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EFFECT OF THE ANNEALING TEMPERATURE ON THE ELECTRONIC AND ATOMIC STRUCTURES OF EXCHANGE-BIASED NiFe–FeMn BILAYERS

J. M. LEE, J. C. JAN, J. W. CHIOU and W. F. PONG*
Department of Physics, Tamkang University, Tamsui 251, Taiwan

M.-H. TSAI
Department of Physics, National Sun Yat-Sen University, Kaohsiung 804, Taiwan

Y. K. CHANG, Y. Y. CHEN and C. R. WANG
Institute of Physics, Academia Sinica, Taipei 107, Taiwan

J. F. LEE
Synchrotron Radiation Research Center, Hsinchu 300, Taiwan

T. YANG, Z. LU, W. Y. LAI and Z. H. MAI
Institute of Physics, Chinese Academy of Science, Beijing, China

In this study we measured the Fe, Mn, and Ni $L_{2,3}$-edge X-ray absorption near-edge structure (XANES) and K-edge extended X-ray absorption fine structure (EXAFS) of the ferromagnetic (FM) NiFe and antiferromagnetic (AFM) FeMn bilayer films prepared with various annealing temperatures. The branching ratios of the white-line intensities in the Fe, Mn, and Ni $L_{2,3}$-edges XANES spectra and consequently the magnetic properties of these exchange-biased FM NiFe − AFM FeMn bilayers are found to depend strongly on the annealing temperature. We find that the first peak in the Fe, Mn, and Ni K-edge EXAFS Fourier transform spectra are very similar, which suggests that the nearest-neighbor bond lengths among Fe, Mn, and Ni atoms are essentially the same in the NiFe–FeMn bilayers. However, the peaks at distances greater than ~ 3 Å appear to be sensitive to the annealing temperature especially for the Fe and Mn K-edge spectra, which suggests that annealing alters the atomic structures of the next-nearest-neighbor and more distant shells surrounding the Fe and Mn atoms in the NiFe–FeMn bilayers.

1. Introduction

The ferromagnetic (FM) NiFe and antiferromagnetic (AFM) FeMn layers with a high degree of exchange anisotropy have recently attracted extensive attention because of their potential application in high magnetic memory sensors and giant magnetoresistive (GMR) spin valve heads. These bilayers have a combination of a high exchange coupling strength and a high blocking temperature T_b (the temperature at which the exchange field, H_{ex}, disappears).[1–4] For memory applications, the high processing temperature requires that the exchange-biased FM–AFM bilayers have thermal stability. Previous investigations[5,6] demonstrated that the annealing process strongly influences the thermal stability and substantially alters the magnetic properties of the exchange-biased FM–AFM bilayers. The exchange

*Author to whom all correspondence should be addressed.

coupling and magnetic properties of the magnetic layers are generally believed to be strongly influenced by their electronic and atomic structures.[7] The study of the electronic and atomic structures of these materials may elucidate the mechanism of the FM–AFM exchange interaction and the GMR properties. However, despite the various studies, which explored the exchange coupling and magnetic properties of FM NiFe – AFM FeMn bilayers (FeMn on top), the dependence of the local electronic and atomic structures in these materials on the annealing temperature, to our knowledge, has not been reported. Thus, we have carried out the measurements of the Fe, Mn, and Ni $L_{2,3}$-edge X-ray absorption near-edge structure (XANES) and K-edge extended X-ray absorption fine structure (EXAFS) to investigate the effect of the annealing temperature on the electronic and atomic structures of the FM NiFe – AFM FeMn bilayers.

