Electronic structure of superconducting MgB$_2$ film

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Abstract. Superconducting MgB$_2$ films were obtained following a two steps approach, using the multilayered structures of MgB$_x$/Mg as precursors deposited at low substrate temperature by sputtering of an MgB$_2$ stoichiometric target, and thermal evaporation of pure Mg. Precursors were subsequently annealed in-situ in the range of 350-600°C. The films showed a zero resistance critical temperature up to 31 K.

The as-obtained MgB$_2$ films were investigated by X-Ray Photoelectron Spectroscopy (XPS) and X-Ray Auger Electron Spectroscopy (XAES) using non-monochromatic Al K$\alpha$ radiation (1486.6 eV) and a double-pass CMA operating in retarding mode. The electronic structure was studied by monitoring the B1s, Mg2p, O1s core-levels and the Mg KL 2,3 L 2,3 Auger peak structure. For comparison, the electronic structure of an MgB$_2$ superconducting sputtering target, of a precursor film and of a non-superconducting sample obtained by sputtering from the MgB$_2$ target have also been investigated. Electron spectroscopy showed that in the superconducting systems the Mg KL2,3 L2,3 Auger peak kinetic energy position is always higher by about 0.7eV with respect to the energy position of the same Auger line measured in the non-superconducting samples.

1. Introduction

Since the discovery of its superconducting behaviour, magnesium diboride has attracted considerable interests under both theoretical and practical points of view. Compared to high-$T_c$ cuprates, MgB$_2$ shows less material complexities, less interface problems, and longer coherence length. All these qualities make MgB$_2$ suitable for electronic applications. Shortcomings to a wide use of MgB$_2$ in superconducting devices can come from thin films fabrication that is affected by two aspects, both correlated to magnesium, that is to say its sensitivity to oxidation and its high volatility.

Apart physical-chemical deposition methods, which are able to give high quality epitaxial films [1] or co-evaporation methods [2], deposition techniques devised so far can be classified as ex-situ or in-situ, according to the way the annealing process to fix the loss of magnesium is performed.

Thin MgB$_2$ films with bulk-like properties can usually be obtained by using ex-situ annealing steps, in which films are held at 700-900 °C in a closed volume in Mg atmosphere [3, 4]; ex-situ processes, however, are not compatible with device technology. In-situ annealing processes generally give better thin films surface quality, but they need further optimization studies as the $T_c$ values are below 36 K.

In this paper, we report about the synthesis of MgB$_2$ obtained by depositing multilayer structures by sequential sputtering from MgB$_2$ stoichiometric targets and Mg evaporation sources. As previously reported [2], by using this in-situ technique it is possible to grow films with good surface properties, and transition temperatures $T_c$ that varies from 25 to 31 K.
In order to study the reason for the lower transition temperature on in-situ low temperature processed MgB$_2$, we have investigated the chemical composition and electronic structure of multilayer films.

To this purpose, samples have been characterized by usual R vs. T scans and by XPS and XAES analysis. XPS and XAES are powerful techniques that can give a useful insight into the electronic structure and composition of surfaces. To our knowledge, only a few XPS and XAES investigations on MgB$_2$ are reported in the literature [5-7] and mostly on bulk samples.

Results obtained so far show the evidence of MgB$_2$ formation, with the presence of oxide and magnesium segregation that can explain the poor superconductive behaviour. In addition, it has been possible correlating the energy position of the Mg KL$_{2,3}$L$_{2,3}$ Auger line with the superconducting properties of the synthesized MgB$_2$ films.

2. Experimental

Deposition setup includes a 1" DC magnetron sputtering gun provided with a commercial MgB$_2$ target (99.5% pure, Superconductive Components), and a thermal evaporation source provided with pure Mg grains (99.98%, Aldrich Chemical Company).

Multilayer structure is obtained by using a swinging arm supporting the sample holder and the heater; thanks to this device, the substrate can be placed alternatively above the sputtering and the evaporation sources so to get a multilayer structure. Resident time on each material source was typically 2 seconds on Mg and 30 seconds on MgB$_2$, but it could be varied as needed. Layers relative thicknesses Mg/MgB$_2$ have been always kept between 1 and 2.

