Analysis and mitigation of defective circular structures in HPCVD-grown MgB$_2$ thin films

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Abstract. In MgB$_2$ films synthesized via hybrid physical-chemical vapor deposition, circular structures containing Mg microparticles were detected, with diameters ranging from 17 to 25 μm. The thinning of MgB$_2$ film was observed inside these circular structures, which formation was found to be induced by rapid heating process and intense evaporation of Mg slugs. Tiny Mg droplets sputtering onto the substrates during rapid heating process influence the growth of MgB$_2$ film and tend to form circular structures around Mg particles, which problem can be mitigated by slowing down the heating process. As a result, MgB$_2$ films with smooth surfaces were obtained, which is instrumental in the fabrication of MgB$_2$ film electronic devices.

1. Introduction

MgB$_2$ with a $T_c$ of 39 K [1] is a promising material for superconducting thin-film electronic devices [2, 3]. The surface quality plays an important role in many MgB$_2$ devices, and MgB$_2$ thin films with smooth surface are usually needed. For example, MgB$_2$ thin films with smooth surface are required for some applications, such as Josephson junctions [4-6] and superconducting quantum interference devices (SQUIDs) [7,8]. Besides, MgB$_2$ thin films with a thickness below 20 nm are preferred for superconducting hot electron bolometers (HEBs) [9-11] used in high-resolution spectroscopy at terahertz frequencies.

So far, many methods are used to fabricate MgB$_2$ thin films, e.g., PLD [12,13], MBE [14] and Sol-Gel [15]. Meanwhile, the hybrid physical-chemical vapor deposition (HPCVD) has been recognized as one of the most efficient ways to obtain high-quality MgB$_2$ films [16,17]. Epitaxial MgB$_2$ thin films with $T_c$ approaching 42 K [18], $J_c$ (1.8 K) up to 1×10$^6$ A·cm$^{-2}$ in a self-field [19] have achieved by HPCVD. The surface morphology, closely related to growth parameters, of MgB$_2$ thin films grown by HPCVD has also been studied widely, which aim to obtain the MgB$_2$ films needed by controlling growth parameters. For example, the surfaces of MgB$_2$ films on different substrates, such as SiC, MgO, and stainless steel [20] or on SiC substrates with different thicknesses [17] show different crystallographic structures. Flower-like MgB$_2$ structures [21] are acquired and the growth mechanism is systematically studied. And the grain size of MgB$_2$ thin films on the SiC buffered-Hastelloy substrates becomes smaller and the the grains are firmly attached [22]. In this work, we observed a kind of circular structures on MgB$_2$ films grown by HPCVD, which has not been reported before. The diameter of the circular structures ranges from ~17 to ~25 μm, with several compact microparticles in each circle. These circular structures are defects that deteriorate the surface quality of MgB$_2$ film-based devices and should be
eliminated. In this study, their characteristics and growth process are analyzed. The circular structures can be eliminated successfully by controlling the heating process. Accordingly, MgB₂ films with smooth and uniform surface can be acquired.

2. Experimental

The MgB₂ thin films were fabricated by the HPCVD technique which has been described in detail elsewhere [19]. Briefly, Mg slugs (purity 99.5%), providing high Mg vapor pressure necessary for thermodynamic stability of MgB₂ phase, were placed around the SiC substrates (commercial (0001) 6H-SiC with square size of 5 mm×5 mm) (TankeBlue, China) on a molybdenum susceptor which is heated to ~700°C. During the whole process purified hydrogen (300 sccm) was continuously introduced and the total system pressure was kept at 4 KPa. The deposition started when the B₂H₆ gas (5% in hydrogen, flow rate 2-3 sccm) was introduced into the reactor, and stopped when the B₂H₆ gas was shut down. The thickness of the films is controlled by adjusting the B₂H₆ flow rate and the deposition time.

Three groups of MgB₂ thin films whose growth parameters are listed in table 1 were prepared here. In order to eliminate accidental influence, a group consists of 3 samples which was prepared simultaneously under the same parameters. The film morphology and distribution of element were investigated by using a scanning electron microscope (SEM, Sigma, Carl Zeiss, Germany) equipped with Energy Disperse Spectroscopy (EDS). The section analysis and 3D image of films were examined by an atomic force microscope (AFM, ICON2-SYS, Bruker Nano Inc., Germany) in the tapping mode. Raman spectra of MgB₂ films were measured by the Raman spectroscopy (inVia, Renishaw, Britain) with laser wavelength 532 nm.

| Sample NO. | B₂H₆ flow rate (sccm) | Deposition time (min) | Heating time from 600 to ~700°C (min) |
|------------|-----------------------|-----------------------|-------------------------------------|
| G1         | 2                     | 2                     | ~12                                 |
| G2         | 3                     | 2                     | ~12                                 |
| G3         | 3                     | 2                     | ~20                                 |

