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Thermodynamics and thin film deposition of MgB$_2$ superconductors

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Abstract
The recently discovered superconductor MgB$_2$ with $T_c$ at 39 K has great potential in superconducting microelectronics. Thermodynamics studies with the calculation of phase diagrams (CALPHAD) modelling technique show that due to the high volatility of Mg, MgB$_2$ is only thermodynamically stable under fairly high Mg overpressures for likely in situ growth temperatures. This provides a helpful insight into the appropriate processing conditions for MgB$_2$ thin films, including the identification of the pressure–temperature region for adsorption-controlled growth. The initial MgB$_2$ thin films were made by pulsed laser deposition followed by in situ annealing. The cross-sectional transmission electron microscopy reveals a nanocrystalline mixture of textured MgO and MgB$_2$ with very small grain sizes. A zero-resistance transition temperature of 34 K and a zero-field critical current density of $1.3 \times 10^6$ A cm$^{-2}$ were obtained. The qualities of these films are limited by the thermodynamic stability conditions, which favour deposition techniques that can maintain a high flux of Mg.

1. Introduction
The recent discovery of superconductivity in MgB$_2$ at 39 K has generated great interest [1, 2]. MgB$_2$ has the highest $T_c$ known for non-oxide compounds. It has been shown that MgB$_2$ is a phonon-mediated BCS superconductor [3] with an energy gap of 5.2 meV at 4.2 K [4] and a coherence length of 50 Å [5]. Its grain boundaries do not have a large detrimental effect on the superconducting current transport [6, 7]. These properties hold tremendous promise for current-carrying large-scale applications in wires and tapes. They also suggest that Josephson junctions of MgB$_2$ may be much easier to fabricate than those made from the high temperature superconductors, which have much shorter coherence lengths. Such junctions could have the performance of conventional superconductor junctions, such as Nb and NbN, but operate at a much higher temperature.

A MgB$_2$ film processing technique compatible with multilayer depositions is needed for Josephson junction applications. Currently, two main types of deposition processes have been used, both involving annealing of films deposited at low temperatures. The first type employs ex situ annealing of low-temperature deposited B or Mg + B films at 900 °C in Mg vapour. The resultant films exhibit bulk-like $T_{c0} \sim 39$ K [8–10] and extremely high critical current density ($\sim 10^7$ A cm$^{-2}$ at low temperatures) [11, 12]. However, the high-temperature ex situ annealing is unlikely to be compatible with multilayer device fabrications. The second type uses an in situ two-step process. Thin films or multilayers of Mg + B or Mg + MgB$_2$ are deposited at low temperatures, and then annealed in situ in the deposition chamber at about 600 °C [8, 13–15]. This process is potentially more compatible with junction fabrications, however the superconducting properties in such films are poorer than in the ex situ annealed films.

Due to the high volatility of Mg, the fabrication of MgB$_2$ thin films by in situ deposition is expected to be difficult. It has been demonstrated for numerous materials containing a volatile constituent that an understanding of
the thermodynamics of the system can help identify the appropriate growth regime for these materials [16–20]. In this paper, we discuss a thermodynamic analysis of the Mg–B system, which shows that the MgB₂ phase is thermodynamically stable only under high Mg partial pressures. The result not only provides helpful insights into appropriate processing conditions for in situ deposition of MgB₂ thin films, but also shows the limitation of the deposition technique involving in situ annealing. The result of MgB₂ thin films made by an in situ process using pulsed laser deposition (PLD) is then presented. It shows that the superconducting properties of these films are weakened by the small MgB₂ grain size of less than 50 Å.