Both sputtering and evaporation processes take place in a 10 mTorr pressure of Ar. Deposition rates were 0.4 nm/s for sputtering and about 2.5 nm/s for Mg evaporation. During film growth, substrate temperature is usually kept at 200 °C. Total deposition time can vary between 5 and 15 minutes, and films have a thickness ranging from 0.3 to 1.0 micron.

In order to form a unique MgB$_2$ phase, immediately after multilayer deposition the reaction chamber is filled with Ar at 450 Torr and the substrate is heated up to the annealing temperature, typically 550 °C, then the sample is kept under these conditions for the annealing time, $t_{\text{ann}}$. Finally, heater power is switched off and the camber is opened after natural cool down.

XPS and XAES data were taken in a UHV chamber (base pressure 1x10$^{-10}$ mbar) using non-monochromatic Al K$\alpha$ radiation (1486.6 eV) and a double-pass CMA operating in retarding mode.

The energy scale was calibrated with reference to the binding energy of the Si2p$_{3/2}$ peak from an atomically cleaned Si(100) sample, measured to be 99.25±0.05 eV with respect to the Fermi level. Samples were etched by several Ar$^+$ sputtering cycles at 1000 eV beam energy. XPS and Auger data were collected after each sputtering cycle.

3. Results

The results presented in this paper have been obtained by studying four different samples. A first set of two un-annealed samples, one of them deposited as a multilayer structure (shortly “MF”) and the other one only from sputtering (“F”), has been used to see any difference in the composition of as-deposited films compared to the starting material. A third sample was a fully processed multilayer film (“SMF”) and the fourth sample was the MgB$_2$ sputtering target (“ST”). By these choices, we have been able to compare the characteristics of the as-deposited and reacted samples with a high quality MgB$_2$ superconductive material coming from the sputtering target.

The first two films are known to have no superconductivity, and in fact their R(T) curve showed no transition. The R(T) curve measured on the sputtering target sample (ST) shows that the transition is relatively high, i.e. $T_c=37.5$ K, and the RRR is about 5, i.e. of the same order of what is reported for crystalline samples, proving that this sample belongs to a different category when compared to our thin films. The multilayer annealed sample SMF has a superconductive transition above 25 K, as shown in Figure 1.
The electronic properties of the samples were studied by monitoring the Mg2p, B1s core levels and the Auger line KL2,3, L2,3 as a function of sputtering time up to $459'$. Figure 2a shows the SMF Mg KL2,3, L2,3 XAES lines for different sputtering times. The kinetic energy (KE) of the Auger lines is referred to the Fermi level. In the as-inserted sample, the Auger line is at $1180.3\pm0.1$eV KE.

After 10' sputtering an intensity increase is registered together with a shift to $1180.9\pm0.1$eV. The KE is unchanged up to 37' sputtering. After 111' sputtering the MgKLL Auger line is observed to decrease in intensity by about a factor 4 and to shift to $1183.7\pm0.1$eV and then, after additional sputtering, it reaches the final stable KE position at $1184.2\pm0.1$eV. The evolution of the SMF Mg2p XPS peak as a function of sputtering time (not shown) reflects the intensity behaviour observed for the Mg KLL line. After 10' sputtering the XPS Mg2p peak intensity increases and the BE shifts to $50.4\pm0.1$eV where it stabilizes. After 111' the Mg2p intensity decreases by about a factor 4 and then remains nearly constant up to the highest sputtering times. The increased relative intensity observed up to 37' sputtering, is probably due to the removal of adsorbed surface contaminants. The B1s XPS core-level (not shown) was below the detection limit up to 37' sputtering. Above that time, the spectral intensity is nearly constant and the BE position is stable at $187.8\pm0.1$eV up to the highest total sputtering times. According to the literature, which reports values of about 1182eV and 50eV for the Mg KLL Auger in MgO and Mg2p core level in MgO respectively [5-7], the as-inserted sample surface appears to be covered by a layer of mostly MgO and/or hydroxides (Mg(OH)$_2$) and carbonates (MgCO$_3$) compounds. The removal of contaminants adsorbed on the surface after initial sputtering causes an increase of the Mg-O related chemical bond photoemission intensity which is reflected in the corresponding Mg Auger and XPS data.

