Effect of Ag as a surfactant on the thermal stability in Cu/Co multilayers

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Abstract. In the present work we studied the effect of Ag as a surfactant in Cu/Co multilayers prepared by ion beam sputtering. Two identical samples of Cu/Co multilayers with 0.2 nm Ag on a Cu buffer layer and without this Ag layer were deposited on Si substrates. It is known that Cu has a lower free energy than Co, and therefore, the Cu/Co interfaces are not symmetric. Addition of Ag alters the kinetics and thermodynamics of the growth and triggers the layer by layer growth as Ag floats on the growing front balancing the surface free energy of Cu and Co. It was found that with addition of Ag surfactant the thermal stability of Cu/Co multilayer improves.

1. Introduction
Ferromagnetic layers separated by non-ferromagnetic layers in a multilayer arrangement are known to exhibit the giant magneto resistance (GMR) [1] through spin-dependent scattering taking place at the interfaces. Therefore the microstructure of the layers plays an important role in determining the GMR in such multilayers. The intermixing between layers due to chemical diffusion, the roughness or the layer curvature, crystallinity of the individual layers strongly influence the electrical and magnetic properties [2, 3]. The Cu/Co multilayers (with layer thickness few nm) are known for high GMR due to the immiscibility of Cu and Co. Though the volume diffusion between Cu and Co is negligible, the grain boundary diffusion of Cu and Co atoms may play a significant role in determining the GMR properties. Further, Cu has a lower surface free energy of 2300 mJ/m² than Co (2700 mJ/m²). Therefore wetting of Cu layer on Co takes place but agglomeration of Co layer on Cu occurs [5]. This means that Cu is energetically preferred on the growth surface during deposition of Co on Cu. This leads to asymmetric interfaces in Cu/Co multilayers. Recently, it was suggested that by adding a ‘surfactant’ during the thin film growth, sharp interfaces can be obtained in a multilayer [4, 5, 6, 7, 8]. A surfactant is chosen in such a way that its free energy allows a balance between the components of multilayers whose surface free energy differs significantly. Generally elements with large atomic volume are chosen as surfactant as it favors their floating out to the surface during growth of overlayer, leaving behind smooth interfaces that are less prone to intermixing. Metals such as Pb, In and Ag have been used as a surfactant to achieve sharp interfaces. However very limited work has been done to quantify the effect of surfactant in terms of inter-diffusion and its ability to
increase the thermal stability. Our aim is to quantify the inter-diffusion in nanometer range thin films using a precise technique like neutron reflectivity. It may be noted that reflectometry or grazing incidence reflection offer a depth resolution down to sub nm level [9]. Therefore precise measurements of inter-diffusion can be done using neutron reflectivity. Here in this work we have used Ag as a surfactant during the deposition of Cu/Co multilayer. The preliminary results obtained in Cu/Co multilayers by using a 0.2 nm Ag layer on a buffer layer of 10 nm Cu layer are reported in this work.

2. Experimental

The samples were prepared using ion beam sputtering technique. The ion beam source used to produce Ar$^+$ ions was a Kaufman type hot cathode ion gun installed in a vacuum chamber at an angle of 45$^\circ$. The Ar$^+$ ion were allowed to fall alternatively on Cu and Co targets to deposit a multilayer structure [Cu 3 nm/Co 2 nm]$^{10}$ on a Si(100) substrate. The Ag target was also mounted on a specially designed target holder which can accommodate four different targets. Prior to the deposition of multilayer, a Cu buffer layer of thickness 10 nm was deposited on the Si substrate. In case of sample prepared with Ag surfactant a 0.2 nm thin layer of Ag was deposited on Cu buffer layer. The pressure during the deposition of the films was of the order of $10^{-3}$ mbar while the pressure obtained before inserting Ar gas in the chamber was about $1\times10^{-6}$ mbar. More details about sample preparation are given in ref. [10].

The samples were measured using laboratory and synchrotron x-rays. The synchrotron measurements were carried out at ID32 beamline of ESRF, France. The x-ray diffraction (XRD) and x-ray reflectivity (XRR) measurements were performed at different energies. The neutron reflectivity (NR) measurements were performed at SINQ/PSI, Switzerland using neutrons of wavelength 0.5 nm. The NR measurements were performed at room temperature in the as-deposited and after annealing the samples in a vacuum furnace at different temperatures for 1h. In addition to NR measurements, the polarized neutron reflectivity (PNR) measurements were also performed. The PNR measurements were performed with an applied magnetic field of 800 G at the samples. The direction of magnetic field was kept parallel to the surface of the samples which is transverse to the direction of the neutron beam.

