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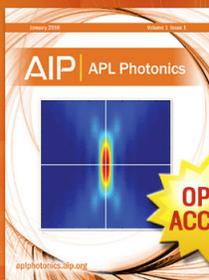
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Thermodynamics of the Mg–B system: Implications for the deposition of MgB₂ thin films

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We have studied the thermodynamics of the Mg–B system with the calculation of phase diagrams modeling technique using a computerized optimization procedure. Temperature–composition, pressure–composition, and pressure–temperature phase diagrams under different conditions are obtained. The results provide helpful insights into appropriate processing conditions for thin films of the superconducting phase, MgB₂, including the identification of the pressure–temperature region for adsorption-controlled growth. Due to the high volatility of Mg, MgB₂ is thermodynamically stable only under fairly high-Mg overpressures for likely growth temperatures. This places severe temperature constraints on deposition techniques employing high-vacuum conditions. © 2001 American Institute of Physics. [DOI: 10.1063/1.1376145]

The recent discovery of superconductivity in MgB₂ at 39 K has generated great interest.^{1,2} MgB₂ has the highest T_c known for nonoxide compounds and appears to become superconducting by the BCS mechanism.³ Its coherence length is longer than those in high-temperature cuprate superconductors, and its grain boundaries have a far less detrimental effect on superconducting current transport.⁴ These properties hold tremendous promise for various large-scale and electronic applications. However, due to the high volatility of Mg, difficulties in fabricating MgB₂ thin films by *in situ* deposition are anticipated. On the other hand, such volatility can greatly simplify composition control by enabling adsorption-controlled film growth⁵ as is extensively used for the growth of III–V and II–VI compound semiconductors. 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 region for these materials.^{6–10}

Although MgB₂ has been known and structurally characterized since the mid-1950s,¹¹ no detailed thermodynamics information is available in the literature.¹² In this letter, we present a thermodynamic analysis of the Mg–B system with the thermodynamic calculation of phase diagrams (CALPHAD) modeling technique using a computerized optimization procedure. We have obtained temperature–composition, pressure–composition, and pressure–temperature phase diagrams under various conditions. We find that the MgB₂ phase is thermodynamically stable only under high-Mg partial pressures. This condition favors deposition techniques that can maintain a high flux of Mg, which may operate in a pressure–temperature window and exploit the automatic composition control benefit that accompanies adsorption-controlled growth.

In the CALPHAD approach, the Gibbs energies of indi-

vidual phases in a system are constructed with models primarily based on the crystal structures of the phases.¹³ For pure elements, the most commonly used model is suggested by the Scientific Group Thermodata Europe (SGTE) and the SGTE data have been compiled by Dinsdale.¹⁴ By combining thermodynamic descriptions of unary systems with binary experimental data, thermodynamic descriptions of binary systems are then developed. In the Mg–B system, there are three intermediate compounds, MgB₂, MgB₄, and MgB₇, in addition to the gas, liquid, and solid (hcp) magnesium phases and the β -rhombohedral boron solid phase.¹⁵ The Gibbs energy for the intermediate compounds is written using the two-sublattice model as

$$G_m^{\text{MgB}_b} = 0G_{\text{Mg}}^{\text{solid}} + b^0G_{\text{B}}^{\text{solid}} + \Delta G_f^{\text{MgB}_b}, \quad (1)$$

where b is 2, 4, or 7 for the three intermediate phases, respectively, ${}^0G_{\text{Mg}}^{\text{solid}}$ and ${}^0G_{\text{B}}^{\text{solid}}$ are Gibbs energies for Mg and B solids, respectively, and $\Delta G_f^{\text{MgB}_b}$ is the Gibbs energy of formation for MgB _{b} . Using the experimentally measured enthalpy of formation and estimated decomposition temperatures, $\Delta G_f^{\text{MgB}_b}$ is evaluated with the Thermo–Calc program¹⁶ for MgB₂, MgB₄, and MgB₇, and the phase equilibria are then calculated.

In Fig. 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 labels “Solid,” “Liquid,” and “Gas” represent the Mg-rich solid, liquid, and gas phases, respectively. The result of our calculation for 1 atm pressure is consistent with the published Mg–B phase diagram,¹² which confirms the powerful capability of the CALPHAD technique. Below 1545 °C and for the atomic Mg:B ratio, $x_{\text{Mg}}/x_{\text{B}}$, greater than 1:2, the MgB₂ phase coexists with the Mg-rich solid, liquid, and gas phases at various temperatures. Above 1545 °C MgB₂ decomposes into a mixture of MgB₄ and Mg vapor. If $1:4 < x_{\text{Mg}}/x_{\text{B}} < 1:2$ and the temperature is below 1545 °C, MgB₂ coexists with MgB₄. When the pres-

