YBaCuO thin films deposited by ion beam sputtering assisted by implantation of : O, Ne, Ar, Cu, Kr, Xe and Ba.

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## Abstract

-Amorphous thin films of YBaCuO are prepared, at room temperature, by ion beam sputter deposition (Kaufman source) assisted by energetic (150 KeV) ion implantation of O, Ne, Ar, Cu, Kr, Xe, and Ba. Influence of the atomic mass of the incoming ions on the stoichiometry, density and dynamic sputtering process is studied. Stoichiometry is measured by RBS. Density and sputtered thickness are measured by grazing X ray reflectometry.

# **INTRODUCTION:**

-Y<sub>1</sub>Ba<sub>2</sub>Cu<sub>3</sub>O<sub>6+x</sub> thin films have been prepared using a variety of methods (1,2,3,4,5,6). For micro-electronic applications it would be desirable to deposit on important technical substrates as, for example, Si substrates. There is therefore a considerable interest in the deposition at rather low temperatures (T< 600°C).

Energetic ion ( $\approx 100$  KeV) beam assisted deposition (EIBAD) offers this possibility as the energy of the deposited species coupled with ion implantation deposited energy allow irradiation enhanced crystallization, densification and can induce texture development.

The deposition conditions of YBaCuO thin films assisted by ion bombardment of the growing film is a field of research which is not well developed yet.(7)

EIBAD has probably a tremendous potential as a technique to produce thin superconducting films with controlled properties such as :

-fully dense films, growth at low substrate temperature, relief of the internal stress in the film, good adhesion with the substrate, texture development through the ion beam induced shift of the orientation toward alignment of the easiest channeling direction along the ion beam axis. This texturing effect which appears to be more pronounced for high energy beam, could have tremendous commercial impact if it was to be extended to produce c-axis oriented films in a rather low temperature deposition process.(8)

Furthermore, the energetic ion beam can be used to compensate for elements deficient in the film, insofar-as oxygen, copper, yttrium and baryum beam have already been used (9). On the other hand, a defined transition temperature and critical current density can be achieved by introducing controlled ion damages or implantation into selected areas or patterns.

Implantation defects can act as pinning centers for the flux lines, leading to the enhancement of the critical current capacity. (10,11)

Therefore, this paper describes some results concerning YBaCuO thin films obtained by ion beam sputtering assisted by ion bombardment of such ions as O, Ne, Ar, Cu, Kr, Xe and Ba.

This study is focused on the early step of the deposition at room temperature. The role played by the implanted atoms on the composition, density and sputtering phenomena is investigated by Rutherford backscattering spectrometry (RBS) and X ray reflectometry.

# **EXPERIMENTAL PROCEDURE :**

-Thin

films of YBaCuO are deposited in an ion beam sputtering chamber which includes a 7 cm diameter Kaufman source. Sputtering is brought about by a beam of argon whose accelerating voltage is 1.2 KV and intensity around 60 mA. A 10 cm, water cooled, sputtering target of stoichiometric  $Y_1Ba_2Cu_3O_{6+x}$  is used at 15 cm from the Kaufman source. (Fig 1). Thin films are deposited at room temperature, on different substrates, as Si, MgO, SrTiO<sub>3</sub>. Thickness of the films are in the range 100-1000 nm.

The sputtering chamber is in line with a 200 KV ion implanter. Assisted deposition are performed by implantation of O, Ne, Ar, Cu, Kr, Xe and Ba with an energy of 150 KeV and a current density around  $1\mu$ A/cm<sup>2</sup>. Total ion fluences received by the thin films at the end of the deposition were in the range  $5.10^{13}$ - $10^{15}$  ions/cm<sup>2</sup>.



Figure 1 : Ion beam deposition system

Composition of the as-deposited amorphous films is analysed by RBS using a 2 MeV helium beam. Experimental spectra are fitted with the RUMP program package (12).

Density variations and sputtering of the deposited films, due to the implanter beam, are measured by mean of X ray reflectometry (13).

Depending upon the quality of the films, this method is able to give the thickness of a thin film with an accuracy of few angstroms.

## **EXPERIMENTAL RESULTS :**

-In this study, all the depositions were carried out at room temperature. The as-deposited thin films are amorphous as shown by TEM and X rays diffraction. Therefore the following results deal with the influence of the atomic mass of the implanted ions on such properties of the amorphous layer of YBaCuO as density, stoichiometry and sputtering of the layer with respect to non-assisted deposition process.

-Stoichiometry:

-Atomic ratio between the different species of the YBaCuO layers are shown in figure 2.Eventhough oxygen peaks in all the RBS spectra are always large, results concerning oxygen are not in the figure 2 because it is rather difficult to extract oxygen concentration from those spectra assuming a Rutherford regime.

A general trend which can be noticed in figure 2, assuming an yttrium stoichiometry of one, is that the Cu/Y and Ba/Y ratios shift from the good values of 3 and 2 respectively. It is not the case for the Ba/Cu ratio which is always near the ideal value of 0.66. For the heaviest incoming ion mentioned in figure 2, i.e. Ba, The Cu/Y and Ba/Y ratios are well under the value of the non-implanted layer.



