FULL PAPER

Development of dynamic aurora pulsed laser deposition equipped with reflection high-energy electron diffraction and effects of magnetic fields on room-temperature epitaxial growth of NiO thin film

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Pulsed laser deposition (PLD) with an electromagnet (dynamic aurora PLD) and reflection high-energy electron diffraction (RHEED) was developed by installing an 11-tuned solenoid coil in a vacuum chamber. This method achieved thin film deposition under a magnetic field of up to 120 mT using dc current of 1,200 A. The electromagnet is a solenoid coil, which produces a magnetic field that is proportional to an electric field without saturation of the magnetic field. This PLD method enables in situ observation of the crystal structure of the thin film surface after turning the electromagnet off, but without breaking vacuum. Many reports have described studies of PLD in a magnetic field. For most such studies, permanent magnets have been used to apply a magnetic field to the plume. Nevertheless, when doing so, carrying out in-situ observation using RHEED is difficult because the magnetic field deflects the electron beam. This case study examined effects of magnetic field application to the plume on the in-plane orientation and resistivity of a NiO thin film deposited on a MgO(001) single crystal at room temperature (25 °C). Results demonstrate that the in-plane orientation (epitaxial growth) is unchanged, whereas thin film resistivity decreases exponentially with the magnetic field intensity during deposition. These results suggest that the Ni³⁺ ion concentration can be expected to increase exponentially with the magnetic field during deposition. The room-temperature resistivity of the NiO thin film deposited under a 120 mT magnetic field was 112 Ω cm.

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1. Introduction

For pulsed laser deposition (PLD) use in preparing thin films, a target surface is irradiated by a focused pulsed laser beam to generate a plasma “plume” that includes electrons, cations, neutral atoms, and their clusters. The respective lifetimes of electrons and cations are very short because of recombination, but their lifetimes can be extended drastically by applying a magnetic field to the plume.¹⁾ In doing so, cations with high energy are deposited on the substrate surface. The first report of PLD in a

magnetic field was presented by Kobayashi et al.,²⁾ who put a rare-earth permanent magnet on the substrate surface. Since that report, numerous researchers have examined the effects of magnetic field application to a plume.³⁾ Typically reported effects on PLD of a magnetic field applied using permanent magnets or electromagnets have included (i) elimination of droplets,^{4,5)} (ii) lowering of the crystallization temperature, improvement of crystallinity, and enhancement of thin film properties,⁶⁻⁸⁾ (iii) change of thin film morphology,⁹⁻¹¹⁾ and (iv) magnetic-field-induced phase separation.¹²⁻¹⁴⁾

Reflection high-energy electron diffraction (RHEED) has been used extensively for in-situ observation of thin film surfaces. In fact, PLD is very commonly used along with RHEED. Nevertheless, using RHEED under a magnetic field is difficult because of electron beam deflection.

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Therefore, if a magnetic field is applied using a permanent magnet, then the following procedure is necessary: (1) breaking vacuum, (2) removing the permanent magnet, (3) evacuating the vacuum chamber again, and (4) conducting RHEED observation. However, exposure to air brings about surface contamination that is expected to cause surface structure alteration. Therefore, RHEED observation for aurora PLD requires magnetic field application using an electromagnet. In this work, the term “in situ observation” is used to mean “observation without breaking vacuum,” not “real-time observation during deposition.” The use of an electromagnet offers compatibility between magnetic field application during deposition and in-situ RHEED observation if the magnetic field is turned off during observation. Furthermore, the electromagnet can be used to produce a “variable magnetic field” during deposition by controlling the electromagnet current. No report of the relevant literature describes PLD development simultaneously with an electromagnet and RHEED. Salient benefits of RHEED observation are that it supports crystal structure analysis for ultrathin films and growth mode analysis for the initial stage of film growth, which are difficult to accomplish using X-ray diffractometer (XRD) alone. The use of an electromagnet instead of a permanent magnet is expected to realize a new crystal structure and functionality for oxide and semiconductor thin films.¹²⁾

