Progress and impact of magnetic field application during pulsed laser deposition (PLD) on ceramic thin films

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When a focused laser beam is irradiated onto a target, electrons and cations are emitted from the target to form a plume (plasma). This phenomenon is referred to as laser ablation (LA). The thin film deposition method using laser ablation is referred to as pulsed laser deposition (PLD). Recombination of electrons and cations usually occurs in the plume before they arrive at a substrate to form a thin film. However, previous reports show that applying a magnetic field to the plume suppresses recombination and enhances electron-impact excitation. The flux of electrons and cations can therefore be controlled by an external magnetic field during PLD. Charged cations can separate from neutral particles or heavy clusters such as droplets. This principle has been used to obtain droplet-free thin films. Applying a magnetic field to the plume also causes ohmic heating and suppression of adiabatic expansion. The electron temperature in a plume with magnetic field application is therefore higher than that in a plume without magnetic field application. This principle has been used to lower crystallization temperatures, improve crystallinity, and enhance thin film properties. Because application of a magnetic field suppresses recombination and enhances electron-impact excitation, several cations exist in the plume. These then rush to the substrates. This principle produces changes in the growth mode, which in turn brings about changes in the thin film morphology. Furthermore, this principle leads to phase separation control. The impingement of cations reportedly brings about lowering of the activation energy for diffusion, which leads to phase separation by spinodal decomposition. A thin film with a spontaneous superlattice structure forms when compositional wave propagation occurs in one direction, but when a cross-linked microstructure is obtained the compositional wave direction of propagation is random. This review presents the influence of application of a magnetic field during deposition.

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1. General theory of the effects of application of a magnetic field to the plume

When a focused laser beam is irradiated onto the surface of a solid (or liquid), the substances on the surface evolve explosively to form a plume (plasma). Electrons and cations as well as neutral atoms or molecules and their clusters are included in the plume (plasma). This phenomenon is referred to as laser ablation (LA). Thin film deposition by LA is generally referred to as pulsed laser deposition (PLD), by which the vapor phase in the plume is deposited onto a substrate to form a thin film. The configuration of PLD is simple compared to those of physical vapor phase deposition methods such as sputtering and molecular beam deposition (MBE). It is therefore easy to install some devices for plume stimulation. In actuality, several experiments on applying an electric field during PLD and introducing nitrogen or oxygen radicals during PLD have been reported. An electric field and irradiation of radicals reportedly improve the quality of thin films including their crystallinity, microstructure, and properties. Because of the simple configuration of PLD, installation of magnets in the vacuum chamber has also been conducted. The effects of magnetic field application on PLD have been reported. In these reports, the direction of application of a magnetic field to the plume can be classified into two types; transverse and longitudinal magnetic fields. The effects of applying a magnetic field to the trajectories of cations have also been considered. Figures 1(a) and 1(b) show simulated trajectories of evaporated cations in a plume in X–Z and X–Y planes without applying a magnetic field. In these trajectories, only the Lorentz force and inelastic scattering are included for the calculation. Figures 1(c) and 1(d) show the estimated trajectories of cations with application of a transverse magnetic field in X–Z and X–Y planes on the basis of discussion by Weißmantel et al. These figures show that the trajectories of cations are spirals focusing close to the center of the substrate, and the radius of the spirals decrease with increases in the magnitude of an electric field and irradiation of radicals.
of a longitudinal magnetic field. The trajectories of electrons are essentially the same as those of cations unless the direction of the spirals is opposite.

The first report on research examining the influence of magnetic field on a plume in vacuum was by Dimberger et al.,8,9) who irradiated a KrF excimer laser onto a metal Mg target. The emission spectra of the magnesium plumes were recorded with and without application of a 0.2 T transverse magnetic field. The authors reported that strong emission peaks of excited neutral magnesium (Mg I) and faint peaks of excited ionized magnesium (Mg II) were observed without application of a magnetic field. However, strong peaks of Mg II were observed with application of a magnetic field. These results indicate that Mg II vanishes with recombination of cations and electrons when magnetic field is not applied. On the other hand, recombination is suppressed when a magnetic field is applied. In addition, Dimberger et al. considered that electron-impact excitation occurs in the plume when a magnetic field is applied. This consideration is based on the fact that they observed Mg I and Mg II peaks up to larger distances, though the lifetime of Mg I and Mg II is very short (517 nm Mg I, 10 ns; 448 nm Mg II, 4 ns). Electron-impact excitation brings about an increase in the electron temperature. To explain how a possible temperature increase might come about, they use a Magneto Hydro Dynamic (MHD) model to describe the expansion of the ionized plume in a magnetic field:40)

\[ E + V \times B = J/\sigma_0 + (J \times B)/n_e e \]  

