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Structural Transition in Cu/Fe Multilayered Thin Films

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ABSTRACT

Microstructural development of Fe and Cu in Cu/Fe multilayers of layer thickness 1.5-10 nm prepared on Si, Ge, and MgO substrates by ion beam sputtering has been studied using x-ray diffraction and cross-sectional transmission electron microscopy (TEM). High-angle x-ray results show an fcc Cu structure and a distorted bcc structure in the Fe layers at 5 nm-layer-thickness and smaller, and bcc Fe (110) and fcc Cu (111) peaks in the 10 nm-layer-thickness samples. Low-angle x-ray diffraction indicates that the layers in the samples grown on MgO substrates have a more uniform and smooth layered structure than the multilayers grown on Si and Ge substrates, which results from larger grains in the MgO substrate samples for the same layer thickness. Relationships among growth, microstructure, and interfaces with layer thickness are discussed.

INTRODUCTION

Since Fe/Cr multilayers exhibited anomalously large negative magnetoresistance,¹ and subsequently, Co/Cu and Fe/Cu showed giant magnetoresistance effects and oscillating magnetic coupling between the magnetic layers when the layers were only a few monolayers thick,²⁻⁴ the interest in understanding the oscillatory magnetic exchange coupling through a non-magnetic layer and its structure, in particular in the Fe/Cu system, has increased tremendously. The Cu/Fe multilayer system is interesting because of the small lattice mismatch between the metastable fcc γ -Fe ($a = 0.359$ nm) and the fcc Cu ($a = 0.36148$ nm), which is favorable for epitaxial growth.⁵ Under equilibrium conditions, fcc Fe only exists at elevated temperatures, but has been observed at room temperature in thin films. As a result, growth and thickness transition of fcc to equilibrium bcc Fe of single Fe films on Cu substrate at room temperature has been studied extensively.⁶⁻⁹ Various techniques show that the first few monolayers of Fe grow epitaxially on Cu and then transform to a distorted bcc structure or the equilibrium bcc structure at roughly 10-11 monolayers.⁸⁻⁹ In the multilayered structure, the reported structures of Fe and Cu layers and their transitions vary widely depending on the individual Fe and Cu layer thicknesses and on the processing conditions.¹⁰⁻¹⁷

The stability of the metastable γ -Fe phase in nanometer-thick Fe/Cu multilayers has not been fully addressed. Under equilibrium conditions, Cu and Fe are mutually insoluble, which suggests sharp interfaces between the layers in a multilayered structure. Micron-thick $\text{Cu}_x\text{Fe}_{1-x}$ non-equilibrium solid solution films, however, have been prepared by a vapor-quenching method such as sputtering at liquid-nitrogen substrate temperature over the whole composition.¹⁸ Phase separation of these solid solutions were generally observed after annealing at around 300°C.¹⁹ X-ray diffraction patterns of a 20 Fe (110)/20 Cu (111) plane period multilayer annealed at 300°C for 10 minutes showed one peak at position between those of the Fe (110) and Cu (111) peaks, similar to that observed in the un-annealed sample, and enhancement of the satellite reflections from the multilayer modulation.¹³

For this project, we are interested in studying the effects of the interfaces on the stability of the metastable γ -Fe phase, and the period-dependent phase separation and recrystallization of Fe/Cu multilayers with individual layer thicknesses ranging from 1.5 to 10 nm on thermal annealing, and their effects on magnetic properties. This paper presents the preliminary results on the microstructure of Fe and Cu in Cu/Fe multilayers as a function of thickness in an equi-layer thickness system, and their magnetic properties.

