Surfactant enhanced antiferromagnetic coupling in magnetron sputtered Cu/Co multilayers: A neutron reflectivity study

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(Dated: May 2, 2014)

In this work we studied Cu/Co multilayers prepared using dc-magnetron sputtering technique with Ag surfactant. It was found that Ag balances the difference in the surface free energy of Cu and Co and this results in removing the asymmetry in the interface roughness of Cu-on-Co and Co-on-Cu interfaces. As the interfaces become symmetric, we observe a significant enhancement in antiferromagnetic coupling and magnetoresistance. Further, a correlation of spin-dependent scattering with the interface roughness is brought by comparing Cu/Co multilayer prepared using different deposition methods. It was found that as interface roughness increases spin-dependent scattering decreases.

I. INTRODUCTION

Magnetic layers separated by a non-magnetic spacer layer are well-known to exhibit the interlayer exchange coupling (IEC) between the magnetic layers.1–3 In particularly, Cu/Co and Fe/Cr multilayers show the giant magnetoresistance (GMR) and an oscillatory exchange coupling with a variation in the thickness of the Cu (Cr) spacer layer. Other than the thickness of the spacer layer, intermixing at the interface (due to chemical diffusion) and interface roughness (σint) strongly influence the GMR.4,5 It is known that the GMR basically originates from the antiferromagnetic coupling (AFC) between magnetic layers and spin-dependent scattering of electrons taking place within a layer (bulk scattering) and at the interfaces.4,6,7 At an interface there is a change in the electronic band structure giving rise to asymmetric spin-dependent electron scattering. As such it is rather difficult to separate the contribution of bulk and interface scattering, some experimental results evidence that scattering is larger at the interface as compared to bulk.8–11 In this context the role of σint is immensely important to control GMR.

Experimental results reveal that Fe/Cr and Cu/Co multilayers show an opposite-type behavior of GMR with the interface roughness. In Fe/Cr multilayers, it was found that the electron scattering at the interface is spin-dependent, irrespective of the deposition method (e.g. sputtering or evaporation).5,12 However, in Cu/Co multilayers results are contradictory. In MBE grown Cu/Co multilayers Hall et al. concluded the electron scattering at the interface is spin-independent13,14 whereas in sputtered multilayers Parkin et al.8 found that the electron scattering at the interface is spin-dependent similar to Fe/Cr multilayers. Such contradictory observations of GMR in MBE grown and sputter deposited Cu/Co multilayer are still debated. In the present work we compare Cu/Co multilayers having different interface roughness and find a strong dependence of electronic scattering on the interface roughness.

In a multilayer, the interface structure depends on several parameters of which adatom energies (Ea, kinetic energy of the atoms being deposited on a substrate), deposition rate (Rd) and surface free energy (γ) of the elements play a very important role on the interface structure.16–18 For example, γ determines the type of growth that takes place while Ea and Rd are characteristic of a deposition process. An element with low γ will wet the surface of elements with high γ and make a smooth interface, whereas high γ element agglomerates over the low γ element surfaces and make a rough interface.19 This leads to asymmetric interfaces in a multilayer structure. In particularly in Cu/Co multilayers, this difference in γ severally affects the growth of multilayer as the average value of γ for polycrystalline Cu and Co are 1.8 J/m² and 2.55 J/m², respectively.20,21 This results in rough Co-on-Cu and smooth Cu-on-Co interfaces.22 It has been shown experimentally that the growth mode of Cu/Co multilayer can be altered by adding a third element known as surfactant.23–25 Various types of surfactants e.g. Ag (γ=1.2 J/m²), Sn(γ=0.65 J/m²), Pb (γ=0.6 J/m²) etc. (γ values for polycrystalline case) have been used in different types of multilayers.29–33 It has been demonstrated that surfactant floats at the surface balancing the γ of the elements, suppress surface diffusion and prevents island formation.34,35 To act as a good surfactant an element must have relatively smaller γ and larger volume so that its incorporation can be avoided.

Other aspects that influence the interface structure are Rd and Ea. For deposition of a particular multilayer, although the γ will not vary, Rd and Ea may change with the choice of deposition method. Generally in magnetron sputtering process both Rd and Ea (~10–20 eV) are large, in thermal evaporation process both Rd and Ea are low with Ea being about two orders of magnitude smaller and Rd typically an order of magnitude smaller. In ion beam sputter (IBS) deposition Ea is large and tunable, Rd is
typically comparable to e-beam methods. Therefore, by depositing samples using these different deposition methods with a surfactant, the $\sigma_{int}$ can be varied precisely.