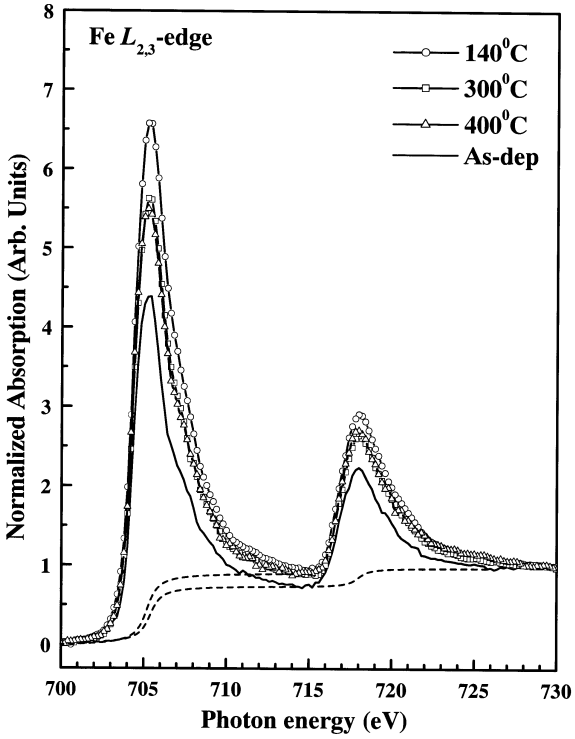
2. Experiment

X-ray absorption spectra were measured using the facility at the Synchrotron Radiation Research Center (SRRC) in Hsinchu, Taiwan, operating with the electron energy of 1.5 GeV and a maximum stored current of 200 mA. The XANES spectra of all samples were obtained from the high-energy spherical grating monochromator beamline using the sample drain current method for Fe and Mn $L_{2,3}$-edges and the fluorescence yield method for Ni $L_{2,3}$-edge respectively, while the K-edge extended X-ray absorption fine structure (EXAFS) spectra were obtained from the wiggler beamline using the fluorescence yield method at room temperature. The exchange-biased NiFe–FeMn bilayers were deposited on the Si(100) substrate by DC magnetron sputtering. Ta layers deposited by RF magnetron sputtering served as the buffer and cap layers. The resultant film compositions were $Ni_{0.8}Fe_{0.2}$ and $Fe_{0.5}Mn_{0.5}$, respectively. The as-deposited Si/Ta(100 Å)/$Ni_{0.8}Fe_{0.2}$(150 Å)/$Fe_{0.5}Mn_{0.5}$(300 Å)/Ta(15 Å) film and the three annealed films with the same configuration are investigated. Annealing was performed in a magnetic field of about 500 Oe for 2 h at temperatures of 140, 300, and 400°C, respectively. The details of the preparation and characterization of these samples are given elsewhere.[8]

