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Highly crystallized as-grown smooth and superconducting MgB₂ films by molecular-beam epitaxy

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We have investigated the growth of superconductive thin films of magnesium diboride (MgB₂) by molecular-beam epitaxy. A Si(111) substrate with a seed layer of MgO was used for the growth of these films by varying parameters such as the growth temperature, Mg:B flux ratio and deposition rate as well as the background pressure. It was found that highly crystallized films could already form at 250 °C; however, only in a narrow window of growth parameters. The highest critical temperature of 35.2 K with a sharp transition (ΔT_C of 0.5 K) was observed for films grown at 300 °C. Using a capping layer of MgO proved to be highly beneficial for the preservation and the smoothness of these films. Together with the fact that MgO proved to be a good seed layer for thin films of MgB₂ makes it an ideal candidate for growing all epitaxial MgB₂ Josephson junctions. © 2002 American Institute of Physics. [DOI: 10.1063/1.1530732]

The observation of superconductivity at 39 K in magnesium diboride¹ has generated much interest since it has twice the transition temperature of Nb-based alloys and the ability to carry strongly linked current flow.^{2–5} For many electronic applications using this material, high-quality thin films are a prerequisite. Most reports on magnesium diboride (MgB₂) thin-film preparation techniques describe a process that requires postdeposition annealing to produce superconducting films.^{6–12} However, as-grown superconducting thin films are favorable for applications utilizing, for instance, Josephson junctions. Two groups^{13,14} reported as-grown superconducting MgB₂ films, however, those films showed poor crystallinity. We report the synthesis of highly crystallized and smooth as-grown thin films of MgB₂ by molecular-beam epitaxy (MBE) with near ideal properties for junction fabrication.

Films were grown on a Si(111) substrate with a 50 Å seed layer of MgO in an MBE chamber with a base pressure of $1-2 \times 10^{-10}$ Torr. Pure metal sources of Mg and B were used: Mg was evaporated from a Knudsen cell (K-cell) and B was deposited by electron-beam evaporation. By proper calibration and real time monitoring of the Mg and B deposition rates by quartz crystal microbalance (QCM), the Mg–B deposition on the substrate could be well controlled.¹⁵ The deposition rates of Mg and B were monitored using two independent QCM whereas the film thickness was typically 600 Å. Various parameters like the growth temperature (T_S), Mg:B flux ratio, deposition rate, and background pressure were varied. T_S was varied between 200 and 350 °C and superconducting films were obtained in the range 200–325 °C. However, not all films grown in that range were superconductive. Some films were insulating or showed normal metallic behavior even down to 4.2 K (no sign of superconductivity), depending on other growth parameters.

This is not in agreement with the work of Liu *et al.*¹⁶ who predicted a thermodynamic stability window of Mg–gas + MgB₂ in which the growth is adsorption controlled, but confirms the observations of Jo *et al.*¹⁴ who had trouble finding this window as well. Auger electron spectroscopy (AES) showed that it is difficult to grow MgB₂ thin films with the right stoichiometry and that they are easily contaminated with oxygen which can be one of the main reasons for the insulating behavior. Each growth temperature had a specific window of growth parameters in which superconductive films were formed.

The AES spectra displayed in Fig. 1 show for films grown; Fig. 1(a) at 310 °C with a Mg:B flux ratio of 1.8, and Fig. 1(b) at 300 °C with a Mg:B flux ratio of 2.0. The numbers in Fig. 1 indicate the atomic concentrations obtained by the spectral intensity analysis. Spectrum (a) is taken from a film which showed a critical temperature (T_C) of 31 K and spectrum (b) is obtained from a film with a T_C of 27 K. The spectra show that the growth is not adsorption controlled but that a higher Mg flux results in a film that contains more Mg. Furthermore, they show that a better stoichiometry results in

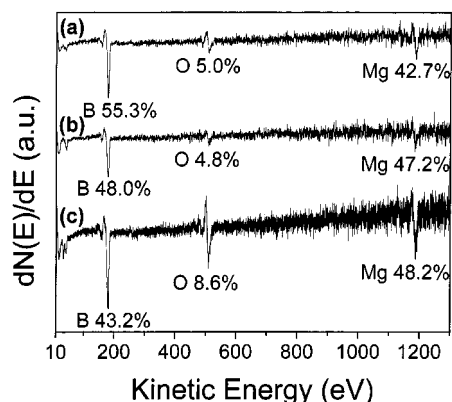


FIG. 1. Auger electron spectra of MgB₂ thin films with a T_C of 31.1 K (a) and 27.0 K (b). The Auger spectrum (c) was taken half an hour later than spectrum (b). Film composition as determined by the peak intensity is also indicated.