2. Thermodynamics of the Mg–B system

Although MgB₂ has been known and structurally characterized since the mid 1950s [21], no detailed thermodynamics information is available in the literature [22]. Our approach of the thermodynamic analysis is the calculation of phase diagrams (CALPHAD), a thermodynamic modelling technique using a computerized optimization procedure. In the CALPHAD approach, the Gibbs energies of individual phases in a system are constructed with models primarily based on the crystal structures of the phases [23]. For pure elements, the most commonly used model is that suggested by the Scientific Group Thermodata Europe (SGTE). The SGTE data used here are compiled by Dinsdale [24]. Using the experimentally measured enthalpy of formation and estimated decomposition temperatures, the Gibbs energy of each phase is evaluated with the Thermo-Calc program [25]. The phase equilibria are then calculated.

In the Mg–B system, there are three intermediate compounds, MgB₂, MgB₄ and MgB₇, in addition to gas and the solution phases, i.e. liquid, hcp magnesium and β-rhombohedral boron [26]. The Gibbs energy of the gas phase assuming ideal mixing is

\[ G_m = \sum y_i G_i + RT \sum y_i \ln y_i \]  

(1)

where \( y_i \) and \( G_i \) are the mole fraction and Gibbs energy of species \( i \) in the gas phase. The Gibbs energy of the solution phases treated as substitutional solutions is

\[ G_m^\Phi = G_m^{hcp} + x \Phi \ln \frac{y_{Mg}}{y_{B}} \]  

where \( \Phi \) is the molar Gibbs energy of the pure element with the structure \( \Phi \) from [24]. The Gibbs energies for the intermediate compounds are written using the two-sublattice model as

\[ G_m^{MgB_i} = G_m^{hcp} + x_i G_i^{\beta-rho} + (1 + x)(aMgB_i + bMgB_i T) \]  

(3)

where \( G_m^{hcp} \) and \( G_i^{\beta-rho} \) are the molar Gibbs energies of the hcp Mg and the β-rhombohedral B, respectively, \( aMgB_i \) and \( bMgB_i \) are the parameters to be determined, and \( \Delta G_m^{MgB_i} = aMgB_i + bMgB_i T \) represents the Gibbs energy of formation of the compound MgBᵢ with \( x \) being 2, 4 and 7, respectively, expressed in per mole of atoms.

Using the aforementioned procedure, the Gibbs energies of formation are obtained for the three compounds:

\[ \Delta G_m^{MgB_2} = -17121–3.815T, \Delta G_m^{MgB_4} = -14441–2.458T \]  

\[ \Delta G_m^{MgB_7} = -13022–0.872T \]  

From these results, binary phase diagrams can be calculated. In figure 1 the calculated temperature-composition phase diagrams for the Mg–B system at (a) 1 atm, (b) 1 Torr and (c) 1 mTorr are plotted. The result for 1 atm pressure is consistent with the published Mg–B phase diagram [22], which confirms the powerful capability of the CALPHAD technique. Above 1545 °C MgB₂ decomposes into a mixture of MgB₄ and Mg vapour. When the pressure is reduced to 1 Torr, the phase diagram changes dramatically. Since the pressure is lower than the triple-point pressure of Mg (650 °C, 2.93 Torr), the liquid phase of Mg disappears completely. The decomposition temperature of MgB₂ decreases to 912 °C. This temperature decreases further to 603 °C at a pressure of 1 mTorr. It is evident that Mg overpressure has a significant influence on the decomposition temperature of MgB₂, which can be very low, thus severely limiting the thin film deposition temperature.

The kinetics of crystal growth require that an in situ film deposition process takes place at sufficiently high temperatures. The optimum temperature for epitaxial growth is typically about one half of the melting temperature, \( T_m \) (in Kelvin), although the minimum temperature can be much lower [27]. For example, the minimum epitaxial growth temperature for metals is about \( T_m/8 \) [28]. Thermodynamic

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\[ \Delta G_m^{MgB_7} = -13022–0.872T \]  

Figure 1. The temperature-composition phase diagrams of the Mg–B system under the pressures of (a) 1 atm, (b) 1 Torr and (c) 1 mTorr.

