A New Method for Preparing Superconducting MgB_2 Films from Diborane *

WANG Dian-Sheng(王殿生)[1,2], FU Xing-Hua(傅兴华)[1**], ZHANG Zheng-Ping(张正平)[1,3], YANG Jian(杨健)[1]

[1]*Department of Physics, Guizhou University, Guiyang 550025*
[2]*Department of Applied Physics, University of Petroleum (East China), Shandong 257061*
[3]*Department of Information and Electronics, Zhejiang University, Hangzhou 310027*

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We report on a new preparation method for magnesium diboride (MgB_2) films by chemical vapour deposition (CVD) from diborane (B_2H_6). It is a two-step ex situ approach, with the precursor boron films grown by CVD from B_2H_6 at 460°C, followed by a post-annealing process in magnesium (Mg) vapour at 830°C. The prepared MgB_2 thin films on Al_2O_3 polycrystalline substrates have an onset transition temperature of 35 K and a zero-resistance temperature of about 24 K. Well-crystallized MgB_2 grains have clearly been observed in the SEM images and confirmed by x-ray diffraction analysis. The advantages of the proposed method are the feasibility to prepare large-area superconducting films and the compatibility with semiconductor technology.

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The discovery of superconductivity with a remarkably high transition temperature of 39 K in binary metallic MgB_2[1] has attracted great interest in both fundamental physics and potential applications.[2–8]

Great efforts have been taken to prepare MgB_2 thin films[9–18] because the availability of the films is of great importance for electronic applications and physical studies. Different methods of MgB_2 film preparation, including pulsed-laser deposition (PLD),[9–12] co-evaporation,[13] deposition from suspension,[14] magnesium (Mg) diffusion,[15–18] and magnetron sputtering,[19] have previously been reported in the literature. Up to now, the Mg diffusion method has been proven to be the best method for the preparation of MgB_2 films, provided that the critical temperature T_c, crystallization and phase purity are taken into account.

In this Letter, we report on a new method based on chemical vapour deposition (CVD). Amorphous boron (B) films were first deposited on Al_2O_3 polycrystalline substrates by CVD using B_2H_6 (99.99%) as the source gas. The dimensions of the substrates were $25 \times 25 mm^2$ and 0.7 mm in thickness. The substrates were heated up to 460°C by a halide lamp heater for the thermal decomposition of B_2H_6. Before introduction into a deposition chamber, B_2H_6 was diluted into about 0.3 vol% with a mixed gas of 95% argon (99.999%) and 5% hydrogen (99.99%). Typically, 2 μm thick B films were formed with a deposition rate of ~10 Å/s, which is greater than that of the PLD method[17] or electron-beam evaporation.[18] Subsequently, the precursor B films together with Mg scraps (99.9%) were put into a tantalum (Ta) container and sealed in an Ar atmosphere, then annealed in a tube quartz furnace. In a typical heat-treatment procedure, the container was heated up to 830°C at a rate of 80°C/min, and held there for 1 h. Then it was quenched to room temperature at a rate of 40°C/min. Ar flow was maintained throughout the annealing process.

The resistance versus temperature curves of MgB_2 films on an Al_2O_3 polycrystalline substrate were measured by a standard four-probe method at a dc current of 100 μA. From the typical curve plotted in Fig. 1, the onset and zero-resistance transition temperatures are 35 K and 24 K, respectively. A rather gradual transition, with a width of about 6 K from 90% to 10% of the normal state resistance, is evident in the inset. This is greater than the reported values for high-quality bulk[4] and film[17] samples.

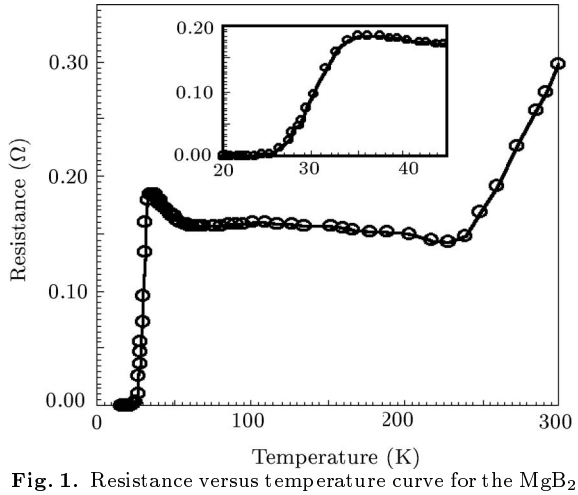

Fig. 1. Resistance versus temperature curve for the MgB_2 film on an Al_2O_3 polycrystalline substrate. The inset shows a magnified view near the transition region.

