Epitaxial growth of superconducting MgB$_2$ thin films with a Mg buffer layer at 110 °C

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Abstract. Since the discovery of MgB$_2$, its application to superconducting electronics has been limited by the absence of proper microfabrication techniques. In this study, we grew crystalline MgB$_2$ thin films using molecular beam epitaxy at a low substrate temperature of 110 °C under ultra-high vacuum of about 10$^{-6}$ Pa. MgB$_2$ thin films were deposited with an epitaxial Mg buffer layer on c-plane 4H-SiC or sapphire substrates. In spite of the low growth temperature, superior crystallinity and surface flatness were confirmed by in situ reflection high-energy electron diffraction and X-ray diffraction measurements. Moreover, we successfully confirmed the occurrence of a sharp superconducting transition at 27 K.

1. Introduction

MgB$_2$ has been expected to apply to various superconducting devices because of its remarkably high superconducting critical temperature $T_c = 39\, \text{K}$[1], small penetration depth $\lambda \simeq 40\, \text{nm}$[2] and extremely short electron-phonon scattering time $\tau_{e-ph} \simeq 3\, \text{ps}$[3]. Superconducting devices made of MgB$_2$ thin films have been limited by the absence of convenient nanofabrication processes partly due to higher growing temperature of high quality MgB$_2$ thin films. Several research groups have developed techniques for the growth of high quality MgB$_2$ film, such as the two step method[4], hybrid physical chemical vapor deposition[5] and sputtering[6]. To fabricate a superconducting thin film, these methods require elevated substrate temperatures at above 700 °C during the deposition or a post-deposition annealing process at temperatures as high as 600 °C–800 °C. High temperature procedures are, however, not preferential for achieving a sharp interface between the superconducting MgB$_2$ and insulator layers in multilayer superconducting devices. Thus, techniques for as-grown synthesis based on low temperature processes have been developed based on the molecular beam epitaxy (MBE)[7, 8, 9, 10], sputtering[11], and co-evaporation[12]. Some studies have attempted to perform a low temperature growth using epitaxial buffer layers with good lattice matching such as AlN (1.9 %)[13], TiZr (3.6 %)[14], and
Ti (4.1 %)[15]. The in-plane axis of MgB$_2$ tends to align with that of the buffer layer, while the substrate temperature remains low during the entire process. In particular, among these bilayer films, MgB$_2$/Ti films, that showed a sharp superconducting transition at $T_c = 36$ K, were obtained by the growth at the lowest temperature of 200°C[15]. This temperature is higher than the applicability limit of the temperature for a standard organic resist. Nanostructures can be fabricated via a conventional lift-off process with an organic resist only at temperatures lower than 150°C. Therefore, a lift-off-like process using an inorganic material as a resist[16], Ar ion milling[17], and focused ion beam (FIB) milling[18] has been applied to the fabrication of MgB$_2$ nano-wire structures. However, the physical dry etching process often causes severe damage to the superconducting film.

We have developed the fabrication method of epitaxial MgB$_2$ thin films at a significantly low substrate temperature of 110°C by the MBE method[19]. In this study, we describe the fabrication of epitaxial MgB$_2$ thin films with epitaxial Mg buffer layer on 4H-SiC or sapphire substrates. We note that the substrate temperature was obtained by radiation heating from the Knudsen cells (K cells) in the chamber. Mg has a hexagonal crystal structure with the lattice constants $a = 3.2125$ Å and $c = 5.2132$ Å. The lattice mismatch between Mg and MgB$_2$ is thus 4.1 %, and is the largest compared with the mismatch values for AlN, TiZr, and Ti. Although good lattice matching is generally effective for promoting epitaxial growth, we note that the wetting at interfaces between the buffer layers and the MgB$_2$ layer is also important for achieving the epitaxial growth. One can expect good wetting at an interface between Mg and MgB$_2$ layers. An as-grown film showed a sharp superconducting transition at $T_c = 27$ K.

