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Comparison of High Pressure DC-sputtering and Pulsed Laser Deposition of Superconducting $Bi_{1.6}Pb_{0.4}Sr_2Ca_2Cu_3O_{10+\delta}$

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Abstract— Superconducting $Bi_{1.6}Pb_{0.4}Sr_2Ca_2Cu_3O_{10+\delta}$ thin films were deposited on Si(111) substrates using two different techniques: dc-sputtering at high oxygen pressure and pulsed laser deposition. The structure and electrical properties of the obtained films were compared. The transition temperature T_c for bulk and films deposited by PLD is 102 K and 97 K respectively, while T_c of films prepared by dc sputtering is 90 K. The structural analysis was carried out by XRD on pellet sample and its annealed and as deposited films .The surface morphology of the films have been studied by using AFM.

Keywords: DC-sputtering; PLD; Thin film superconductors

I. INTRODUCTION

The development of reproducible and stable processes for homogeneous deposition of high quality and large area high T_c films is crucial for fabrication of many superconducting devices. Many different techniques have been widely employed and proved suitable for the deposition of high temperature superconductor HTSc especially BSCCO thin films, but the most common technique are pulsed laser deposition and sputtering [1, 2].

Kula et al,[3] have reported the investigation of the 110 K $Bi_2Sr_2CaCu_3O_x$ phase formation in superconducting thin films of Bi-based cuprates. The films were dc magnetron sputtered from single Bi(Pb)-Sr-Ca-Cu-O targets of various stoichiometries, and subsequently annealed in air at high temperatures. It has been found that heavy Pb doping considerably accelerated formation of the 110K phase reducing the film annealing time to less than 1 hour. The films were *c*-axis oriented,with 4.5 K wide superconducting transition, and zero resistivity at106 K.

Hiroki wakamatsu et al. [4] studied the superconducting properties of (Cu, C) Ba_2CuO_y thin films deposited by RF magnetron sputtering from targets with a nominal composition of $Ba_2Cu_{1.5}O_y$. The thin films were grown in mixed Ar (5~40 mTorr), O_2 (0~1.2 mTorr) and CO_2 (0~1.8 mTorr) atmosphere. By optimizing deposition conditions, the excellent (Cu, C)Ba_2CuO_y thin film with T_c = 62K and superconducting transition width ΔT_c = 1.5 K was successfully obtained.

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Ayhan [5] studied the composition of as-deposited Bi-2212 thin films as a function of the rf magnetron sputtering variables, i.e. substrate to target distance, total sputtering gas pressure and aging of the target, in an on-axis configuration. They found that after 12 hours pre-sputtering a target can have a steady state for a long subsequent period of 60 hours or over for an rf-power of 50 watt. Sputtering chamber Ar gas pressure has a strong effect on the Bi ratio of the as-deposited film composition, while other metallic cations, Sr and Ca are not much affected by chamber pressure. Bi ratio in the as-deposited film composition increases with increasing gas pressure in the chamber. The peeling of mechanism for ex-situ annealed thin films was investigated and found that the main reason is wrong composition within certain limits. Bi/Sr ratio should be kept between 0.9-1 (which is also essential for stoichiometry) to prevent the peeling of in as-deposited Bi-2212 thin films during the high temperature annealing process. For some extreme values of Bi/Sr ratio (too high or too low) the film may stay on the substrate. However as expected, this unstoichiometric composition does not allow good superconducting properties. Kim et al. [6] deposited thin films of Bi-Sr-Ca-Cu-O on (100) cubic zirconia by PLD from a bulk superconducting target of nominal composition $BiSrCaCu_2O_x$ had investigated by dc resistance. It has shown that the film quality is affected by the substrate temperature and the annealing process. They indicated that the films are oriented with the *c*-axis perpendicular to the film plane.