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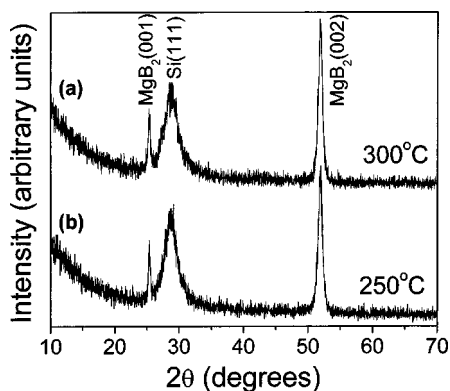


FIG. 2. XRD 2θ - θ patterns of MgB_2 thin films grown at 250 °C and 300 °C on Si(111) with a MgO seed layer.

a higher critical temperature and that the films are contaminated with oxygen. Spectrum (c) was obtained for the same film as in (b) but was taken half an hour later to investigate the oxidation rate. It shows that the oxygen concentration almost doubled, even while the film was exposed to a background pressure of only 6.0×10^{-10} Torr.

The detrimental effect of oxygen was demonstrated by varying the background pressure (partial oxygen pressure) during film deposition. Films were grown at a background pressure in the range from 3.5×10^{-9} to 1.0×10^{-7} Torr and it was found that, independent of other growth parameters, all the films that were grown at a pressure higher than $\sim 3.0 \times 10^{-8}$ Torr showed insulating behavior. It was also found that the specific window of growth parameters in which the superconductive films were formed became larger with a lower background pressure.

The quality of the MgB_2 thin films was also strongly dependent on the deposition rate of Mg and B. This was varied between 0.5 and 2.3 Å/s and it was found that films grown with a deposition rate below ~ 1.5 Å/s were all insulating and that the films that were grown with the highest deposition rate had the highest T_C . The negative effect of low deposition rates is probably caused by the low partial Mg pressure when depositing at low rates. Because of its

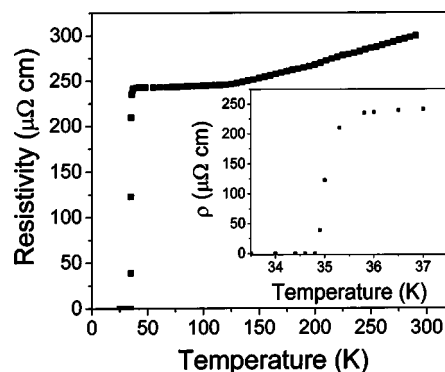


FIG. 3. Resistivity vs temperature data for a MgB_2 thin film grown at 300 °C.

volatility, a high partial Mg pressure is necessary to obtain good quality films at the required growth temperatures. Furthermore, at low deposition rates the chance of oxidation is higher. Higher deposition rates were limited by the maximum rate that could be used for the evaporation of B. When the deposition rate was not constant during growth, it had a negative effect on the quality of the film as well.

In Fig. 2 is displayed two x-ray diffraction (XRD) patterns for MgB_2 films showing that highly crystallized films can already form even at a growth temperature of 250 °C. For the MgB_2 thin films grown at 250 °C and 300 °C, the full width at half maximum of the (002) peak is 0.70° and 0.69° , respectively, corresponding to a grain size of about 740 Å.¹⁷ Not every film grown in the range of 250–300 °C showed this high degree of crystallinity. Films that were insulating showed no XRD peaks, whereas films with a lower T_C showed a reduced crystallinity, having smaller MgB_2 (00L) peaks in their spectra which were sometimes accompanied by a small Mg (002) peak, depending on the growth parameters. Even very poorly crystallized films still showed superconductivity which is in agreement with the results of Ueda *et al.*¹³ However, in our case, a higher T_C corresponded with the higher degree of crystallinity while their films remained poorly crystallized even when having a T_C of 32.8 K.