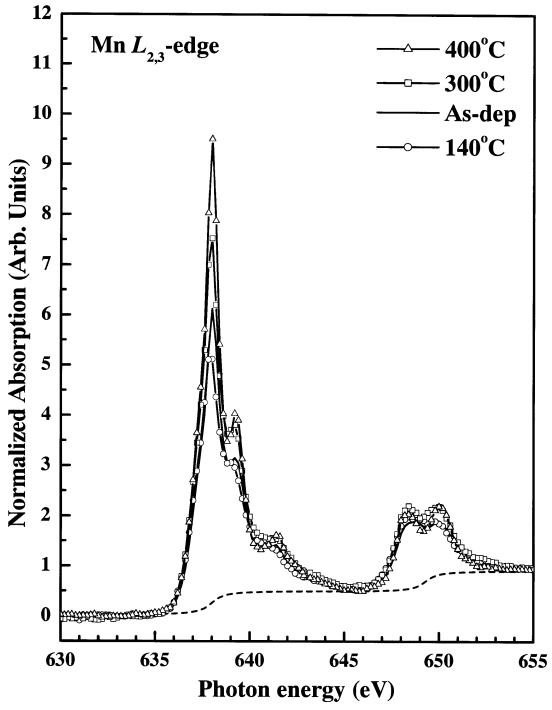
3. Results and Discussions

Figures 1(a)–1(c) display, respectively, the normalized Fe, Mn, and Ni $L_{2,3}$-edge XANES spectra of the as-deposited and three annealed NiFe–FeMn bilayer films. According to the dipole-transition selection rule, the dominant transition is from Fe (Mn & Ni) $2p_{3/2}$ and $2p_{1/2}$ to the unoccupied Fe (Mn & Ni) $3d$ electron states. The area beneath the white-line feature in the Fe (Mn & Ni) $L_{2,3}$-edge XANES spectra is predominantly a convolution of the absolute square of the transition matrix element and the unoccupied densities of states of the d character. The general line shapes in the Fe (Mn & Ni) $L_{2,3}$-edge XANES spectra of the as-deposited and the three annealed NiFe–FeMn bilayers display similar features above the Fe (Mn & Ni) $L_{2,3}$-edge, except for the intensity near the threshold of the Fe (Mn & Ni) $L_{2,3}$-edge XANES spectra. Figures 1(a)–1(c) illustrate a systematic reduction in the intensity of the feature near the Fe and Ni $L_{2,3}$-edge for the three annealed NiFe–FeMn bilayers with the increase of the annealing temperature. In contrast, the variation of the intensity in the Mn $L_{2,3}$-edge XANES spectra shows exactly the opposite trend for the features of the three annealed NiFe–FeMn bilayers, which display increasing intensity of the Mn $L_{2,3}$-edge XANES with the increase of the annealing temperature for the NiFe–FeMn bilayers, as presented in Fig. 1(b).

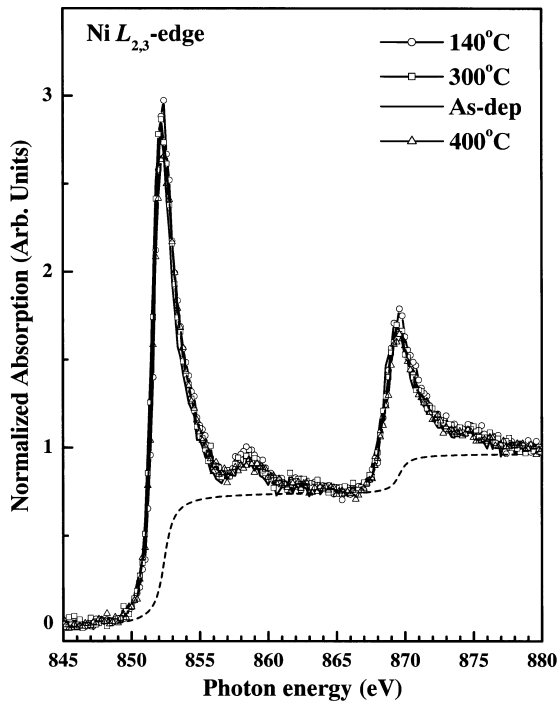
Generally, the lower the intensities of the features near the threshold in the Fe (Mn & Ni) $L_{2,3}$-edge XANES spectrum, the fewer the unoccupied Fe (Mn & Ni) $3d$ states the material has. The line shape of the $L_{2,3}$-edge white-line absorption spectra of $3d$ transition-metal ions depends strongly on the crystal-field symmetry and ligand-field splitting parameter $10D_q$.[9] In a study of how the Fe (Mn & Ni) $3d$ electronic structure and the magnetic property of the NiFe–FeMn bilayers change with the annealing temperature, Thole and van der Lann noted that[10] the branching ratio of the white-line intensity $I(L_3)/[I(L_3) + I(L_2)]$ is highly sensitive to the spin states of the $3d$ transition-metal ions. They found that the high-spin states have a relatively large white-line branching ratio. Thus, in this study we have investigated the branching ratio to understand the spin states and the magnetic properties of the NiFe–FeMn bilayers. An arctangent function



(a)



(b)



(c)

Fig. 1. Normalized (a) Fe $L_{2,3}$-edge (b) Mn $L_{2,3}$-edge, and (c) Ni $L_{2,3}$-edge XANES spectra of the as-deposited and three annealed NiFe–FeMn bilayers. The dashed line is a best-fitted arctangent shape background and the center of the continuous step of the arctangent function was selected at the inflection point of the threshold.