(1)

In this equation, \( E \) and \( B \) represent the electric field and the magnetic flux density, and \( V \) represents the mass flow velocity. \( J \) stands for the current density, \( \sigma_0 \) denotes the conductivity, and \( n_e \) signifies the electron density. This equation shows that ohmic heating by induced currents maintains the electrons at a sufficiently high temperature to continue to excite Mg I and Mg II in the expanding plume, explaining the enhancement of the emission at large distances from the target. Without magnetic field application, adiabatic expansion of the electron gas produces a rapid decrease in the electron temperature, thereby halting excitation and emission.41) Furthermore, similar phenomena in which transverse magnetic field application to the plume enhances the formation of excited ionized species have been reported for graphite10,11) and carbon nitride.12)

As concern longitudinal magnetic fields, Tachiki et al. observed the emission spectra of SrTiO3 plumes at the target position and substrate position with and without application of a strong magnetic field of 0.45 T.13) Figures 2(a) and 2(b), respectively, portray changes in the emission spectra with and without magnetic field application. In these figures, “Sr” and “Ti”, respectively, denote excited neutral peaks. Also, “Sr” and “Ti”, respectively, denote excited ionized peaks. These figures demonstrate that ionized peaks can be observed at the target position, irrespective of magnetic field application. At the substrate position, however, strong ionized peaks are still observed in the spectra with magnetic field application, although only very faint ionized peaks are apparent in spectra without magnetic field application. These results demonstrate that recombination of ions and electrons occurs rapidly in the plume to produce neutral atoms without magnetic field application. Magnetic field application during deposition suppresses recombination while also causing electron-impact excitation in the case of longitudinal magnetic field application.

2. Purpose of this review

As discussed above, a number of reports described the influence of the application of magnetic fields on PLD.31–39) In most of those studies, permanent magnets of materials such as SmCo5, Sm2Co17,
or Nd$_2$Fe$_{14}$B have been used to apply a transverse or longitudinal magnetic field to the plume. In this case, the maximum magnetic field is reported to be approximately 0.45 T. For the following reasons, however, the use of permanent magnets might not be preferred for thin film deposition:

1. It is difficult to change the magnetic field because the magnetic field is determined by the remanent magnetization of the permanent magnets.

2. It is difficult to deposit thin films at elevated temperatures, because the deposition temperature should be below the maximum operating temperature $T_{\text{max}}$. The $T_{\text{max}}$ of SmCo$_5$, Sm$_2$O$_{17}$, and NdFe$_{14}$B are 250, 350 and 120°C, respectively.42

3. It is difficult to produce a uniform magnetic field around a substrate unless a permanent magnet with a wide area is used.

These difficulties can be overcome with the use of an electromagnet. In fact, we have developed a PLD with a solenoid coil installed in a vacuum chamber and realized thin film deposition under conditions of longitudinal magnetic fields up to 0.2 T and substrate temperatures as high as 800°C (Fig. 3).30,31,38,39 The magnetic field magnitude can be changed dynamically. We therefore, referred to this PLD as a “Dynamic Aurora PLD”. The PLD with a solenoid coil was developed by Okuyama et al.33,34 They installed a solenoid coil with an oxide-superconductive tape set in a liquid nitrogen container to realize a 0.4 T longitudinal magnetic field and substrate temperature of 600°C (magnetic field-assisted PLD). Recently, Zhang et al. incorporated a PLD system with a superconducting magnet to realize thin film deposition under conditions of a high longitudinal magnetic field up to 8 T and a substrate temperature up to 800°C (high magnetic field-assisted PLD [HMF-PLD]).36,37

In this review, the influence of magnetic field application on PLD is described briefly from the following four points of view. The direction of the magnetic field is mainly transverse or longitudinal with some derivative.