3. Results and discussion

The SEM images of the MgB₂ films of the 3 groups are shown in figure 1. Here, only one sample per group is shown, because three samples in each group have the same characteristics. It reveals that the surface of G1 and G2 films present circular structures, which are not seen in G3 film. Further observation shows that the circular structures on G1 and G2 films present some common characteristics. For example, there are a few of compact micro particles in every circle and the morphology in the circle, except small area near the particles, is greatly different from that of MgB₂ film outside the circle. Meanwhile it can be seen that the growth of MgB₂ film follows the Volmer-Weber mode [23], isolated islands are formed at first and then coalesced into continuous film. The MgB₂ films with different thickness show different morphology based on which the thickness can be approximately estimated. The typical surface morphology of thin and thick MgB₂ films [17] is observed in figures 1(b) and 1(f) outside the circle. And the thickness of G1, G2 can be inferred to be ~20 and ~40 nm. The thickness of G3 is approximately equal to 40 nm since G2 and G3 films were grown with same B₂H₆ flow rate and the deposition time.
Figure 1. SEM images of MgB$_2$ film: circular structure on G1 film (a) & (b) & (c); surface of G3 film (d); circular structure on G2 film (e) & (f).

Figure 2 shows the AFM images of the MgB$_2$ films and circular structures. The diameter of the circle ranges from $\sim$17 to $\sim$25 $\mu$m, as shown in figure 2(e) and 2(f). It is easy to find that the growth of MgB$_2$ film follows the Volmer-Weber mode in figure 2(a), isolated islands are firstly formed, and continuous film is then formed, as shown in figure 2(d). The 3D images in figures 2(b) and 2(c) and section analysis of circular structures in figures 2(e) and 2(f) reveal that the circular structures sink in the MgB$_2$ film, and the height of particles in the circle is much higher than that of the film around them. It is obvious that the more particles appear in the circle, the larger the circle diameter is.
The EDS analysis of one of the circular structures on G2 MgB$_2$ film is shown in figure 3. It presents that the main elements detected in the sample are Si, C, O and Mg in figure 3(a), among which Si and C almost come from SiC substrate. So here we focus on the distribution of Mg. The line distribution, crossing the circle and particles in figure 3(b), of Mg shows that the amount of Mg in the circle is less than that of Mg outside the circle, which results from the thinner film in the circle. In addition, the amount of Mg on the particles is the most, which are also consistent with Mg mapping result shown in
figure 3(c). So it can be concluded that the particles in the circle are almost made of Mg. Combining with film growth parameters, we can deduce the formation process of circular structures as follows. In experiments Mg slugs begin to melt at about 600°C. So the heating process from 600°C to ~700°C (starting reaction temperature) influences the melting process of Mg slugs. No matter thin film G1 or thick film G2, if the heating process is too fast, micro Mg liquid drops would be sprayed from Mg slugs onto the SiC substrate and then evaporated. Therefore the local Mg vapor pressure changes, which influence the growth of MgB$_2$ film. Mg or Mg compound deposits and tends to form a circular structure on the substrate around the Mg particles. If the heating process from 600 to ~700°C is extended for instance from 12 to 20 min, Mg slugs melt slowly and there is no Mg liquid drops are sprayed, which will not lead to the increase of local Mg vapor pressure. As a result, smooth MgB$_2$ films without circular structures can be obtained like G3 films.

![Fig 3](image_url)

**Figure 3.** EDS analysis of circular structure on G2 film: elemental type analysis (a), elemental line distribution (b) and Mg mapping (c).

![Fig 4](image_url)

**Figure 4.** Raman spectra of four positions in G2 MgB$_2$ film and SiC substrate.
Figure 4 shows the room-temperature Raman spectra of four positions in the G2 MgB$_2$ film around the circular structure and SiC substrate. It provides some information of MgB$_2$ film growth inside the circle in positions 2#, 3#, 4# and outside the circle in position 1#. The four bonds marked as black diamond come from SiC substrate. The broad E$_{2g}$ symmetry phonon centered around 620 cm$^{-1}$ [24] is seen, which means that MgB$_2$ is formed in all positions. Moreover, it is noteworthy for the Raman spectra in position 3#, that a strong bond around 620 cm$^{-1}$ almost coincides with that in position 1#. It can be inferred that MgB$_2$ films in these two areas, near the particles and outside the circle, are almost identical. The SEM images shown in figures 1(b) and 1(c) are also consistent with that conclusion. However, the exact growth mechanism of MgB$_2$ film near the particles is yet unknown and will be further investigated.

4. Conclusions
The circular structures on MgB$_2$ films fabricated by HPCVD are observed and investigated. The diameter of the circular structures, each containing several compact Mg microparticles, is about 20 μm. The MgB$_2$ films in these circular zones are thinner than outside them, and Mg particles protrude from the flat film surface. Rapid heating process and intense evaporation of Mg slugs are the main reasons for the formation of circular structures. The Mg microdroplets sputtering onto the substrates influence the growth of MgB$_2$ film around them and tend to form defective circular structures, which can be eliminated by decreasing the heating rate. Thus, the surface quality of MgB$_2$ film can be improved, providing some guidance for the preparation of MgB$_2$ thin films. Moreover, the reasons why a small area of MgB$_2$ film close to the particles is not influenced by the Mg droplets are worth studying in the future.

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