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calculation shows that MgB\textsubscript{2} melts congruently at 2430 °C (~2700 K) with an equilibrium vapour pressure exceeding 49000 Torr. Therefore, the optimum temperature for the deposition of epitaxial MgB\textsubscript{2} films is around \(\sim 1080 \text{ °C} \) (1350 K). For MgB\textsubscript{2} to be stable at 1080 °C, a Mg partial pressure of at least 11 Torr is required. Converting the Mg partial pressure to Mg flux, \( F \), from the deposition source using the formula \( F = P / \sqrt{2\pi mk_B T} \), where \( m \) is the mass of Mg atom [29, 30], 11 Torr is equivalent to an incident Mg flux of \( 2 \times 10^{21} \text{ Mg atoms/cm}^2 \text{ s} \), or a Mg deposition rate of 0.5 mm s\(^{-1}\) if all the Mg atoms stick and form a Mg layer with bulk density. This is impossible for most thin film deposition techniques.

Figure 1, however, illustrates the automatic composition control benefit that accompanies adsorption-controlled growth as is extensively used for III–V and II–VI compound semiconductors [31]. As long as the Mg:B ratio is above the 1:2 stoichiometry, any amount of extra Mg above this stoichiometric amount will vaporize and the desired MgB\textsubscript{2} phase will result. The most critical requirement for controlling the stoichiometry is thus to avoid insufficient Mg supply, which will lead to MgB\textsubscript{4}, MgB\textsubscript{7} or solid B phases.

From a thermodynamic perspective, deposition of a single-phase MgB\textsubscript{2} film becomes easy when the growth conditions (substrate temperature and Mg overpressure) fall within a window where the thermodynamically stable phases are the desired MgB\textsubscript{2} phase and gas phases. Within this growth window MgB\textsubscript{2} does not decompose and excess Mg does not condense on the MgB\textsubscript{2} surface, thus the formation of single-phase MgB\textsubscript{2} is adsorption controlled and automatic. This window (the ‘Gas + MgB\textsubscript{2}’ region) is best illustrated by the pressure–temperature phase diagram shown in figure 2. For a given deposition temperature, one can find the Mg partial pressure range to keep the MgB\textsubscript{2} phase thermodynamically stable. As shown in the figure, this range extends over about three orders of magnitude. The boundaries of the growth window can be approximately expressed by the following equations: \( \log(P) = -(7561/T + 8.673) \) (the upper boundary with solid Mg) and \( \log(P) = (-10142/T + 8.562) \) (the lower boundary with MgB\textsubscript{2}), where \( P \) is in Torr and \( T \) in Kelvin.

While the applicability of equilibrium thermodynamics to thin film growth has been established for many material systems, the non-equilibrium nature of specific deposition techniques can be quite important. For MgB\textsubscript{2}, a recent study has revealed a significant kinetic barrier to the thermal decomposition of MgB\textsubscript{2} [32]. This opens the possibility of using non-equilibrium routes to drive the formation reaction of MgB\textsubscript{2} to mitigate by as much as a factor of \( 10^{-3} \) the high Mg pressures described in this paper.

The implications of the thermodynamic analysis to the \textit{in situ} MgB\textsubscript{2} film deposition can be demonstrated by examining the necessary Mg overpressures for several possible deposition conditions. As discussed above, the optimum epitaxial growth temperature is \( \sim 1080 \text{ °C} \) for MgB\textsubscript{2}, which requires a Mg flux of \( 2 \times 10^{21} \text{ Mg atoms/cm}^2 \text{ s} \) or a Mg deposition rate of 0.5 mm s\(^{-1}\). The lower bound for epitaxial growth is unknown. For metals it is about \( T_m/8 \) [28], which would be 50 °C for MgB\textsubscript{2}. However, there has been no observation of MgB\textsubscript{2} epitaxy for a deposition temperature lower than 400 °C. From the phase diagram in figure 2, a deposition temperature of 850 °C corresponds to a Mg overpressure of 340 mTorr, or a Mg flux of \( 6 \times 10^{19} \text{ Mg atoms/cm}^2 \text{ s} \) or a Mg deposition rate of 15 \( \mu \text{m s}^{-1} \). For 600 °C, the necessary Mg overpressure is 0.9 mTorr, which corresponds to a Mg flux of \( 2 \times 10^{17} \text{ Mg atoms/cm}^2 \text{ s} \) or a Mg growth rate of 500 \( \AA \text{ s}^{-1} \). Clearly, these conditions favour deposition techniques that can maintain a high Mg overpressure during the deposition. This is further complicated by the oxygen contamination during the deposition in non-UHV systems. The Mg flux reacts with residual oxygen in the background, which effectively reduces the Mg overpressure thus pushing the system to the thermodynamically unstable region.

