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## Experimental study of MgB<sub>2</sub> decomposition

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The thermal stability of MgB<sub>2</sub> has been studied experimentally to determine the role of thermodynamic and kinetic barriers in the decomposition process. The MgB<sub>2</sub> decomposition rate approaches one monolayer per second at 650 °C and has an activation energy of 2.0 eV. The evaporation coefficient is inferred to be  $\sim 10^{-4}$ , indicating that this process is kinetically limited. These values were inferred from in situ measurements using a quartz crystal microbalance and a residual gas analyzer, in conjunction with ex situ measurements of redeposited material by Rutherford backscattering spectroscopy and secondary ion mass spectroscopy. The presence of a large kinetic barrier to decomposition indicates that the synthesis of MgB<sub>2</sub> thin films conditions may be possible with vacuum processing, albeit within a narrow window in the reactive growth conditions. © 2001 American Institute of Physics. [DOI: 10.1063/1.1383804]

The discovery of MgB<sub>2</sub>, a binary metal with a superconducting transition temperature of 39 K (Ref. 1), is of both fundamental and practical importance. This compound is reported to be an isotropic superconductor with conventional Bardeen-Cooper-Schrieffer electron-phonon coupling.<sup>2</sup> It has been fabricated into powders, wires<sup>3</sup> and thin films.<sup>4,5</sup> To date, almost all of the MgB<sub>2</sub> bulk samples have been synthesized at elevated temperatures and large Mg overpressures. There is an increasing effort to prepare MgB<sub>2</sub> thin films. High transition temperature films have been produced only by using a high-temperature high-Mg-pressure annealing step, which follows a lower-temperature deposition step. Recently, the Twente group<sup>4</sup> has made thin films using a twostep process involving low-temperature deposition, followed by a somewhat rapid thermal annealing in inert gas. Despite the progress so far, the preparation of stoichiometric thin films with transition temperatures comparable to those of bulk samples, using a single-step in situ vapor deposition process, has eluded researchers to date. It is already clear that the volatility of Mg is a key factor in this limited progress.

A recent report has used thermodynamics to predict the conditions under which MgB<sub>2</sub> synthesis would be possible under vacuum conditions.<sup>6</sup> However, it is well known that thermodynamics alone are not sufficient to predict growth. There are systems in which synthesis does not occur under thermodynamically predicted growth conditions. Two examples include GaN and diamond.

Below, we briefly describe the criterion that distinguishes when thermodynamics can be used to accurately predict conditions of synthesis. For many systems, bulk thermodynamic data can be used to predict the rate and species of decomposition, indicative of the limit where kinetic barriers to the reverse reaction are absent.<sup>7</sup> Metals, for example, are found to vaporize as monatomic species with an evaporation rate equal to within experimental accuracy of the thermodynamically predicted value due to the absence of a kinetic barrier to decomposition and desorption. Many other solids including semiconductors such as Si, GaAs, and InP, oxides such as Al<sub>2</sub>O<sub>3</sub>, Ga<sub>2</sub>O<sub>3</sub>, In<sub>2</sub>O<sub>3</sub>, and ionic compounds such as LiCl, decompose at a rate of 1.5 to 3 times slower than the maximum predicted value due to a small kinetic barrier to this process. The ratio of the observed rate to the thermodynamically predicted rate is labeled the evaporation coefficient,  $\alpha$ . In all of these cases,  $\alpha$  is 0.3 to 0.7, thus the kinetic barrier is sufficiently small that rapid decomposition prevents growth except at (or very near) conditions when the synthesized compound is thermodynamically stable. For example, Tsao has shown that bulk thermodynamics accurately predict successful molecular-beam epitaxy conditions by using conditions in which the III-V compound and a vapor are the only thermodynamically stable phases.<sup>8</sup>

