Arrays of ferromagnetic FeCo and FeCr binary nanocluster wires

Department of Chemistry, College of Natural Sciences, Kyungpook National University, Taegu 702-701, South Korea

H.-C. Ri
Materials Science Laboratory, Korea Basic Science Institute, 52 Yeoeun-Dong, Yusung-Ku, Taejon 305-333, South Korea

Bongsoo Kim b)
Department of Chemistry, KAIST, Taejon 305-701, South Korea

J. H. Park
Department of Chemistry, Korea University, Jochiwon 339-700, South Korea

(Received 25 November 2002; accepted 27 June 2003)

We report fabrication of the arrays of ferromagnetic FeCo and FeCr binary nanocluster wires (NCWs) by thermally decomposing the Fe(CO)₅/Co₂(CO)₈ and Fe(CO)₅/Cr(CO)₆ metal carbonyl vapors, respectively, with a resistive heater placed in the middle of a pair of permanent disc magnets. The NCWs are produced through the pileup of binary nanoclusters along the lines of magnetic flux, perpendicular to the substrates attached to a pair of permanent disc magnet surfaces. For both arrays of FeCo and FeCr binary NCWs, the diameter of individual NCWs ranges from 8 to 20 nm and the NCWs exist as bundles with their length up to 2–3 mm. We observed compositional dependence of structure. © 2003 American Institute of Physics. [DOI: 10.1063/1.1602955]

I. INTRODUCTION

The ferromagnetic nanowires (NWs) are important because they may be applied to a high density perpendicular magnetic recording with their high coercivity and ratio of remanence to maximum saturation magnetization (M_r/M_s) close to 1. The latter arises from a zero demagnetization factor along the wire direction. Due to this importance, a variety of fabrication methods for the arrays of ferromagnetic NWs have been reported. These include the electrochemical deposition of metals into the well defined arrays of nanopore templates made of either aluminum oxides or polymer membranes. These methods may be used in fabricating a variety of the arrays of ferromagnetic NWs by controlling the nanopore diameters and lengths, and the separation between the nanopores in the templates.

Although both FeCo and FeCr binary nanoparticles and their thin films have been studied theoretically and experimentally due to their potential applications to high temperature magnets and magnetic recording heads as well as their interesting magnetic properties, there exist only a few studies on their arrays of NWs. Recently, Qin et al. observed high coercivities and large M_r/M_s in the array of Fe₉₀Co₃₀ nanowires fabricated on the aluminum oxide template through the electrochemical deposition of Fe and Co which may be suitable for a high density perpendicular magnetic recording.

In this article, we report the fabrication of the arrays of ferromagnetic FeCo and FeCr binary nanocluster wires (NCWs) by using the method recently developed in our laboratory. The FeCo and FeCr binary nanoclusters are initially produced by thermally decomposing the gas mixtures of Fe(CO)₅/Co₂(CO)₈ and Fe(CO)₅/Cr(CO)₆ metal carbonyl vapors, respectively, by using a resistive heater placed in the middle of a pair of permanent disc magnets. And then, the binary nanoclusters formed near to the resistive heater environment are pulled by the magnetic field to the substrates attached to a pair of permanent disc magnet surfaces and then, are grown (or piled up) vertically to become the arrays of NCWs. We studied the structure of the arrays of Fe₉₀Co₆₀ NCWs by varying composition x.

II. EXPERIMENTAL DETAILS

The arrays of FeCo and FeCr binary NCWs are fabricated by thermally decomposing the gas mixtures of Fe(CO)₅/Co₂(CO)₈ and Fe(CO)₅/Cr(CO)₆ metal carbonyl vapors, respectively, by using a resistive heater placed in the middle of a pair of permanent disc magnets (Fig. 1). Briefly, the reaction chamber is a small stainless steel vacuum chamber which houses a pair of permanent disc magnets, a tube spacer, a resistive heater, and two substrates. A pair of permanent disc magnets, separated from each other by a glass tube spacer provide a magnetic field strength of 3000–4000 G at the center. A glass tube spacer with an inner diameter of 14 mm and a tube length of 15 mm is used to separate a pair of permanent disc magnets. A resistive heater (a nichrome alloy wire in the present experiment) placed in the middle of the glass tube spacer is used to decompose the metal carbo-
FIG. 1. A schematic for the fabrication of the arrays of FeCo and FeCr binary NCWs.

