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Ultra-high-vacuum epitaxial growth of MgB₂(0001) thin films on Mg(0001) via molecular beam epitaxy

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Abstract

Ordered MgB₂ thin films have been successfully grown on Mg(0001) by molecular beam epitaxy (MBE). By simply depositing B on the Mg substrate a maximum film thickness of about 4 ML can be achieved, while thicker layers can be obtained by co-deposition or alternated deposition of Mg and B. Thick films show hexagonal low energy electron diffraction patterns and the photoemission and x-ray absorption features typical of MgB₂.

1. Introduction

It has recently been demonstrated that superconductivity is present at 39 K in MgB₂ [1], a discovery that generated large interest in the scientific community because this is the highest superconducting transition temperature among intermetallic compounds, second only to cuprates.

Although MgB₂ has been around since the 1950s and it can be produced by a simple method (from low cost and non-toxic reagents), the synthesis of high-quality phase-pure samples is still very challenging. The growth of high-grade single crystals [2] has opened up a route for several important physical studies [2–11], but the sub-millimetre size of these crystals, the low chemical stability of MgB₂ and the need to expose the crystals to air before any experimental investigation, have limited the application of many techniques. Photoemission experiments, as well as other important investigations like scanning tunnelling microscopy and spectroscopy, transport measurements or de Haas–van Alphen studies, will take great advantage from the development of an adequate ultra-high-vacuum (UHV) *in situ* growth of ordered phase-pure

MgB₂ thin films. In addition, the controlled growth of high quality epitaxial MgB₂ thin films is also a critical step to realize MgB₂-based superconducting devices [12].

Ideally, the synthesis of MgB₂ films should be as simple as possible and as clean as possible due to the strong reactivity of Mg. Mg and B would be deposited on a substrate, at the highest possible vacuum and the lowest possible growing temperature compatible with the achievement of clean stoichiometric 'crystalline' MgB₂ films.

The simplest way to make a film of MgB₂ is to first deposit B, or a mixture of Mg and B, at a relatively low temperature, and then anneal it in the presence of Mg vapour to about 900 °C [13]. Alternative methods involve the deposition of a mixture of Mg and B at a lower temperature with typically an excess of Mg, either by sputtering [14], laser ablation [15], co-evaporation [16], or hybrid physical–chemical vapour deposition with B₂H₆ [17]. These different synthesis techniques, and the different thermodynamic parameters used, produce polycrystalline samples with slightly different electronic and superconducting characteristics, mainly ascribed to the effect of impurities, structural defects (i.e. Mg vacancies) and lattice strains [13–18]. Moreover, since all of these works involved a deposition pressure at best in a low vacuum range ($>10^{-7}$ mbar), the deposited films always suffered the presence of oxides due to the high chemical reactivity of MgB₂ and of Mg as well in the presence of oxygen and/or water.

However, one clear indication emerges from these studies: substrates having a surface with hexagonal symmetry and with in-plane lattice parameters close to those of MgB₂ must be preferred for the film growth. In this respect, Mg(0001) substrate is potentially one of the best candidates since the in-plane lattice parameter is 3.19 Å, only 3.5% larger than that of MgB₂ (3.085 Å), and the expected diffusion of Mg atoms from the substrate hopefully favours the MgB₂ formation in the first stages of growth. On the other hand, the strong reactivity of the Mg substrate asks for UHV conditions and, as a consequence, the growth can be performed only at low substrate temperature because of the vapour pressure of Mg in ultra-high-vacuum ($\sim 10^{-9}$ mbar at 250 °C). This may hinder the MgB₂ formation.

Figure 1 shows the phase diagram for the Mg–B system, as reported by Liu *et al* [19] down to a pressure of 10^{-6} Torr, for which we have extrapolated the low pressure (below 10^{-6} Torr down to 10^{-10} Torr) and temperature (below 230 °C) ranges according to some published works [16, 20, 21], whose growing pressure and temperature regions are also reported on the phase diagram. The diagram suggests that the thermodynamics conditions for MgB₂ formation may be compatible with the use of a Mg substrate in UHV.