3. Results and discussions

Fig. 1 shows the grazing incidence x-ray diffraction pattern of the samples prepared with and without Ag surfactant. It was found that the XRD pattern of the sample prepared with Ag
The grain size $g_s$ for the sample prepared with Ag was about 7 nm while for the sample prepared without Ag it was 8.3 nm. This indicates that in presence of Ag, the grain growth of Cu is somewhat restricted.

In order to observe the effect of Ag layer on the interfaces of the multilayer, the x-ray reflectivity measurements were performed near the absorption edges of Cu (8.97 KeV) and Co (7.696 KeV) and at a higher energy of 10 KeV. Fig. 2 show the measured reflectivity for both samples at different energies. The choice of these energies was made to increase the scattering contrast between Cu and Co. In both cases near the absorption edges of Cu and Co, the XRR pattern of sample without Ag showed a higher roughness compared to the sample prepared with Ag. However at the higher energy of 10 KeV, the reflectivity of both samples appears together. The positions of the Bragg peaks in case of samples prepared with and without Ag surfactant are slightly shifted relative to each other. This may happen due to error in thickness caused during the deposition process. The fitting of the measured data taken at the absorption edges of Cu and Co was done using Parratt’s formalism [11]. From the fitting of the data it was observed that the roughness of the Cu buffer layer is the same in both cases however the interface roughness of Cu-on-Co is 0.5 nm while that of Co-on-Cu is 0.3 nm for the sample prepared without surfactant. For the sample prepared using Ag surfactant, the interface roughness of both interfaces is almost equal to 0.4 nm. This indicates the surfactant yields interfaces with similar roughness amplitude. The surfactant effect allows a more homogeneous distribution of the interfacial defects.

The neutron reflectivity pattern of the samples prepared with and without Ag as a surfactant are shown in Fig 3. The measurements were performed in the as-deposited samples and after annealing the samples at 373 K, 473 K, 573 K and at 673 K for 1 hour at each temperature. The annealing were performed in a vacuum furnace with a base pressure of the order of $1 \times 10^{-6}$ mbar.
Table 1. The inter-diffusion length ($L_d$) and magnetic moment per Co atom obtained from the neutron data.

| Sample | Co magnetic Moment with Ag ($\mu_B$) | Co magnetic Moment without Ag ($\mu_B$) | $L_d$ with Ag (nm) | $L_d$ without Ag (nm) |
|--------|-------------------------------------|---------------------------------------|--------------------|------------------------|
| As-deposited | 1.7                                | 1.5                                   | -                  | -                      |
| 373 K   | 1.7                                | 1.6                                   | 0.8                | 1.05                   |
| 473 K   | 1.7                                | 1.6                                   | 2.05               |                        |
| 573 K   | 0.6                                | 0.25                                  | 2.5                |                        |
| 673 K   | 0                                  | 0                                     | -                  | -                      |

Figure 3. Neutron reflectivity pattern of the Si/[Cu 10 nm/Ag 0.2 nm|Cu 3 nm/ Co 2 nm]$_{10}$ samples (a) and Si/[Cu 10 nm|Cu 3 nm/ Co 2 nm]$_{10}$ samples (b). The measurements were performed in the as-deposited sample and after annealing the samples in the temperature range of 373 K to 673 K with a step of 100 K. The annealing of the samples was performed in a vacuum furnace.

The Bragg peak corresponding to the multilayer period appears at nearly the same angles in both samples. The intensity of the Bragg peak is expected to decay due to the inter-diffusion as the annealing temperature is raised. This decay is seen to be faster in the samples when no surfactant was used.

In case of the sample prepared using Ag surfactant the Bragg peak intensity decreases marginally up to an annealing temperature of 473 K. However in case of sample where no Ag surfactant was used even at 473 K there is significant decrease of Bragg peak intensity. At 573 K the Bragg peak completely disappears for the sample where no surfactant was used while for the sample with 0.2 nm Ag the Bragg peak could still be seen however its intensity is significantly reduced. At 673 K the Bragg peak completely disappears in both cases. This result
clearly demonstrates that the thermal stability of the Cu/Co multilayer is improved with Ag surfactant. From the measured neutron reflectivity data the inter-diffusion in both samples can be quantified and the decay of the Bragg peak intensity can be used to calculate the diffusion coefficient using the expression \[ I(t) = I(0) \exp \left( -\frac{8\pi^2 n^2 D}{\ell^2} t \right), \] where \( I(0) \) is the intensity before annealing and \( I(t) \) is the intensity after annealing time \( t \) at temperature \( T \), \( \ell \) is the bilayer periodicity \( n \) is the order of reflection which is equal to unity for 1st order Bragg peak. With known diffusion coefficient \( (D) \) calculated using eq 1 the inter-diffusion length \( (L_d) \) can be calculated with the expression \( L_d^2 = 6Dt \) in the direction normal to the multilayer [14]. The inter-diffusion lengths obtained in this way are given in table 1. As can be seen from the table the \( L_d \) is significantly smaller for the sample prepared with Ag surfactant as compared to the sample prepared without any surfactant. This result clearly shows that by using Ag surfactant the inter-diffusion in Cu/Co multilayers can be reduced.