(i) Elimination of droplets by magnetic field application.
(ii) Lowering of the crystallization temperature, improvement of crystallinity, and enhancement of thin film properties by magnetic field application.
(iii) Change of thin film morphology by magnetic field application.
(iv) Magnetic field-induced phase separation.

3. Elimination of droplets by magnetic field application

As described above, a plume consists of electrons, cations, and neutral atoms or molecules and their clusters. In addition to these species, micrometer-sized particulates called “droplets” occasionally evolve from the target to be deposited onto the substrate, which is detrimental to PLD. To avoid the evolution of droplets from a target, or adhesion of droplets to a substrate, the following methods have been reported: using a dense target,43 polishing the target,44 using a velocity selector,45 using “eclipse” method by which a plate is introduced between the target and substrate to eliminate droplets in the plume,46,47 and using “off-axis” method by which the substrate is placed parallel to the plume to prevent adhesion of droplets to the substrate.48

In addition to these methods, another method of eliminating droplets application of a magnetic field to the plume has been reported.14–15 It is not certain whether the droplets are neutral or charged. If the droplets are neutral, then the Lorentz force does not work for them although it works for cations and electrons. The droplets flight direction is therefore unaffected by the application of a magnetic field, while that of the cations and electrons is deflected. If the droplets are charged, then the flight direction of the droplets is also deflected. The radius of the droplet curvature is considerably greater than those of cations or electrons, however because the droplet mass is much greater than those of cations or electrons. It is therefore, possible to separate the flow of droplets from that of cations and electrons using an applied magnetic field.

In the literature, this approach is classified into two categories.

One method is to use a curved solenoid coil, as depicted schematically in Fig. 4(a). Where this method is used, the magnetic field is in the axial direction. The flow of cations occurs along the solenoid coil, therefore, although the droplet direction is unchanged. Jordan et al. developed a PLD with a 90° stainless-steel curved duct.16 Copper wire was wound around the duct surface to generate a magnetic field up to 0.07 T. In addition, the duct can be positively or negatively biased with respect to the ground. The results showed that a droplet-free copper thin film was obtainable as a result. The results also showed that application of both a magnetic field (0.04 T) and dc bias voltage (100 V)
are necessary, however, to guide the plasma (plume) to the substrate. Minami et al. developed a PLD with a curved solenoid coil.\textsuperscript{15} They deposited carbon thin film with and without an applied magnetic field of 0.3 T. They found that the use of a magnetic guide field reduces inclusion of droplets in the film. Additionally, they found that the sp\textsuperscript{3} fraction in the carbon thin film increased when using a magnetic guide field, which means that a better-quality diamond-like-carbon film is obtained through deposition using a pure ion component in the plume.

The second approach is to use a transverse magnetic field, as depicted schematically in Fig. 4(b). Fernández et al. developed a PLD with two magnets: one was a solenoid coil that applied a longitudinal magnetic field (0.25 T) to guide the plasma; the other was a Hallbach cylinder that applied a transverse magnetic field (0.42 T) to change the plasma flight direction.\textsuperscript{17} The authors confirmed that droplet-free, low-roughness metals (Mo, Cu and Fe) thin films are deposited compared with conventional PLD without magnetic field application. Weißmantel et al. simulated the angular distribution of the ablated species and the thickness of hexagonal-BN film thickness distribution with and without application of a homogeneous transverse magnetic field by a permanent magnet (1.1 T).\textsuperscript{18} Their results showed that transverse magnetic field application increases the deposition rate for the substrate mounted above and sideways, and that the area density of droplets can be decreased. Additionally, they confirmed the simulation results using experimentally obtained results.

4. Lowering of the crystallization temperature, improvement of crystallinity, and enhancement of thin film properties by magnetic field application

As described above, applying a magnetic field to the plume suppresses recombination of cations and electrons. In addition to this effect, Dirrberger et al. considered three effects: electron-impact excitation, suppression of adiabatic expansion and ohmic heating.\textsuperscript{8} They pointed out that, without magnetic field application, adiabatic expansion of the electron gas produces a rapid decrease in the electron temperature, thereby halting excitation and emission.\textsuperscript{41} Magnetic field application suppresses adiabatic expansion, however because of the Lorentz force. A high electron temperature is consequently maintained at substrate position.