In this paper we investigate the possibility to grow MgB₂ thin films on a clean Mg(0001) surface by molecular beam epitaxy (MBE). The quality and stoichiometry of the films, obtained under different growing conditions, were characterized *in situ* by measuring the photoemission core levels (XPS) as well as the valence band spectra (UPS), the B K-edge x-ray absorption spectrum (XAS) and by observing the low energy electron diffraction (LEED) pattern. We show that stoichiometric, clean and well-oriented MgB₂ thin films, suitable for angle-resolved photoemission spectroscopy (ARPES), can be grown on Mg(0001) in UHV at temperatures as low as 185 °C.

2. Experimental details

The experiments were performed in the UHV apparatus of the analytical division of the TASC laboratory and in the UHV end-station of the SuperESCA beamline at Elettra (base pressure 5×10^{-11} mbar in both experimental systems). The Mg(0001) substrate was cleaned and ordered by subsequent cycles of sputtering and annealing at 220 °C. Pure metal sources of Mg slugs (99.95%) and B pieces (99.5%) were used. Mg was evaporated from a resistively

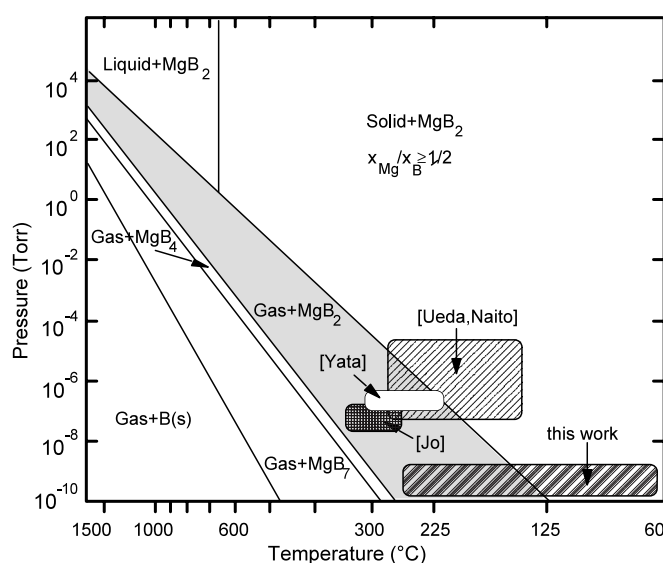


Figure 1. The pressure–temperature phase diagram for the Mg–B system. The grey ‘Gas + MgB₂’ area represents the thermodynamically stable region for the formation of MgB₂. Also shown are the pressure–temperature regions corresponding to the growing conditions of MgB₂ films reported by Ueda and Naito [16], Jo *et al* [20], Yata *et al* [21] and used in the present work.

heated Ta cell and B was evaporated using an electron-beam gun. Mg and B evaporators were carefully cleaned with several days of degassing.

In the TASC experimental apparatus Mg and B were evaporated separately (or co-evaporated) in the 3×10^{-10} to 2×10^{-9} mbar range. Boron layers were deposited on the clean Mg(0001) at 80 °C (a complete B layer in 20 min) and the formation of MgB₂ was studied as a function of the B thickness and annealing temperature of the deposited films up to 225 °C. Co-deposition was performed with an Mg:B atomic flux ratio of 3:2 on the clean substrate held at 185 and 205 °C with the formation of one complete layer of MgB₂ in ~14 min. XPS spectra were obtained using a Mg K α x-ray source, while UPS spectra were obtained using an He I resonance lamp. The photoelectrons were collected using a hemispherical 150 mm Leybold electron energy analyser at normal emission, integrating over 6°, with an overall energy resolution of 1 eV for XPS and 100 meV for UPS. The same XPS and UPS results were obtained by using Mg:B atomic flux ratio up to 2:3.

In the SuperESCA end-station, Mg and B were co-deposited with an atomic flux ratio of 2:3 on the clean substrate held at 220 °C. During the co-deposition, the pressure was maintained in the range 1×10^{-9} mbar $< p < 2 \times 10^{-9}$ mbar. Under these conditions, the evaporation rate was such as one complete layer of MgB₂ (in the following we define 1 ML = one plane of Mg + one plane of B in MgB₂(0001)) is formed in 7 min. Photoemission and x-ray absorption spectra were obtained using synchrotron radiation and collecting the emitted electrons by means of a double-pass hemispherical electron energy analyser with an angular resolution of $\pm 0.5^\circ$. The overall energy resolution was about 40 meV for valence band measurements and better than 200 meV for core level spectra.