Generally speaking, substrate heating is necessary to achieve epitaxial growth of oxide ceramics. However, epitaxial growth of NiO thin films has been reported even at room temperature.^{6),15),16)} Although the room-temperature resistivity of pure stoichiometric NiO crystals is as high as $10^{13} \Omega \text{ cm}$, the resistivity of NiO is reportedly low from the perspective of defect chemistry.¹⁷⁾ Usual NiO is not stoichiometric. It includes an excess of oxygen that is accommodated by nickel vacancies. To preserve overall electrical neutrality in the crystal, some Ni^{2+} ions must be converted to Ni^{3+} ions, which are then responsible for the conduction of NiO.¹⁸⁾ For NiO thin films deposited by sputtering, thin film resistivity reportedly changes with substrate temperature during deposition. This result has demonstrated that the Ni^{3+} ion concentration changes with substrate temperature because sputtering is far from an equilibrium state of the material.¹⁹⁾

Because thin film deposition under a magnetic field (dynamic aurora PLD) at room temperature is also regarded as far from an equilibrium state, the resistivity of room-temperature grown NiO thin films is expected to be controllable by the magnetic field that is used during deposition. Therefore, this work serves two purposes: development of PLD with an electromagnet (dynamic aurora PLD) and RHEED; and assessment of the effects of magnetic field application on the crystal structure and examination of ceramic thin film properties. As an example of the second purpose, the effects of magnetic field application during deposition on a crystal structure and electrical conductivity of a room-temperature deposited NiO thin film were examined.

2. Development of dynamic aurora PLD with RHEED

Figure 1 portrays a schematic drawing of dynamic aurora PLD apparatus equipped with RHEED. The distance between the target top and the substrate bottom is 55 mm. In this gap, a 50 mm-thick electromagnet was installed under the RHEED beamline. **Figure 2(a)** presents a photograph of an electromagnet (solenoid coil) made of an 11-tuned hollow conductor and its stand. The hollow conductor cross-section is $10 \text{ mm} \times 10 \text{ mm}$ square copper having a $6 \text{ mm} \phi$ through hole. The hollow conductor surface was covered with polyimide tape and was rolled up. **Figure 2(b)** presents a photograph of an electromagnet installed in the vacuum chamber. To prevent charging by the RHEED electron beam, the electromagnet surface was covered with conductive aluminum tape. For this electromagnet, dc current of up to 1,200 A and 6 L/min of cooling water were applied. **Figure 3** presents the relation between the magnetic field and the electromagnet current. The magnetic field was measured at the center of the electromagnet's upper edge. This figure shows a linear relation because the electromagnet is a solenoid coil without saturation of the magnetic field. As this figure shows, a 120 mT magnetic field is obtained when using 1,200 A of dc current.

Fig. 1. Schematic drawing of dynamic aurora PLD equipped with RHEED.

Fig. 2. Photographs of (a) an electromagnet (solenoid coil) made of an 11-tuned hollow conductor on a stand and (b) an electromagnet installed in the vacuum chamber. The electromagnet surface was covered with aluminum tape to prevent charging by the RHEED electron beam.

Fig. 3. Relation between the magnetic field and electromagnet current.

Fig. 4. Change of the NiO thin film deposition rate at room temperature with an applied magnetic field.

Table 1. Deposition conditions of NiO thin films

Laser	Nd:YAG laser ($\lambda = 266$ nm)
Repetition rate/Hz	10
Target	NiO
Substrate	MgO(001)
Fluence/J/cm ²	2.0
Magnetic field/mT	0–120
Substrate temperature/°C	25
Oxygen pressure during deposition/Pa	1.33×10^{-2}

3. Experimental

Using this dynamic aurora PLD with a Nd:YAG laser ($\lambda = 266$ nm), NiO thin films were deposited on MgO(001) substrates. For this study, thin film deposition was done at room temperature under a 0–120 mT magnetic field. A sintered NiO ceramic disc was used as the target. Detailed deposition conditions are presented in **Table 1**.