3. Nanocrystalline MgB\textsubscript{2} thin films by an \textit{in situ} annealing process

Before an \textit{in situ} MgB\textsubscript{2} thin film deposition technique that satisfies the thermodynamic stability conditions is developed, techniques involving post-deposition annealing are being investigated. We have used PLD with an \textit{in situ} annealing procedure similar to those described by Blank et al [13], Christen et al [14] and Shinde et al [8], which is potentially more compatible with junction fabrications than the \textit{ex situ} annealing process. The early reports from various groups on \textit{in situ} MgB\textsubscript{2} thin films show lower \( T_{\text{c0}} \) around or below 25 K [8, 13–15]. Our result shows a much higher \( T_{\text{c0}} \) of 34 K. From the structural analysis, we find that our films are nanocrystalline and the small MgB\textsubscript{2} size limits their superconducting properties.

The MgB\textsubscript{2} films were deposited on (0001) Al\textsubscript{2}O\textsubscript{3} substrates from targets prepared by pressing Mg powder with MgB\textsubscript{2} powder at room temperature. The Mg:MgB\textsubscript{2} molar ratio was varied between 4:1 and 2:1. The films were deposited at 250–300 °C in an Ar atmosphere (99.999% gas purity) of 120 mTorr. The background vacuum was in the low to mid
Figure 3. (a) Resistivity versus temperature curve for a 4000 Å thick MgB$_2$ film. (b) The ac susceptibility of the same film.

Figure 4. The temperature dependence of the zero-field $J_c$ of a 4000 Å thick MgB$_2$ film. The inset shows the $M$–$H$ loop at $T = 10$ K.

$10^{-7}$ Torr range. The energy density of the laser beam was 5 J cm$^{-2}$ and the repetition rate was 5 Hz. The deposited films were then heated at a rate of 40 °C min$^{-1}$ to 630 °C and held there for 10 min. The atmosphere during the heating and annealing was the same as during the deposition. After the in situ annealing, the films were cooled to room temperature in ~20 Torr Ar.

The film deposited at 250–300 °C was a likely mixture of Mg and amorphous MgB$_2$ or B. Several processes are involved in the in situ annealing: Mg evaporation, MgB$_2$ phase formation, which is determined by the thermodynamics [33] and forward kinetics [32], nucleation and growth of crystallites, and MgB$_2$ decomposition, which is determined by the thermodynamics [33] and a kinetic barrier [32].

High quality films are constrained by the balance of these processes, and a careful adjustment of the heating and annealing parameters such as temperature and duration is necessary.

In figure 3(a) we plot the resistivity versus temperature curve for a 4000 Å thick MgB$_2$ film. It shows a metallic behaviour with a residual resistance ratio, $\text{RRR} = R(300 \text{ K})/R(40 \text{ K})$, of 1.4 and the resistivity at room temperature is ~150 µΩ cm. Compared to high-density bulk samples, where $\text{RRR} = 25.3$ and $\rho(300 \text{ K}) = 9.6 \mu\Omega \text{ cm}$ [34], the residual resistance ratio of the MgB$_2$ film is much smaller and the resistivity much higher. This is likely to be due to the small grain sizes and existence of MgO in the film since precipitates of MgO at the grain boundaries will act as series-connected resistors to the MgB$_2$ grains. The superconducting transition temperature of the film, characterized by the zero resistance temperatures, is 34 K. The superconducting transition is further characterized by the ac susceptibility, the result of which is shown in figure 3(b). The transition is relatively sharp with a full width at the half maximum of the imaginary-part signal being ~0.8 K.