2. Experimental method

Thin films of MgB$_2$ were grown by the MBE method. The pressure during the growth process was about $2 \times 10^{-6}$ Pa. The elementary materials Mg and B were deposited by the K cells. The temperature of each K cell was stabilized at the set point within $\pm 0.1$ °C during deposition. This ensured the high stability of each deposition rate for the whole duration of the film deposition. The (001) surface of a 4H-SiC or sapphire was used as a substrate. The substrate temperature was determined to remain at 110°C within the accuracy of 5°C by the several irreversible thermo-labels placed on top surface of the substrate holder. It increased due to the radiation heating from the K cells while we did not use the substrate heater for intentional heating. The deposition rate was monitored by a quartz oscillating monitor located below the substrate. We evaluated a deposition rate by monitoring a resonant frequency change at intervals of 1 minute to recover a very low rate. We found that the deposition rate thus obtained was well stabilized within $\pm 0.014$ Å/min with respect to the deposition rate of 0.7 Å/min. The Mg buffer layer was deposited at the typical deposition rate of 3 Å/min to form a 20 to 30-nm-thick film. After the deposition of the Mg buffer layer, the MgB$_2$ layer was deposited by the co-evaporation of Mg and B. The deposition-rate ratio between Mg and B was 1:2, which is the same as the MgB$_2$ stoichiometric ratio. This is in marked contrast with the preceding reports on MgB$_2$ films, where excess Mg was supposed to be necessary to grow MgB$_2$ films. The typical deposition rate and film thickness of the MgB$_2$ layer were 0.7 Å/min and 60 to 100 nm, respectively. Surface flatness and crystallinity during the deposition were monitored by the reflection high energy electron diffraction (RHEED). The structure of the films was investigated using the X-ray diffraction (XRD) method and the surface flatness of the films was measured using an atomic-force microscope (AFM). The resistivity measurements were performed using the conventional four-probe method.

3. Result and discussion

Figures 1 (a) and (c) show the RHEED patterns for Mg layer on the 4H-SiC and sapphire substrates with the layer thickness of 30 and 22 nm, respectively. The Mg RHEED image shows
Figure 1. RHEED images for (a) Mg and (b) MgB$_2$ on a 4H-SiC substrate and (c) Mg and (d) MgB$_2$ on a sapphire substrate.

A sharp streak pattern, indicating epitaxial growth with good crystallinity and atomic-scale surface flatness of Mg thin films. On the other hand, RHEED images of the MgB$_2$ with the layer thickness of 100(62) nm on the 4H-SiC(sapphire) substrate are spot-like, implying relatively rough surface (see Figs. 1 (b) and (d)). With the rotation of the incident direction of the electron beam, both patterns changed, ensuring an inplane alignment of Mg and MgB$_2$ thin films.

The presence of a relatively rough MgB$_2$ film surface detected by RHEED was directly confirmed by examining the AFM image of MgB$_2$ films shown in Figs. 2 (a) and (b) on the 4H-SiC and sapphire substrates, respectively. While some protuberances are seen in the images, we estimate the average surface roughnesses to be 3.4 nm and 2.1 nm on the 4H-SiC and sapphire substrates, respectively. Although the origin of these protuberances is not fully understood as of now, it is possible that excess Mg, B, and MgO may have given rise to such protuberances.

Figures 3 (a) and (b) show the interplane XRD pattern for the MgB$_2$/Mg bilayer films grown on the (001) surface of the 4H-SiC and sapphire substrate, respectively. As shown in Figs. 3 (a) and (b), (001) and (002) peaks of MgB$_2$ and (002) and (004) peaks of Mg are observed. This is clear evidence of the successful growth of the MgB$_2$/Mg bilayer thin films. We also observed a contamination peak at around 44° marked by †: the origin of this peak has not been identified yet. Exclusive appearance of the (00l) peaks in MgB$_2$ and Mg revealed that the film has a distinct c-axis oriented structure. The XRD rocking-curve measurements performed for the (002) MgB$_2$ peak and for the (002) Mg peak of MgB$_2$/Mg/sapphire are shown in Figs. 3 (c) and (d), respectively. The 0.55° full width at half maximum (FWHM) of the (002) Mg peak is much smaller than the 1.91° FWHM of the (002) MgB$_2$ peak. This corresponds to the fact that

Figure 2. Atomic force microscope image for MgB$_2$ on a (a) 4H-SiC and (b) sapphire substrate.
Figure 3. Interplane X-ray diffraction pattern for MgB$_2$ on a (a) 4H-SiC and (b) sapphire substrate. Substrate peaks are shown by *. Impurity peak appears at 44°, as shown by †. Rocking curves for (c) MgB$_2$ (002) peak and (d) Mg (002) peak on a sapphire substrate.

The RHEED pattern of Mg is noticeably sharper than that of MgB$_2$, as shown in Fig. 1 (c) and (d). We note that almost the same rocking-curves are obtained in MgB$_2$/Mg/4H-SiC, as 0.25° FWHM of the (004) Mg peak and 1.54° FWHM of the (002) MgB$_2$ peak, respectively[19].

Figure 4. In-plane X-ray diffraction pattern for MgB$_2$ on a (a) 4H-SiC and (b) sapphire substrate. $\phi$-scan of the MgB$_2$ (c) (103) peak on a 4H-SiC substrate and (d) (1T0) peak on a sapphire substrate.
Figure 5. Reciprocal lattice mapping around the MgB$_2$ (103) peak for a MgB$_2$/Mg/4H-SiC.