The NiO thin films were characterized based on RHEED observations conducted after turning off the electromagnet, but without breaking vacuum. The electron gun was operated at 20 kV with an incident angle of around 3° . Then the NiO thin film was taken out of the vacuum chamber. Following measurement, it was carried out in air at room temperature. The film thickness was measured using an X-ray fluorescence spectrometer (Minipal; Malvern Panalytical, UK) equipped with the FP multi-software module. The crystal structure and pole figure of the thin film were examined using a high-resolution XRD (X'pert MRD; Malvern Panalytical, UK). The NiO thin film resistivity was measured using a resistance meter (4339B; Agilent Technologies Inc., USA).

4. Results and discussion

Figure 4 portrays the change of the NiO thin film deposition rate according to changes of the applied magnetic field during deposition. The film thickness was measured at the center of the thin film. As this figure shows, the deposition rate increases almost linearly with the magnetic field intensity. Applying a magnetic field to the plume focuses the plume because the Lorentz force applied to the flying cations serves as a centripetal force. The high deposition rate is a benefit of applying the magnetic field to the plume.

Fig. 5. XRD patterns of NiO thin film deposited at room temperature on MgO(001) under magnetic fields of (a) 0 and (b) 100 mT. (c) (111) X-ray pole figure of NiO thin film deposited under a magnetic field of 100 mT.

Figures 5(a) and 5(b) respectively portray XRD patterns of NiO thin films deposited at room temperature on MgO(001) in magnetic fields of 0 and 100 mT. The left panel of the figure shows two peaks marked “*” derived from the MgO(001) substrate. **Figure 5(b)** shows that a film deposited under a magnetic field of 100 mT exhibits a 001 orientation. No such peak is observed for **Fig. 5(a)**. However, a broad peak is observed around at 42° at 2θ . This broad peak is expected to indicate that the NiO film is crystalline but composed of nanocrystals. **Figure 5(c)** shows a (111) X-ray pole figure of NiO thin film deposited under a magnetic field of 100 mT. Four poles are observed at every 90° in ϕ at 54° in φ , which proves epitaxial growth of the NiO thin film on MgO(001).

Figures 6(a) and 6(d) respectively depict RHEED images of MgO(001) single-crystal from [100] and [110] azimuth. **Figures 6(b) and 6(e)** respectively show those of NiO thin film deposited under a magnetic field of 0 mT from [100] and [110] azimuth. **Figures 6(c) and 6(f)** respectively show those of NiO thin film deposited under a magnetic field of 100 mT from [100] and [110] azimuth. In **Figs. 6(b) and 6(e)**, a streak pattern can be observed clearly. This result agrees with the consideration that the NiO thin film deposited without application of a magnetic field is crystalline, as described in **Fig. 5(a)**. These RHEED images depict that the in-plane orientation of NiO thin film is unchanged between 0 and 100 mT, and that epitaxial growth on MgO(001) is realized. This in-plane orientation is observed for thin films deposited under 120

Fig. 6. (a) and (d) RHEED images of MgO(001) single-crystal from [100] and [110] azimuth. (b) and (e) RHEED images of NiO thin film deposited under a magnetic field of 0 mT from [100] and [110] azimuth. (c) and (f) RHEED images of NiO thin film deposited under a magnetic field of 100 mT from [100] and [110] azimuth.

mT, although the images are not shown here. As presented in Fig. 5(a), the thin film deposited without applying magnetic field appears to be amorphous from XRD, whereas Figs. 6(b) and 6(e) show epitaxial growth. This result suggests that the crystallinity of NiO thin film deposited without applying a magnetic field during deposition is low, but in-plane crystallinity can be observed using RHEED. Kobayashi et al. deposited a NiO thin film on MgO(001) substrate at room temperature without applying a magnetic field. They found that the NiO thin film crystallinity depends on oxygen pressure during deposition.⁶⁾ According to their results, NiO thin films deposited at 1.33×10^{-5} Pa of O_2 are amorphous from the point of view of XRD and crystalline from the point of view of RHEED, whereas a NiO thin film deposited at 1.33×10^{-4} Pa of O_2 is epitaxial by both XRD and RHEED. These results indicate that room temperature epitaxial growth of NiO thin film is very sensitive to the deposition condition. In our work, the NiO thin film was deposited at 1.33×10^{-2} Pa of O_2 . Therefore, direct comparison of our results with theirs is difficult. It can be inferred that an amorphous thin film examined using XRD can often show in-plane orientation when examined using RHEED.

