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Growth of Fe_4N epitaxial layers displaying anomalous light reflectivity modulated by an external magnetic field†

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Cubic Fe_4N epitaxial layers have been grown on a MgO (100) substrate by atmospheric pressure halide vapor-phase epitaxy using $FeCl_3$ and NH_3 as the starting materials. The full width at half maximum of the X-ray (200) diffraction peak for the Fe_4N epitaxial layer was about 0.05°. Transmission electron diffraction measurements revealed a diffraction pattern similar to that of a single crystal with cubic structure. The saturation magnetization and coercive force of an Fe_4N epitaxial layer deposited at 600 °C were 182.0 emu g^{-1} and 30 Oe, respectively. It was found, for the first time, that the epitaxial layer of Fe_4N displayed anomalous light reflectivity modulated by an external magnetic field.

1. Introduction

The iron–nitride system has been one of the main subjects of the research on metal nitrides because of its remarkable mechanical and magnetic properties. Early interest in iron nitrides came from the steel industry to improve the abrasive strength of steels by nitridizing the surface.[1,2] Recently, however, the magnetic properties of iron nitrides, especially high saturation magnetization and high coercivity, have received more attention than their mechanical properties because they are amenable to high-density magnetic recording.

Iron forms three metastable compounds with nitrogen, Fe_8N, Fe_4N and Fe_2N, which are stable at room temperature. It is also known that ferromagnetic iron nitrides of formulae Fe_xN with $2<x<8$ have high mechanical hardness, and that their chemical stability is superior to that of the pure metal. In particular, their magnetic properties have attracted attention to these compounds. The saturation magnetization of Fe_4N, for example, is considerably higher than that of γ-Fe_2O_3 although it is slightly lower than that of metallic iron. However, other characteristics apart from magnetic and mechanical properties have not been clarified yet. This is because single crystals of Fe_8N, Fe_4N and Fe_2N have not been successfully prepared although there have been almost the same number of papers dealing with thin films[3–5] and with fine particles.[6–8]

We have shown previously that atmospheric pressure halide chemical vapor deposition (AP-HCVD) is an appropriate technique for the preparation of metal nitride films.[9–11] This paper, therefore, describes the results of the investigation of the vapor-phase epitaxy of Fe_4N onto an MgO (100) substrate using a halide source, and of the change in light reflection of Fe_4N epitaxial layers associated with magnetic-field modulation.

2. Experimental

The horizontal quartz reactor used in this study is the same as that described earlier.[9,10] Fe_4N epitaxial layers were grown on MgO (100) under atmospheric pressure. The used substrate was a MgO (100) single crystal. The surface of the MgO substrate was mirror-polished using 0.25 μm diamond paste and then heated to 1050 °C in a furnace for 2.5 hours in air prior to deposition. The mean square roughness (R_{ms}) in a 30 × 30 μm square of the polished MgO substrate was less than 0.4 nm. $FeCl_3$ and NH_3 were used as the Fe and N sources, respectively. $FeCl_3$ was evaporated from a source boat at a temperature of 250 °C, and supplied to the growth zone. Purified N_2 was used as a carrier gas. The input partial pressures of $FeCl_3$ and NH_3 were varied by varying the flow rate of the carrier gas. Typical experimental conditions are summarized in Table 1.

The crystallographic structures of the iron nitride films deposited were examined using a Rigaku RINT 2000 X-ray diffractometer. Their crystallinity was assessed both by double crystal X-ray diffraction analysis and by transmission electron diffraction. The thickness of iron nitride films were evaluated by scanning electron microscopy (SEM). Surface morphologies were examined by atomic force microscopy (AFM). XPS spectra were measured using a Shimadzu XRTOS-XSAM 800 X-ray photoelectron spectrometer. The magnetic properties of the films were measured using a Toei Kogyo VSM-2 vibrating sample magnetometer, in which a magnetic field up to 2 T was

Table 1 Typical growth conditions

Substrate	MgO (100)
$FeCl_3$ source temperature/°C	250
$FeCl_3$ partial pressure/atm	1.5×10^{-6}
NH_3 partial pressure/atm	1.7×10^{-2}
Carrier gas	N_2
Total flow rate/cm^3 min^{-1}	590
Growth temperature/°C	600

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†Electronic supplementary information (ESI) available. AFM image of an Fe_4N epitaxial layer. See http://www.rsc.org/suppdata/jm/b1/b103465k/