For strongly bound nitrogen-containing compounds, such as AlN<sup>9</sup>, BN<sup>9</sup>, Mg<sub>3</sub>N<sub>2</sub>,<sup>7</sup> and GaN,<sup>10</sup> the process of breaking the strong surface metal-N bonds results in the decomposition rate being kinetically-limited with  $\alpha$  being  $10^{-3}$  for the first three compounds and  $10^{-8}$  for GaN. For these compounds, the growth of high quality thin films can be performed under metastable conditions if the forward reaction is driven with activated species. Successful growth results when the rate of arrival of the activated species (i.e., the maximum rate of the forward reaction) is greater than the

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thermal decomposition reaction rate (i.e., the minimum rate of the reverse reaction). In the case of GaN, the decomposition reaction is sufficiently slow such that reactive nitrogen can be used to drive the synthesis reaction. Under these conditions, the GaN compound is formed under a nitrogen pressure that is over eight orders of magnitude lower than needed to achieve thermodynamic stability of the GaN phase.

In order to address this key issue of the kinetic barrier to decomposition and evaporation relevant to the successful synthesis and thermal processing of  $MgB_2$  in a vacuum, we have characterized the decomposition process experimentally. We will show that the *small evaporation coefficient* for the  $MgB_2$  system might give a window in the reactive processing conditions to allow *in situ* growth. We give the processing conditions including the substrate temperature, and flux of reactants necessary to achieve this outcome.

The MgB<sub>2</sub> samples were synthesized from a high purity, 3 mm diameter Mg rod and isotopic  $_{11}$ B (Eagle Picher, 98.46 at. %  $_{11}$ B). The Mg rod was cut into pieces about 4 mm long and mixed with the  $-200 \text{ mesh} _{11}$ B powder. The reaction was done under moderate pressure (50 bars) of ultra high purity grade Argon at 850 °C. At this temperature, the gas– solid reaction was complete in about 1.5 h. The samples were contained in a crucible with a closely fitting cover made from boron nitride (BN) (Advanced Ceramics Corp. HBC grade BN). There was no reaction between the reactants and the BN crucible. X-ray diffraction showed the material was impurity free to within our resolution.

The rate of the MgB<sub>2</sub> decomposition process and each species volatilization was measured using a quartz crystal microbalance and a residual gas analyzer in UHV. For improved accuracy, we also used Rutherford backscattering (RBS) and secondary ion mass spectroscopy (SIMS) to determine the chemical composition of the desorbed material. The MgB<sub>2</sub> power was loaded in a tantalum crucible with a diameter of 0.5 cm and a height of 2.5 cm. The temperature was measured by a thermocouple, which was attached to the wall of the crucible by spring force. The evaporation species and the related partial pressures were measured by a modified Stanford Research Systems (Model RGA200) Residual Gas Analyzer (RGA). The samples were initially outgassed at 300 °C for 1 h to remove volatile impurities and any excess Mg, if present. There was no desorption of Mg or B detected during this process. The filament of the RGA is located 7 cm above the outlet of the crucible. The partial pressure measured by the RGA was calibrated to a flux using conventional Knudsen analysis in conjunction with thickness determinations from a moveable water-cooled quartz crystal microbalance positioned 3.5 cm above of the outlet of the crucible.

The onset of significant Mg and B evaporation (i.e.,  $>10^{-9}$  Torr) was observed near 425 °C and 650 °C, respectively. For a given temperature, the flux of Mg is found to be at least two orders higher than any other species. Chemical analysis of the redeposited material using RBS confirmed that the flux of B is less than a few percent. SIMS measurements indicated that the maximum desorbed B concentration is on the order of 0.1%. Up to the highest temperature measured, 900 °C, evaporation of only Mg and B was observed. There was no unambiguous evidence for MgB, MgB<sub>2</sub>,



FIG. 1. (a) Ahhenius plot of kinetically-limited Mg evaporation pressure, as deduced from the experiment is shown. An activation energy of 2.0 eV is found. For comparison, the thermodynamic stability line is given for the decomposition of stoichiometric MgB<sub>2</sub> to MgB<sub>4</sub>+gas (from Ref. 6). An evaporation coefficient of  $\sim 10^{-4}$  is determined. (b) Measured Mg evaporating flux and inferred MgB<sub>2</sub> decomposition rate in monolayers per second (ML/s) as a function of temperature are presented.

