Control of Crystal Orientation by Imposition of a High Magnetic Field in a Vapor-Deposition Process

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The nonmagnetic elements of zinc and bismuth were deposited onto a glass substrate under a high magnetic field of 5 T. The substrate was set parallel to the magnetic field, in a chamber kept at a pressure of $10^{-3}$ Pa. Bismuth was deposited in the c-plane orientation which agreed with the theoretical prediction based on the magnetization energy. The experimental result that the orientation index in the c-plane increased with an increase in the distance between the target and the substrate, suggests that the radiation heat due to the laser heat source interrupted the crystal orientation in the vicinity of the target. On the other hand, the orientation of zinc which has a smaller absolute value of magnetic susceptibility than bismuth, did not clearly appear in a magnetic field of 5 T. It has been found that from the viewpoint of magnetization energy, the crystal orientation due to a magnetic field needs a magnetization energy density more than 100 J/m$^3$.

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1. Introduction

It is well known that the physical properties of materials such as electrical, magnetic and mechanical, can be improved by controlling crystal orientation. The development of superconducting magnet technologies has enabled one to introduce magnetic fields as high as 10 T in academic laboratories. Under such high magnetic fields, the magnetization force acting on nonmagnetic materials is not negligible any more. Furthermore, materials have different magnetic susceptibilities depending on each direction of their unit crystal cells. Taking account of this physical characteristic and utilizing the function of a high magnetic field, we now have the possibility to develop a new method to align crystals in a favorable direction. The aim of this study is to investigate the effects of a high magnetic field on the crystal orientation in films deposited by use of a YAG laser.

2. Theory

Both zinc and bismuth have hexagonal crystal structures which show a magnetic anisotropy depending on each direction of their unit crystals. Magnetic susceptibilities along the a- or b-axis and the c-axis of zinc are $\chi_{a,b} = -1.81 \times 10^{-5}$, $\chi_c = -1.33 \times 10^{-5}$, and those of bismuth are $\chi_{a,b} = -1.24 \times 10^{-4}$, $\chi_c = -1.76 \times 10^{-4}$ respectively. The magnetization energy given in eq. (1) determines the favorable crystal direction depending on the magnetic susceptibility of each crystal axis in a given magnetic field.

$$U = -\frac{\chi}{2\mu_0(1 + N\chi)^2}B^2,$$

where $\chi$ is the magnetic susceptibility, $\mu_0$ is the permeability in vacuum, $N$ is the demagnetization factor, and $B$ is the applied magnetic field. When a crystal is set in a magnetic field, the crystal tends to align to a favorable crystal direction with the lowest magnetization energy. Substituting values of the magnetic susceptibility of zinc and bismuth into eq. (1), we get $U_c < U_{a,b}$ in the case of zinc and $U_{a,b} < U_c$ in the case of bismuth. These results tell that the c-axis of zinc crystal and the a- or b-axis of bismuth are the favorable crystal directions in parallel to a magnetic field. When a substrate is set in parallel to a magnetic field as shown in Fig. 1, the a- or b-axis orientation in zinc and the c-axis orientation in bismuth can be expected to appear on the substrate.

![Figure 1: Favorable crystal orientations in zinc and bismuth under a magnetic field.](image-url)
3. Experimental

A schematic view of the experimental apparatus is shown in Fig. 2. A vacuum chamber was set in the 90 mm diameter bore of a superconducting magnet. A glass plate was used as the substrate which was prepared by cleaning in ethanol bath with an ultrasonic cleaner to eliminate organic materials on its surface. The vacuum chamber was evacuated up to $10^{-3}$ Pa by use of diffusion and rotary pumps. The target material was vaporized by use of a YAG laser beam operating at a wavelength of 1064 nm. In order to control the temperature of the substrate, electric current was imposed in Fe-30 mass%Cr wire which was installed behind the substrate holder and the temperature was monitored by a thermocouple connected to it.

The orientation index of the deposited films on the substrate was calculated from the intensity of X-ray diffraction lines measured by means of an X-ray diffraction analyzer.

