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MgB_2 films prepared by rapid annealing method

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ABSTRACT

The experiment for preparing MgB_2 thin films by electron beam (e-beam) annealing of Mg–B multilayer is reported. The annealing process lasts less than 1 s, which effectively suppresses the volatility of Mg as well as the reaction of Mg and oxygen. The influence of annealing parameters on the film quality including exposure time, accelerating voltage and beam current is investigated. It is found that e-beam with lower accelerating voltage can acquire MgB_2 film with smaller annealing energy density. Also, double e-beam scan annealing process helps to obtain more uniform MgB_2 thin films than the single scan. This rapid annealing method synthesizes MgB_2 thin films with critical temperature T_c of 35 K and critical current density J_c at 15 K of 7.6×10^6 A cm^{-2}.

1. Introduction

The discovery of superconductivity in magnesium diboride at 39 K [1] has attracted a great deal of interest in preparing MgB_2 thin films for electronics applications [2–5], due to its relatively high transition temperature, long coherence length [6], large energy gap [7] and simple chemical structure. There are a series of difficulties in the MgB_2 thin film fabrication including the volatility of Mg, phase stability of MgB_2 and the reactivity of Mg and oxygen. In the last decade, much effort has been devoted to depositing MgB_2 thin films. As a result, several techniques have been developed for producing high quality MgB_2 thin films. The earliest successful technique is annealing B or Mg–B precursor film in high Mg vapor at high temperature [8–12]. With this method Kang et al. obtained MgB_2 thin film with T_c of 39 K [8]. Then some *in situ* annealing methods [13] as well as *in situ* one-step methods [14–16] have been explored for the synthesis of MgB_2 films. Specially, hybrid physical–chemical vapor deposition (HPCVD) method obtains *c*-axis oriented epitaxial MgB_2 thin film with $T_c \sim 40$ K and residual resistivity $\rho_0 \sim 0.1$ μΩ cm [15].

Recently, we have explored a rapid annealing of Mg–B precursor method to prepare MgB_2 thin films [17]. This method provides us medium qualities MgB_2 thin films. Although the film property is not as good as that from HPCVD method, this method avoids the toxic gas of diborane and the production process will be safer. In this approach, e-beam is introduced to complete a very quick heating process. The total annealing duration lasts less than 1 s. The volatility of Mg, the reaction of Mg and O_2 can be considerably suppressed due to the short annealing time. As a result, a no extra Mg vapor and Ar gas protected annealing process is achieved. Large area MgB_2 films and tapes can be also expected by adjusting e-beam scan lines on various precursor films. In this paper, we make a systematic study on different annealing conditions of the rapid electron beam annealing method.

2. Experimental details

Mg–B multilayer was deposited at room temperature on 6H–SiC (001) substrate using e-beam evaporation. The chamber was evacuated to a base pressure of 5.0×10^{-6} Pa. Commercial magnesium (99.5%) and boron (99.5%) was used as the evaporation source. The precursors had the construction of $[B(10\ nm)/Mg(15\ nm)]_{N=4}$/SiC. The thickness ratio, Mg:B = 3:2, satisfy the atomic ratio of Mg:B = 2:1 expected from their specific densities. The total thickness of Mg–B multilayer was 100 nm. Since the precursor was obtained, experiments were followed by e-beam annealing. Samples were moved to EBW-6 e-beam welder with base vacuum of 5.0×10^{-3} Pa. Then e-beam was introduced scanning the samples (Fig. 1). The multilayer films were heated to the sintering temperature instantaneously, when Mg and B rapidly reacted to form MgB_2 films. The reaction time was limited to less than 1 s. In the annealing process, partial Mg in precursor vaporized and formed a fairly high Mg vapor locally around the samples, making MgB_2 thermodynamically stable [18]. As soon as the e-beam stopped, the heat quickly spreads from MgB_2 thin film to the substrate. The temperature of MgB_2 thin film dropped to the room

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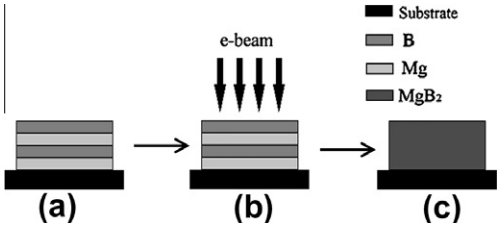

Fig. 1. The electron beam annealing process. (a) Precursor, (b) e-beam annealing, and (c) MgB_2 thin film.

temperature rapidly and the annealing process finished. In this paper, different annealing conditions were attempted. The exact annealing parameters were presented in Table 1.

The film crystallinity was investigated by X-ray diffraction (XRD, D-MAX-RA-12KW). Film surface morphology was measured by scanning electron microscope (SEM, Nova Nano SEM 430) and atomic force microscope (AFM, Veeco). The superconducting and transport properties of MgB_2 film was characterized by standard four-point method and Quantum Design magnetic property measurement system (MPMS).