 $MgB_4$ ,  $MgB_6$ , or  $MgB_7$  evaporation. Boron solid has a significantly lower vapor pressure than that measured, indicating that  $MgB_2$  must decompose, yielding elemental boron that presumably desorbs directly from the surface.

Figure 1 shows the magnesium evaporation pressure as a function of MgB<sub>2</sub> temperature. Arrhenius analysis indicates that the Mg desorption process has an activation energy of 2.0 eV. In the graph, the thermodynamically predicted pressures are also shown for comparison. An evaporation coefficient of  $\sim 10^{-4}$  can be inferred.

To achieve high quality thin films, thermal energies are used to overcome the kinetic steps involved in epitaxy, including for example, surface diffusion, nucleation, and adatom incorporation into the lattice. In the past, empirical observations have been used to develop methods that overcome the kinetic barriers of epitaxy. For example, the optimal substrate temperature used to grow almost all high quality single-crystal thin films is >1/2 to 2/3 of the melt temperature.<sup>8,11,12</sup> In the Mg–B system, since a number of stable phases occur below the melt temperature of ~2300 °C, it is not clear how high a temperature is required to attain high quality epitaxy. Most bulk growth techniques have used a temperature over 900 °C to achieve optimal stoichiometry and high superconducting transition temperatures. The Twente group was able to attain improved transition temperatures with somewhat rapid thermal anneals at  $600 \,^{\circ}$ C of a film deposited at lower temperatures. Thus, it appears that epitaxy might be possible for substrate temperatures in the range of  $600-850\,^{\circ}$ C, if conditions to achieve stoichiometric films could be defined.

Reactive synthesis using vacuum process techniques (e.g., sputtering, and pulsed laser deposition.) can readily drive the forward synthesis reaction at a few monolayers per second. The heat of Mg and/or B condensation, or the use of activated reactant species, could provide sufficient energy required to form the desired  $MgB_2$  phase under nonequilibrium conditions.

At a temperature of 650 °C, the Mg desorption rate from the surface of the film will be nearly one monolayer per second. If the Mg sticking coefficient is on the order of unity at this substrate temperature, successful synthesis at a rate on the order of a monolayer per second could be achieved with Mg fluxes of a few  $10^{15}$  cm<sup>-2</sup> s<sup>-1</sup>. Even higher substrate temperatures would be possible if larger Mg fluxes are used. However, if the sticking coefficient is significantly less than 0.1 at these temperatures, much larger Mg fluxes would be necessary. Several other options could also be tried. One would be to deposit the reactants at a reduced substrate temperature where the sticking coefficient is much higher (i.e., order of unity). The temperature of the thin film could then be increased to higher temperatures for time periods sufficiently short to result in small levels of Mg loss. These temperature excursions could be executed cyclically during growth, or at the end of the process, as was done by the Twente group. Another alternative would be to increase the sticking coefficient by using high kinetic energy Mg bombardment  $(> \sim 30 \text{ eV})$  so that this reactant is buried below the surface. This process would improve the sticking coefficient, but might also give other deleterious effects including an enhanced decomposition rate and/or creation of subsurface defects.

In summary, the evaporation of  $MgB_2$  in a vacuum was studied to provide insight into the proper conditions for *in situ*  $MgB_2$  thin film growth and thermal processing. At moderately high temperatures, near and above 425 °C,  $MgB_2$  decomposes and magnesium is desorbed. At a temperature of 650 °C, the desorption rate of MgB<sub>2</sub> is nearly one monolayer per second. The MgB<sub>2</sub> decomposition rate is found to have an activation energy of 2.0 eV. The evaporation coefficient is inferred to be  $\sim 10^{-4}$ , indicating that this process is kinetically limited. The presence of the large kinetic barrier to decomposition indicates that the synthesis of MgB<sub>2</sub> thin films will be possible with *in situ* vacuum processing methods, albeit within a narrow window in reactive growth conditions.

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