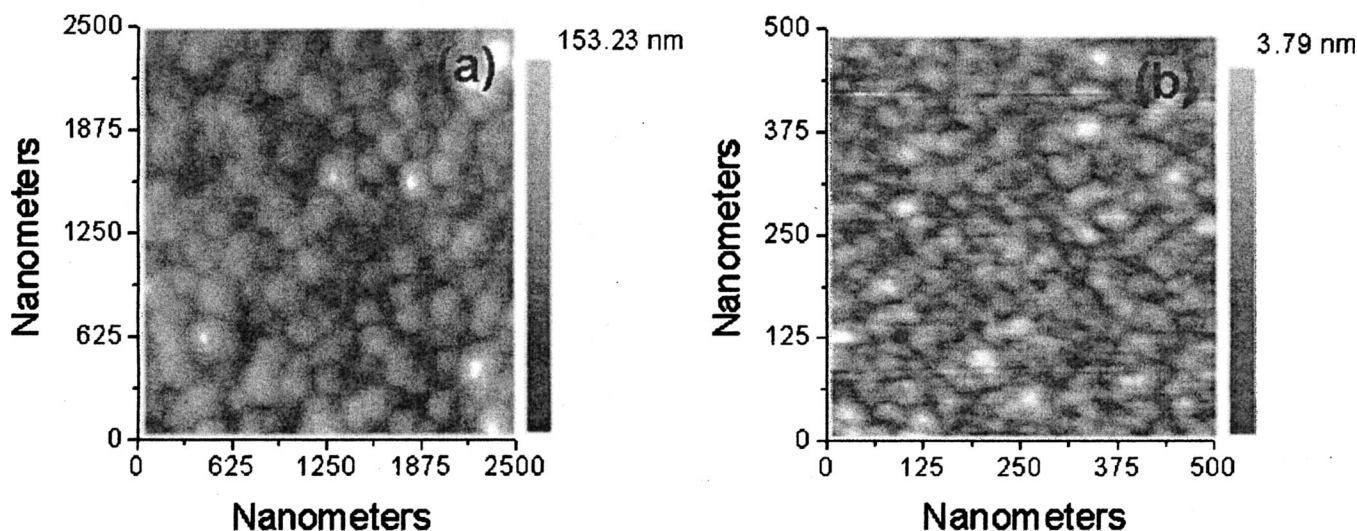


FIG. 4. AFM pictures of a MgB_2 thin film without a MgO capping layer (a) and with a MgO capping layer (b).

Figure 3 shows the resistivity versus temperature curve for the same MgB₂ film grown at 300 °C that was displayed in Fig. 2. It was grown at a deposition rate of 2.2 Å/s and with a Mg:B flux ratio of 1.5. The transition temperature range ($T_C^{\text{onset}} - T_C^{\text{zero}}$) of the film is 35.4–34.9 K (with a ΔT_C of 0.5 K). In spite of the high crystallinity, the T_C of this film is still well below the best bulk T_C , probably because of the contamination with oxygen and possible presence of off-stoichiometric material in grains or at the grain boundaries. Furthermore, the lattice constant of MgO is 4.21 Å, whereas it is 3.05 Å for MgB₂ implying a lattice mismatch of 28%. This would mean that MgB₂ cannot grow with good epitaxy directly on top of the MgO seed layer, but that there is some interface layer that is highly stressed which can also cause a reduced T_C .¹⁸ However, a 45° in-plane rotation of the MgB₂ film with respect to the MgO(001) direction results in a lattice mismatch of only ~3% for two unit cells of MgB₂ on a MgO unit cell, which would make epitaxial growth possible.¹² More experiments are needed to investigate the possibility of such an orientation.

We also characterized the film surface by atomic force microscopy (AFM). Figure 4(a) shows an image of a film grown at 300 °C that had a T_C of 35.2 K and no capping layer of MgO. It has a root-mean-square (rms) roughness of 255 Å and the average size of the features in the picture is about 3200 Å, which is about four times larger than the grain size obtained by XRD measurements of the same film. In Fig. 4(b), an AFM image is shown of a film grown at 250 °C, having a critical temperature of 32.7 K that had a 30 Å thick MgO capping layer. It has an rms roughness of 4.2 Å and an average feature size of 480 Å which is comparable with the grain size obtained by XRD for that film. This shows that having a MgO capping layer is highly beneficial for the smoothness of the films. It was also observed that films quickly degraded when exposed to air without a capping layer. Together with the fact that it proved to be a good seed layer for the growth of MgB₂ films, it can be an ideal candidate for serving as a barrier in MgB₂ Josephson junctions.

In conclusion, we have investigated the properties of as-grown MgB₂ films on a Si(111) substrate with a MgO seed layer under different conditions. Mg:B flux ratios, growth temperature, deposition rate, and background pressure were varied to determine the conditions to provide the highest-quality films for the fabrication of tunnel junctions. It was found that it is difficult to obtain high-quality films, because for each growth temperature, there is a specific window of growth parameters in which superconductive films were formed. However, when this window is found highly crystallized and very smooth MgB₂ thin films already form at

250 °C. This study thus shows the high potential for growing *in situ* Josephson junctions for applications.

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