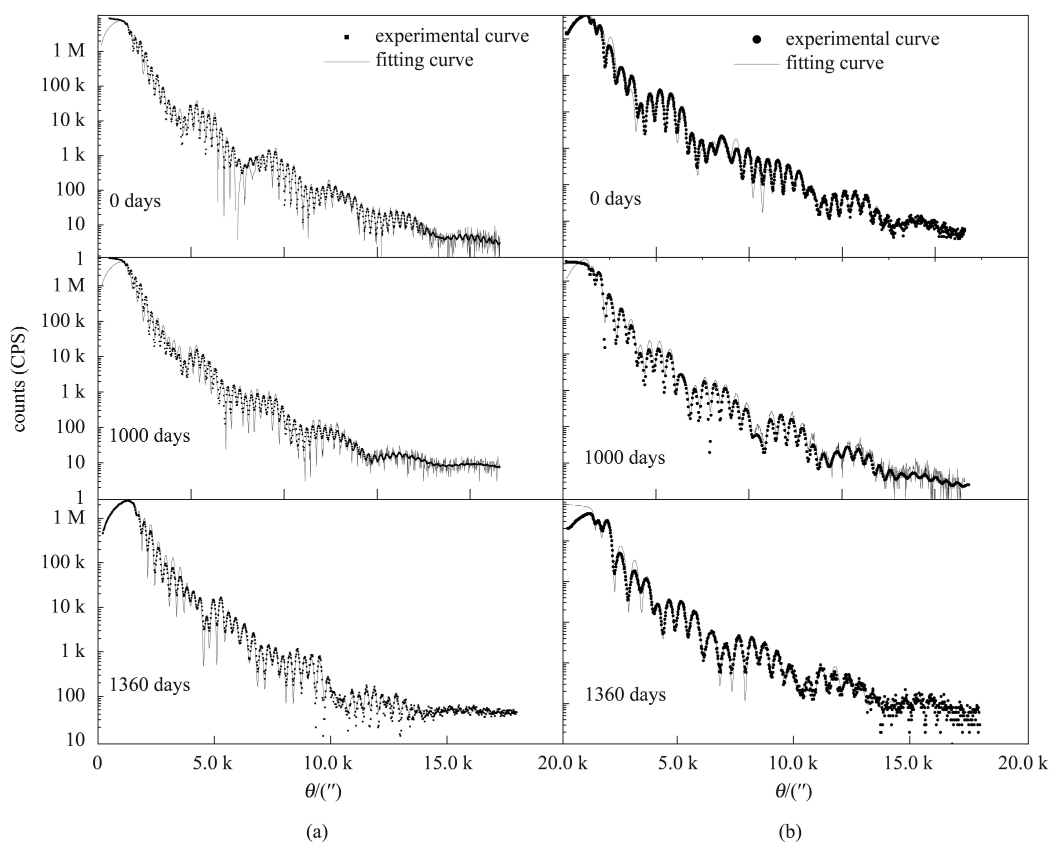

Fig. 1. Experimental data and the best fitting curve of XRR for BSV (a) and TSV (b) after annealed for 0, 1000 and 1360 days.

for about four years. The roughness at the interfaces, however, was obviously changed with the annealing time expanding. It is worthwhile to note the time dependence of the roughness at the interfaces of NiO/Co and Co/Cu which plays an important role in deciding the performance of the spin valves. The roughness at the interface of NiO/Co has a direct effect on the exchange-bias effect and the reflectivity of the conduction electrons at NiO/Co interface. Our previous results have shown that the decrease of roughness at the interface of NiO/Co will increase the MR of spin valve. And the maximum value of MR of 15% was obtained by improving the roughness at the interface of NiO/Co. Many studies have shown that the roughness at the interface of Co/Cu may influence the exchange coupling effect between the two Co layers, and change the MR effect. The time dependence of the roughness at the NiO/Co and Co/Cu interface was listed in Table 3. With the annealing time expanding, the roughness at NiO/Co interface almost decreases for both BSV and TSV. The decreased roughness at NiO/Co interface is in favor of increasing the MR value, which is consistent with the results obtained from the samples annealed at high temperature. However, the time dependence of the roughness at Co/Cu interface is absolutely different from that at NiO/Co interface for BSV and TSV.

