High-quality Superconducting MgB$_2$ Thin Film Preparation on Plastic Substrates

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Abstract. We have synthesized as-grown superconducting MgB$_2$ thin films on polyimide film substrates, making use of a low substrate temperature growth of MgB$_2$ thin films, and found that $T_c$'s above 30 K were obtained on polyimide films, like on Al$_2$O$_3$-C substrates. For high-quality MgB$_2$ thin film fabrication on substrates completely out of lattice-matching with MgB$_2$ lattice, we have examined Ti/Ag double-layered buffers on glass substrates, and clarified that a double-layered buffer composed of Ag bottom layer 50 nm thick and Ti upper layer 50 nm thick prepared at an ambient temperature is effective for this purpose.

1. Introduction

MgB$_2$, having the highest critical temperature of 39 K [1] of all intermetallic compound superconductors, is a candidate for applications of superconductivity at operating temperatures above 20 K. For superconducting device applications, the preparation of high-quality MgB$_2$ thin films is important. To date, as-grown superconducting MgB$_2$ film preparation methods have been categorized into two groups; one is a low temperature process [2], [3] and the other a high temperature process [4], [5]. The low temperature process is characterized by substrate temperatures below 300ºC and $T_c$'s of about 30–35 K. Though the $T_c$'s of the films synthesized by this process is lower than those by the high temperature process, the low temperature process is suitable for the fabrication of multilayer devices because an abrupt interface between adjacent layers can be obtained. Furthermore, there is another possibility due to low substrate temperatures, that is, low substrate temperatures enable us to use heat-resistant plastic substrates (such as polyimide) as a substrate. MgB$_2$ thin film synthesis on plastic substrates provides us with additional applications such as flexible superconducting films.

In this paper, we will report a preparation method and superconducting properties of MgB$_2$ thin films on polyimide films, glass and Ti/Ag-buffered glass substrates. Here “Ti/Ag” means a double layer composed of Ti layer on Ag bottom layer. A Ti/Ag double-layered buffer was used to make high quality MgB$_2$ thin films grow on substrates completely out of lattice-matching with MgB$_2$ lattice. The reason that we use the buffer is the following. We have found MgB$_2$ thin films grown on the lattice-near-matched buffer-layer have high crystallinity and good superconducting properties [6]. Usually the growth direction of Ag deposited on any substrates is [111] orientation [7], and the growth direction of
Ti deposited on Ag (111) plane is expected to be c axis orientation because lattice mismatch between Ag (111) plane and Ti (001) plane is only 2.1%. Consequently, MgB₂ films may grow with good crystallinity on Ti (001) plane, which is the lattice-near-matched plane for MgB₂ (001) plane.

2. Experimental
In this experiment, we used a commercial polyimide film with 25 μm in thickness (UPILEX® 25S, Ube Industries, Ltd.). MgB₂ thin films were deposited in the substrate temperature (Tₛ) range from 200˚C to 300˚C by coevaporation of Mg and B, which were evaporated using an effusion cell and electron beam gun, respectively. The deposition rates of Mg and B were 1.2~1.8 nm/s and 0.3~0.36 nm/s, respectively. The background pressure of the deposition chamber was 2×10⁻⁷ Torr, and increased to about 2.0×10⁻⁶ Torr during deposition. The bottom Ag buffer-layer was deposited by the effusion cell and the upper Ti buffer-layer by an electron beam gun. The deposition rates of Ag and Ti for Ti/Ag buffers were both 0.1 nm/s. After the fabrication of the double buffer-layer, MgB₂ was prepared consecutively in the same vacuum process.

Tₜ measurements were performed using a standard four-probe method. Crystallinity of thin films was examined by X-ray diffraction (XRD). Thin film surface morphology was observed using a high-resolution scanning electron microscope (SEM).

3. Results and discussion
Figure 1 shows the temperature dependence of resistivity of MgB₂ films 300 nm in thickness deposited on polyimide films at substrate temperatures ranging from 225˚C to 275˚C. These Tₛ values were measured by a thermocouple which is equipped with the substrate holder. In our previous study, the optimum Tₛ of MgB₂ thin films grown on Al₂O₃-C substrate was 270˚C [6]. On the other hand, for MgB₂ films grown on polyimide films at Tₛ of 270˚C, their Tₛ's became lower and resistivities higher than those of the films on Al₂O₃-C. This fact is believed to be caused by a difference in the actual surface temperature between the polyimide film and Al₂O₃-C substrate, and this difference results from the radiation absorption characteristic and thermal conductivity of substrate materials and substrate thickness, where the thickness of Al₂O₃-C substrates is 0.5 mm. The optimum Tₛ for polyimide film substrates is 235˚C, and MgB₂ thin films with T_c² at 30 K were obtained under this substrate temperature, as is shown in Fig. 2. Figure 3 shows the temperature dependence of resistivity of MgB₂ films of 300 nm and 100 nm in thickness. T_c² of 300 nm-thick MgB₂ film is 30.9 K, whereas that of 100 nm-thick MgB₂ film 28.0 K. We consider the decrease in T_c is caused by small grain size and poor crystallinity in grains of the initially deposited 100 nm-thick MgB₂ layer. The results of XRD measurements, shown in Fig. 4, support the above-mentioned results. In the XRD result, any diffraction peaks from MgB₂ phase are not observed in 100 nm-thick films.