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applied perpendicular to the film plane. The diamagnetic contribution from the glass substrate was found to be negligibly small compared with the magnetization of the films. The experimental set-up to measure light reflectivity changes associated with magnetic field modulation is shown in Fig. 1, in which a magnetic field of approximately 100 Oe was perpendicularly applied to the (100) direction of the Fe_4N film. A helium–neon (He–Ne: 632.8 nm) laser was used as a light source. The polarization direction of the laser beam was adjusted using a $\lambda/4$ plate and polarization plate. A 10×10 mm^2 film surface was irradiated with p-polarized light at an incident angle of 30°. The reflected light intensity was detected through a photo-detector (Optofocus ET-2010) by an oscilloscope. The detector window is not sensitive to the polarisation of the incoming light. All the measurements were carried out at room temperature.

3. Results and discussion

Fig. 2 shows a typical X-ray diffraction profile of an as-grown film under the conditions given Table 1, in which the growth rate was about 8 µm h^{-1}. An intense diffraction peak appearing at 47.8° is assigned to the (200) diffraction of Fe_4N with a cubic structure. The full width at half-maximum (FWHM) value for the Fe_4N epitaxial layer is about 0.05°. Another peak at 42.8° is due to the (200) diffraction of the MgO substrate. This implies that the Fe_4N films were grown epitaxially under atmospheric pressure using $FeCl_3$ and NH_3. The lattice constant was calculated to be $c = 3.780$ Å utilizing the observed (200) diffraction; this is slightly smaller than the reported value of 3.795 Å for Fe_4N powder.[11] This observation is probably due to the lattice mismatch between Fe_4N and MgO.

A representative transmission electron diffraction pattern for an Fe_4N epitaxial layer is shown in Fig. 3. It is immediately noticed that the observed spots have a pattern typical of cubic Fe_4N with good crystallinity. 100 and 110 spacings of 3.795 and 2.684 Å, respectively, were calculated from the TEM image, in accord with JCPDS data for Fe_4N. It is of note that the crystallinity of the Fe_4N films is good despite a large lattice mismatch between Fe_4N ($a = 3.795$ Å) and MgO ($a = 4.2212$ Å) of approximately 10%. Single crystals of MgO have been conventionally used as substrates for the preparation of cubic GaN and YBaCuO and have led to good quality crystals although a large lattice mismatch of 6–10% is present. A similar lattice mismatch is found in this work for the metastable cubic Fe_4N phase. Given that the cubic phase of Fe_4N is metastable, its formation is not favorable under high vacuum growth conditions as used for sputtering, chemical vapor deposition (CVD) or molecular beam epitaxy (MBE). By contrast, a specific chemical reaction is utilized for the preparation of the Fe_4N epitaxial layer by means of AP-HVPE.[9,10] Adduct formation of $FeCl_3 \cdot NH_3$ in the gas phase plays an important role in the epitaxial growth.[12]

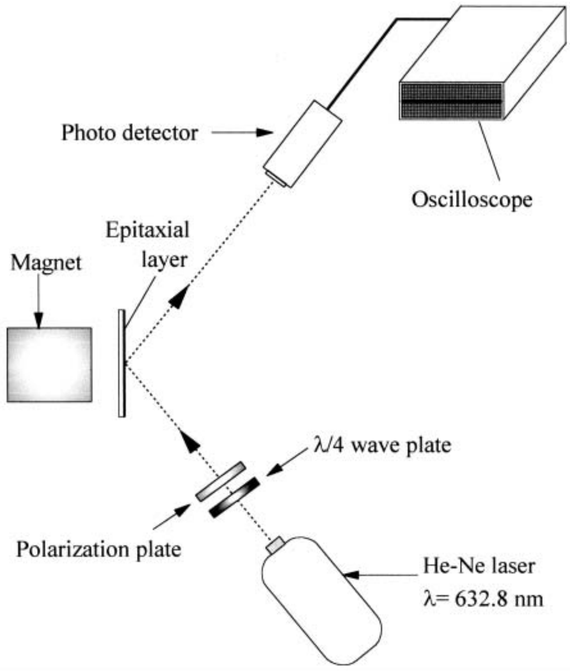

Fig. 1 Schematic diagram of the apparatus used to measure the photoresponsive of Fe_4N films.