In addition, the PNR measurements yield the magnetic moment of Co in these samples. PNR is a technique which is able to yield the absolute value of a magnetic moment per atom in a magnetic thin film with high accuracy [15]. In contrast to the bulk magnetization magnetometer techniques, e.g. dc extraction, VSM, or SQUID, no correction due to the magnetic signal from the substrate has to be applied in PNR. Further, the sample dimensions and mass do not play a crucial role in the determination of the magnetic moment. During the experiment, polarized neutrons with spin parallel or anti-parallel (also termed as spin +/up, or spin −/down) to the direction of magnetization on the sample are reflected off the surface of a sample at grazing incidence. The measurements were performed with an applied field of 800 G, which is sufficient to reach the saturation magnetization in all the layered samples.

Fig. 4 show the PNR pattern of the sample prepared using Ag surfactant. Since the PNR pattern of a sample prepared with or without surfactant is similar in shape, therefore pattern corresponding to one sample is shown. The measured PNR pattern were fitted using SimulReflec software [16]. Table 1 show the obtained values of the magnetic moment per Co atom in units \( \mu_B \) obtained after fitting the PNR data in both cases. In the fitting routine the magnetic profile of Co is assumed to be constant throughout the layer. It was found that in the Co magnetic
moment was slightly smaller in case of sample prepared without Ag surfactant. Also the decay of Co magnetic moment was faster as the annealing temperature was increased in case of sample prepared without Ag. This could be understood from the results obtained with NR data and it was found that inter-diffusion is faster as the annealing temperature is increased in case of sample prepared without Ag. A faster inter-diffusion indicates an intermixed layer of Cu-Co resulting in a decreased value of Co magnetic moment. The obtained result demonstrates that the thermal stability of Cu/Co multilayers can be improved using Ag as a surfactant.

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References
[1] Baibich M N, Broto J M, Fert A, Van Dau F Nguyen, Petroff F, Etienne P, Creuzet G, Friederich A and Chazelas J 1998 Phys. Rev. Lett. 61 2472
[2] Nagamine L C C M, Biondo A, Pereira L G, Mello A, Schmidt J E, Chimendes T W, Cunha J B M and Saitovitch E B 2003 J. Appl. Phys. 94 5881
[3] An Y, Zhang H, Dai B, Mai Z, Cai J and Wu Z 2004 J. Appl. Phys. 100 023516
[4] Steigerwald D A and Egelhoff W F Jr 1989 J. Vac. Sci. Technol. A 7 2167
[5] Chopra H D, Yang D X, Chen P J and Egelhoff W F 2002 Phys. Rev. B 65 094433
[6] Yang D X, Shashishekar B, Chopra H D, Chen P J and Egelhoff W F 2001 J. Appl. Phys. 89 7121
[7] Camarero J, Ferron J, Cros V, Gomez L, De Parga A L V, Gallego J M, Prieto J E, De Miguel J J and Miranda R 1998 Phys. Rev. Lett. 81 850
[8] Larson D J, Petford-Long A K, Cerezo A, Bozeman S P, Morrone A, Ma Y Q, Georgalakis A and Clifton P H 2003 Phys. Rev. B 67 144420
[9] Gupta M, Gupta A, Stahn J, Horisberger M, Gutberlet T, and Allenspach P 2005 Phys. Rev. B 70 184206
[10] Gupta M, Gupta A, Phase D M, Chaudhari S M, and Dasannacharya B A 2003 Appl. Sur. Sci. 205 309
[11] Parratt L G 1954 Phys. Rev. 95 359
[12] Rosenblum MP, Spaepen F, Turnbull D. 1980 Appl. Phys. Lett. 37 184
[13] Speakman J, Rose P, Hunt JA, Cowlan N, Somekh RE, Greer A L 1996 J. Magn. Magn. Mat. 156 411
[14] Schmidt H, Gupta M, Gutberlet T, Stahn J and Bruns M 2008 Acta Materialia 56 464
[15] Blandell S J and Bland J A C 1992 Phys. Rev. B 46 3391
[16] SimulReflec: Reflectivity curve simulations and fitting, online at http://www-llb.cea.fr/prism/programs/simulreflec/simulreflec.html