Table 1. The simulation model of XRR curve of BSV without annealing.

material	thickness/Å	density(%)	roughness/Å
Ta_2O_5	22.04	81,43	2.10
Ta	32.82	105.54	1.98
Co	43.57	98.01	4.23
Cu	22.32	93.21	3.45
Co	44.27	105.60	3.58
NiO	450.34	101.74	3.98
Ta	41.55	104.90	3.77
SiO_2	25.43	120.22	5.12
Si	constant	100	3.52

Table 2. The simulation model of XRR curve of TSV without annealing.

material	thickness/Å	density(%)	roughness/Å
Ta_2O_5	30.23	90,13	1.95
Ta	25.12	103.51	2.97
NiO	183.71	95.11	8.34
Co	42.33	98.25	3.81
Cu	24.22	101.61	3.55
Co	45.34	111.24	3.50
Ta	43.51	102.92	4.10
SiO_2	20.13	80.12	4.32
Si	constant	100	2.76

Table 3. The time dependence of the roughness at the interface of NiO/Co and Co/Cu for BSV and TSV.

roughness/Å	BSV		TSV	
	NiO/Co	Co/Cu	NiO/Co	Co/Cu
0 day	3.98	3.58	8.34	3.50
1000 days	3.65	4.22	7.22	3.05
1360 days	3.57	4.40	7.81	2.78

The roughness at Co/Cu interface monotonously increases for BSV but decreases for TSV. A large roughness at Co/Cu interface may increase the coupling effect between the two ferromagnetic Co layers. A large coupling effect between the two ferromagnetic Co layers is not in favor of the completely antiparallel alignment of them, which will reduce the MR effect.

Considering that the deposition condition of the corresponding layer is the same in BSV and TSV, the different time dependence of the roughness at NiO/Co and Co/Cu interface is ascribed to the mechanism and the order of deposition for spin-valve multilayer. Generally, the roughness at the interface of multilayer originates from two kinds of mechanisms. One is from the inter-diffusion of non-homogeneous atoms at the interface, and the other one is from the packing of homogeneous atoms, which are shown in Fig. 2 and hereafter named chemistry and geometry roughness respectively. The time dependence of the rocking curve of the sample annealed at 100 ℃ was measured and is shown in Fig. 3 in order to explore the origin of the roughness at the interface of the multilayer. As seen from Fig. 3, the intensity of the diffuse scattering keeps weak and almost unchanged with the annealing time, while that of the specular reflection increases obviously. It can be concluded that the roughness of the interface is mainly originated from the accumulation of homogeneous atoms, and the inter-diffusion of non-homogeneous atoms is weak. The interface becomes more flat because of the migration of homogeneous atoms by annealing. However, the inter-diffusion of non-homogeneous atoms always exist and becomes serious with the interface away from the substrate. The composition of the roughness at the interface of NiO/Co and Co/Cu is different because of their different positions in the structure of BSV and TSV. Cu/Co has a slightly positive mixing heat. As a consequence, the sputtered samples generally show either sharp interfaces or can easily be demixed by a mild annealing step if there is no other additional influence. In BSV，however, it is separated from the substrate by NiO layer with thickness of about 400Å, and there is an additional interface of NiO/Co.

Therefore, the percent of the chemistry roughness at Co/Cu interface in BSV increases compared with the geometry one, and the energy of Co/Cu interface may reach a minimal value with a part of Co and Cu atoms interdiffusing at the interface. So the inter-diffusion of non-homogeneous atoms becomes serious resulting in an increase of the roughness with the annealing time. In TSV, however, because the Co/Cu interface is next to the substrate, the roughness at the interface of Co/Cu is mostly originated from the accumulation of homogeneous atoms, and the energy of interface may keep a minimum with the Co and Cu arranging orderly. Therefore, the roughness at the interface of Co/Cu decreases with the annealing time expanding. The NiO/Co interface is most close to the substrate in the BSV, which leads to the roughness decreasing monotonously with the annealing time at NiO/Co interface because of a little inter-diffusion of non-homogenous atoms. For TSV, however, the percent of the chemistry roughness increases because the NiO/Co interface is farthest from the substrate, which results in the slight increase of roughness with the annealing time expanding. However, because the thickness of Co/Cu/Co sandwiches is only about 110Å, the chemistry roughness at NiO/Co interface in TSV still has small shares compared with the geometry one. So the general trend of the roughness at NiO/Co interface in TSV was decreasing in four years. Therefore, the roughness at the NiO/Co interface is improved in both BSV and TSV as time goes by. It is concluded from the comprehensive comparison of the time dependence of the roughness at the NiO/Co and Co/Cu interfaces that spin valve with NiO layer on the top of Co/Cu/Co is more beneficial to the stability of the microstructures and is more suitable for application.