representing the background intensity, as displayed by dashed lines in Figs. 1(a)–1(c) was first subtracted from the intensities $I(L_3)$ and $I(L_2)$. Then $I(L_3)$ (between 700.0 and 714.2 eV for Fe, 634.2 and 646.2 eV for Mn, 847.0 and 863.0 eV for Ni) and $I(L_2)$ (between 714.2 and 730.0 eV for Fe, 646.2 and 654.0 eV for Mn, 863.0 and 878.0 eV for Ni) were integrated separately for the as-deposited and the annealed films. Figure 2 shows the results of the branching ratio $I(L_3)/[I(L_3)+I(L_2)]$ as a function of the annealing temperature. The trend of the branching ratio $I(L_3)/[I(L_3) + I(L_2)]$ in the Fe $L_{2,3}$-edge spectra is very different from those in the Mn and Ni $L_{2,3}$-edge spectra. First, the Fe $L_{2,3}$-edge branching ratio $I(L_3)/[I(L_3) + I(L_2)]$ remains constant up to the annealing temperature of about 140°C, then decreases with the increase of the annealing temperature. In an opposite trend, the Mn and Ni $L_{2,3}$-edge branching ratios increase with the increase of the annealing temperature above 140°C. These trends suggest that the spin moments of the Fe, Mn, and Ni 3*d* states are not affected by the annealing treatment up to 140°C. However, the spin moments of the Fe (Mn & Ni) 3*d* states are significantly reduced

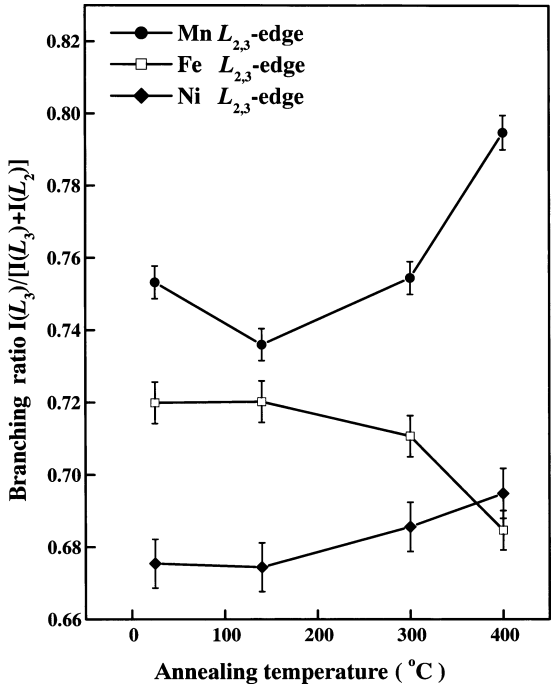


Fig. 2. The branching ratio $I(L_3)/[I(L_3) + I(L_2)]$ as a function of the temperature at the Fe, Mn, and Ni $L_{2,3}$-edge.

(enhanced) when the annealing temperature of the NiFe–FeMn bilayers exceeds 140°C. The substantial decrease in the spin moment of the Fe 3*d* states is most likely caused by the formation of bcc Fe in the top fcc FeMn layer.[6] This result suggests that the Fe ions approaches the low-spin state, while Mn & Ni ions approach the high-spin state when the annealing temperature exceeds 140°C. The major contribution to the desirable magnetic properties of the NiFe–FeMn bilayers is primarily from the significant change of the Fe, Mn, and Ni 3*d* spin states in the NiFe and FeMn layers following annealing. The critical annealing temperature of around 140°C, below which the spin moments of the Fe, Mn, and Ni atoms remain unaffected, is close to the observed blocking temperature T_b, at which H_{ex} disappears, of $\sim$ 150°C in the NiFe–FeMn films.[2,3,11] This critical annealing temperature for the spin moments of the Fe, Mn, and Ni atoms may be closely related to the lowering of the Néel temperature from that of the bulk FeMn of $\sim$ 220°C.[3] Since the existence of H_{ex} is caused by a unidirectional anisotropy arising from the nearest-neighbor exchange coupling, which is proportional to the spin moments,[1] H_{ex} will roughly follow the dependence of the overall spin moments of the Fe, Mn, and Ni 3*d* atoms on the annealing temperature.