In both experimental systems the evaporation rates were determined on the basis of the attenuation of the Mg 2p substrate peak as a function of the evaporation time in XPS (in the case of co-deposition the Mg flux was estimated by depositing Mg on a copper plate and

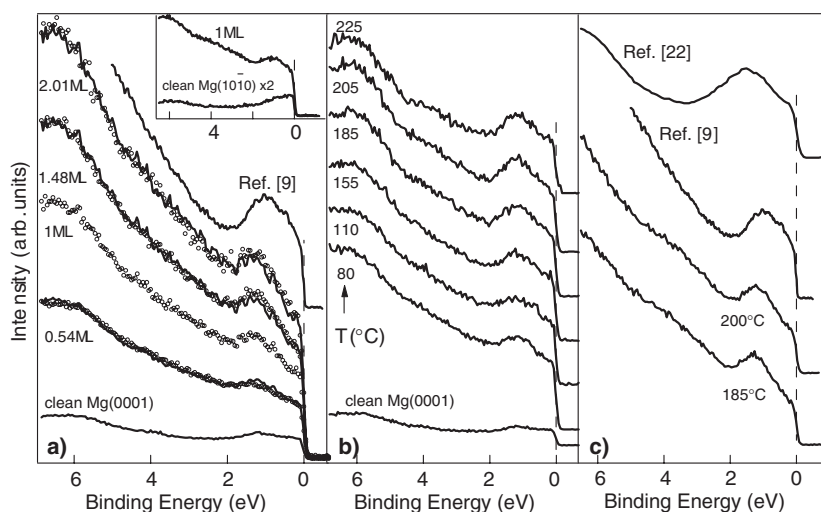


Figure 2. (a) UPS spectra of deposited B layers on the clean Mg(0001) corresponding to deposition times of 7 min (0.54 ML), 14 min (1 ML), 21 min (1.48 ML) and 28 min (2.01 ML). The simulations (continuous curve) according to a layer-by-layer growth (see the text) are superimposed to the experimental data (empty dots). The inset shows the UPS spectra of the clean Mg(10 $\bar{1}$ 0) surface and of 1 ML of B deposited on it. (b) Dependence of the UPS features in 1 ML of B on Mg(0001) on increasing post-deposition annealing temperatures. (c) UPS spectra of \sim 7 ML films obtained by co-depositing B and Mg at two different substrate temperatures, using an Mg:B atomic ratio of 3:2. MgB₂ reference photoemission spectra are also shown [9, 22].

measuring the attenuation of the Cu 2p_{3/2} signal) and the order of the grown film was checked using LEED.

The measurements were performed at room temperature.

3. Results and discussion

First, on the basis of the attenuation of the Mg 2p XPS signal (electron mean free path at 1200 eV kinetic energy of 28.5 Å) we have determined the formation of one single layer of B on the clean Mg(0001) kept at 80 °C (corresponding to the same number of atoms present in one complete B layer in MgB₂), whose UPS spectrum is shown in figure 2. For comparison the clean Mg(0001) spectrum is also shown. The intensities are normalized to the photon flux. Already at this growth temperature the UPS spectral shape of the deposited film presents features similar to MgB₂ [9, 22] (for this reason we call it 1 ML), whose reference spectrum [9] measured at Γ is shown on the top. Although the intensity is much higher than the clean Mg(0001) spectrum, one may argue that apparently the same features are already present in the clean Mg. To convince the reader that the observed lineshape of 1 ML is typical of a reacted B–Mg system and does not come from the Mg(0001) substrate, we show in the inset of figure 2(a) the spectrum of one complete layer of B deposited on Mg(10 $\bar{1}$ 0). The lineshape of the clean Mg(10 $\bar{1}$ 0) is completely different from that of Mg(0001), but the spectrum of the deposited film looks the same and, as above, is similar to MgB₂.

It seems, therefore, that after the deposition of a complete layer of B, the system reacts to form something similar to 1 ML of MgB₂. This growth seems to proceed layer-by-layer, as demonstrated by measuring the photoemission spectra as a function of the deposition time. In figure 2(a) we also report the spectra corresponding to an exposure to B flux 0.5, 1.5 and 2 times longer than that corresponding to the formation of 1 ML.