Figure 5 shows XRD patterns of MgB₂ films grown on glass and Ti/Ag-buffered glass substrates. We prepared buffer-layers of different thickness combinations of Ti/Ag, that is, 100 nm/50 nm at Tₛ of 200˚C and 50 nm/50 nm at Tₛ of an ambient temperature. Here we designate MgB₂ films on glass

![Fig. 1. Temperature dependences of resistivity of MgB₂ thin films on polyimide films.](image1)

![Fig. 2. Temperature dependence of resistivity of the optimized MgB₂ film/polyimide film.](image2)
(standard sample), Ti(100 nm)/Ag(50 nm)/glass and Ti(50 nm)/Ag(50 nm)/glass as samples A, B and C, respectively. The diffraction pattern of sample B indicates the existence of MgB₂, AgMg and Ti phases, whereas in sample C, diffraction peaks from MgB₂, Ag and Mg phases are identified and AgMg phase is not detected at all. The formation of AgMg is a feature of sample B, and is considered to originate from inadequate covering of Ti layer on Ag bottom layer, that is, Ti island growth, which causes a reaction between Ag layer and evaporated Mg atoms. Another feature in sample B is that (002) MgB₂ diffraction peak becomes sharp in comparison with those of other samples, which may result from an enhanced MgB₂ crystal growth by a heat of formation of AgMg compound. Sample C is characterized by existences of a trace of Mg single phase, suggesting that the $T_s$ for MgB₂ growth of sample C is slightly lower than the optimum $T_s$, and noticeably grown Ag single phase. The latter fact means that a covering of Ti layer on Ag bottom layer is complete. For estimating the degree of preferred orientation of Ag layer in sample C, we employed the following equation: $\alpha = \frac{I_{Ag(111)} + I_{Ag(200)} + I_{Ag(200)} + I_{Ag(311)}}{I_{Ag(111)} + I_{Ag(200)} + I_{Ag(220)} + I_{Ag(311)}}$, where $I_{Ag(111)}$, $I_{Ag(200)}$, $I_{Ag(220)}$ and $I_{Ag(311)}$ are the integrated intensities from Ag(111), Ag(200), Ag(220) and Ag(311) diffraction peaks, respectively. Here, the $\alpha$ value is 1/4 when the growth direction is perfectly random, and is 1 when the perfect (111) preferred orientation is realized. Since the estimated $\alpha$ for sample C is 0.75, the preferential growth in [111] direction is achieved in Ag layer of sample C. The (002) MgB₂ diffraction peak of sample C becomes clearer than that of sample A, indicating that the Ti/Ag buffer layer is effective for the synthesis of high-quality MgB₂ thin films on completely out-of-lattice-matching substrates.

Figure 6 shows SEM photographs of the surface views of Ag layers with a nominal thickness of 50 nm deposited on glass substrates, where (a) is sample B ($T_s$: 200°C) and (b) sample C ($T_s$: an ambient temperature). In Fig. 6 (a), Ag layer shows a strong island growth nature, indicating the height of individual islands is much larger than the nominal thickness of 50 nm, which promotes poor covering of the upper Ti layer over the bottom Ag layer. In Fig. 6 (b), a smooth surface of Ag layer can be seen,
due to an ambient temperature deposition. Consequently, the upper Ti layer of 50 nm in thickness can cover the bottom Ag layer entirely, and the result is consistent with the XRD result.

Figure 7 shows the temperature dependence of resistivity of sample A and resistance of samples B and C. Here we have not yet measured the resistivities of Ti/Ag buffer layers independently, the results on samples B and C are shown in resistance. For sample C, the $T_c$ is equivalent in that of sample A, whereas, for sample B, the $T_c$ shows a double-transition. In sample B, therefore, there exist two phases which relate to superconductivity. The one is the same phase as those in samples A and C with a $T_c$ above 30 K, and the other is a low $T_c$ phase. Though the reason of the formation of the low $T_c$ phase is not clear at present, we presume the following origin. In sample B, an unnegligible amount of Mg reacts with Ag, and Mg-deficient MgB$_2$ phase may form in the film. We consider that the coexistence of this nonstoichiometric MgB$_2$ phase will provide double-transition behavior.

4. Summary

In the present work, we have synthesized as-grown superconducting MgB$_2$ thin films on polyimide film substrates, making use of a low substrate temperature growth of MgB$_2$ thin films, and found that $T_c$'s above 30 K is obtained on polyimide films, like on Al$_2$O$_3$-C substrates. For high-quality MgB$_2$ thin film fabrication on substrates completely out of lattice-matching with MgB$_2$ lattice, we have examined Ti/Ag double-layered buffers on glass substrates, and clarified that a double-layered buffer composed of Ag bottom layer 50 nm thick and Ti upper layer 50 nm thick prepared at an ambient temperature is effective for this purpose. It is successively necessary for us to demonstrate that this Ti/Ag double-layered buffer is also effective for plastic film substrates.

5. Acknowledgment

The authors express their thanks to M. Asahi and Y. Ohki of NTT Advance Technology, Inc. for their surface observation using high-resolution SEM technique.

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