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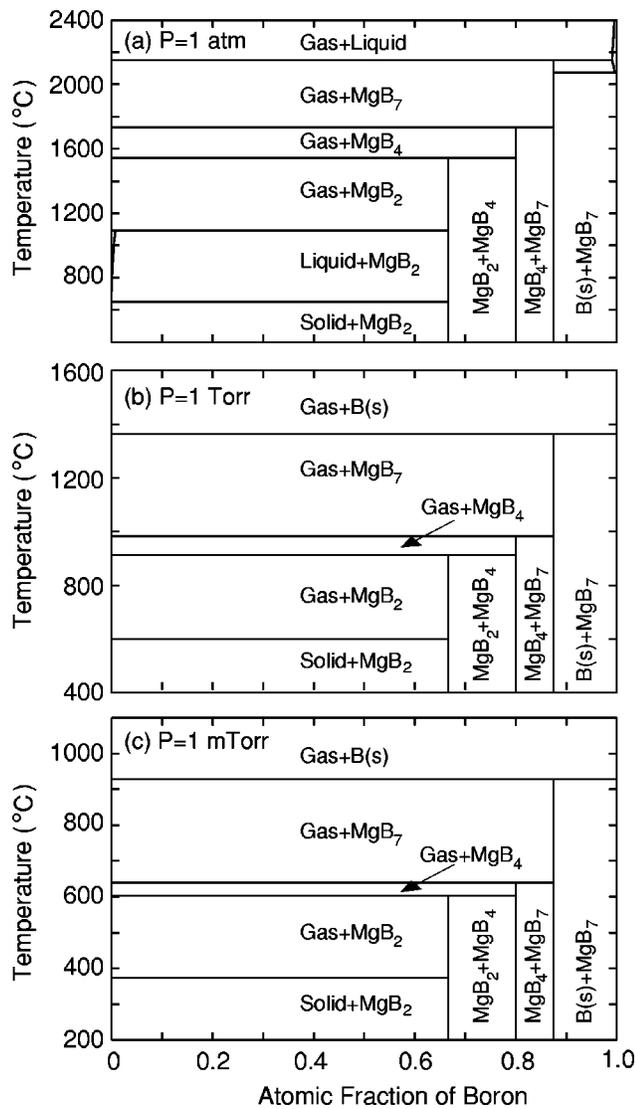


FIG. 1. Temperature-composition phase diagrams of the Mg-B system under the pressures of (a) 1 atm, (b) 1 Torr, and (c) 1 mTorr.

sure 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 completely disappears. The decomposition temperature of MgB_2 decreases to 912 °C. This temperature decreases further to 603 °C at the pressure of 1 mTorr. Evidently, the pressure has significant influence on the decomposition temperature of MgB_2 , 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.¹⁷ For example, the minimum epitaxial growth temperature for metals is about $T_m/8$.¹⁸ Thermodynamic calculation shows that MgB_2 melts congruently at 2430 °C (~ 2700 K) with pressure higher than 49 000 Torr, therefore, the optimum temperature for deposition of epitaxial MgB_2 films is around ~ 1080 °C (1350 K). For MgB_2 to be stable at 1080 °C, a Mg partial pressure of at least 11 Torr is required, which is impossible for many thin film deposition tech-

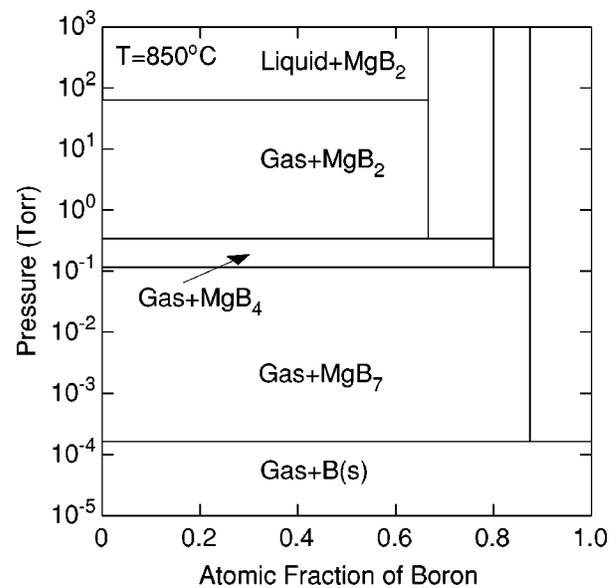


FIG. 2. Pressure-composition phase diagram of the Mg-B system at 850 °C.

niques. This encourages film growth at temperatures lower than optimal but nonetheless sufficient for epitaxial growth. In Fig. 2, the pressure-composition phase diagram at 850 °C is shown. At this temperature, MgB_2 is thermodynamically stable only above a Mg partial pressure of 340 mTorr. Below this pressure MgB_2 will decompose and only Mg vapor, MgB_4 , MgB_7 , or solid B can be obtained.