Jannah *et al* [7] studied the properties of BSCCO thin film deposited by pulse laser deposition .Thin films of $Bi_{1.6}Pb_{0.4}Sr_2Ca_2Cu_3O$ have been grown on (100) MgO and the oxygen pressure during the deposition was ~2 x 10^{-3} mbar using Nd: YAG pulse laser beam. The as-deposited films were annealed under oxygen flow at the temperatures between 820ºC to 850ºC for 2 hours with heating rate 3ºC/min. Morphological and structural analysis of thin films produced were performed by an SEM, X-ray diffractometer and AFM. The electrical properties of the bulk and film were measured using a four point probe system. Their results show that annealing at 850ºC for 2 hours improved the superconducting properties of the film. The XRD patterns and T_c measurement with zero resistivity temperature at about 60 K indicate that the film were mainly grown in 2212 phase, with 2223 phase which is detected in small structures on the film surface. The aim of this search is fabrication of thin film superconductor of $Bi_{1.6}Pb_{0.4}Sr_2Ca_2Cu_3O_{10+\delta}$ by two ways (DC-magnetron sputtering and PLD) and investigate the role of annealing on appearing the phases of superconductivity, and getting on T_c for film and make comparison with bulk.

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II. EXPERIMENTAL DETAILS

The target preparation plays an important role in achieving the required superconducting properties. The targets were prepared by conventional calcinating at 810 ºC for 24 h using bismuth and lead oxide, strontium carbonate and copper oxide as the starting materials., pressed as a pellet at 0.5 GPa., diameter of the pellet is 13 mm and thickness (2-3) mm and sintering procedures at 860 ºC for 140h This pellet used as a target to deposited as a thin film on Si(111) substrate using two different technique dc-sputtering at high oxygen pressure and pulsed laser deposition. The deposition conditions for dc sputtering substrate target distance 3cm, chamber pressure 10^{-2} mtorr and dc voltage 400V. These followed by a suitable thermal treatment of film at 810 ºC and 840ºC for 2 h. Immediately after the deposition, the oxygen pressure was increased from the operating value to around 10 mbar and kept for 15min.

In PLD the $Bi_{1.6}Pb_{0.4}Sr_2Ca_2Cu_3O_{10+\delta}$ target was mounted in vacuum chamber 10^{-4} mbar, and ablated by a double frequency with Q- switched Nd:YaG pulsed laser operated at 532 nm, pulse duration of about 7 n sec and a (0.4 -8) J/cm^2 energy density was focused on the target to generate plasma plume. The distance between target and substrate 5cm, substrate temperature of 300°C with oxygen back ground pressure of $2*10^{-3}$ mbar, the number of pulses are 150. The sample was thermally treated in the furnace with a heating rate of 15 °c/min, the films heated typical to the range of 820 ºC in an atmosphere of oxygen with flow rate 2 lit/min .

The resistivity of the bulk sample and its film is measured using a four-probe resistance measurement and was examined by X-ray diffraction type (Philips) with the CuK_α source. The surface morphology of $Bi_{1.6}Pb_{0.4}Sr_2Ca_2Cu_3O_{10+\delta}$ thin films carried out by using atomic force microscope (AFM) model AA3000, Angstrom.

III. RESULT AND DISCUSSION

Structural analysis was carried out by XRD on bulk pellet sample of superconducting $Bi_{1.6}Pb_{0.4}Sr_2Ca_2Cu_3O_{10+\delta}$ as shown in Fig.(1).The result of d-spacing experimental is for compound with atomic dimension a=5.350233Aº, b=5.543269 Aº , c=37.13874 Aº . Results indicate that the samples have polycrystalline orthorhombic structure. Two main phases were observed in the XRD spectra: high T_c-phase and low T_c-phase, beside of these phases there is an unknown phase which is due to creation of the stacking faults which leads to deform the structure and delay onset of long range phase coherence to appear at transition temperature to stay Copper pairs longer distance.