FIG. 2. The SEM micrographs of the arrays of FeCo and FeCr binary NCWs: (a) $x = 10.7$, (b) $x = 11.4$, (c) and (d) $x = 57.4$, and (e), (f), and (g) $x = 83.2$.

nyl vapors into the metal atoms and the COs. The two glass substrates attached to a pair of permanent disc magnet surfaces are used for the substrates onto which the arrays of NCWs are grown (or piled up). The FeCo or FeCr binary nanoclusters are produced near to the resistive heater environment through numerous collisions between the decomposed neutral metal atoms and then, are pulled by the magnetic field. They pile up vertically to become the arrays of NCWs. Here, the resistive heater temperature is kept at 300–400 °C in order to break only the metal atom-CO bond. Above this temperature, the CO itself can be also dissociated into C and O, from which both undesirable metal carbides and oxides can be produced. The metal carbonyl vapor pressures [i.e., Fe(CO)$_3$, Co$_2$(CO)$_8$, and Cr(CO)$_6$] used in the present experiment range from 1 to 20 Torr. In order to vary the composition of binary nanoclusters, the mole ratios of the two metal carbonyl vapors are changed. The exact mole ratios of binary NCWs are then determined through the elemental analysis by using an inductively coupled plasma atomic emission spectrometer. The mole ratios of Fe$_{x}$Co$_{100-x}$ binary NCWs range from $x = 0$ to 100 because both Fe and Co are strongly drawn by the magnetic field whereas those of Fe$_{x}$Cr$_{100-x}$ binary NCWs range from $x = \sim 80$ to 100 because the Cr is not drawn by the magnetic field. Note that the NCWs are fabricated through the pile up of magnetic nanoclusters inside a magnetic field. Also, note that Fe and Co mix almost completely because of their high solubility whereas Fe and Cr do not because of their low solubility. According to the bulk solubilities, we expect the Fe structure above 26 Fe mole % and the Cr structure below about 26 Fe mole % in FeCo nanoclusters whereas we expect the Fe structure above about 92 Fe mole % and then, phase separation into Fe and Cr phases below about 92 Fe mole % in FeCr nanoclusters.

The arrays of NCWs are characterized with the scanning electron microscope (SEM, Hitatch S-4200) operated at 5–15 kV, the high resolution transmission electron microscope (HRTEM, JEOL JEM 3010) operated at 300 kV, and x-ray diffraction spectrometer (XRD, Philips X-PERT) with Cu Kα radiation.

III. RESULTS AND DISCUSSION

A. Arrays of FeCo binary NCWs

The arrays of FeCo binary NCWs are presented in Figs. 2(a)–2(g). As presented in Fig. 2, the NCWs exist as bundles [i.e., one bundle in both (b) and (g), and two bundles in (d) are shown] with their length up to a few millimeters. The HRTEM micrographs of single FeCo binary NCWs are presented in Figs. 3(a)–3(f). The diameter of NCWs ranges from 8 to 20 nm. Figure 3(b) is a magnified micrograph of the arrow part in Fig. 3(a) and is presented in order to show that the NCWs consist of nanoclusters even though the individual FeCo binary nanoclusters are barely distinguishable due to severe aggregation between them. Figure 3(c) represents a branched NCW. Note that the straightness and compactness of the NCWs become slightly worse with increasing Fe mole % [i.e., as we go from (a) to (f)]. This likely arises from the fact that Co is more strongly drawn by the magnetic field (i.e., more ferromagnetic) than Fe, as can be noticed from the higher coercivity of pure Co NCWs than that of pure Fe NCWs.

The XRD diffraction patterns of FeCo binary NCWs are presented in Fig. 4. Since the NCWs are composed of FeCo binary nanoclusters, the XRD patterns should originate from the structure of FeCo binary nanoclusters. Figure 4 shows that the structure of FeCo binary NCWs changes from the body centered-cubic (bcc) structure of Fe nanoclusters to the face centered-cubic (fcc) structure of Co nanoclusters, like the structural evolutions in the FeCo binary nanoparticles and the bulk alloy. Here, the fcc structure of pure Co NCWs arises from the particle size effects of Co
nanoclusters\(^{31}\) [i.e., for Co nanoclusters, the fcc structure is a more stable structure than the bulk hexagonal close-packed (hcp) structure when the particle diameter is in the nanometer range]. Since the bcc \((110)\) peak \((2\theta=44.8^\circ)\) of Fe nanoclusters occurs very closely to the fcc \((111)\) peak \((2\theta=44.3^\circ)\) of Co nanoclusters, they are not resolved in the XRD patterns. However, by estimating the lattice constants of FeCo binary NCWs by assuming both bcc and fcc structures and then, by plotting them as a function of Co mole percent (Fig. 5), we can roughly estimate the range where the Fe bcc structure changes into the Co fcc structure. Clearly, there is a sudden change in the lattice constant at the 88.6 Co mole %. Since there is a gap in Co mole % between 79.1 and 88.6, we can just say that above the 88.6 Co mole %, the structure of FeCo binary NCWs is the fcc Co structure whereas below the 79.1 Co mole %, the structure of FeCo binary NCWs is the bcc Fe structure. This is roughly consistent with the bulk FeCo alloy in which the Co fcc structure appears above the \(-74\) Co mole %.\(^{29}\)