The residual resistance ratio (RRR), $R_{RR} = R(300\,K)/R(40\,K)$, of about 1.7 is comparable to the values of the films grown on single-crystal $SrTiO_3$ substrates by PLD in an *ex situ* annealing procedure.[10] However, compared to the films also grown on single-crystal $SrTiO_3$ substrates by PLD in an *in situ* annealing process, where $R_{RR} = 18$,[11] the RRR values

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** Author to whom any correspondence should be addressed.
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of our films are much smaller. The reason for the large difference among the RRR values associated with the preparation method is still being debated.[10] Besides, we attribute the non-monotonic temperature dependences of the resistance in Fig. 1 to the multiple crystalline phases. The x-ray diffraction (XRD) patterns are shown in Fig. 3.

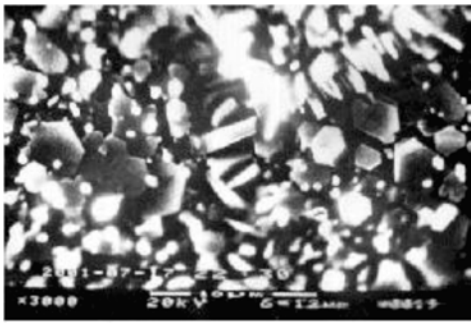

Fig. 2. SEM image of surface morphologies for the MgB_2 film on an Al_2O_3 polycrystalline substrate.

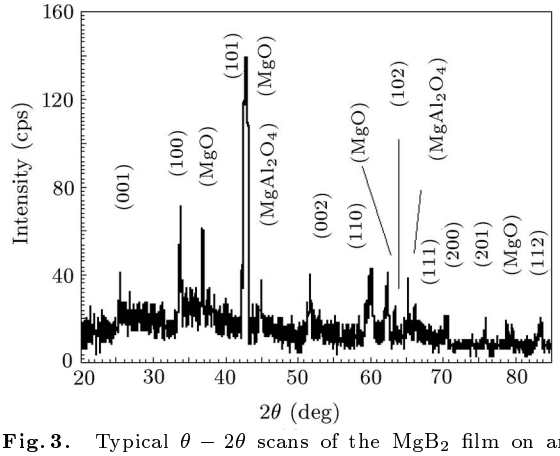

Fig. 3. Typical $\theta - 2\theta$ scans of the MgB_2 film on an Al_2O_3 polycrystalline substrate. The diffraction peaks are indexed to MgB_2, and the substrate peaks have been subtracted.

The surface morphologies and grain sizes of the prepared MgB_2 films were examined using a scanning electron microscope (SEM). As shown in Fig. 2, well-defined large hexagonal grains with dimensions of about 2μm can be clearly observed in the film. From the SEM image, the MgB_2 grains in the film seem to grow independently of each other, indicating that the nucleation of these grains is likely to occur at the film surface.[10]

Typical $\theta - 2\theta$ scans of the prepared films are presented in Fig. 3, confirming that polycrystalline MgB_2 films have been grown on the Al_2O_3 polycrystalline substrates. In addition to the MgB_2 phase, MgO and $MgAl_2O_4$ phases have also been detected in the film. The existence of MgO and $MgAl_2O_4$ impurities is the most plausible reason for the larger transition width shown in the inset of Fig. 1. The $MgAl_2O_4$ phase may result from the reaction of MgO with Al_2O_3. This may imply that the Al_2O_3 polycrystalline substrates are not chemically highly stable during the heat treatment at high temperatures.

In summary, we have successfully prepared superconducting MgB_2 films on Al_2O_3 polycrystalline substrates using precursor B films deposited by CVD from B_2H_6, followed by a post-annealing process in Mg vapour at high temperature. The fabricated MgB_2 films have an onset transition temperature of 35 K and a zero-resistance temperature of 24 K. The surface morphology of the films shows well-defined MgB_2 crystallines with a grain size of about 2 μm. XRD patterns indicate that the MgB_2 films are polycrystalline with MgO and $MgAl_2O_4$ phases. The formation of $MgAl_2O_4$ is most likely due to the chemical instability of Al_2O_3 polycrystalline substrates at high temperature and the existence of the MgO impurities. Our results suggest that high-quality superconducting MgB_2 films can be prepared by the present approach on single-crystal or polycrystalline substrates, such as Al_2O_3, MgO and $SrTiO_3$, by further optimizing the deposition conditions and the post-annealing procedure. The new method of preparing superconducting MgB_2 films by CVD from B_2H_6 is compatible with the present semiconductor technology, and has a few advantages for potential device applications.

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