Fabrication of Epitaxial Interface between Transition Metal Cyanides

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Nanoporous materials are currently attracting the interest of materials scientists, because nanopores can transfer and accommodate guest cations. We may realize a rapid cation transfer from one material to another through an epitaxial interface. In this study, we fabricated bilayer films of nanoporous transition metal cyanides by an electrochemical deposition technique. Scanning electron microscopy (SEM) images as well as X-ray diffraction patterns strongly suggest that the cyanide layers are epitaxially connected to each other. We compared the current–voltage (i–V) properties of the epitaxial bilayer films with those of the monolayer films.

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**Abstract**

Transition metal cyanides, \(A_nM_x[MB(CN)_6]_2H_2O\) (\(A\) is an alkali metal and \(M_8\) and \(M_6\) are transition metals) have a nanoporous structure. These compounds are face-centered cubic,\(^{1,2}\) \((Fm\overline{3}m; Z = 4)\) and consist of a three-dimensional cyano-bridged network of transition metals, \(-CN-M_8-NC-M_6-CN-M_8-NC-\). The guest species of these compounds, i.e., alkali cations and water molecules, are accommodated in the cubic nanopores, 5 Å on each side. These compounds are currently attracting the interest of materials scientists, because they can be utilized as the positive electrode\(^{3-6}\)) of lithium ion secondary batteries and electronic paper.\(^7,8\) Imanishi and coworkers\(^9,10\) reported lithium intercalation into a host framework as well as charge–discharge behavior in a series of cyano-bridged transition metal compounds with \(M_8 = V, Mn, Co, Ni, and Cu,\) and \(M_6 = Fe.\) The charge capacity of the Cu compound reaches 140 mAh g\(^{-1}\), which is comparable to that of the actually used material, LiCoO\(_2\) (capacity is 140 mAh g\(^{-1}\)). Recently, Moritomo and Shibata\(^{9}\) and Shibata and Moritomo\(^{10}\) have fabricated an all solid device using two cyanide films without an electrolyte solution, and realized a direct cation transfer from one film to another through a solid–solid interface. They demonstrated electromagnetism\(^9\) as well as fast electrochromism,\(^10\) although the interface was formed by the physical connection of the two cyanide films. Thus, the interface between the nanoporous materials is a key to controlling the cation transfer from one material to another.

In this paper, we report the fabrication and characterization of the bilayer films of nanoporous transition metal cyanides. In Fig. 1, we show the schematic structure of the epitaxial interface between the cyanides. On the basis of scanning electron microscopy (SEM) images as well as X-ray diffraction (XRD) patterns, we conclude that the surface layer is epitaxially grown on the buffer layer. We further investigated the electronic properties of the epitaxial bilayer films in the current-perpendicular-to-plane (CPP) configuration at 300 K and compared them with those of the monolayer films.

A \(Na_{x}Co[Fe(CN)_{6}]_{1-x}H_2O\) (denoted as NC0F71) film with high \((111)\) orientation was used as the buffer layer. The film was electrochemically grown on an indium–tin oxide (ITO) transparent electrode in an aqueous solution containing 0.5 mmol/L \(K_2[Fe(CN)_{6}]\), 1.25 mmol/L \(MnCl_2\), and 1 mol/L \(NaNO_2\). To enhance the \((111)\) orientation, a sawtooth-type electrostatic potential (between \(-0.85\) and \(-0.15\) V at 36 Hz) was applied.\(^{11}\) The film thickness was typically \(\sim 700\) nm. The XRD pattern revealed that the compound is face-centered cubic and has a lattice constant \((a)\) of 10.25(2) Å. The film consists of \((111)\) oriented rodlike crystals, \(\sim 600\) nm in length and \(\sim 130\) nm in area.\(^{12}\) Three types of surface layers, \(Fe[Cr(CN)_{6}]_{0.47}H_2O\) (FCr67), \(Na_{1.32}Mn[Fe(CN)_{6}]_{0.33}H_6O\) (NMF83), and \(Na_{1.45}Co[Fe(CN)_{6}]_{0.90}2H_2O\) (NCoF90), were electrochemically grown on the buffer film under a potentiostatic condition at \(-0.5\) to \(-0.45\) V vs a standard Ag/AgCl electrode. The buffer film was immersed in an aqueous solution containing 5.0 mmol/L \(K_2[Cr(CN)_{6}]\) and 7.5 mmol/L \(FeCl_3\) for the FCr67 film, 1.0 mmol/L \(K_2[Fe(CN)_{6}]\), 1.5 mmol/L \(MnCl_2\), and 1.0 mol/L \(NaCl\) for the NMF83 film, and 0.8 mmol/L \(K_2[Fe(CN)_{6}]\), 0.5 mmol/L \(Co(NO_3)_2\), and 5.0 mol/L \(NaNO_2\) for the NCoF90 film. Thus, we prepared three bilayer films, i.e., the NCoF71/FCr67, NCoF71/NMF83, and NCoF71/NCoF90 films.