The plasma temperature can be estimated using a Boltzmann plot according to the following equation:\textsuperscript{49,50}

\[
\log \left( \frac{I_{\text{exc}} A_{\text{exc}}}{g_{\text{exc}} A_{\text{exc}}} \right) = \frac{4.34 E_{\text{exc}}}{kT} + C \quad (C: \text{constant}) \tag{2}
\]

In this expression, \( I_{\text{exc}}, A_{\text{exc}}, g_{\text{exc}}, A_{\text{exc}}, E_{\text{exc}}, k \) and \( T \) respectively represent the emission intensity of the \( \lambda \)-wavelength line from the excited level, wavelength, statistical weight of this level, considered probability of transition, excitation energy, Boltzmann’s constant, and temperature. We measured the emission spectra of excited ionized titanium (Ti\textsuperscript{+}) peaks in the plume generated from a SrTiO\textsubscript{3} target with and without application of a 0.2 T longitudinal magnetic field using a spectrometer (PMA-11; Hamamatsu Photonics K. K.). Figure 5 presents the results of the Boltzmann plot. From the slope of this plot, the plasma temperature of SrTiO\textsubscript{3} with and without magnetic field application was estimated, respectively, as 1650 and 1470 K. These results show that magnetic field application (0.2 T) increased the plasma temperature by approximately 180 K. A high plasma temperature can lower the crystallization temperature and improve the thin film crystallinity. Improvement of crystallinity enhances the material properties. Several examples are presented below.

Kobayashi et al. reported room temperature heteroepitaxial growth of NiO thin films on MgO(001) substrates using the “Aurora-Eclipse” method with application of a maximum longitudinal magnetic field of 0.36 T.\textsuperscript{23} Without a magnetic field applied, NiO thin films become polycrystalline. Similar results were reported for SrTiO\textsubscript{3} thin films deposited at 500°C with application of a maximum longitudinal magnetic field of 0.45 T.\textsuperscript{24} Additionally, they reported that a very smooth film surface was obtained by magnetic field application during deposition. For ZnO thin films deposited on a quartz glass substrate at low temperature using the “Aurora PLD” method with application of a 0.4 T longitudinal magnetic field, they reported that the photoluminescence intensity and carrier density of the films were equal to those of thin films deposited at 100°C using conventional PLD without magnetic field application.\textsuperscript{25} This finding suggests that magnetic field application during deposition is equivalent to lowering the deposition temperature of approximately 80°C. Suzuki et al. deposited Al-doped ZnO thin films and Ti-doped ZnO thin films on glass substrates at temperatures lower than 230°C with application of a 1.25 T transverse magnetic field during deposition.\textsuperscript{26-28} They found that the crystallinity of the films deposited with magnetic field application is higher than that deposited without magnetic field application. Rafique et al. deposited BaFe\textsubscript{12}O\textsubscript{19} (BaM) thin films at 300°C under transverse magnetic fields of 0.6 T.\textsuperscript{29} Although the crystallinity of their films was very low, they found that the thickness, anisotropy field, saturation magnetization, and band gap energy increase with the presence of a magnetic field during deposition. These findings suggest that the properties of BaM thin films can be controlled by transverse magnetic field application during deposition.