B. The arrays of FeCr binary NCWs

The arrays of FeCr binary NCWs are presented in Figs. 6(a)–6(f). As can be seen in Fig. 6, the NCWs exist as bundles [i.e., one bundle is shown in (c)] with their length up to a few millimeters. The HRTEM micrographs of single FeCr binary NCWs are presented in Figs. 7(a)–7(c). The diameter of single NCWs ranges from 8 to 20 nm. We could produce Fe\(_x\)Cr\(_{100-x}\) binary NCWs ranging from \(x=\sim 80\) to 100 because the FeCr binary nanoclusters below \(x=80\) are not easily drawn by the magnetic field. We also noticed that a lot of FeCr binary nanoclusters were deposited in the NCWs at \(x=80.5\) [see Figs. 6(d) and 6(e)]. This is because the FeCr binary nanoclusters with a large Cr mole % are hardly drawn by the magnetic field and thus, are just randomly deposited into the NCWs.

The XRD diffraction patterns of the arrays of FeCr binary NCWs are presented in Fig. 8. Since the NCWs are composed of FeCr binary nanoclusters, the XRD patterns

FIG. 3. The HRTEM micrographs of single Fe\(_x\)Co\(_{100-x}\) binary NCWs: (a), (b), and (c) \(x=10.7\), (d) \(x=57.5\), (e) \(x=74.1\), and (f) \(x=83.2\). (b) is a magnified HRTEM micrograph of the top part of (a).

FIG. 4. The XRD diffraction patterns of Fe\(_x\)Co\(_{100-x}\) binary NCWs.

FIG. 5. The plot of lattice constants of Fe\(_x\)Co\(_{100-x}\) binary NCWs vs Co mole percent assuming bcc structure (filled triangle) and fcc structure (filled circle).
should also originate from the structure of FeCr binary nanoclusters. We can roughly estimate the range where the Fe bcc structure changes into the Cr bcc structure by plotting the lattice constants as a function of Cr mole % (Fig. 9), as done in FeCo binary NCWs. Clearly, there is a sudden change in the lattice constant at the 19.5 Cr mole %. Since there is a gap in Cr mole % between 4.9 and 19.5, we can just say that above the 19.5 Cr mole %, the structure of FeCr NCWs is the Cr bcc structure. Note that the phase separation in bulk FeCr alloy occurs above about 8 Cr mole %. Thus, in addition to this structural change, we also expect a phase separation at 19.5 Cr mole % (i.e., into Fe and Cr phases) in FeCr binary nanoclusters due to their low solubility. Since there is a gap in Cr mole % between 4.9 and 19.5, we can just say that the phase separation occurred above the 19.5 Cr mole %.

In fact, the estimated lattice constant (i.e., 0.2874 nm) of FeCr binary NCWs is very close to the average of the lattice constants of Fe and Cr (i.e., 0.286 and 0.289 nm for the bulk bcc Fe and bcc Cr metals, respectively), supporting this phase separation.

**IV. CONCLUSION**

In this work, we fabricated both arrays of FeCo and FeCr binary NCWs by thermally decomposing the gas mixtures of Fe(CO)$_5$/Co$_2$(CO)$_8$ and Fe(CO)$_5$/Cr(CO)$_6$ metal carbonyl vapors, respectively, by using a resistive heater placed in the middle of a pair of permanent disc magnets. Their structures correspond to the FeCo and FeCr binary nanoclusters, respectively, because the NCWs consist of the corresponding FeCo and FeCr binary nanoclusters, respectively. For both arrays of FeCo and FeCr binary NCWs, the diameter of individual NCWs ranges from 8 to 20 nm and
the NCWs exist as bundles with their length up to 2–3 mm. We observed structural changes from the bcc structure of Fe to the fcc structure of Co in FeCo NCWs and from the bcc structure of Fe to the bcc structure of Cr in FeCr NCWs with increasing Co and Cr mole %, respectively. We could fabricate arrays of Fe$_{1-x}$Co$_x$NCWs for all x because both Fe and Co are ferromagnetic and thus, were drawn by magnetic field whereas we could fabricate Fe$_{2-x}$Cr$_x$NCWs only up to x=about 20 because Cr is nonmagnetic.

**ACKNOWLEDGMENTS**

The authors thank the Korea Basic Science Institute (KBSI) for allowing us to use their SEM and XRD at a membership rate and the Materials Science Laboratory at the KBSI for allowing us to use their MPMS through the cooperation project. This work is supported by the KOSEF (R05-2003-000-10141-0). B.K. thanks the Center for Electro-Optics at KAIST for financial support.