The presence of the MgO at the surface is expected due to the known Mg surface segregation and subsequent oxidation upon air exposition. By further sputtering a decrease of the Mg KLL and Mg2p intensities is observed. The decrease is accompanied by a shift towards higher KE of the Mg Auger peak. That could indicate the onset of a more “metallic” character of Mg in the sample which is a hint of the presence of a superconducting MgB$_2$ phase which is known to be metallic [6]. In the 1184.7eV Mg KLL line the bump at 1180.9eV is indicating residual MgO like compounds which are observed to disappear at the longer sputtering times. XPS measurements performed for comparison on the superconducting ST sample (not shown) confirmed the results reported for the annealed multilayer sample (SMF). Similarly to the case of the SMF sample, the Auger Mg KLL line was observed at 1184.3±0.1eV. XPS data measured on the two non-superconducting samples F and MF (not shown) give, similarly to the superconducting samples, the usual value 187.8±0.1eV for the B1s core-level BE. On the other hand, the Mg 2p core level is measured in both samples at 50.7±0.1eV after the longest sputtering time. Figure 2b shows some XAES Mg KL2,3, L2,3 taken on sample MF after different sputtering times.

After initial sputtering the Auger lines show lower KE features which can be associated to Mg (hydro) oxides or carbonates. By increasing the sputtering time, the lower KE features intensities decrease and the main line shifts to $1183.2\pm0.1$eV, the highest measured KE value. By comparison with the results...
obtained on the superconducting samples, the non-superconducting ones show a lower Mg KLL KE and a higher Mg 2p BE. This behaviour can be related the presence of oxides (and carbonates) in the whole film. Due to the remarkable KE difference (about 1eV) registered between the Mg KLL lines of the superconducting and non-superconducting samples and the favourable XPS spectral emission intensity of the Auger line compared to the Mg 2p core-level, these results indicate that the Mg KL2,3,L2,3 kinetic energy is a reliable spectral parameter for determining the superconducting properties of the MgB2 films.

4. Conclusions
In order to find the best deposition conditions for our in-situ processed, multilayer MgB2 samples, we have studied the presence of chemical compounds responsible for the low transition temperature and poor electrical characteristics.

Results obtained so far show the evidence of MgB2 formation, with the presence of oxide and magnesium segregation that can explain the poor superconductive behaviour. These compounds are present in as-deposited films, and annealing process tends to segregate impurities to the surface.

In addition, it has been possible correlating the energy position of the Mg KL2,3,L2,3 Auger line with the superconducting properties of the synthesized MgB2 films.

References
[1] Zeng X H, et al. 2002, Nature Materials 1, 35.
[2] Grassano G, Besi Vetrella U, Boffia V, Celentano G, Gambardella U, Mancini A, Petrisor T, Rufoloni A, Vadrucci M 2003, proceedings of 6th European Conference on Applied Superconductivity, 1367.
[3] Kang W N, Kim H J, Choi E M, Jung C U, Lee S I 2001, Scienze 292, 1521.
[4] Eom C B, et al. 2001, Nature 411, 558.
[5] Vasquez R P, Jung C U, Park M S, Kim H J, Kim J Y, Lee S I 2001, Phys Rev B 64, 052510.
[6] Goldoni A, Larciprete R, Lizzit S, La Rosa S, Bianco A, Bertolo M 2002, Phys Rev B 66, 132503.
[7] Wang S F, Zhou Y L, Zhu Y B, Zhang Q, Dai S Y, Xie K, Chen Z H, Lu H B, Yang G Z 2003, Physica C390, 1.