EXPERIMENTAL TECHNIQUES

Cu/Fe multilayers with individual layer thicknesses ranging from 1.5 to 10 nm were prepared by ion beam sputtering on cleaned Ge (100), MgO (100), and oxidized Si (100) substrates at 100°C with a 20 nm thick buffer layer of either Cu or Fe. The multilayers that were terminated

with an Fe layer were coated with a Cu capping layer for consistency with other samples and to prevent iron oxidation. The base pressure of the chamber was in the 10^{-8} Pa range, and the sputtering gas during deposition was Ar at 2.5×10^{-4} Pa. The deposition rate of Fe was approximately 0.04 nm/sec and that of Cu was 0.05 nm/sec. The thickness of the Cu and of the Fe layers was kept equal in each multilayer, and the nominal thickness of the each layer was monitored by a quartz crystal. The bilayer period and the number of bilayer pairs were varied to obtain a total thickness of 200 nm in all samples for magnetic measurement comparison.

The samples were studied by low- and high-angle x-ray diffraction, and cross-sectional and plan-view transmission electron microscopy (TEM). The x-ray diffraction measurements were performed using a Rigaku x-ray diffractometer and Cu K_{α} radiation. The TEM specimens were prepared by mechanical grinding followed by ion milling in a cold stage.²⁰ They were then studied in a high-resolution JOEL 200CX microscope operating at 200 kV, at the National Center for Electron Microscopy, Lawrence Berkeley National Laboratory (LBNL). The magnetic hysteresis loops of the samples were studied in a Vibrating Sample Magnetometer (VSM).

RESULTS

In general, low-angle x-ray diffraction indicates that the samples grown on MgO substrates have better layering than those grown on Si and Ge substrates, especially at small layer-thicknesses, while high-angle scans show similar microstructures in all the samples. Small layer-thickness (5 nm and smaller) samples exhibit a preferred growth of a lattice near that of the fcc Cu (111) or bcc Fe (110) planes, and a lower peak at the Cu (200) position.

Figure 1 shows the low-angle x-ray profiles of equal layer-thicknesses of 1.5 and 2.5 nm multilayers grown on a Cu-buffered layer on MgO and Si substrates. For Cu/Fe multilayers, only first order Bragg's peak and at most two orders are usually observed due to the low scattering power difference between the layer materials. Since the layers in the samples grown for this study were prepared nominally equal to each other, second order peaks may not be observed. At 1.5 nm layer-thickness, the first order peak of the MgO substrate sample is observed at $2\theta = 3.05^{\circ}$, while that of the Si substrate sample is not present, which suggests a weaker modulated structure than that in the MgO substrate sample. Both 2.5 nm samples grown on MgO and Si substrates show the first order peak at $2\theta = 1.97^{\circ}$. A weak second order peak, however, is observed in the MgO substrate sample, which suggests that the Fe and Cu layers in the sample are not exactly equal in thickness. Low-angle diffraction of longer layer-thickness samples prepared for this study (5 nm and 10 nm) does not show any Bragg's peaks, since their first order positions, according to these thicknesses, are smaller than the critical reflection angle, and their third order peaks are too weak even in an ideal structure ($< 1\%$) to be observed for the number of bilayer pairs deposited. The multilayers grown on MgO substrates seem to have better layering than those grown on Si substrates. Smooth layers in the MgO substrate samples are evidenced by the presence of thickness

Figure 1. Low angle x-ray diffraction of 1.5 and 2.5 nm multilayers on MgO and Si substrate. Both 2.5 nm multilayers show Bragg's peaks while at 1.5 nm, the peak is observed only in the sample on MgO substrate indicating better modulation than that on Si.

Figure 2. Typical high angle x-ray diffraction of Cu/Fe multilayers showing a strong peak between Cu (111) and Fe (110) positions, and a Cu (200) peak. This sample was prepared on a Si substrate.