We have assessed the effects of longitudinal magnetic field application on magnetic properties of ZnFe\textsubscript{2}O\textsubscript{4} (ZF) thin films deposited on Y\textsubscript{0.15}Zr\textsubscript{0.85}O\textsubscript{1.925} (YSZ) buffered Si(001) substrates at various deposition temperatures using the Dynamic Aurora PLD.\textsuperscript{30} Figure 6 shows the changes of magnetization-magnetic field curves of ZF thin films deposited at various temperatures with application of a 0.2 T longitudinal magnetic field. This figure shows that the \( M-H \) curve shape is ferrimagnetic up to 500°C. The shape becomes paramagnetic at temperatures above 600°C. In addition, as this figure shows, the saturation magnetization of ZF thin film increases with the deposition temperature to as high as 500°C, but it decreases drastically to almost zero at temperatures higher than 600°C. Bulk ZF is paramagnetic at room temperature because Zn\textsuperscript{2+} and Fe\textsuperscript{3+} cations, respectively, occupy the A-site (tetrahedral site) and B-site (octahedral site) of the spinel structure (regular spinel structure). The spins of Fe\textsuperscript{3+} in the B-site align
antiparallel to cancel the magnetic moment. However, previous reports show that ZF powders synthesized by co-precipitation, ball milling, mechanical activation, rapid quenching and ZF thin films deposited at room temperature show ferrimagnetic properties. These ferrimagnetic properties are regarded as derived from the exchange of Zn\(^{2+}\) and Fe\(^{3+}\) cations between A- and B-sites. Therefore, the results presented in Fig. 5 can be interpreted as follows. At temperatures as high as 500°C, the ZF thin film is in a non-equilibrium state. The degree of exchange can be controlled by the application of a magnetic field during deposition. At temperatures higher than 600°C, thermodynamics dictate that the ZF thin film has a regular spinel structure in which no ferrimagnetism is observed. We also examined the effects of longitudinal magnetic field application (0.2 T) on magnetic properties of BaM thin films deposited on Y\(_{0.15}Zr_{0.85}O_{1.925}\) (YSZ) buffered Si(001) substrates at 800°C.\(^3\) The results showed that the saturation magnetization decreases with the magnetic field during deposition. It is noteworthy that this tendency is opposite to that reported by Rafique et al. described above.\(^2\) At present, the reason for this discrepancy remains unclear. However, the results might depend on the experimental conditions, i.e., the difference in deposition temperatures (300°C\(^2\) and 800°C\(^3\)), and the directions of the magnetic field (transverse\(^2\) and longitudinal\(^3\)) to the plume. This point must be clarified in future studies, but the findings presented above indicate that magnetic field application during deposition can modify the thin film properties.

5. Changes in thin film morphology with magnetic field application

Reportedly, magnetic field application during deposition alters the microstructure of thin films considerably. Suzuki et al. deposited ZnO thin film on glass substrates at 160–300°C with and without transverse magnetic field application.\(^26\),\(^27\) They found that films deposited with a magnetic field contain lattice defects at the interface between the substrate and thin film, whereas films deposited with no magnetic field include no such defects. Ehsani et al. deposited Co thin film on Si(001) substrates at room temperature with and without application of a 0.1 T transverse magnetic field.\(^21\) They found that the grain size of Co thin film deposited with a magnetic field applied is larger than that deposited with no magnetic field application. They explained that application of a magnetic field during deposition provides more kinetic energy for the ad-atoms. Ad-atom migration is consequently enhanced, thereby improving grain growth. It is noteworthy that the deposition temperature reported by Suzuki et al. and Ehsani et al. is not very high. Okuyama et al. deposited BiFeO\(_3\)-CoO\(_2\)-O\(_3\) (BFCO) thin films on Pt/Ti/SiO\(_2\)/Si substrates at 600°C with and without application of a 0.4 T longitudinal magnetic field.\(^3\) They found that the BFCO thin film deposited with magnetic field application shows a columnar structure, while that deposited without magnetic field application shows a grain-like microstructure. Additionally, they calculated the trajectories of the charged particles in the plume under a magnetic field and simulated the formation process of the columnar structure of a BiFeO\(_3\) (BFO) thin film based on the facet growth mechanism.\(^3\)