We further electrochemically synthesized monolayer FCr67, NMF83, and NCoF90 films on the ITO electrode in the respective aqueous solutions. The sawtooth-type electrostatic potentials, between \(-0.8\) and \(-0.2\) V at 36 Hz for the FCr67 film and between \(-0.8\) and \(-0.1\) V at 36 Hz for the NMF83 and NCoF90 films, were applied. The \((111)\) orientations of these films were worse than that of the NCF71 film (see Table 1). The chemical compositions\(^{13}\) of the monolayer films were determined by the inductively coupled plasma (ICP) method and the CNH organic elementary analyzer (Perkin-Elmer 2400 CHN elemental analyzer).

The upper panels of Fig. 2 show the cross-sectional SEM images of the \(a\) NCoF71/FCr67, \(b\) NCoF71/NMF83, and \(c\) NCoF71/NCoF90 bilayer films. The interface regions are

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Table 1. Magnitude of $S (= \frac{v_{111}^{\text{film}}}{v_{200}^{\text{film}}} / \frac{v_{111}^{\text{powder}}}{v_{200}^{\text{powder}}})$ is the volume fraction of the \((hkl)\)-oriented domain for monolayer and bilayer films.

| Film           | Buffer layer | Surface layers |
|----------------|--------------|----------------|
|                | NCoF71       | FCr67 | NMF83 | NCoF90 |
| Monolayer      | 200          | 17    | 5     | 5     |
| Bilayer        | —            | 500   | 140   | 200   |

Fig. 2. Cross-sectional (top) and surface (bottom) SEM images for (a) NCoF71/FCr67, (b) NCoF71/NMF83, and (c) NCoF71/NCoF90 bilayer films. Dotted lines in the upper panels represent the epitaxial interfaces. Insets in the bottom panels show the surface SEM images of the buffer NCoF71 film. The acceleration voltage was set to be 2 kV.

Fig. 3. (Color online) (a) Magnified XRD patterns of FCr67 and NCoF71/FCr67 films at 300 K. (b) Magnified XRD patterns of NMF83 and NCoF71/NMF83 films at 300 K. (c) Magnified XRD patterns of NCoF90 and NCoF71/NCoF90 films at 300 K. The suffix indicates that the reflection originates from the NCoF71 buffer layer.

Now, let us investigate the structural properties of the films in more detail. The lower patterns of Fig. 3 show the XRD patterns of the monolayer films: (a) FCr67, (b) NMF83, and (c) NCoF90 films. The diffraction patterns of (a) FCr67 and (b) NMF83 revealed that the compounds are fcc wurtzite having lattice constant \(a\) values of 10.59(2) and 10.53(2) Å, respectively. On the other hand, (c) NCoF90 is rhombohedral and has the lattice constants \(a = 10.37(2)\) Å and \(c = 91.6(2)\) Å. These lattice constants are slightly larger than that \([a = 10.25(2)\) Å\] of the buffer NCoF71 film. The upper patterns of Fig. 3 show the XRD patterns of the bilayer films: (a) NCoF71/FCr67, (b) NCoF71/NMF83, and (c) NCoF71/NCoF90 films. In the (a) NCoF71/FCr67 and (b) NCoF71/NMF83 films, the (111) reflection is much stronger than that in the monolayer film. Similarly, both the (111) and (111) reflections in the (c) NCoF71/NCoF90 film are much stronger than those of the monolayer film. These observations clearly indicate that the (111) orientation is enhanced when the film is grown on the (111)-oriented buffer layer.