We have reproduced the spectral lineshape I_{tot} assuming a layer-by-layer growth mode, according to the following equation:

$$I_{\text{tot}} = I_c e^{-nd/\lambda} (1 - R + R e^{-d/\lambda}) + I_{\text{ML}} \left(R e^{-nd/\lambda} + \frac{e^{-nd/\lambda} - 1}{e^{-d/\lambda} - 1} \right).$$

Here, I_c is the photoemission signal (spectrum) of the clean Mg(0001), I_{ML} is the signal coming from one complete MgB₂ overlayer (that we assume to be the experimentally measured photoemission signal of 1 ML minus the attenuated signal of the clean substrate), n is the number of completed layers, and R is the fraction of the $(n + 1)$ th layer (the coverage is $\theta = n + R$). Finally, d is the thickness of one layer and λ the electron inelastic mean free path.

With this equation, the spectra at different B coverages have been well reproduced by assuming a layer thickness $d = 3.521 \text{ \AA}$ (i.e. the c -lattice parameter of MgB₂) using only two fitting parameters, the coverage θ and the electron inelastic mean free path λ . The resulting coverages, as reported in figure 2(a), are 0.54, 1.48 and 2.01 ML in agreement with the corresponding evaporation times, while λ is $14.0 \pm 0.3 \text{ \AA}$.

This layer-by-layer growth of the reacted B–Mg system, however, proceeds at 80 °C up to 4 ML only. Above this coverage, unreacted B layers form, as observed by XPS and UPS.

In figure 2(b) we show the effect of a post-deposition annealing of ~5 min on 1 ML film. By heating from 80 to 110 °C, no main changes are observed in the photoemission spectra. By annealing in the range 185–220 °C, a narrowing of the peak at ~1.2 eV is observed. This peak is mainly a MgB₂ surface state [9, 23], but also a minor contribution from σ -bands is expected due to the angular acceptance (6°) of the analyser. Thus, the enhancement of the surface peak suggests an improved order of the film surface. Above 220 °C, we observe a decrease in intensity of the whole spectrum (about 23% less after 5 min at 225 °C), indicating that the film starts desorbing, probably because of the sublimation of the Mg substrate. It seems, therefore, that the best growing temperature for the Mg–B films on Mg(0001) in UHV lies between 185 and 220 °C.

In order to obtain films thicker than 4 ML we co-deposited B and Mg on Mg(0001) keeping the Mg:B flux ratio with an excess of Mg with respect to the MgB₂ stoichiometry (see experimental details), and the substrate temperature between 185 and 220 °C. Figure 2(c) compares the UPS spectra of 7 ML films deposited at 185 and 200 °C, with reference spectra of MgB₂ powders [22] and single crystal [9]. As above, the lineshape is very similar to that of MgB₂, with an even more pronounced surface state compared to thinner films.

It is worth noting that the grown films, in particular the thicker ones for which the substrate signal should be almost completely attenuated, displayed a sharp hexagonal LEED pattern and both XPS and UPS spectra did not show the presence of oxygen or other contaminants.

To confirm whether these films are really MgB₂ we moved to the synchrotron. Figure 3 shows the XPS wide spectrum measured at 655 eV photon energy and the corresponding LEED pattern of a film obtained after 2 h of co-deposition with the Mg(0001) substrate kept at 220 °C. The measured Mg 2s/B 1s area ratio of 0.30 is consistent with stoichiometric, Mg-terminated MgB₂, as results from the equation

$$\frac{I_A}{I_B} = \frac{n_A \sigma_A}{n_B \sigma_B} \frac{1 - e^{-d/\lambda_B}}{1 - e^{-d/\lambda_A}} e^{d/2\lambda_B}$$

valid for an A-terminated multilayer structure ABAB... with distance $d/2$, i.e. half of the c -lattice parameter of MgB₂, between the slabs.

Here $I_{A(B)}$ is the photoemission signal of a representative core level peak of A(B) coming from one single slab A(B), $n_{A(B)}$ is the atomic density of A(B), $\sigma_{A(B)}$ is the photoemission cross section and $\lambda_{A(B)}$ is the electron inelastic mean free path of the core level of A(B). This equation gives for the Mg 2s/B 1s area ratio a value of 0.30 ± 0.02 for an Mg-terminated,