4. Results and Discussion

Zinc was deposited on the substrate (10 mm × 10 mm × 0.7 mm) placed at a position with the maximum intensity of magnetic field. The X-ray diffraction patterns of zinc are shown in Fig. 3, where the difference between the results of with and without the magnetic field trials is not clearly seen. The magnetic susceptibility value of about $10^{-5}$ for zinc is not large enough to align zinc crystals in a magnetic field of 5 T. On the other hand, the X-ray diffraction patterns of bismuth given in Fig. 4 show that the peak of (012) has appeared in the case of 0 T, but the peak of the $c$-plane is revealed in the magnetic field of 5 T. This result agrees with the theoretical prediction described in chapter 2. The magnetic field of 5 T is large enough to align bismuth crystals with a magnetic susceptibility of about $10^{-4}$. SEM photographs of bismuth thin films are shown in Fig. 5, where the surfaces of the samples were covered with minute particles in the case of 0 T and with rather large particles in the case of 5 T, respectively.

The magnetization energy difference due to the difference in magnetic susceptibilities is given by eq. (2) by using eq. (1).

$$\Delta U = \left\{ \frac{x_{a,b}}{2 \mu_0 (1 + N x_{a,b})^2} - \frac{x_c}{2 \mu_0 (1 + N x_c)^2} \right\} B^2$$

$$\approx \frac{|\Delta \chi|}{2 \mu_0} B^2 \quad (0 < N < 1, \chi \ll 1)$$

(2)

where $|\Delta \chi| = |x_{a,b} - x_c|$ is the absolute value of the difference between the magnetic susceptibilities depending on each crystal direction, and the values for zinc and bismuth are $|\Delta \chi|_{Zn} = 4.8 \times 10^{-6}$ and $|\Delta \chi|_{Bi} = 5.2 \times 10^{-5}$, respectively. The relations between the orientation index and the magnetization energy density are shown in Fig. 6. The broken line with a value of unity shows the standard orientation index obtained from the JCPDS card. A significant effect of the magnetic field on the crystal orientation is clearly seen in the region over 100 J/m$^3$.

On the plane representing the relation between the difference in magnetic susceptibilities and the magnetic field intensity, the area to have a magnetization energy density over the value of 100 J/m$^3$ is shown in Fig. 7. For exceeding the value of 100 J/m$^3$, bismuth which has a magnetic susceptibility difference of $5.2 \times 10^{-5}$ is sufficient with a magnetic field of 2 T, but zinc which has a magnetic susceptibility difference of $4.8 \times 10^{-6}$ needs a magnetic field over 7 T. Hence, this is the reason why the crystal orientation for zinc was not clearly seen at the magnetic field of 5 T.

In order to clarify the mechanism for the crystal orienta-
tion by imposition of a magnetic field, a bismuth film which was deposited on a glass plate without a magnetic field was again heated in a magnetic field of 5 T. X-ray diffraction patterns before and after this treatment should be different under the hypothesis that the crystal orientation due to the magnetic field takes place after vaporized atoms adhere to the substrate surface. As no difference is seen in the X-ray diffraction patterns of both samples as shown in Fig. 8, the mechanism of crystal orientation is considered as follows: A particle which has grown enough to feel the magnetization force during flying from the target to the substrate rotates in a favorable direction in the magnetic field and adheres to the substrate.

Next, substrates were set in a comparatively uniform magnetic field region in the superconducting magnet and a number of bismuth films were obtained by changing the magnetic field intensity. The orientation indexes of the c-plane (003) in these films were evaluated and plotted with respect to the distance between the target and the substrate in Fig. 9. In the case of 0 T no specific orientation is clearly observed at every place, but the orientation indexes obtained under imposition of the magnetic fields of 3 and 5 T clearly increase with the increase in the magnetic field intensity and the distance from the target.

Furthermore, the thermal effect on crystal orientation was investigated by changing the temperature of the substrate. The results obtained in 0 and 5 T are shown in Figs. 10 and
11, respectively. The values of the orientation index seen in Fig. 10 are less than or near unity. This fact implies that the crystal orientation did not take place under 0 T so that any effect regarding the substrate temperature was not observed. The other hand, it is seen in Fig. 11 that the orientation indexes larger than unity were clearly suppressed with rising in the substrate temperature under 5 T. In particular, the orientation was obviously suppressed in the vicinity of the target.