The critical current densities of the MgB$_2$ films were determined using both the magnetization and transport methods. In figure 4(a), the temperature dependence of $J_c$ is plotted for a 4000 Å thick MgB$_2$ film. A zero-field $J_c \sim 1.34 \times 10^6$ A cm$^{-2}$ was obtained at 7.5 K. The $M$–$H$ loop at 10 K for magnetic field $H \perp$ film surface, which is 5 mm × 4 mm in size, is shown in the inset. It shows a severe instability in flux pinning or flux jump, which causes the collapse of circulating critical current so that the magnetization...
the MgB$_2$ grain size and superconducting properties is further
grain size was appreciably smaller. The correlation between
films revealed no discernable film peaks, indicating that the
peaks [11, 10], x-ray diffraction scans of our
found in bulk MgB$_2$ [6]. The temperature dependence
of the transport $I_c$ is plotted in figure 4(b) for a 2500 Å
thick MgB$_2$ film. A narrow bridge with a width of 7 μm
was photolithographically patterned and the electrodes were
formed by pressed indium. A criterion of 1 μV was used to
determine the critical current. As shown in the figure, a $I_c$
value of $1.4 \times 10^6$ A cm$^{-2}$ was obtained at low temperatures.

Compared to the early reports of in situ MgB$_2$ thin films
[8, 13–15] where $T_c$ is around or below 25 K, the $T_c$ value
shown here is much higher. The reason may be due to the
different microstructures in these films. We have studied the
structure of our films by both x-ray diffraction and cross-
sectional transmission electron microscopy (TEM). In contrast
to ex situ annealed MgB$_2$ films with bulk-like $T_c$ of 39 K, which
has a MgB$_2$ grain size of ~100 Å and clear x-ray diffraction
peaks [11, 10], x-ray diffraction scans of our in situ annealed
films revealed no discernable film peaks, indicating that the
grain size was appreciably smaller. The correlation between
the MgB$_2$ grain size and superconducting properties is further
corroborated by the TEM results of two MgB$_2$ films of different
$T_c$ values.

The TEM result for a MgB$_2$ film with $T_c = 32$ K is shown
in figure 5, and its $R$ versus $T$ curve is shown in figure 6. The
dark-field image in figure 5(a) shows that the film consists of
two layers with different contrast. Figure 5(b) is a selected-
area electron diffraction pattern taken from region I near
the film/substrate interface. By measuring the position and
intensity distribution of the diffraction rings, it is determined
that they all belong to the rock salt MgO phase. Figure 5(c)
is a diffraction pattern taken from region II close to the
film surface using the same size selected-area aperture as for
figure 5(b). In addition to the diffraction rings corresponding to

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure5.png}
\caption{Figure 5. (a) Dark-field TEM image showing a cross-sectional view of a MgB$_2$ thin film with $T_c = 32$ K. Selected-area electron diffraction patterns from (b) region I and (c) region II.}
\end{figure}

the MgO phase, it also shows diffraction spots corresponding
to the hexagonal MgB$_2$ phase. The diffraction spots indicated
by the circles are due to the (001) planes, while those by the
arrow heads arise from diffraction by the (110) planes of MgB$_2$.
The (021) MgB$_2$ reflections are also detected. The discrete
spots appear in figure 5(c) instead of nearly continuous rings
in figure 5(b), indicating a larger grain size in region II. In both
regions, the result indicates substantial oxygen contamination.
The MgB$_2$ grain size in region I must be less than about
50 Å to account for the absence of MgB$_2$ rings or spots in
figure 5(b).