Layer thickness (nm)	Average grain size (nm)
1.5	4.0
2.5	4.6
5	6.9
10	6.8 (Cu 111)
10	7.6 (Fe 110)
100	18.7

Figure 3. High angle x-ray diffraction around the Cu 111 and Fe 110 peaks of the multilayers on Si substrate. The 1.5, 2.5, and 5 nm layer thick samples show one broad peak, while the 10 nm sample shows double peaks according to Cu 111 and Fe 110 lattices. Diffraction from a 100 nm single Fe film is also shown.

oscillation in the low-angle scan of the 1.5 nm sample. Low-angle scans of all multilayers grown on Si and Ge substrates with a Fe buffer layer show a pronounced oscillation corresponding to an approximately 20 nm-thick layer, while this oscillation is not observed in any samples grown on a Cu buffer layer.

Most of the high-angle scans show similar characteristics to each other. Figure 2 shows a high-angle symmetric scan of the 2.5 nm layer-thickness sample on Si. The scan exhibits a prominent peak at a position near that of the fcc Cu (111) and the bcc Fe (110) peaks, and a lower peak near the fcc Cu (200) position. Figure 3 plots x-ray profiles around the positions of the fcc Cu (111) and the bcc Fe (110) peaks of the samples grown on a Cu-buffer layered Si substrate. For reference, the plot also indicates the positions of the equilibrium bulk fcc Cu (111) and bcc Fe (110). Also included for comparison is the scan from an 100 nm-thick single Fe film grown on Cu buffer layer on Si substrate. Other peaks (α -Fe 200 and 211) are also present in this film but are very weak indicating that the Fe thick film grows preferentially on its close-packed plane (110). The position of the (110) peak of this sample is very near that of the equilibrium Fe bulk. Of the multilayered films, except for the thickest sample under study (10 nm layer-thick), the x-ray patterns from all samples show a broad peak at a position between that of the fcc Cu (111) and the bcc Fe (110) structure, which suggests that the Fe grows in some sort of a bcc structure, probably a distorted bcc structure as has been reported,⁹ and that both the Cu and Fe layers are strained to match with each other's lattice. No satellite reflections from the modulation are observed. The 10 nm layer-thickness sample shows double peaks - one very near the 43.3° position of the fcc Cu (111) and one close to that of the α -Fe (110) lattice. Therefore at this thickness, the Fe layer has grown toward a more equilibrium bcc structure close to that of the bulk. The width of the peaks is observed to increase with decreasing layer thickness, which indicates a decreasing average grain size with decreasing layer thickness. Figure 3 also presents the average grain size of the crystallites at this orientation, determined from the Scherrer's equation.

Cross-sectional TEM was used to study the layered periodicity in the longer layer thickness multilayers. Figure 4 shows a bright field (BF) and a dark field (DF) cross-sectional TEM image of a 5 nm layer-thickness Fe/Cu multilayered sample on a Fe-buffer layer on Si substrate, and their corresponding selected area diffraction (SAD) pattern. Present in the images are the Si substrate, a thin layer of approximately 2-3 nm between the substrate and the buffer layer, the Fe buffer layer with an intended thickness of 20 nm, 40 layer pairs of nominally 5 nm Cu and 5 nm Fe, and a 5 nm Cu capping layer. The images show that the layered structure in this sample is apparent though the layers and interfaces are not quite flat. The diffraction pattern (Fig. 4c) shows the diffraction spots from the Si substrate, a strong and broad ring corresponding to a length near that of the fcc Cu (111) and the bcc Fe (110) lattice, and weaker rings of the fcc Cu structure and possibly of copper oxides. It is believed that the oxides arise from an oxide layer on top of the multilayer before TEM specimen preparation and not from a coat on the TEM prepared specimen. A preferred orientation is observed from the diffraction pattern of the Cu (111) and (222) rings approximately 12° from the normal [200] direction of the Si substrate. Close examination of the diffraction pattern (Fig. 4d) reveals rings that correspond to the reflection from the fcc Cu (222) and bcc Fe (220) lattices which are very close to each other. The DF image (Figure 4b) was taken with an aperture shown in the SAD pattern displaced from the main beam. As shown, many reflections of different structures are allowed through which results in bright grains in both the multilayer and the