Figures 3–5 show the Fe, Mn, and Ni *K*-edge Fourier transform (FT) of the EXAFS oscillation $k^3\chi$ data for the as-deposited and the annealed NiFe–FeMn bilayers. The inset shows the corresponding Fe, Mn, and Ni *K*-edge EXAFS oscillation $k^3\chi$ data, respectively. The first peaks in the FT curves shown in Figs. 3–5 (marked by the first vertical arrow) correspond to the nearest-neighbor (NN) bond lengths. The first peaks of the as-deposited and the annealed bilayers appear to roughly have the same location, height and full width at the half maximum. This result suggests that the NN atomic structures around the absorbing Fe, Mn, and Ni atoms in the annealed bilayers closely resemble that of the as-deposited film. Since a substantial element diffusion across the interfaces may occur in the NiFe–FeMn bilayers after extended annealing,[1] this result also indicates that Ni–Ni, Ni–Fe, Fe–Fe, Fe–Mn, Mn–Mn, Mn–Ni bond lengths are approximately the same. This result is consistent with the observation that the backscattering amplitudes of the Fe, Mn, and Ni atoms are very similar and that the covalent radii of

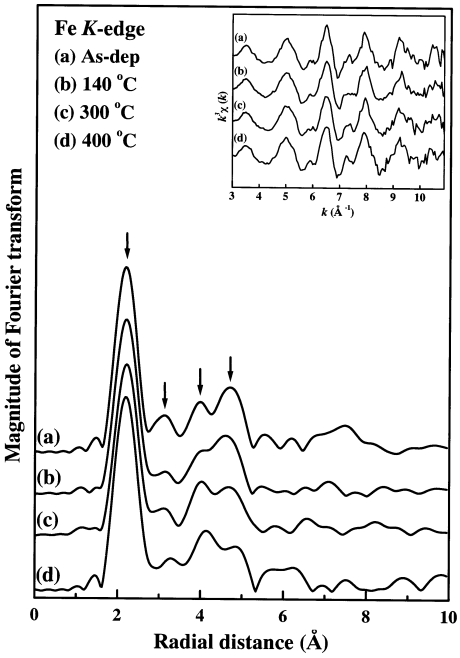


Fig. 3. Fourier-transform amplitudes of the EXAFS $k^3\chi$ data at the Fe K-edge from $k = 3.2$ to 11 Å^{-1} for the as-deposited and three annealed NiFe–FeMn bilayers. The inset represents the Fe K-edge EXAFS oscillation $k^3\chi$ data.

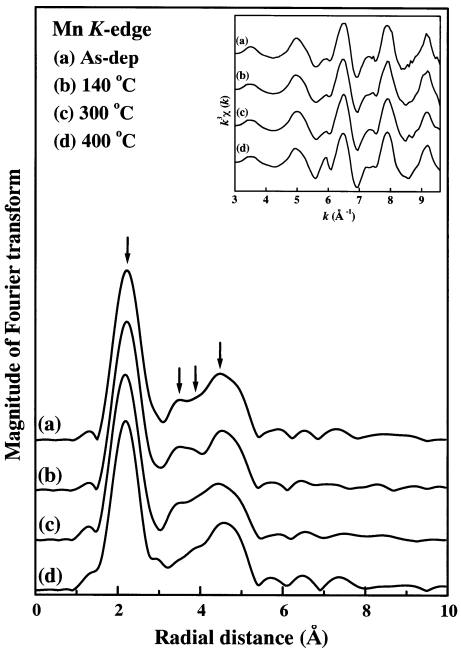


Fig. 4. Fourier-transform amplitudes of the EXAFS $k^3\chi$ data at the Mn K-edge from $k = 3.2$ to 9.7 Å^{-1} for the as-deposited and three annealed NiFe–FeMn bilayers. The inset represents the Mn K-edge EXAFS oscillation $k^3\chi$ data.