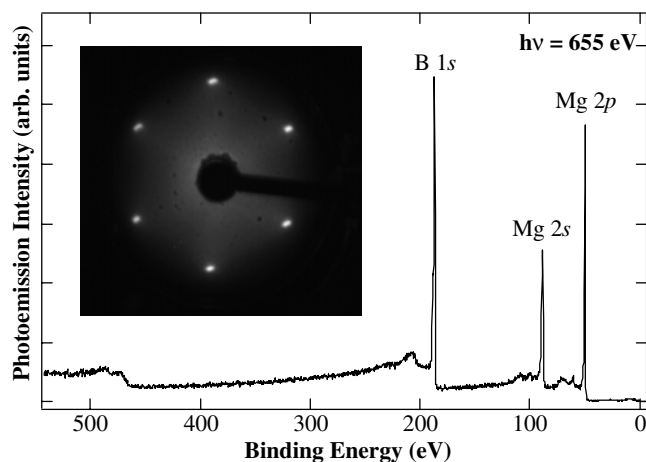


Figure 3. XPS spectrum of a 17 ML thick epitaxial film obtained by co-depositing boron and magnesium on the Mg(0001) substrate kept at 220 °C. The corresponding LEED pattern, at primary electron beam energy of 52 eV, is also shown.

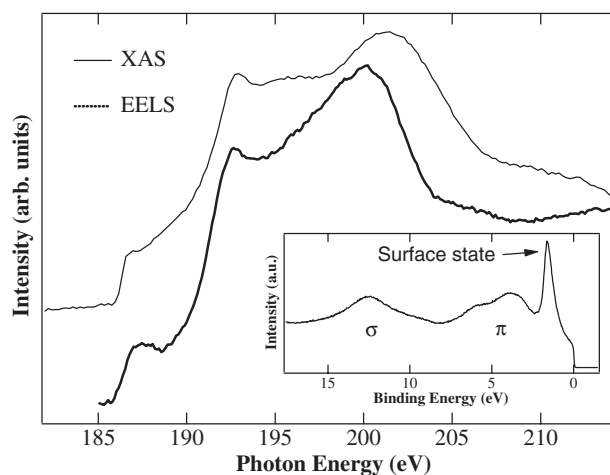


Figure 4. XAS spectrum at the B 1s threshold of a 17 ML thick epitaxial film obtained by co-depositing boron and magnesium on the Mg(0001) substrate kept at 220 °C, compared to the EELS spectrum measured on a MgB₂ crystal [24]. The corresponding valence band photoemission spectrum measured at $h\nu = 105$ eV is also shown. Note the enhancement of the surface state at this photon energy.

stoichiometric MgB₂ film, while for a boron-terminated film it gives 0.23 ± 0.02 . The error on the value of this ratio is due to the uncertainty in $d/\lambda_{A(B)}$.

The estimated film thickness is about 18 ML. Even in this case, it can be seen that no other elements apart from boron and magnesium are present. Figure 4 shows the XAS spectrum at the B 1s threshold measured on this film, with the linear light polarization at 45° from the surface, compared with the electron energy loss spectrum (EELS) [24] at the B 1s threshold, measured on a single crystalline grain with the electron momentum \mathbf{q} parallel to the c -axis. The XAS spectrum compares quite well with the MgB₂ EELS data, the only notable difference being at high energies where, however, the EELS spectra may be affected by multiple scattering

effects. We also observe a strong polarization dependence of the XAS spectra (not shown here) that is in agreement with theoretical calculations for MgB₂ [25].

Finally, the inset of figure 4 shows the valence band photoemission spectrum of the co-deposited film taken at 105 eV of photon energy near the Γ point. All of the observed features are in good agreement with band structure calculations for MgB₂ and, as shown elsewhere [26], the band dispersion of the σ and π bands (both in-plane and perpendicular to the planes) follows the calculated MgB₂ electronic structure. Moreover, the in-plane dispersion of the surface state compares with the theoretical calculations for the Mg-terminated MgB₂(0001) surface [27].

4. Conclusions

Deposition of B or co-deposition of Mg and B on Mg(0001) in UHV and in a temperature range between 185 and 220 °C allows the epitaxial formation of ordered MgB₂ films as confirmed by low-energy electron diffraction, x-ray photoemission and absorption spectroscopy and ARPES. This growth method ensures a very clean sample (free of oxygen and other contaminants) and allows important *in situ* measurements like ARPES, scanning tunnelling microscopy and spectroscopy, transport measurements or de Haas–van Alphen studies to be performed without exposing the MgB₂ samples to air. This controlled UHV MBE-growth of clean MgB₂ films may enable the controlled doping of this material, as well as it could be used to realize MgB₂-based superconducting devices.

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