To reveal the crystal orientation under the imposition of a magnetic field, the magnetization energy should be larger than the thermal one. This condition is given in eq. (3),

$$\frac{|\Delta \chi|}{2\mu_0} B^2 V \geq k_B T, \quad (3)$$

where $V$ is the volume of a particle, $k_B$ is Boltzmann’s constant, and $T$ is the temperature in Kelvin. By taking account

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**Fig. 7** Feasible region for crystal orientation in the plane of magnetic flux density and absolute difference of magnetic susceptibilities.

**Fig. 9** Distributions of orientation index of Bi(003) with respect to the distance from the target under different magnetic field intensities.

**Fig. 8** X-ray diffraction patterns before and after applying a magnetic field.
of the experimental results given in Figs. 10 and 11 and the condition of eq. (3), it can be understood that the crystal orientation could be suppressed in the vicinity of the target due to the thermal energy introduced by the laser source. On the basis of eq. (3), the relation between the temperature and the critical size of bismuth particles, over which the magnetization energy in a particle is larger than the thermal energy, is shown in Fig. 12. Since it is difficult to measure the temperature of a flying particle and to see the shape of it, its temperature and shape are assumed to be the same as that of the substrate and spherical, respectively. It can be found that the crystal orientation due to a magnetic field becomes tangible with an increase in the particle volume. Thus, the mechanism of the crystal orientation in a vapor-deposition process in a magnetic field can be imaged as follows: Molecules evaporated from the surface of a target become a particle through agglomerating process during travelling from the target to the substrate. When the particle volume exceeds a certain value satisfying the condition of eq. (3), the particle feels a magnetization force stronger than the thermal disturbance force and rotates to a favorable crystal orientation before adhering to the substrate.

The substrate was set in a region with a large magnetic field gradient in the superconducting magnet and the vapor-deposition of bismuth was carried out under a magnetic field of 5 T. In Fig. 13 the orientation indexes of the c-plane (003) in bismuth films are plotted with respect to the distance between the target and the substrate. The orientation indexes increase with the increase in the distance from the target. The relations between the square of magnetic field intensity, which is proportional to the magnetization torque force and the orientation index, and those between the product of the magnetic field and its gradient, which is in proportion to the magnetization force and the orientation index, are shown in Figs. 14 and 15, respectively. As can be seen from the correlation coefficients of $R = 0.89$ in Fig. 14 and $R = 0.29$ in Fig. 15, it has been found that the crystal orientation due to a high magnetic field is related not to the product of the magnetic field and its gradient, but to the square of the magnetic field intensity. Hence, the mechanism of the crystal orientation is considered to stem from the magnetic torque as written in $\tau = M \times B$, which arises in the vector outer product of
the magnetic field $B$ and the magnetization $M$ as shown in Fig. 16.

5. Conclusion

In order to clarify the mechanism of the crystal orientation in a high magnetic field, zinc and bismuth were deposited under the imposition of a high magnetic field. The observed results have been discussed from the theoretical viewpoint, and the following information has been obtained.

(1) The crystal of bismuth deposited under a magnetic field of 5 T was aligned to the $a$- or $b$-axis parallel to the magnetic field line and its orientation index increased with increase in magnetic field strength and the distance from the target.

(2) The orientation of zinc was not clearly detected under a magnetic field of 5 T, because zinc has a smaller absolute value of magnetic susceptibility than bismuth.

(3) A magnetization energy difference over 100 J/m$^3$ is required to reveal the crystal orientation in vapor-deposition processes. The crystal orientation due to a magnetic field be-

![Fig. 16 The concept of the crystal rotation due to a magnetic field ($\tau = M \times B$).](image)

comes tangible when the magnetization energy stored in a particle exceeds the thermal energy.

(4) A particle, to which evaporated molecules agglomerate, rotates to a favorable direction in the magnetic field during flying from the target to the substrate and then adheres to the substrate.

(5) The rotation mechanism of a particle stems from the magnetization torque force which is induced by the interaction of an applied magnetic field and the magnetization induced in the particle.

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