Interfacial structure of epitaxial MgB$_2$ thin films grown on (0001) sapphire

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The recent discovery of superconductivity above 39 K in intermetallic MgB$_2$ has re-sparked interest in nonoxide superconductors from both the fundamental and technical perspectives.$^{1,2}$ Among the prominent properties of MgB$_2$, are the record-breaking transition temperature ($T_c$) in metallic superconductors and the ability to carry strongly linked current flow.$^{3-5}$ Growth of single crystal is of particular importance in probing the fundamental properties of MgB$_2$, such as the superconducting mechanism and the anisotropy in properties. Unfortunately, a peritectic decomposition of MgB$_2$ thin films were characterized by transmission electron microscopy. It was found that the MgB$_2$ films grow epitaxially on the substrate with an orientation relationship with respect to the substrate as: (0001)MgB$_2$||(0001)Al$_2$O$_3$ and [1120]MgB$_2$|[1010]Al$_2$O$_3$. At the film/substrate interface, both MgO and MgAl$_2$O$_4$ phases were observed, which also grow epitaxially on the (0001) Al$_2$O$_3$ substrate. The formation of these intermediate phases is ascribed to the existence of oxygen during the annealing. © 2002 American Institute of Physics. [DOI: 10.1063/1.1489101]

The chemical composition of the film was studied by energy dispersive spectroscopy (EDS) and electron energy-loss spectroscopy (EELS) using a field emission gun analytical electron microscope JEOL-2010F. High-resolution transmission electron microscopy (HRTEM) image simulations were performed using the EMS software.

A well lattice-matched substrate is critical to ensure an epitaxial growth. MgB$_2$ has a hexagonal structure with space group $P6/mmm$ (No. 191) and lattice constants of $a=3.086$ and $c=3.524$ Å at room temperature.$^{19}$ Al$_2$O$_3$ possesses a hexagonal structure with space group $R-3C$ (No. 167) and lattice constants of $a=4.758$ and $c=12.991$ Å at room temperature.$^{19}$ One can see that the basal plane of MgB$_2$ and Al$_2$O$_3$ possess the same six-fold symmetry and an identical atomic configuration. While an $a$-to-$a$ alignment between MgB$_2$ and Al$_2$O$_3$ results in $\sim23\%$ lattice mismatch, being unfavorable for the epitaxial growth, a $30^\circ$ angular off the $a$-to-$a$ alignment, namely [1120]MgB$_2$|[1010]Al$_2$O$_3$, provides a small lattice mismatched ($\sim11\%$) alignment to possibly allow an epitaxial growth.

Low-magnification TEM and electron diffraction studies were performed to examine the overall microstructure as well as to establish the epitaxial orientation relationships. Figure 1(a) is a low-magnification cross-sectional TEM image showing a portion of the film. The film has an average thickness of 400 nm, with a peak-to-valley surface roughness of approximately 80 nm. Figures 1(b) and 1(c) are selected-area electron diffraction patterns recorded from the film and the substrate, respectively. The patterns were recognized as the [1120] zone axis diffraction pattern of hexagonal MgB$_2$ and the [1010] zone axis diffraction pattern of Al$_2$O$_3$. These studies indicated that a MgB$_2$ thin film grows on the (0001) Al$_2$O$_3$ substrate, with epitaxial orientation relationships of (0001)MgB$_2$||(0001)Al$_2$O$_3$ and [1120]MgB$_2$|[1010]Al$_2$O$_3$, respectively. Note that there is indeed a $30^\circ$ angular off the $a$-to-$a$ alignment between the basal plane of MgB$_2$ and the Al$_2$O$_3$ substrate. Additionally, two thin layers in the vicinity of the film-substrate interface show noticeably different contrast features from the film, indicating the formation of interfacial microstructures.

To understand the orientation relationship between the
MgB$_2$ film and the (0001) Al$_2$O$_3$ substrate, which is important for understanding the growth mechanisms and the physical properties of the film, the interfacial structure was studied using HRTEM technique combined with computer image analysis. Figure 2(a) shows an HRTEM micrograph taken from the film/substrate interface with the incident electron beam aligned along the $[10\overline{1}0]$ zone axis of Al$_2$O$_3$. Four layers with distinct structural characteristics are seen. The top layer was determined to be MgB$_2$, oriented with its $[11\overline{2}0]$ axis parallel to the $[10\overline{1}0]$ direction of Al$_2$O$_3$. This study confirmed the orientation relationship between MgB$_2$ and Al$_2$O$_3$, revealed by selected area electron diffractions. Between the MgB$_2$ film and the substrate, two intermediate layers exist, which are unexpected for the overall epitaxial relationship between the film and substrate. Fourier transform studies and computer image simulations revealed that two intermediate layers correspond to the $(11\bar{1})$ oriented, epitaxial MgO (upper) and the MgAl$_2$O$_4$ (lower) phase. This conclusion is further confirmed by spatially resolved x-ray EDS and EELS. Detailed TEM studies showed that the intermediate layers (MgO and MgAl$_2$O$_4$) are continuous along the film/substrate interface, in which MgAl$_2$O$_4$ layer lies underneath the MgO layer. Both MgO and MgAl$_2$O$_4$ grow epitaxially on the Al$_2$O$_3$ substrate, with orientation relationship of