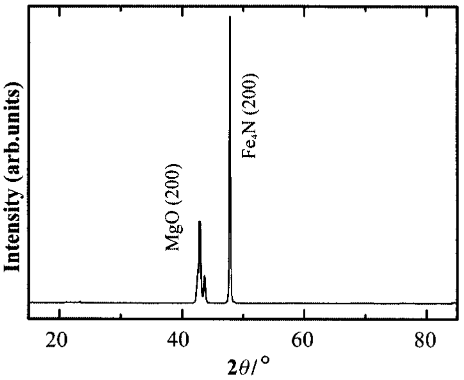

Fig. 2 XRD pattern of an as-grown Fe_4N film deposited on an MgO (100) substrate.

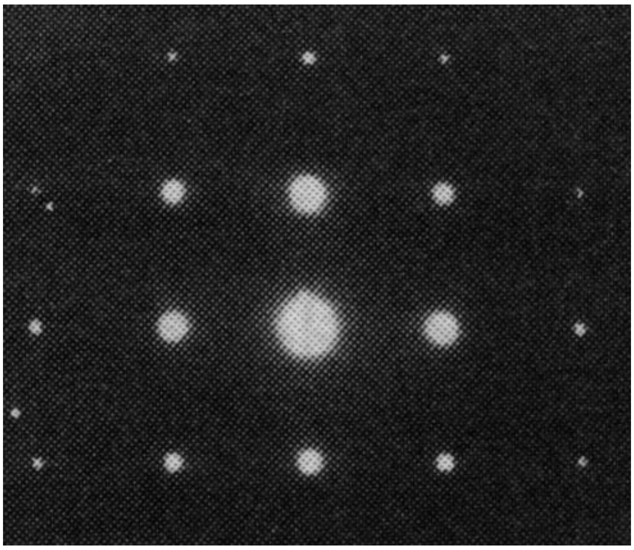

Fig. 3 Transmission electron diffraction pattern of an as-grown Fe_4N film deposited on an MgO (100) substrate.

The surface morphology of the Fe_4N film deposited at 600 °C was examined by AFM. The mean square roughness for a 5×5 µm^2 square of the Fe_4N film is less than 0.5 nm, suggesting that the surface is flat and smooth. Also, it was found that the surface morphology is smoother than that of Fe_3N films prepared on glass substrates by AP-HCVD.[10]

The nitrogen content in the Fe_4N film was determined by XPS. Fig. 4 shows XPS spectra of the as-deposited films at 600 °C together with plots of the intensity ratio of N 1s to Fe $2p_{3/2}$ peaks *versus* the N content. Calibration was carried out using standard iron nitride powder samples. XPS analysis suggested that the epitaxial layer prepared in this study has an atomic ratio of Fe to N of approximately 4 : 1 as shown in Fig. 4. Oxygen was not assayed on the top surface of the film, and no chlorine was detected even near the surface. In the

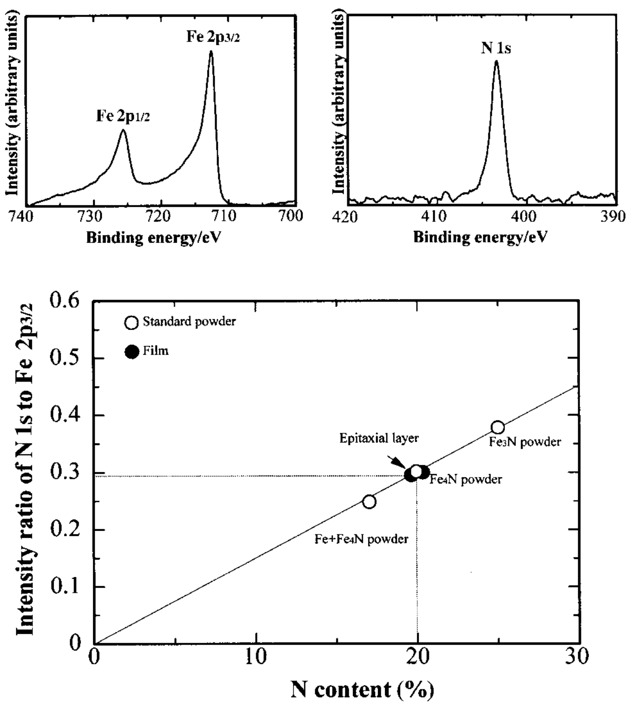

Fig. 4 Intensity ratio of N 1s to Fe $2p_{3/2}$ XPS peaks as a function of N atom concentration in standard Fe–N powder samples along with Fe_4N films used in this study.

inside of the Fe_4N film prepared in this study, it was confirmed that the C and Cl percentages are below 1 atom% (the identification limit).