Figure 4. Cross-sectional TEM bright-field (a), dark-field (b) images, and corresponding electron diffraction patterns (c and d) of 5 nm layer thickness sample grown on Si substrate with a Fe buffer layer. The images in a) and b) show the layered structure and grain size. The DF image is taken with an aperture shown in c). Enlargement of the diffraction pattern in c) shows rings of Cu (222) and Fe (220) which suggest that the Fe is of a bcc type structure.

buffer layer; nevertheless, it provides an idea of the grain size in the films. Similar to the results obtained from the x-ray diffraction pattern, the lateral grain size in this sample ranges from the thickness of one layer to about twice that size, which corresponds to approximately 5 to 10 nm. The average value determined from the x-ray diffraction is near 7 nm.

Observation of the 10 nm layer-thickness sample grown on Si substrate shows more well-defined layers than those in the 5 nm layer thickness sample. The grains seem to be on the same order as that of the layer thickness, which is consistent with the value determined from the x-ray diffraction pattern. A thick layer of approximately 7 nm of a different contrast is observed between the Si substrate and the Cu buffer layer. This layer is probably a silicide layer which results from reaction of the Cu and Si substrate during deposition that has also been reported in sputtered Cu buffer layers on Si substrate.¹⁵ The thickness of the Cu buffer is measured to be about 15 nm, significantly less than the intended growth thickness of 20 nm.

Preliminary magnetic measurements of the samples show that the magnetization and coercivity increases with layer-thickness of the multilayers. The values measured are in the same order of magnitude as those reported by Cheng et al., in which they observed a distorted bcc Fe structure in the films.⁵ The difference in the grain size of Fe in the samples may explain for this difference in the coercivity. It has been reported that the coercivity of sputtered Fe is roughly proportional to the sixth power of the grain diameter below 20 nm, and is proportional to the reciprocal of the grain diameter at larger values.²¹ Detailed magnetic results will be presented in another report.

DISCUSSION

The structural evolution with thickness observed in this study is consistent with reported results. The Cu layers have an fcc structure at all thicknesses studied, as evidenced by the presence of other lattice reflections in the x-ray diffraction and electron diffraction patterns, while the Fe layers exhibit a distorted bcc structure at small thicknesses that approach the parameters of the bulk structure as the thickness increases. Observation of the bcc Fe (220) ring in the electron diffraction pattern confirms that the Fe structure is of a bcc type at these thicknesses. No clear evidence of the γ -Fe structure is observed in the thickness range of the samples in this study. The thinnest sample 1.5 nm in this study, whose layer corresponds to approximately 7 monolayers of Cu (111) or Fe (110) planes, is near the reported critical value for the growth of γ -Fe by vacuum deposition in a temperature range 20-100°C.¹⁰ For sputtered multilayers with individual layers nearly equal in thickness to each other, metastable γ -Fe has been observed only in those that are less than approximately 1 nm thick.¹¹⁻¹⁴

Comparatively, higher layered quality in samples grown on MgO substrate than those on Si and Ge substrates, especially at small layer thickness, can be explained by the difference in the grain size in the layers. High angle x-ray diffraction of these samples show similar structure, namely a strong peak at a position near that of the fcc Cu (111) and the bcc Fe (110) lattice, and a reasonable peak at the Cu (200) position. Other fcc Cu peaks are occasionally observed, though very faint. The width of the strong peak near that of the fcc Cu (111) and the bcc Fe (110) lattice of the MgO substrate samples, however, is significantly narrower than that of the Si substrate samples. The average grain size of the 2.5 nm layer thickness sample on MgO substrate, for example, is determined from Scherer's equation to be approximately 19 nm, which is more than 4 times the average grain size of the sample deposited concurrently onto the Si substrate. The grain size difference is related to the preferred growth orientation of the buffer layer and subsequently the multilayers on the different crystal structures of the substrates. All the substrates used have a cubic structure and a lattice parameter that would promote the growth of Cu (100) planes. There are thus two competing growth orientations for the fcc Cu buffer layer: its close-pack planes (111) and the lower interfacial energy (100) planes. The closer match of the Si (110) lattice to that of the Cu (100) planes ($\sim 6.24\%$) as compared with the MgO (100) lattice ($\sim 16.6\%$) suggests that more Cu (200) grows on Si substrate than on MgO substrate. Epitaxial growth of thin (200) Cu planes on Si in fact has been reported, and as the thickness increases, (111) growth also appears.¹⁷