$$(0001)[11\overline{2}0]MgB_2\|([111][1\overline{1}0]MgO\|([11\overline{1}])$$

$$(1\overline{1}0)MgAl_2O_4\|([0001][1\overline{1}0]Al_2O_3).$$

The orientation relationships between MgO and Al$_2$O$_3$ established here are similar with those found in the MgO films grown on the (0001) Al$_2$O$_3$ substrate by molecular beam epitaxy, except that no twin variants were observed in the present MgO layer. In addition to the epitaxial MgO and MgAl$_2$O$_4$ layers, isolated secondary-phase inclusions were observed at the interface. The region marked by the dashed-line box in Fig. 2(a) shows a secondary phase inclusion adjacent to the MgO layer, which has different image characteristics from that of MgB$_2$. Chemical analysis by EDS and EELS, combined with structural analysis by Fourier-transform and HRTEM image simulations, reveals that this secondary phase has the MgB$_4$ structure. However, unlike the MgO and MgAl$_2$O$_4$ layers, MgB$_4$ layers are discontinuously distributed at the interface with very low population.

The formation of MgB$_2$ is believed to proceed through the diffusion of Mg vapor into the boron film, a process being analogous to that involved in the fabrication of MgB$_2$ wires. Given that vapor pressure of Mg is approximately 50 Torr at 850 °C, the MgB$_2$ phase would be thermodynamically stable according to the pressure-temperature-composition phase diagram calculated by Liu et al. This is confirmed by our TEM observations in the present work. The formation of the intermediate epitaxial MgO layer is likely to be the result of a reaction between oxygen and magnesium during the course of annealing, or in part through the reaction of MgB$_2$ with oxygen. In the latter case, excess boron would likely further react with MgB$_2$, resulting in a formation of MgB$_4$, which agrees with the observation of small

FIG. 1. (a) Low magnification cross-sectional bright-field TEM image of a MgB$_2$ film grown on the (0001) Al$_2$O$_3$ substrate. (b) and (c) selected-area diffraction pattern taken from the film and the substrate with the electron beam incident along the same direction.

FIG. 2. HRTEM image of the interface between MgB$_2$ film and the Al$_2$O$_3$ substrate along the [11\overline{2}0] zone axis of MgB$_2$. Interfacial microstructure consisting of MgO and MgAl$_2$O$_4$ epitaxial layers is seen. An isolated thin layer composed of MgB$_4$ is also seen at the interface as indicated by the dashed line box.

FIG. 3. (a) HRTEM image of the MgB$_2$–MgO interface with the imaging electron beam along the [11\overline{2}0] direction of MgB$_2$. The insert in the middle is a computer simulated image (thickness=3 nm and defocus=-50 nm) that optimally fits the experimental one. (b) An atomic structure of the interface deduced from the HRTEM and computer simulations.
MgB$_4$ inclusions adjacent to the MgO layer. However, the formation of epitaxial MgO prior to the growth of MgB$_2$ cannot yet be completely ruled out. More experiments are underway to clarify this issue. The epitaxial MgAl$_2$O$_4$ is thus not yet be completely ruled out. More experiments are under- way to clarify this issue. The epitaxial MgAl$_2$O$_4$ is thus the product of solid state reaction between MgO and Al$_2$O$_3$, which was predominantly observed in MgO–Al$_2$O$_3$ system annealed at high temperature. The formation of MgO phase at the interface between MgB$_2$ and Al$_2$O$_3$ substrate is energetically favorable due to the similarity of the oxygen sublattices in both MgO and Al$_2$O$_3$. Hence, the existence of oxygen plays a key role in developing the observed epitaxial MgO and MgAl$_2$O$_4$ at the interface. The oxygen may result from the quartz tube at high temperature and oxygen impurity in the sputtered B film.

Atomic structure of the MgB$_2$/MgO interface was examined by HRTEM combined with computer image simulations. Figure 3(a) is an HRTEM image of the MgB$_2$/MgO interface imaged with the electron beam incident along the [1120] direction of MgB$_2$. The interface is sharp and clean. Computer simulated image that optimally fits the experimental image is inserted in the middle. The accordingly resolved atomic structure of the interface is schematically shown in Fig. 3(b). MgO has a cubic structure with space group $Fm\bar{3}m$ (No. 225) and lattice constant $a = 4.220$ Å. The in-plane alignment of $[\bar{1}10]$ MgO with $[11\bar{2}0]$ MgB$_2$ results in a lattice mismatch of $-3.3\%$. Thus, misfit dislocations were observed at the interface, essentially due to the lattice mismatch in the observed in-plane orientation relationship between MgB$_2$ and MgO. Figure 4 is a HRTEM image of the MgO–MgB$_2$ interface containing one dislocation. The Burgers vector, determined by the Burgers circuit shown as black lines in the image, is $\frac{2}{3}[1\bar{1}00]$ of MgB$_2$, which is a characteristic of partial misfit dislocation.

In conclusion, the microstructure and interfacial atomic structure of epitaxial MgB$_2$ thin films grown on the (0001) Al$_2$O$_3$ substrate have been studied by high-resolution transmission electron microscopy and analytical electron microscopy. Epitaxial MgO and MgAl$_2$O$_4$ layers were found between the MgB$_2$ film and the Al$_2$O$_3$ substrate, due to the presence of oxygen in the annealing process. The orientation relationships between these phases were determined to be (0001)[1120]MgB$_2$/[111][110]MgO/ (111)[010]Al$_2$O$_3$. The 30° angular offset of the a-to-a alignment between the basal plane of MgB$_2$ and Al$_2$O$_3$ results in a small lattice mismatch between the MgB$_2$ thin film and the (0001) Al$_2$O$_3$ substrate.

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