In our recent works the effect of Ag surfactant on the $\sigma_{int}$ was studied in Cu/Co multilayers prepared using IBS$^{27,36}$ and e-beam evaporation.$^{28}$ Although the values of $\sigma_{int}$ in these deposition processes were different ($\sigma_{int} = 0.1$ nm in IBS and 1 nm in e-beam), it was found that in both cases Ag surfactant helps in removing the asymmetry of $\sigma_{int}$ caused due to different $\gamma$ of Cu and Co. In the present work we apply dc-magnetron sputtering (dc-MS) technique to study the effect of Ag surfactant in Cu/Co multilayers and found that Ag surfactant yield symmetric Cu/Co and Co/Cu interfaces. Here the value of $\sigma_{int}$ was found to be in between that of IBS and e-beam. A correlation of $\sigma_{int}$ with MR normalized with antiferromagnetic fraction (AFF) clearly shows that spin-dependent electron scattering at the interface of Co/Cu multilayers decreases with increasing $\sigma_{int}$. The obtained results are presented and discussed in the following sections.

II. EXPERIMENTAL DETAILS

We deposited Cu/Co multilayers on silicon substrates using dc-MS technique with following structure: Cu (10 nm)/x/[Cu (3 nm)/Co (2 nm)]$_{10}$, with $x =$ one monolayer of Ag or 0 (reference sample without Ag surfactant). With a base pressure of $\sim 1 \times 10^{-7}$ mbar, the deposition was carried out at $2 \times 10^{-3}$ mbar pressure using 5 sccm Ar gas for sputtering. Circular targets of (75 mm diameter) of pure Cu, Co and Ag (purity 99.999%) were sputtered at power of 50 W. All targets were cleaned by pre-sputtering for about 10 minutes. The deposition rates obtained were 31.3 nm/min, 13.4 nm/min and 40 nm/min for Cu, Co and Ag, respectively. Since Ag surfactant should be about a monolayer thick, a 10 nm slit was placed below Ag target which reduced Ag deposition rate to about 5 nm/min. The substrates were oscillated linearly with respect to a central position of a target for better uniformity of deposition area.

As-deposited Cu/Co multilayers were studied using unpolarized neutron reflectivity (NR) and polarized neutron reflectivity (PNR). These measurements were performed at the AMOR reflectometer at Swiss Spallation Neutron Source (SINQ) at PSI, Switzerland$^{37}$ in the time of flight geometry using neutrons of wavelength 0.15 nm $< \lambda < 1.3$ nm. The polarization efficiency of Fe-CoV/Ti:N supermirror polarizer was about 97%. X-ray diffraction (XRD) measurements were done in $\theta$-2$\theta$ geometry using x-rays of wavelength 1.54 Å in standard diffractometer (Bruker D8 Advance). The x-rays were detected using a fast counting detector based on Silicon strip technology (Bruker LynxEye detector). Magnetoresistance (MR) measurements were performed using four point probe method at room temperature. During the MR measurement direction of the magnetic field was along the direction of the current flowing in the sample.

Magnetization (M) versus magnetic field (H) hysteresis loop of the samples were recorded using superconducting quantum interference device (SQUID)-vibrating sample magnetometer (SVSM; Quantum Design Inc., USA).

III. RESULTS

A. X-ray diffraction measurements

Fig. 1 shows the XRD pattern of Cu/Co multilayers prepared with and without Ag surfactant using dc-MS method. Bragg peaks corresponding to Cu (111) and Cu (200) reflections can be seen around 2$\theta = 44.5$ deg. and 50.6 deg., respectively. The average grain size can be estimated using Scherrer formula and found to be around 6 nm in both samples. It appears that the grain growth is not significantly affected due to the presence of Ag surfactant in the Cu/Co multilayers. This is in agreement with Cu/Co multilayers prepared using Ag surfactant with other deposition methods.$^{27,28}$

B. Neutron reflectivity measurements

NR and PNR measurements were performed to probe the interface structure in Cu/Co multilayer samples. Fig. 2(a, b) shows the NR pattern of Cu/Co multilayers prepared without and with Ag surfactant. The NR measurements were performed without exposing the samples to any magnetic field. The reflectivity pattern of samples shows first order nuclear Bragg peak around momentum transfer vector $q_z = 0.11$ Å$^{-1}$ ($q_z = 4\pi \sin \theta /\lambda$, where $\theta$ is incidence angle and $\lambda$ is wavelength of neutrons). This correspond to a bilayer period of about 5.6 nm. The sample prepared with Ag surfactant shows in addition a half-order peak around $q_z = 0.055$ Å$^{-1}$. This half-order Bragg
peak originates as Co layers gets antiferromagnetically coupled and give rise to additional magnetic superstructure at twice the period of nuclear structure. No such magnetic peak could be observed in the NR pattern of sample where Ag surfactant was not used. To understand the observed results, the interface structure of the samples prepared with and without Ag surfactant should be analyzed. The fitting of the NR pattern provides detailed information about the Cu/Co and Co/Cu interfaces. The NR patterns were fitted using Parratt’s formalism, the fitting parameters are given in table I. As can be seen from the table, the interface roughness of Co-on-Cu and Cu-on-Co interfaces becomes almost equal when Ag surfactant is added.