Figure.2:composition of the deposited films versus the atomic mass of the incoming ions.

#### -Density:

Thin films of amorphous YBaCuO obtained without implantation have a density of 4 g/cm<sup>3</sup> which is around 62% of the density of the crystalline phase (6.38 g/cm<sup>3</sup>). A densification effect appears with implantation of neon, increases substantially with argon and then seems slightly to decrease (Fig3).



Figure.3: Density of the deposited films versus the atomic mass of the incoming ions

## -Sputtering of the thin films:

-All the process which include energetic ion bombardment are limited by the sputtering phenomena, particularly with such heavy ion as barium.

In this case, one ion of barium whose energy is 150 KeV which impiges the film at 45° induces a sputtering of approximately 10 ions of the YBaCuO layer.



FIG.4 : Experimental sputtering yield of the deposited films versus the atomic mass of the incoming ions (units correspond to the sputtered thickness, per unit area, for one incoming ion)

Owing to the high resolution possibilities of the X rays reflectometry, the thickness of the thin films realized by implantation assisted deposition have been measured. The thickness which have been sputtered away as a function of atomic mass of the implanted ions are shown in figure 4. In this figure, the sputtered thickness is rationalized by the total ion fluence received by the film



FIG.5 : Experimental sputtering yield of figure 4 compared to the theoretical sputtering deduced from TRIM calculations.

It is worthy of mention that the sputtered thickness dramatically increases toward the mass of argon ion. This surprising behavior of the experimental sputtering is compared with the theoretical sputtering computed with the TRIM code (14) (Fig 5).

An other interesting point is the similarity of the two curves in the xenon and barium region.For those heavy ions experimental sputtering could be explained on the basis of theTRIM computations.

## **DISCUSSION OF THE RESULTS :**

This study of thin films of YBaCuO, elaborated at room temperature, by ion implantation assisted ion beam sputtering deposition is focused on the early step of the elaboration process where the as-deposited layers are amorphous.

Parameters under investigation are stoichiometry, density and sputtered thickness as a function of the atomic mass of the implanted ions.

### -Stoichiometry:

Without implantation, the stoichiometry is not very far from the 1,2,3 ratios. With implantation,Cu/Y and Ba/Y shift away from those values. This observation can be explained in terms of preferential sputtering. Nevertheless, the Ba/Cu ratio exhibits a rather constant value.

#### -Density:

It is worth noting that the curve which represents the density versus atomic mass substantially increases up to the argon ion mass and then slightly decreases.

The efficiency of ion beam assistance can be suggested in terms of the energy transfer factor of the binary collision approximation defined as:  $T=4m_1m_2/(m_1+m_2)^2$  where  $m_1$  and  $m_2$  are the target and incoming ion mass respectively. When T=1, the energy transfer is maximum. Values of this factor for the different atoms of the film, Y,Ba,Cu and O are shown figure 6, together with a component whith a mean atomic mass of 51 which corresponds to the atomic mass of YBaCuO weighted by the stoichiometry 1,2,3,7. The maximun of T is then at  $m_2=51$ . When a mean value of T for the different target atoms is calculated, T is maximum at  $m_2=31$ .

In both cases, the general trend of this coefficient versus the atomic mass of the incoming ions, suggests a ballistic effect in the densification process.

-Sputtering of the deposited layer The salient features of the sputtering behavior due to the implantation assisted deposition are: : The curve which represents the total sputtered thickness versus implanted ion mass exhibits a maximum in the argon region.



-Experimental and theoretical sputtered thickness obtained from the TRIM calculations (14) are very different. The ratio between both results is greater than 50 for atomic mass around 40.

-The discrepancy between experimental and theoretical sputtering decreases and finally disappears for atomic mass around 130(Xe, Ba). Obviously, this dynamic sputtering phenomena which takes place, as growing amorphous layer of YBaCuO proceeds, cannot be explained in terms of the classic theory of sputtering. By comparison with molecular dynamic simulation of atomic rearrangements produced by impact of bombarding ions on films with porous structure (15), an explanation can be suggested from the results concerning density and sputtered thickness versus atomic mass.

The non-assisted as-deposited layer exhibits a rather "defective" structure whose density is around 60% of the theoretical density of the cristalline structure.Both surface morphology and atom arrangement in the bulk of the growing amorphous layer are very irregular. Owing to this defective-like structure, links between atoms or "islands" of atoms can be very weak. The result is a dramatic sputtering sensitivity to energetic ion bombardment which increases with ion mass. But, as ion mass increases, the density increases up to the mass of argon, leading to smoother surface and internal densification very likely by forward recoils or deplacements of film atoms and some increasing mobility mechanism which gives a more densely packed configuration. Therefore, as atomic mass of the incoming ions increases, the dynamic sputtering yield decreases and becomes a more "classic" sputtering phenomena.

In conclusion, a lot of work is still to be done on the early step of the ion bombardment assisted deposition of the amorphous thin films of YBaCuO. Structural aspects as density and stoichiometry, together with the dynamic sputtering mechanism involved during the growth of the film, might be of prime importance for the further step of recrystallisation which will give the quality of the superconductor

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