Here, we introduce the parameter \(S (= \frac{v_{111}^{\text{film}}}{v_{200}^{\text{film}}} / \frac{v_{111}^{\text{powder}}}{v_{200}^{\text{powder}}})\) of the film as a measure of the degree of the (111) orientation. Using \(S\), the intensity ratio of the Bragg reflection of the film is described as

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\frac{I_{111}^{\text{film}}}{I_{200}^{\text{film}}} = \frac{S}{m_{111}}, \quad \frac{F_{111}^{\text{film}}}{F_{200}^{\text{film}}} = \frac{m_{111}}{m_{200}},
\]

where \(I_{hkl}^{\text{film}}\), \(I_{hkl}^{\text{powder}}\), \(F_{hkl}^{\text{film}}\), \(F_{hkl}^{\text{powder}}\), \(v_{hkl}^{\text{film}}\), \(v_{hkl}^{\text{powder}}\), \(m_{hkl}\) are the intensity, structural factor, and multiplicity, respectively. In the case of the powder samples, we obtained

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\frac{I_{111}^{\text{powder}}}{I_{200}^{\text{powder}}} = \frac{F_{111}^{\text{powder}}}{F_{200}^{\text{powder}}} = \frac{m_{111}}{m_{200}}.
\]

The magnitude of \(R_{s} = \frac{I_{111}^{\text{film}} / I_{200}^{\text{film}}}{I_{111}^{\text{powder}} / I_{200}^{\text{powder}}}\) was estimated to be 0.044, 0.090, 0.006, and 0.032 for the NCoF71, FCr67, NMF83, and NCoF90 films, respectively. Then, the magnitudes of \(S = (v_{111}^{\text{film}} / v_{200}^{\text{film}}) / (v_{111}^{\text{powder}} / v_{200}^{\text{powder}})\) are easily calculated from the diffraction patterns and are listed in Table I. In the bilayer film, the magnitudes of \(S\) for the surface layers are comparable to that of the monolayer NCoF71 film. Thus, we concluded that the surface layers are epitaxially grown on the buffer NCoF71 film.

We further investigated the electronic properties of the cyanide films in the CPP configuration. In our measurements, we slightly introduced the holes \(\delta\) into the transition metal sites by the oxidation of the film at 0.4 V versus a standard Ag/AgCl electrode in 0.5 mol NaNO\(_3\). The magnitude of \(\delta\) was estimated from the total charge used in the oxidation process. The electronic contact on the surface side was formed by physical connection with the ITO electrode. All the monolayer films show the ohmic behavior. To estimate the bulk resistivity of a monolayer film, we should subtract the contact resistance \(R_c\) between the cyanide film and the ITO substrate as well as the sheet resistance \(R_s = 80 \Omega\) of the ITO electrode. To estimate \(R_s\), we investigated the film resistance against the film thickness. The magnitude of \(R_s = 5 \Omega \text{cm}^2\) is one order smaller than that of the typical material resistance (\(\sim 30-40 \Omega \text{cm}^2\) for 1 mm thickness; see Table II). We evaluated the resistivity

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Table II. Bulk resistivity ($\rho$) values of several transition metal cyanides at 300 K. The parameter $\delta$, which is defined by a chemical formula, represents the doping level of a hole.

| Material       | $\delta$ | $\rho$ (\Omega cm) |
|---------------|---------|--------------------|
| NCoF71        | Na$_{0.84}$Co[Fe(CN)$_{6}$]$_{17}$3.8H$_{2}$O | 0.04 | 3.8(7) x $10^4$ |
| FC67          | Fe(Cr(CN)$_{6}$)$_{3}$4.1H$_{2}$O | — | 3.2(3) x $10^5$ |
| NMF83         | Na$_{0.20}$Mn[Fe(CN)$_{6}$]$_{13}$3.6H$_{2}$O | 0.27 | 4.1(3) x $10^5$ |
| NCoF90        | Na$_{0.40}$Co[Fe(CN)$_{6}$]$_{9}$2.9H$_{2}$O | 0.40 | 3.9(1.2) x $10^5$ |

Fig. 4. (Color online) (a) $I$–$V$ properties in the CPP configuration of the NCoF71/FCr67 film ($\delta = 0.00$) at 300 K. The film thickness was 900 nm (600 nm) for the buffer (surface) layer. (b) $I$–$V$ properties of the NCoF71/NMF83 film ($\delta = 0.04$) at 300 K. The film thickness was 900 nm (120 nm) for the buffer (surface) layer. (c) $I$–$V$ properties of the NCoF71/NCoF90 film ($\delta = 0.06$) at 300 K. The film thickness was 900 nm (800 nm) for the buffer (surface) layer. $\delta$ is formally defined by the buffer NCoF71 film as Na$_{0.84}$Co[Fe(CN)$_{6}$]$_{17}$3.8H$_{2}$O.