The TEM result for a second MgB$_2$ film with $T_c = 21$ K
is shown in figure 7, and its $R$ versus $T$ curve is shown in figure 8.
From the dark-field image in figure 7(a) one can see that region
I is thinner than that in the higher $T_c$ film. As shown in
figure 7(b), in both regions I and II, the MgB$_2$ diffraction
patterns were absent. The absence of the MgB$_2$ patterns
indicates that the MgB$_2$ grain size in this film is less than 50 Å.
When the grain size is close to the coherence length of MgB$_2$,
the superconducting properties will be affected. While the
900 °C annealing in the ex situ process provides enough
thermal energy for crystallization and texturing, the lower
temperature during the in situ annealing limits the extent of
these processes. The reason that the $T_c$ value reported here is
much higher than those in the early reports of in situ MgB$_2$
films [8, 13–15] may be that the grain size in our film is
larger due to the details of the processing conditions.

The results of both figures 5 and 7 show severe oxygen
contamination in the films. The diffraction patterns from
MgO dominate both images. A separate XPS measurement
of two films with different $T_c$, 17 and 32 K, respectively,
shows that there is no appreciable difference in the oxygen
content between the two films, and the Mg:B:O atomic ratio
is 1.0:1.1:1.2. The extent of the detrimental effects of oxygen
contamination is not well understood, and Eom et al even
suggest that it may help to enhance the flux pinning [11].

4. Conclusion

In order to realize the potential of MgB$_2$ in superconducting
digital applications, epitaxial or polycrystalline film produced

![Figure 6. Resistance versus temperature curve for the film in figure 5.](image-url)
MgB\textsubscript{2} phase is constrained by the balance of several processes. However, because the formation and crystallization of the MgB\textsubscript{2} phase is thermodynamically stable only under fairly high to very high Mg partial pressures at the temperature range appropriate for epitaxial growth. Therefore, a large Mg flux must be delivered from the deposition source for in situ film deposition. This requirement favours deposition techniques that can maintain a large Mg flux over those where a large Mg flux is impractical. At present, no deposition techniques that can maintain a large Mg flux over multilayer deposition, it is important to demonstrate that high c\textsubscript{0} and b\textsubscript{0} and c\textsubscript{0} obtained is much higher than those previously reported in situ using a processing technique compatible with multilayer deposition.

by a processing technique compatible with multilayer depositions is needed. Using the CALPHAD technique we find that MgB\textsubscript{2} is thermodynamically stable only under fairly high to very high Mg partial pressures at the temperature range appropriate for epitaxial growth. Therefore, a large Mg flux must be delivered from the deposition source for in situ MgB\textsubscript{2} film deposition. This requirement favours deposition techniques that can maintain a large Mg flux over those where a large Mg flux is impractical. At present, no report of such deposition technique exists.

Lacking an in situ MgB\textsubscript{2} film deposition technique, we have deposited MgB\textsubscript{2} thin films by pulsed laser deposition using an in situ annealing process. The $T_{c0}$ obtained is much higher than those previously reported in situ films and $J_c$ is comparable to those of the polycrystalline bulk samples even though the grain size in the films is extremely small. Because this deposition process is more compatible with multilayer deposition, it is important to demonstrate that high $T_{c0}$ and $J_c$ can be obtained using this process. Our results are a step towards making the in situ annealing technique a viable candidate for MgB\textsubscript{2} Josephson junction technologies. However, because the formation and crystallization of the MgB\textsubscript{2} phase is constrained by the balance of several processes and by thermodynamic phase stability conditions and kinetics, it is difficult to achieve films with large grain sizes. An in situ film deposition technique is much more desirable for the MgB\textsubscript{2} Josephson junction technologies.

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Figure 7. (a) Dark-field TEM image showing a cross-sectional view of a second MgB\textsubscript{2} thin film with $T_c = 21$ K. (b) Selected-area electron diffraction pattern.

Figure 8. Resistance versus temperature curve for the film in figure 7.