The influence of longitudinal magnetic field application during deposition on the morphology is readily apparent for thin films deposited under a high magnetic field. Zhang et al. deposited La\(_0.9\)Sr\(_0.1\)MnO\(_3\) (LSMO) and La\(_0.9\)Ca\(_0.1\)MnO\(_3\) (LSCO) thin films on (LaAlO\(_3\))\(_{0.3}\) (Sr\(_2\)AlTaO\(_6\))\(_{0.7}\) (LSAT) substrates at 650°C with and without application of an 8 T magnetic field.\(^3\) The change in the microstructure of the LSMO thin film with longitudinal magnetic field application during deposition is depicted in Fig. 7.\(^3\) They found that LSMO thin film deposited without magnetic field application was a continuous planar thin film [Fig. 7(a)], suggesting a typical Frank–van der Merwe layer-by-layer growth mode. They found that LSCO thin film deposited with application of a 0.5 T magnetic field shows a two-layer structure. Thus, a continuous planar layer is grown first. A nanorod layer is then grown on the continuous planar layer [Fig. 7(b)], suggesting the Stranski–Kranatov layer-plus-island...
growth mode. LSCO thin film deposited with application of an 8 T magnetic field also shows a two-layer structure. However, the thicknesses of the continuous layer and the nanorod layer are thinner and thicker, respectively, than those deposited with application of a 5 T magnetic field [Fig. 7(c)]. These findings indicate that magnetic field application during deposition enhances the columnar structure. They also reported that the columnar structure brings about magnetic anisotropy. The value of the longitudinal magnetic field of 5–8 T is larger by at least 10 times than those used in other papers. As shown in Figs. 1(g) and 1(h), the radii of the spirals decrease with increases in the magnitude of the magnetic field. This suggests that the recombination of ions and cations would be extensively suppressed, in addition, that the electron-impact excitation would also be enhanced. The effects of enhanced suppression of recombination and electron-impact excitation on the properties of thin film should be clarified in the future.

6. Magnetic field induced phase separation

We observed spontaneous superlattice formation on epitaxial SrTiO$_3$ thin films with A-site excess composition (Sr$_{1.4}$TiO$_{3.4}$) deposited on Nb-doped SrTiO$_3$ (001) substrates at 700°C with longitudinal magnetic field application (0.2 T) during deposition using the Dynamic Aurora PLD [Fig. 8(b)]. As shown in this figure, no spontaneous superlattice formation is observed on films without magnetic field application. Furthermore, no spontaneous superlattice formation is observed on stoichiometric composition thin films with or without magnetic field application, as portrayed in Fig. 8(a). Spontaneous superlattice formation is confirmed by cross-sectional scanning transmission electron microscopy (STEM) observation (bright field) and energy dispersive X-ray spectroscopy, as shown in Fig. 8(d). The period of superlattice determined by X-ray diffraction (XRD) according to the following formula is 25.6 nm where $\theta_B$ is the Bragg angle and $m$ is the order of reflection:

$$\sin \theta_m = \sin \theta_B \pm m\lambda / 2\Lambda$$

This value shows good agreement with that observed by STEM image (30 nm). To consider the cause of spontaneous superlattice formation, we first considered the possibility of formation of the Sr$_7$Ti$_4$O$_{15}$ phase because the composition of our film (Sr$_{1.4}$TiO$_{3.4}$) is close to this value. This possibility was rejected however because the lattice parameter of Sr$_7$Ti$_4$O$_{15}$ along the c-axis was reportedly $\epsilon = 2.038$ nm, which is one order smaller than the...
observed superlattice period described above. In addition, if this phase is formed, then the peaks of (008), (0012) and (0014) should be observed respectively near 35, 54, and 64° in 2θ. No such peak was observed, however as portrayed in Fig. 8(c). Therefore, we considered another possibility for Ruddlesden–Popper (RP) phases having the general formula Sr1+xTiO3+(x-1). According to Ohnishi et al. the lattice parameter of Sr1+xTiO3+(x-1) along the c-axis can be expressed as a sum of the SrTiO3 (STO) lattice parameter (a_{STO} = 0.3905 nm) and the inter-layer distance of the SrO bilayer (d_{SrO-SrO} = 0.2380 nm), i.e. c = 2(a_{SrO} + d_{SrO-SrO}). In these compounds, the lattice parameter along the c-axis can be considered as coinciding with the superlattice period. Applying this formula to our thin film, we estimated the n value as approximately n = 32, because the superlattice period determined using XRD was 25.6 nm. If n = 32, then the Sr/Ti ratio turned out to be (1 + 32)/32 = 1.03, which is definitely different from the composition of our thin film (Sr1.4TiO3.4). Therefore, the possibility of formation of other RP phases was also denied. In the Sr–Ti–O system, another type of superlattice with the general formula Sr_mTiO_{2m+2} (m = 1–5) has also been reported. The possibility of formation of this type was also denied however, because of the difference in XRD patterns. These findings indicate that the structure of the spontaneously formed superlattice shown in Figs. 8(b) and 8(d) differs from the structures reported to date. Figure 8(e) is a high-resolution TEM (HRTEM) image of a cross section of the film portrayed in Fig. 8(d). In this image, insertion of an extra SrO double layer is suggested. We therefore, considered that the crystal structure of the Sr–Ti–O thin film with a spontaneously formed superlattice is fundamentally a perovskite-type structure in which SrO double layers are distributed randomly to form the spontaneous superlattice period. Applying this formula to our thin film deposition in the Dynamic Aurora PLD. Figure 8 shows this to be the reason why spontaneous superlattice formation is observed. Actually, in our work, the apparent activation energy was estimated at 0.25 eV. This value is one order smaller than that reported for Ti diffusion in La-doped SrTiO3 single crystals (3.3 eV). This strongly suggests that lowering of the apparent activation energy is brought about by the “Q-of-φ” term. Similar low apparent activation energy (0.1 eV) has been reported for BaSnO3 thin film with a spontaneous superlattice structure. It is noteworthy moreover that Sr–Ti–O (Sr1.4TiO3.4) thin film with a spontaneous superlattice structure shows ferroelectricity although SrTiO3 bulk is quantum paraelectric. which also suggests that extra properties are induced for films deposited using magnetic field application. Figure 9 shows the relationship between the fluence (source laser power) and the spontaneous superlattice period. This figure indicates that the superlattice period drastically increases with the source laser power. This result suggests that the density and speed of cations evaporated from the target increase with laser power, which would increase the density and radius of the trajectories of the ions. This enhances the ion-impingement and lowers the activation energy to increase spontaneous superlattice period.