The resistivity ($\rho$) of the film by considering the external component ($R_{\text{ext}} = R_{\text{int}} + R_{\text{ext}}$) to the external component of the epitaxial interface makes a sharp contrast with that of the physically formed interface.\(^{9,10}\) The resistance of the NCoF90/ NCoF90 bilayer film with the physically formed interface is dominated by $R_{\text{int}}$: $R_{\text{int}} = 12500 \Omega$. $R_{\text{ext}} = 1800 \Omega$, $R_{\text{mat}} = 1100 \Omega$, and $R_{\text{int}} = 9600 \Omega$.\(^{10}\) Such a large $R_{\text{int}}$ is ascribed to the disconnection of the cyano-bridged network.

In summary, we fabricated an epitaxial interface between nanoporous transition metal cyanides. The interface shows a negligible resistance ($R_{\text{int}} \sim 0 \Omega$), reflecting a perfect cyano-bridged network. Our technique is easy and low-cost, and is applicable to other network polymer materials.

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1) A. Ludi and H. U. Gueld: *Struct. Bonding* 14 (1973) 1.
2) F. Herren, P. Fischer, A. Ludi, and W. Halg: *Inorg. Chem.* 19 (1980) 956.
3) N. Imanishi, T. Morikawa, J. Kondo, Y. Takeda, O. Yamamoto, N. Kimugasa, and T. Yamagishi: *J. Power Source* 79 (1999) 215.
4) N. Imanishi, T. Morikawa, J. Kondo, R. Yamane, Y. Takeda, O. Yamamoto, H. Sakaue, and M. Tabuchi: *J. Power Source* 81–82 (1999) 530.
5) M. Okubo, D. Asakura, Y. Mizuno, J.-D. Kim, T. Mizokawa, T. Kudo, and I. Honma: *J. Phys. Chem. Lett.* 1 (2010) 2063.
6) T. Matsuda and Y. Moritomo: *Appl. Phys. Express* 4 (2011) 047101.
7) A. Gotoh, H. Uchida, M. Ishizaki, T. Satoh, S. Kaga, S. Okamoto, M. Obta, M. Sakamoto, T. Kawamoto, H. Tanaka, M. Tokumoto, S. Hara, H. Shiozaki, M. Yamada, M. Miyake, and M. Kurihara: *Nanotechnology* 18 (2007) 345609.
8) S. Haru, H. Shiozaki, A. Omura, H. Tanaka, T. Kawamoto, M. Tokumoto, M. Yamada, A. Gotoh, M. Moritomo, and M. Sakamoto: *Appl. Phys. Express* 1 (2008) 104002.
9) Y. Moritomo and T. Shibata: *Appl. Phys. Lett.* 94 (2009) 043502.
10) T. Shibata and Y. Moritomo: *Appl. Phys. Express* 2 (2009) 105502.
11) F. Nakada, H. Kamioka, Y. Moritomo, J. E. Kim, and M. Takata: *Phys. Rev. B* 77 (2008) 224436.
12) T. Shibata and Y. Moritomo: *Jpn. J. Appl. Phys.* 49 (2010) 094101.
13) The chemical composition of the surface layer is considered to be the same as that of the monolayer film, because their lattice constants are the same within the experimental error.
14) Y. Moritomo, K. Igarashi, T. Matsuda, and J. E. Kim: *J. Phys. Soc. Jpn.* 78 (2009) 074602.
15) The magnitudes of $I_{\text{on}}^{\text{max}}$ and $I_{\text{off}}^{\text{max}}$ were estimated from synchrotron radiation XRD patterns. In our measurements, the films were carefully removed from the ITO glass with a microspatula, and then the fine powder samples were filled into a glass capillary, 300 mm in diameter. The capillary was sealed and put on a Debye–Scherrer camera at the BL02B2 beamline of SPring-8.
16) Conventional techniques, e.g., vacuum evaporation and sputtering, are not applicable to our transition metal cyanide film, because the vacuum process causes serious cracking of the film.
17) The $I$–$V$ behavior cannot be ascribed to the cation transfer within the film, because their lattice constants are the same within the experimental error.
18) Y. Kurihara, H. Funashima, M. Ishida, N. Hamada, T. Matsuda, K. Igarashi, H. Tanida, T. Uruga, and Y. Moritomo: *J. Phys. Soc. Jpn.* 79 (2010) 044710.
19) T. Shibata and Y. Moritomo: *Jpn. J. Appl. Phys.* 49 (2010) 094101.