Further to confirm that this half-order peak appearing in the Ag surfactant sample indeed has magnetic origins, we performed PNR measurement by applying an external magnetic field of 0.5 T parallel to the sample. This magnetic field strength is sufficient to saturate the samples magnetically. Fig. 3 shows the PNR data of samples around the critical angle. PNR gives a precise information about the absolute magnetic moment per atom in a magnetic sample and this is independent of substrate magnetism (often paramagnetic or diamagnetic) or sample volume as in case of bulk magnetization techniques e.g. SQUID, VSM or extraction methods. This makes PNR a unique technique to measure absolute magnetic moment in magnetic samples. The PNR data of the samples were fitted using a computer software and it reveals that the Co magnetic moment in both samples is about 1.7 \( \mu_B \) per atom, which is close to bulk Co magnetic moment. This indicates that Ag surfactant has no influence on the magnetic moment of these samples. Fig. 2 (c,d) shows the spin down (\( R^- \)) PNR pattern for both samples to higher \( q_z \). It may be noted that the contrast with polarized neutrons for Cu and Co is larger for spin-down neutrons. For neutrons the nuclear scattering length density (SLD) for Cu and Co is \( 6.55 \times 10^{-6} \text{ Å}^{-2} \) and \( 2.26 \times 10^{-6} \text{ Å}^{-2} \), respectively whereas magnetic SLD of Co is \( 4.22 \times 10^{-6} \text{ Å}^{-2} \). For spin-up neutrons the contrast between Cu and Co becomes \( 6.55 \times 10^{-6} \text{ Å}^{-2} \) and \( 6.48 \times 10^{-6} \text{ Å}^{-2} \) whereas for spin-down neutrons it is \( 6.55 \times 10^{-6} \) and \( -1.96 \times 10^{-6} \text{ Å}^{-2} \), obviously a larger contrast for spin-down neutrons permits to probe the Cu/Co multilayers more accurately. As can be seen from Fig. 2 (d) the half order peak has disappeared completely after applying a magnetic field of 0.5 T, confirming that the half order peak was indeed arisen due to antiferromagnetic coupling of alternate Co layers. A detailed fitting of PNR data reveals that the \( \sigma_{int} \) in the multilayers are similar to those obtained with NR data. This confirms that the structural roughness of Cu-on-Co and Co-on-Cu interfaces become equal when Ag surfactant was used.

C. Magnetotransport measurements

Fig. 4 shows the M-H hysteresis loop of the samples prepared with and without Ag surfactant. As can be seen, there is no appreciable change in the coercivity and saturation magnetization (\( M_s \), also confirmed by PNR measurements) of the samples but the remanent magnetization (\( M_r \)) is significantly different. As discussed before, the addition of Ag surfactant enhances the AFC in Cu/Co multilayer (see Fig. 2 b). The AF coupled region can be quantified as AFF = \( 1- M_r/M_s \). We find that the AFF for the sample prepared without Ag surfactant is about 18.8% and increases to about 39.2%.
TABLE I. Cu-on-Co and Co-on-Cu interface roughness ($\sigma_{\text{int}}$) of the Cu/Co multilayer samples prepared with and without Ag surfactant with nominal structure of Si(100)/Cu(10 nm)/[Cu(3 nm)/Co(2 nm)]$_{10}$ using dc-Magnetron sputtering (dc-MS), ion beam sputtering (IBS) and e-beam evaporation techniques.

| Deposition Method | $\sigma_{\text{int}}$ (nm) | No surfactant | Ag surfactant | Ref.     |
|------------------|---------------------------|---------------|---------------|---------|
| dc-MS            | $\sigma_{\text{Co-on-Cu}}$ | 0.74±0.05      | 0.4±0.05      | Present work |
|                  | $\sigma_{\text{Cu-on-Co}}$ | 0.32±0.05      | 0.4±0.05      | 27      |
| IBS              | $\sigma_{\text{Co-on-Cu}}$ | 0.36±0.05      | 0.11±0.05     | 28      |
|                  | $\sigma_{\text{Cu-on-Co}}$ | 0.18±0.05      | 0.10±0.05     |         |
| e-beam           | $\sigma_{\text{Co-on-Cu}}$ | 1.6±0.1        | 1.1±0.05      |         |
|                  | $\sigma_{\text{Cu-on-Co}}$ | 1.0±0.1        | 1.0±0.05      |         |