The NiO thin film resistivity was measured at room temperature for 120-nm-thick thin films. As portrayed in Fig. 4, the deposition rate depends on the magnetic field during deposition, the NiO thin film deposition was controlled by changing the deposition time. **Figure 7** presents the change of resistivity with the magnetic field measured at room temperature. As this figure shows, the NiO thin film resistivity decreases exponentially with the magnetic field during deposition. For this work, two-point probe method was used to evaluate resistivity. Resistivity ρ of the NiO thin film was corrected as shown below.

Fig. 7. Change of resistivity of NiO thin film deposited at room temperature with an applied magnetic field.

$$\rho = R \frac{w\pi}{\ln 2} \quad (1)$$

Therein, R and w respectively represent the resistance measured using the two-point probe method and the thin film thickness. For the two-point probe method, the effect of contact resistance must be considered. For this work, the contact resistance was estimated by comparing the calculated resistance with the measured resistance for a 0.25-mm-thick metal Ni sheet. Because the resistivity of metal Ni at room temperature is $6.84 \times 10^{-6} \Omega \text{ cm}$,²⁰⁾ the resistance is calculated as $6.04 \times 10^{-5} \Omega$ based on Eq. (1). The measured resistance obtained using the two-point method was 0.9Ω . The measured resistance is much larger than the calculated value. Therefore, the measured resistance (0.9Ω) is believed to correspond to the contact resistance. Figure 7 depicts that the least resistivity is obtained for NiO thin film deposited under a magnetic field of 120 mT. For this film, the resistance value was $2.05 \times 10^6 \Omega$. Because this resistance value is much larger than the estimated contact resistance, one can neglect the contact resistance effects. The fact that the NiO thin film resistivity decreases exponentially with the magnetic field suggests that the Ni^{3+} ion concentration would increase exponentially with the magnetic field during deposition according to the analogy of sputtered NiO thin films.¹⁹⁾ For a sputtered NiO thin film, the reported resistivity is 0.3–0.8 $\Omega \text{ cm}$. This magnitude of resistivity is 2–3 orders lower than that portrayed in Fig. 7. If the NiO thin film resistivity depends simply on the Ni^{3+} concentration, then the concentration in a NiO thin film deposited under the magnetic field is much lower than that in a sputtered NiO film. Reportedly, Li-doping can control NiO thin film resistivity. For example, the resistivity of a 0.05 % Li-doped NiO thin film has been reported as 750 $\Omega \text{ cm}$ at room temperature.¹⁷⁾ This resistivity is almost equal to that of a NiO thin film deposited under a magnetic field of 80 mT. Therefore, results of this study clarified that, without Li-doping, the NiO thin film resistivity can be controlled by the magnitude of magnetic field application during deposition.

5. Conclusions

For this work, PLD along with an electromagnet

(dynamic aurora PLD) and RHEED was developed by installing an 11-tuned solenoid coil in the vacuum chamber. This method achieved thin film deposition under a magnetic field of up to 120 mT using 1,200 A of dc current. Because the electromagnet is a solenoid coil, the magnetic field is proportional to the electric field without saturation of the magnetic field. After turning off the electromagnet, but without breaking vacuum, this PLD method can allow in situ observation of the crystal structure of the thin film surface. Many reports of the literature describe studies of PLD in a magnetic field. In most such studies, permanent magnets have been used to apply a magnetic field to the plume. However, in this case, carrying out in-situ observations using RHEED is difficult because the magnetic field deflects the electron beam.

This case study examined the effects of a magnetic field applied to the plume on the in-plane orientation and resistivity of NiO thin film deposited on MgO(001) single crystal at room temperature (25 °C). Results demonstrate that the in-plane orientation (epitaxial growth) is unchanged, whereas the thin film resistivity decreases exponentially with the magnetic field during deposition. These findings suggest that the Ni^{3+} ion concentration can be expected to increase exponentially with the magnetic field during deposition. The room-temperature resistivity of NiO thin films deposited under a magnetic field of 120 mT was 112 Ωcm . Results clarified that the NiO thin film resistivity can be controlled by the magnitude of the magnetic field applied during deposition without Li-doping.

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