Fig. 5 shows the *M*–*H* characteristics of the Fe_4N epitaxial layer deposited at 600 °C. It is evident that the observed curve shows a typical superparamagnetic behavior with little hysteresis. The saturation magnetization and coercive forces of the Fe_4N epitaxial layer were 182 emu g^{-1} and 30.0 Oe, respectively. The saturation magnetization of the Fe_4N epitaxial layer is slightly lower than that reported for powdered Fe_4N.[13]

Fig. 6 shows the dependence of reflected light intensity from an Fe_4N epitaxial layer with an applied magnetic field, in which a He–Ne laser of 632.8 nm was used as a light source. It is apparent that the reflection intensity decreases to 50% by applying a magnetic field of 100 Oe, and recovers to 100% when the magnetic field was removed. That means that the epitaxial layer of Fe_4N is "an optically smart material". We denote this behavior as opto-agilent. Fig. 7 shows the change in the reflection intensity in a series of on–off cycles of the magnetic field. As is seen in Fig. 7, a rapid response of the reflection intensity to the magnetic field is observed. It is interesting that the response is not diminished even after 1000 cycles. Clearly applying a magnetic field alters the reflectivity of the cubic Fe_4N epitaxial layer. Consequently, it is concluded that cubic Fe_4N epitaxial layers are promising materials for optical switching devices.

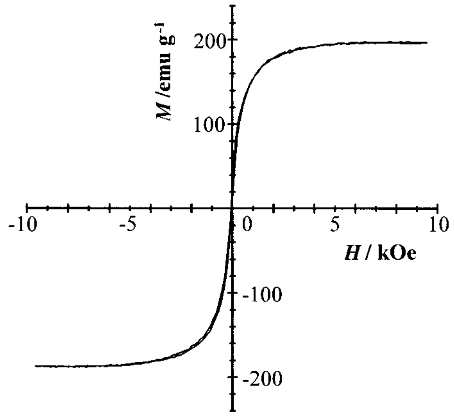

Fig. 5 Hysteresis curves for an as-grown Fe_4N film deposited on an MgO (100) substrate.

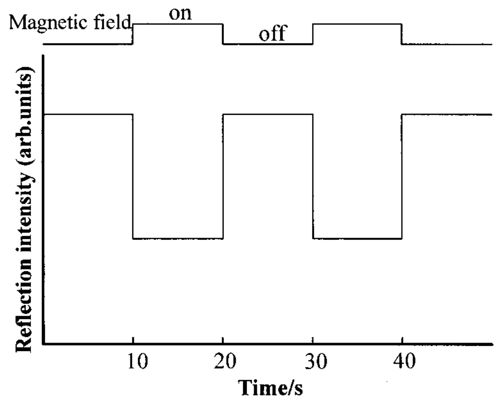

Fig. 6 The dependence of reflected light intensity from an Fe_4N epitaxial layer with an applied external magnetic field.

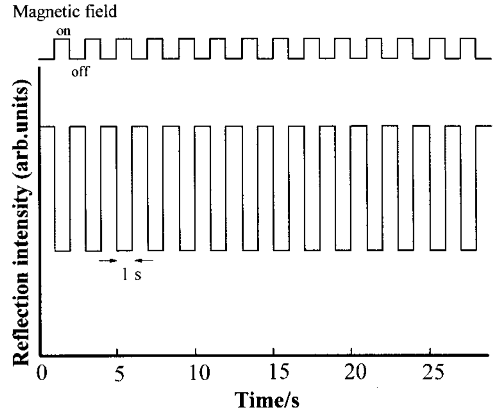

Fig. 7 The change in the reflection intensity in a series of on–off cycles of magnetic field.

4. Conclusions

Epitaxial layers of Fe_4N were grown on an MgO (100) substrate by AP-HVPE using $FeCl_3$ and NH_3 in a hot-wall reactor. The formation of an Fe_4N epitaxial layer with cubic structure is supported by X-ray diffraction, transmission electron diffraction, AFM and XPS measurements. The saturation magnetization and coercive forces of Fe_4N deposited at 600 °C were 182.0 emu g^{-1} and 30 Oe, respectively. It was clarified, for the first time, that the epitaxial layer of Fe_4N shows an anomalous light reflectivity modulated by an external magnetic field.

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