3. Result and discussion

Using the method mentioned above, MgB_2 thin films were prepared in three series (Table 1). In series 1, different dwell time with the fixed accelerating voltage of 24 kV and e-beam current of 12.3 mA was chosen (Fig. 2). A sample with magnetic $T_{c(onset)}$ of 34.2 K is obtained with the annealing time as short as 0.35 s. It indicates that Mg and B have a very fast reaction rate, which provides the foundation of rapid annealing method to prepare MgB_2 thin film. The magnetic $T_{c(onset)}$s and magnetization value at 5 K tends to increase with the annealing time up to 0.44 s and decrease with the time above 0.44 s. Films with annealing time of 0.37–0.47 s show a consistent $T_{c(onset)}$ of 35–36.1 K. When the e-beam radiation time increases to 0.56 s, the $T_{c(onset)}$ sharply drops bellow 5 K and the films are basically non-superconducting. It indicates a crucial decomposition reaction at 0.47–0.56 s. We attribute this phenomenon to the gradually elevation of the substrate temperature. In the annealing process, high energy electrons collide with the sample. The kinetic energy continually transforms to the thermal energy at the sample surface. Film temperature increases gradually during annealing time. In the longer annealing time of 0.47–0.56 s, the sample temperature has reached the decomposition temperature of MgB_2 phase under our annealing conditions.

Table 1
The comparison of reaction conditions of the three series sample.

Series 1. Accelerating voltage: 24 kV; current: 12.3 mA		
Sample number	Dwell time (s)	Energy density (J/cm^2)
1	0.36	68.9
2	0.37	71.4
3	0.44	84.4
4	0.47	89.5
5	0.56	107.1
Series 2. Accelerating voltage: 32 kV; dwell time: 0.37 s		
Sample number	Current (mA)	Energy density (J/cm^2)
6	9.9	75.5
7	10.7	81.6
8	12.8	97.6
9	13.3	101.4
10	14	106.7
Series 3. Accelerating voltage: 32 kV; dwell time in single scan: 0.27 s		
Sample number	Current (mA)	Energy density (J/cm^2)
11	13.4	76.6
12	14.5	82.9
13	15	85.8
14	16	91.5
15	17	97.2

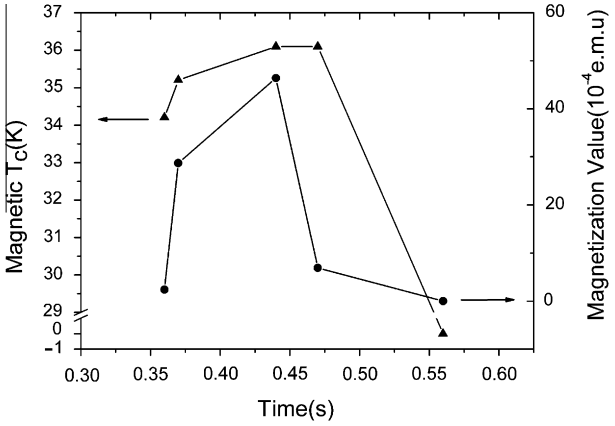

Fig. 2. Annealing time dependence of the magnetic T_c and magnetization value at 5 K of MgB_2 films.

Fig. 3 shows the XRD θ–2θ scans of series 1 (Table 1). Except those from the substrate and MgB_2 no other peaks appear in the XRD pattern. The unknown peaks appearing every 6° were confirmed from SiC substrate. It suggests a pure phase compared to the traditional post annealing film [13]. The obviously appearance of MgB_2 (002) peaks implies that the films contain significant amount of MgB_2 *c*-axis grains. However, the MgB_2 (002) peak is weaker than the epitaxial films [19,20] and MgB_2 (001) peak cannot be observed with the strong background noise. These demonstrate that the film is a *c*-axis orientation polycrystalline MgB_2 film. The strongest MgB_2 (002) peak is corresponding to the film annealing for 0.44 s. This trend is also accordance with the strongest magnetization signal at 5 K in Fig. 2.

Fig. 4a–c presents the morphology of sample 1, 3 and 4 in series 1 (Table 1), with annealing time of 0.36 s, 0.44 s and 0.47 s respectively. Sample 3 (Fig. 4b) has a well connected hexagonal crystallites and smooth surface. In samples 1 and 4, more cavities appear. The three samples represent the annealing process in three phases. In the beginning of the annealing process, Mg and B react and form MgB_2 grain (Fig. 4a). When prolong the annealing time, MgB_2 grains begin to join together. Compact films are obtained at the optimal annealing time of 0.44 s (Fig. 4b). After annealing

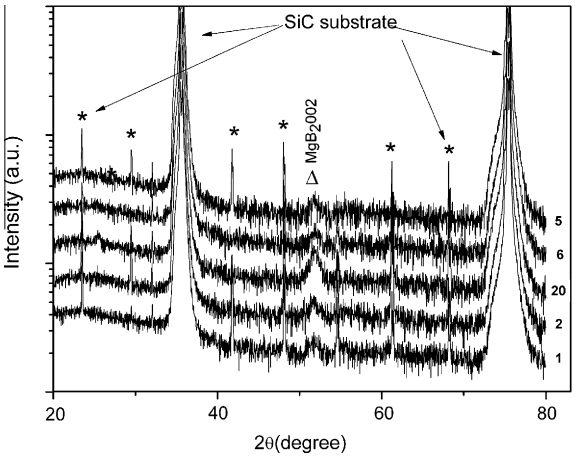

Fig. 3. X-ray diffraction spectra of the samples in series 1.