TABLE II. Average value of adatom energy ($E_a$) and deposition rate ($R_d$) for Cu/Co multilayer samples prepared using dc-Magnetron sputtering (dc-MS), ion beam sputtering (IBS) and e-beam evaporation techniques.

| Deposition Method | $E_a$ (eV) | $R_d$ (nm/min) |
|------------------|------------|----------------|
| dc-MS            | ~18        | ~30            |
| IBS              | ~22        | ~4.5           |
| e-beam           | ~0.2       | ~1.2           |

When Ag surfactant is used. This enhancement of AFF for the sample prepared with Ag surfactant re-confirms our observation from NR measurements, where the intensity of half-order peak gets enhanced when Ag surfactant is added.

For studying the effect of Ag surfactant, on the MR of the samples we performed MR measurements using the four-probe method. Fig. 5 shows the MR of the samples prepared with and without Ag surfactant. Here MR is defined as $\text{MR}= (R_0 - R_s)/R_0$, where $R_0$ is the resistance in the absence of magnetic field and $R_s$ is the resistance under the saturation magnetic field. The MR of the samples prepared with and without Ag surfactant are about 3.1% and 1.9% respectively. It may be noticed that there is significant increase in MR for the sample prepared using Ag surfactant.

IV. DISCUSSION

We observe that the addition of Ag surfactant helps in removing the asymmetry in the $\sigma_{\text{int}}$ of Cu-on-Co and Co-on-Cu interfaces independent of deposition method (see table I). Similar observation were also made by several other groups in Cu/Co multilayers. However, an enhancement in MR and AFC as observed in NR measurement is remarkable as: (i) the thickness of Cu layer corresponds to third and weakest maxima of the oscillatory exchange coupling (ii) the number of bilayer repetitions taken were only 10.
larger than the IBS technique. With the help of known deposition techniques are given in table II(calculated using SRIM simulations). In case of e-beam island type deposition techniques are different either in term of $E_a$ or $R_d$ which leads to the difference in the $\sigma_{int}$ in Cu/Co multilayers. The average value of $E_a$ and $R_d$ involved in different deposition techniques are given in table II(calculated using SRIM simulations). In case of e-beam evaporation technique $E_a$ directly translates to melting temperature of Cu, Co and Ag whereas in case of IBS and dc-MS, $E_a$ varies with Ar$^+$ energy. As can be seen from table II that $E_a$ values for IBS and dc-MS are not significantly different but the $R_d$ is an order of magnitude larger than the IBS technique. With the help of known $E_a$ and deposition rates, the growth mode of Cu/Co multilayers can be estimated. In case of e-beam island type growth is well-known and roughness keeps on increasing slow deposition rate result in almost layer-by-layer type growth. This explains different values of $\sigma_{int}$ obtained in these samples.

We can now compare the spin-dependent scattering with $\sigma_{int}$ in samples prepared using different methods with Ag surfactant. In magnetic multilayers, MR originates due to the competitive process of spin dependent scattering and AFC and MR normalized with AFF exhibits only the spin dependent scattering.7,51,52 A plot of MR/AFF in fig. 6 shows a decreases in it as $\sigma_{int}$ increases. This is a clear evidence showing that the spin-dependent scattering decreases with an increase in interface roughness in Cu/Co multilayers. This essentially implies significance of scattering from the interfaces in Cu/Co multilayers.

V. CONCLUSIONS

We observe Ag surfactant leads to symmetric interfaces in Cu/Co multilayers. Symmetric interface roughness enhances the AFC in Cu/Co multilayer which give rise to enhanced MR in the sample. A comparison of the Cu/Co multilayers prepared using different techniques - ion beam sputtering, e-beam evaporation and dc-magnetron sputtering reveal that spin-dependent scattering at the interface decreases with increase in $\sigma_{int}$. Observed results help in establishing the fact that spin-dependent electron scattering is significant in Cu/Co multilayers.

ACKNOWLEDGMENTS

This work is partially based on experiments performed with neutron reflectometer AMOR at the Swiss spallation neutron source SINQ, Paul Scherrer Institute, Villigen, Switzerland. We acknowledge DST, Government of India for providing financial support to carry out NR experiments under its schemes ‘Utilisation of International Synchrotron Radiation and Neutron Scattering facilities’. We are thankful to M. Horisberger and S. Potdar for their help in sample preparation. We are also thankful to Dr. R. J. Chaudhary for SVSM measurement. Continuous support and encouragements received from Dr. P. Chaddah is gratefully acknowledged.

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