To clarify whether ion impingement brings about spontaneous superlattice formation in other crystal structures, we examined the effect of magnetic field application on the epitaxial growth of cobalt ferrite thin film with a spinel structure. Figure 10 presents the changes in the XRD patterns of CoFe2O4–CoO (CoF) thin films deposited on MgO(001) substrates at 700°C with the activation energy for diffusion according to the following equation:

\[
D^*(0) = D_0 \exp \left( -\frac{Q - \alpha I}{kT} \right)
\]

Herein, \(D^*(0), D_0, Q, \alpha, \) and \(I\) respectively represent the enhanced diffusion coefficient at the surface (z = 0), pre-exponential factor, activation energy, enhancement factor with a positive constant, and energy of flux of ion impingement. These indicate that ion impingement (ion bombardment) during deposition lowers the activation energy for “up-hill diffusion”. Spinodal decomposition is consequently induced to bring about spontaneous superlattice formation. It should be remembered that application of a magnetic field to the plume suppresses the recombination of electrons and ions, and enhances the electron-impact excitation. Therefore, ion impingement occurs during thin film deposition in the Dynamic Aurora PLD. Figure 8 shows this to be the reason why spontaneous superlattice formation is observed. Actually, in our work, the apparent activation energy was estimated at 0.25 eV. This value is one order smaller than that reported for Ti diffusion in La-doped SrTiO3 single crystals (3.3 eV). This strongly suggests that lowering of the apparent activation energy is brought about by the “Q-of-φ” term. Similar low apparent activation energy (0.1 eV) has been reported for BaSnO3 thin film with a spontaneous superlattice structure. It is noteworthy moreover that Sr–Ti–O (Sr1.4TiO3.4) thin film with a spontaneous superlattice structure shows ferroelectricity although SrTiO3 bulk is quantum paraelectric. which also suggests that extra properties are induced for films deposited using magnetic field application. Figure 9 shows the relationship between the fluence (source laser power) and the spontaneous superlattice period. This figure indicates that the superlattice period drastically increases with the source laser power. This result suggests that the density and speed of cations evaporated from the target increase with laser power, which would increase the density and radius of the trajectories of the ions. This enhances the ion-impingement and lowers the activation energy to increase spontaneous superlattice period.