The grazing-incidence XRD profile for a MgB$_2$/Mg/4H-SiC and MgB$_2$/Mg/sapphire films are shown in Figs.4 (a) and (b), respectively. The (200)((1T0)) MgB$_2$ peak and the (100)((300)) peak of the 4H-SiC(sapphire) substrate are observed, indicating that MgB$_2$ grains were grown with the MgB$_2$[100]||4H-SiC[100]|MgB$_2$[100]|sapphire[1T0]). Observation of the finite (1T0) ((100)) MgB$_2$ peak in MgB$_2$/Mg/4H-SiC (MgB$_2$/Mg/sapphire) films indicates the existence of unoriented grains. We also determined the degree of epitaxy for Mg buffer layer by employing Mg[100]|4H-SiC[100] and Mg[100]|sapphire[1T0] in the grazing-incidence XRD measurements. Figures 4 (c) and (d) show the $\phi$-scan pattern of the (103) and (1T0) MgB$_2$ peak for MgB$_2$/Mg/4H-SiC and MgB$_2$/Mg/sapphire films, respectively. Clear six-fold peaks are observed, consistent with the six-fold symmetry of MgB$_2$. Based on the RHEED and XRD patterns, we conclude that we have successfully obtained partially epitaxial MgB$_2$ films, while some of the grains are randomly oriented for the in-plane axis.

Figure 6. Temperature dependence of the electrical resistance for MgB$_2$ on a (a) 4H-SiC and of the electrical resistivity for MgB$_2$ on a (b) sapphire substrate.
Figure 5 shows the X-ray reciprocal lattice mapping for MgB$_2$/Mg/4H-SiC. The (103) MgB$_2$ peak is clearly observed; using the peak position, we determined the MgB$_2$ lattice constants as $a = 3.075$ Å and $c = 3.576$ Å. These results are accurate within 0.4% and 1.5% for the bulk $a$ and $c$ values, respectively, thus showing a fairly good agreement with the bulk values. The 0.98° FWHM of the (103) MgB$_2$ peak in the rocking curve was comparable with that of the (002) peak. The average coherent domain size $D$ is estimated as 57 nm by applying the Debye-Scherrer formula $D = \frac{0.9\lambda}{\beta \cos \theta}$, where $\lambda$ is the X-ray wave length, $\beta$ is a FWHM for a diffraction peak in the $\theta$ scan.

Temperature dependence of the electrical resistance $R$ for MgB$_2$/Mg/4H-SiC and of the electrical resistivity $\rho$ for MgB$_2$/Mg/sapphire are shown in Figs. 6 (a) and (b), respectively. Below room temperature, $R$ increases with decreasing temperature because of the influence of a semiconducting resistance by 4H-SiC substrate. As shown in the inset of Fig. 6 (b), $\rho$ decreases with decreasing temperature as expected in a normal metal in MgB$_2$/Mg/sapphire because sapphire is a good insulator in contrast with semiconducting 4H-SiC. Superconductivity appears below $T_c = 27.2$ K(26.9 K), with a relatively narrow superconducting transition width $\Delta T_c = 0.9$ K(0.5 K) for MgB$_2$/Mg/4H-SiC(MgB$_2$/Mg/sapphire).

It is well-known that annealing drastically improves $T_c$ in MgB$_2$. Shibata et al. indicated that the film surface of MgB$_2$ is deteriorated in air[18]. Therefore, the lower $T_c$ values of our as-grown MgB$_2$ thin films relative to that of the bulk samples are due to the absence of post-deposition-annealing and to surface oxidization.

4. Summary
We have grown superconducting MgB$_2$ thin films with a buffer layer of epitaxial Mg on the (001) 4H-SiC or sapphire substrate surface. We have successfully grew MgB$_2$ thin films with the substrate temperature lower than 110° C. To the best of our knowledge, this is the lowest deposition temperature for a partial epitaxial growth of MgB$_2$ thin films. $T_c$ values of the present thin films are comparable to the previously reported results; the observed suppression of thin film $T_c$ is known to be related to the increased substrate temperature. The presence of the Mg buffer layer is crucial for reducing the epitaxial temperature. MgB$_2$ thin films with relatively good crystallinity and superconducting properties were obtained. We believe that this offers a new process for fabricating nanostructured MgB$_2$ films with the aid of an organic-based lift-off resist. Our new MgB$_2$ thin film growth process is promising for the development of a convenient nano-fabrication technique for MgB$_2$ thin films based on a standard lift-off process with a commercial organic resist. We think that our innovative method will have a strong impact on the expansion of utilizing the MgB$_2$ materials in future.

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