The effects of the Fe and Cu buffer layer on the structure and the magnetic properties of the multilayers are still under study. The oscillation corresponding to an approximately 20 nm-thick layer observed in the low angle x-ray diffraction of samples grown on a Fe buffer layer probably arises from the scattering from the buffer layer. This oscillation is not observed in the diffraction pattern of samples grown on a Cu buffer layer probably because of the presence of a large compositional-variant layer at the interface of the substrate and the buffer layer due to the diffusion of the Cu atoms into the substrate to form compounds during deposition. Preliminary comparison of the magnetic measurements of the 1.5 nm samples grown on different buffer layers and substrates seems to indicate a higher magnetization for those grown on a Fe buffer layer than those grown on a Cu buffer layer, which is similar to the results found in Cu/Co grown on these two buffer layers.²² The use of a Fe buffer layer has shown a more well-defined layering of Co/Cu superlattice structure than structure grown on a Cu buffer layer,²² though this effect is not clear from the results in this study.

Mechanisms for growth of metastable fcc γ -Fe on fcc Cu have been discussed briefly. Clemens et al. suggest that the interfacial energy may be particularly significant in controlling the extent of the fcc thickness and fcc $\rightarrow$ bcc transformation in single Fe layer grown on Cu.⁹ The interfacial energy between the structures, in fact, probably governs the structure of the layers near the interfaces. Similar phenomenon of structural transition with layer thickness has also been observed in other nanometer multilayers such as Al/Ti.²³ In this system, it was found by high resolution TEM that the structure contains hcp Ti/hcp Al at thin layer period (5.2 nm), and changes to fcc Ti/fcc Al at 9.8 nm, and to equilibrium hcp Ti/fcc Al at longer period.²³ First principle calculations of the interfacial energies with an in-plane strain and allowed relaxation in the other direction in the layers indeed show a transition in the minimum total energy of the system according to the structures observed experimentally and in the nanometer-scale range.²⁴ Therefore, the role of interfacial energies is important in nanoscale multilayers in which the

dimension of the interfacial layers approaches that of the layers. In the Cu/Fe system, however, the transition of the minimum energy probably also depends on the thickness of the individual layers and on the substrate. The argument suggests that the metastable structure is stable at these thicknesses in the layered structure. The effects of annealing on the stability of the metastable phase will be addressed in a later report.

SUMMARY

Microstructural development in nanometer thick Cu/Fe multilayered thin films prepared by ion beam sputtering on various substrates has been studied by x-ray diffraction and cross-sectional TEM. High-angle x-ray results show little differences in the microstructure among the samples on different substrates. Thicker layer samples (10 nm) show the presence of both bcc Fe and fcc Cu structures, while thinner layer samples (5 nm and below) exhibit a fcc Cu structure and a distorted bcc structure in the Fe layers. Low-angle x-ray diffraction indicates that the layers in the samples grown on MgO substrates have a more uniform and smooth layered structure than the multilayers grown on Si and Ge substrates, which results from larger grains in the MgO substrate samples for the same layer thickness. Cross-sectional TEM observation of the 5 and 10 nm thick layer samples shows that the layered structure is apparent, and the electron diffraction patterns exhibit rings of the fcc Cu phase similar to the results obtained by x-ray diffraction. A distorted bcc Fe structure observed in thin layer thickness Cu/Fe multilayers is a result of interfacial energy reduction which is dominant in nanoscale multilayered structures.

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