To clarify whether ion impingement brings about spontaneous superlattice formation in other crystal structures, we examined the effect of magnetic field application on the epitaxial growth of cobalt ferrite thin film with a spinel structure. Figure 10 presents the changes in the XRD patterns of CoFe2O4–CoO (CoF) thin films deposited on MgO(001) substrates at 700°C with...
magnetic field application during deposition. This figure shows that only one peak of spinel (004) is observed for a film deposited without magnetic field application. For films deposited with magnetic field application during deposition, no satellite peaks, which are characteristic of spontaneous superlattice formation, were detected, although peak splitting was observed. This peak splitting suggests phase separation by spinodal decomposition. It is noteworthy that the deposition was conducted for 20 min with no annealing. Phase separation was confirmed by observation of the morphology. Figure 11 presents scanning electron microscopy (SEM) photographs with EDS mapping along with corresponding atomic force microscopy (AFM) images. This figure depicts a cross-linked microstructure resembling the microstructure of glass after spinodal decomposition. A phase diagram of a CoFe2O4–Co3O4 system, has been reported by Robin, Masse and Muan. They found a miscibility gap (spinodal curve) in the spinel region. The phase diagram was revised; and the kinetics of spinodal decomposition was examined by Takahashi et al.85–87 In their work, the samples were aged for from 200 h to 36 days at 500–700°C. Hirano et al.87 and Kim et al., respectively observed spinodal decomposition for sol–gel derived CoF thin films after aging for 7.5–60 h at 700°C and for 4 h at 800°C. It is noteworthy that no phase separation was observed for as-synthesized bulk or as-deposited thin films. Aging for an extended period is necessary to cause spinodal decomposition. Therefore, it can be considered that magnetic field application during deposition enhances spinodal decomposition. In spinodal decomposition, compositional non-homogeneity occurs because of compositional wave propagation. As described above, spinodal decomposition in Sr–Ti–O thin films with magnetic field application occurs during deposition to form a spontaneous superlattice, whereas that in the CoF thin film occurs to form a cross-linked structure. We therefore consider that the direction of the propagating compositional wave is perpendicular to the substrate to form spontaneous superlattice in the Sr–Ti–O thin films. In the CoF thin films however, the direction of the propagation compositional wave is random to form a cross-linked microstructure. Figures 12(a) and 12(b) show reciprocal space maps around SrTiO3 (103) for the film portrayed in Fig. 12(b) and around CoF (226) for the film presented in Fig. 10 (0.2 T). Figure 12(a) shows that the in-plane lattice parameters of Sr–Ti–O thin film agree closely with those of the Nb–SrTiO3 substrate, suggesting coherent growth. In Fig. 12(b), a reciprocal point of a MgO substrate (113) and two reciprocal points of CoF thin film (226) by phase separation are observed. The averaged in-plane lattice parameter for these two reciprocal points is smaller than that for the MgO substrate, suggesting incoherent growth. Based on these findings, we have developed the following hypothesis: In the case of Sr–Ti–O thin film, coherent growth occurs. It is thus considered difficult for up-hill diffusion to occur in the in-plane direction since such diffusion would impede coherent growth. In this case, the compositional
wave that brings about spinodal decomposition propagates along the out-of-plane direction only, leading to form spontaneous superlattice formation. In the case of CoF thin film, coherent growth does not occur. The compositional wave can therefore be propagated in any direction to form a cross-linked structure. This hypothesis requires verification by future investigation.

7. Summary

Magnetic field application during PLD has several effects on the morphology, crystal structure, and their properties of thin films. This review introduces a brief history of its use and effects. The use of magnets to apply a magnetic field during deposition is classifiable into three methods using permanent magnets, electromagnets, and superconducting magnets. In this review, the influence of magnetic field application during PLD is described from four perspectives: (i) Elimination of droplets by magnetic field application; (ii) Lowering of crystallization temperatures, improvement of crystallinity and enhancement of the properties of thin film by magnetic field application; (iii) Changing of thin film morphology by magnetic field application; and (iv) Magnetic-field induced phase separation. Among these, magnetic-field induced phase separation is especially promising because phase separation by spinodal decomposition can be achieved for a system without a spinodal curve in the phase diagram such as a Sr–Ti–O system. A Sr–Ti–O thin film with a spontaneous superlattice structure due to spinodal decomposition shows room temperature ferroelectricity. Films deposited under magnetic field might show extraordinary properties, therefore that are not observed in the bulk. Magnetic field application during deposition is consequently expected to open new avenues for progress in the field of materials science.

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