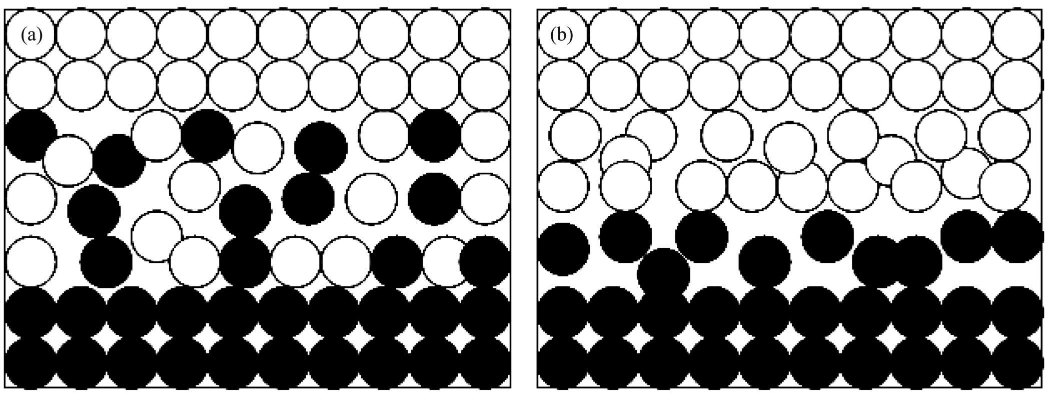

Fig. 2. Sketch figures of the origin of the two kinds of the roughness at the interface: the inter-diffusion of non-homogeneous atoms (a) and the accumulation of homogeneous atoms (b).

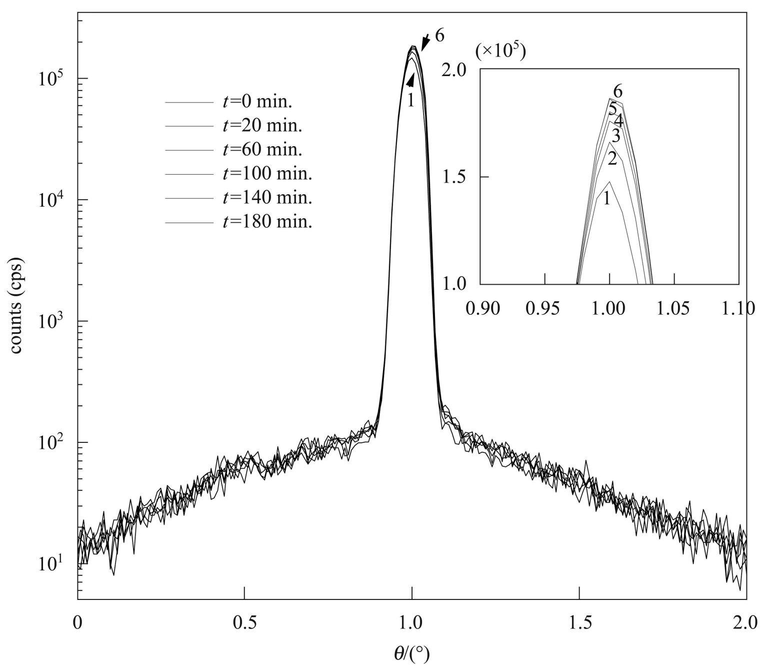

Fig. 3. The time dependence of intensity for X-ray transverse diffusing scattering at 100 ℃.

4 Conclusions

The time dependence of the microstructure of NiO-containing Co/Cu/Co spin valves has been studied by synchrotron radiation X-ray diffraction. With the annealing time expanding, the interfacial roughness at NiO/Co interface decreases for both TSV and BSV, and the interfacial roughness at Co/Cu interface increases for BSV while it decreases for TSV. The above results indicate that the structure of TSV is more stable than that of BSV, and TSV may be more suitable for working in spin valve based devices.

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