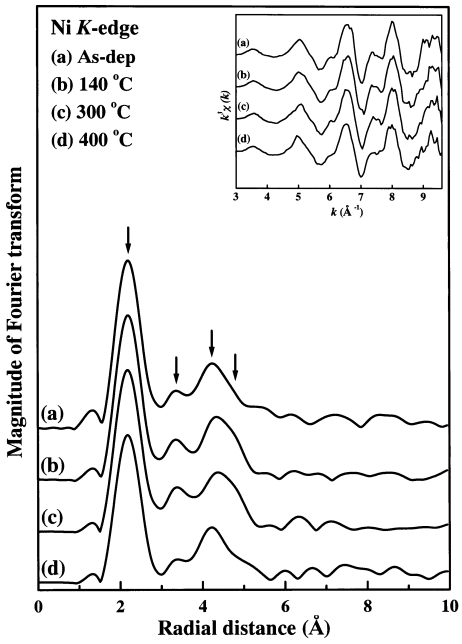


Fig. 5. Fourier-transform amplitudes of the EXAFS $k^3\chi$ data at the Ni K-edge from $k = 3.2$ to 9.7 Å^{-1} for the as-deposited and three annealed NiFe–FeMn bilayers. The inset represents the Ni K-edge EXAFS oscillation $k^3\chi$ data.

the Fe, Mn, Ni atoms are approximately the same (1.17 Å, 1.17 Å and 1.15 Å, respectively, for Mn, Fe, and Ni).[12] However, the peaks at a distance greater than ~ 3 Å (marked by the second, third, and fourth vertical arrows) differ considerably, especially for Fe and Mn atoms, as shown in Figs. 3 and 4. The differences suggest that the thermal effect in the NiFe–FeMn bilayers gives rise to bond distance distortion and/or different degrees of atomic disorders in next-nearest-neighbor and more distant shells surrounding the X-ray absorbing Fe and Mn atoms, which may significantly influence the exchange bias in the NiFe–FeMn bilayer films. On the other hand, Fig. 5 shows that the line shapes and intensities of the shells between 3 Å and ~ 5 Å in the Ni K-edge FT spectra remain more or less the same. For more distant shells the line shapes and intensities differ for different annealing temperatures similar to those of the Fe and Mn K-edge FT spectra. This property suggests that the coordination of the Ni atoms with neighboring atoms remains more or less unchanged up to shells about 5 Å away from the Ni atom upon heating. The Auger composition analysis[1] reported substantial Ni diffusion into the FeMn layer near

the interface after extended annealing at $\sim$ 260°C causing the formation of NiMnFe ternary alloys that display a strong antiferromagnetic order and are coupled to the NiFe to produce a much stronger exchange bias. The Auger composition analysis in conjunction with our Ni K-edge FT result seems to suggest that the atomic structure in the interface region and about 5 Å deep in the FeMn layer more or less has the fcc structure of the NiFe layer.

4. Conclusion

In summary, this study has investigated the electronic and atomic structures of the as-deposited and three annealed FM NiFe – AFM FeMn bilayers using X-ray absorption spectroscopy and found substantial variation of the branching ratio $I(L_3)/[I(L_3)+I(L_2)]$ for the Fe, Mn, and Ni $L_{2,3}$-edge at an annealing temperature above 140°C in the NiFe–FeMn bilayers. These results suggest that the spin moments of the Fe, Ni & Mn atoms are unaffected by annealing up to about 140°C. Beyond 140°C, the spin moments of the Fe atoms decrease significantly while those of the Ni and Mn atoms increase significantly with the increase of the annealing temperature. The EXAFS results show that annealing causes changes in the next-nearest-neighbor and higher-order shells surrounding the Fe and Mn atoms in the NiFe–FeMn bilayers.

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