Figures 1 and 2 illustrate the automatic composition control benefit that accompanies the adsorption-controlled growth. From a thermodynamic perspective, deposition of a single-phase MgB_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_2 phase and gas phases. Within this growth window MgB_2 does not decompose and excess Mg does not condense on the MgB_2 surface, thus the formation of single-phase MgB_2 is adsorption-controlled and automatic. From the figures we find that this composition window, marked as “Gas+ MgB_2 ,” is large. As long as the Mg:B ratio is above the stoichiometric 1:2, any amount of extra Mg above the stoichiometry will be vaporized and the desired MgB_2 phase will result. The more critical requirement for controlling the stoichiometry is to avoid insufficient Mg supply, which will lead to MgB_4 , MgB_7 , or solid B phases.

The thermodynamic stability window for MgB_2 film deposition (the “Gas+ MgB_2 ” region) is best illustrated by the pressure-temperature phase diagram shown in Fig. 3. This phase diagram is essentially the same for all compositions with $x_{\text{Mg}}/x_{\text{B}} \leq 1:2$. If the Mg overpressure is too low, it is thermodynamically favorable for MgB_2 to decompose into MgB_4 (+Gas). If it is too high, it is thermodynamically favorable for Mg to condense on to the MgB_2 surface. For a given deposition temperature, one can find the Mg partial pressure range to keep the MgB_2 phase thermodynamically stable. As seen 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

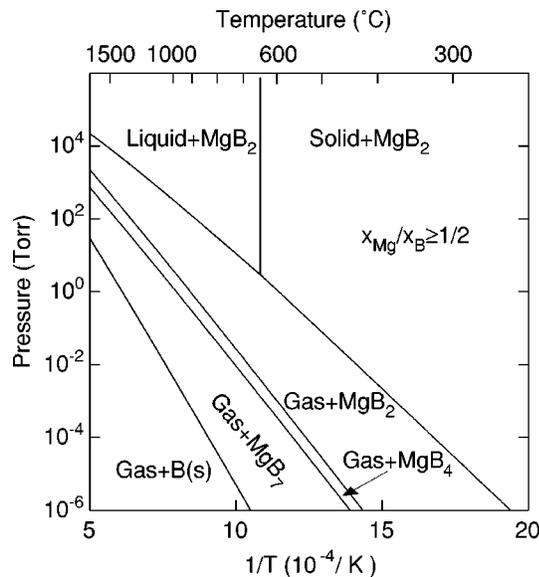


FIG. 3. Pressure–temperature phase diagram for the Mg:B atomic ratio $x_{\text{Mg}}/x_{\text{B}} \geq 1/2$. The region of Gas+MgB₂ represents the thermodynamic stability window for the deposition of MgB₂ thin films.

equations: $\log(P) = -7561/T + 8.673$ (the upper boundary with solid Mg), and $\log(P) = -10142/T + 8.562$ (the lower boundary with MgB₄), where P is in Torr and T in Kelvin.

The Mg partial pressure can be converted 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,^{19,20} to determine the film deposition parameters. For example, at the optimum temperature of 1080 °C, the required Mg partial pressure of about 10 Torr is equivalent to an incident Mg flux of 2×10^{21} Mg atoms/(cm²s), or a Mg deposition rate of 0.5 mm/s if all the Mg atoms stick and form a Mg layer with bulk density. This is impossible for most thin film deposition techniques. One can sacrifice epitaxy for phase stability by lowering the growth temperature. For example, the highest tolerable Mg pressure for molecular beam epitaxy (MBE) is typically 10^{-4} Torr.²⁰ From Fig. 3, this implies a maximum substrate temperature of about 534 °C (807 K) for MBE.

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 MgB₂, a recent study has revealed a significant kinetic barrier to the thermal decomposition of MgB₂.²¹ This opens the possibility of using non-equilibrium routes to drive the formation reaction of MgB₂ to mitigate by as much as a factor of 10^{-3} the high Mg pressures described in this letter.

In conclusion, the CALPHAD technique was used to develop a thermodynamic description of the Mg–B system. We find that MgB₂ is thermodynamically stable only under fairly high to very high Mg partial pressures at the temperature range appropriate for *in situ* epitaxial growth, implying that a large Mg flux must be delivered from the deposition source. This requirement favors deposition techniques that can maintain a large Mg flux over those where a large Mg flux is impractical. It should be pointed out that our approach considers only the equilibrium thermodynamic conditions, and the kinetics of the thin film growth could change the details of the phase stability window.

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