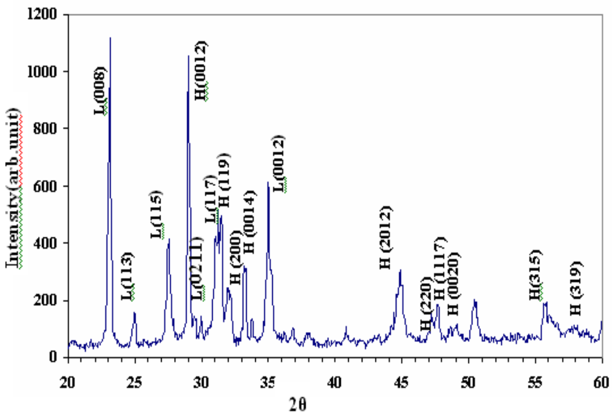

Fig. (1).XRD pattern of bulk $Bi_{1.6}Pb_{0.4}Sr_2Ca_2Cu_3O_{10+\delta}$

Fig (2,a,b,c) shows the XRD Patterns, measurements using a $Cu_{K\alpha}$ source for as-deposited and annealed films at 810°C and 840°C prepared by dc- sputtering respectively. X-ray diffraction showed number of diffraction peaks. The XRD patterns of as-deposited BPSCCO films show broad structures characteristics of amorphous material. During the annealing treatment a crystalline order is established and showed a number of diffraction peaks. The possible reasons for such behavior are an improvement of the films morphology, optimization of oxygen content and a change of the phase composition of the films [8]. Peak with (o) is from the substrate and the structure at the base of the Si(111) reflection is due to the absorption edge of Si. The XRD plot of Fig(2) shows that a film annealed at 810°C is c-axis oriented and emergence of peaks while film annealed at 840°C shows a slight angular shift and broad of some peaks at H(0012), H(0016), H(1113), H(317).The reason may attributed to the change in the oxygen content of the film as Ishii et al.[9]referred.

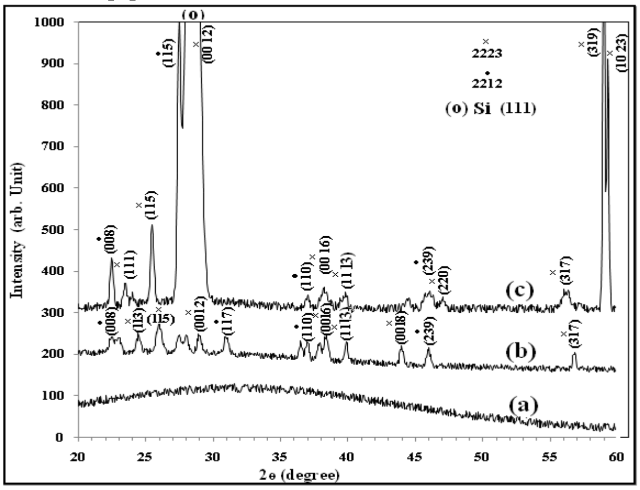

Fig (2) XRD pattern of BiPbSrCaCuO film (a) as deposited (b) annealed at 810°C (c) annealed at 840°C prepared by dc- sputtering.

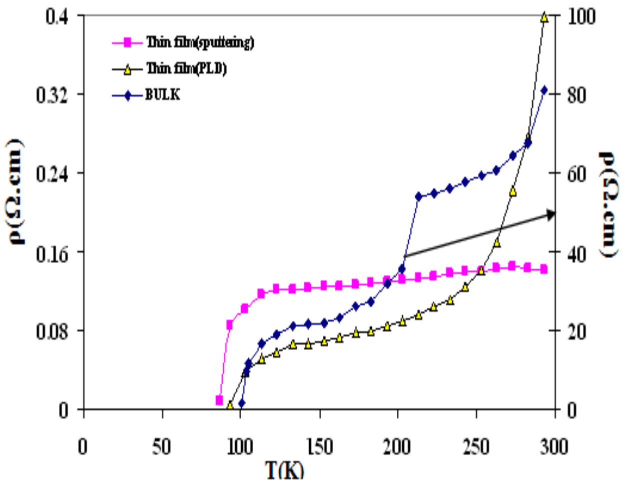

Fig (3) shows the XRD of film prepared by PLD and annealed at 820 °C. It is interesting to note that heat treatment may be enough to increase the degree of crystallinity of the film. This could be explained as: PLD yields almost uniform transport of ablated atoms to the substrate and results in high crystal quality films with stoichiometry close to the target element contents compared to sputtering techniques [10]

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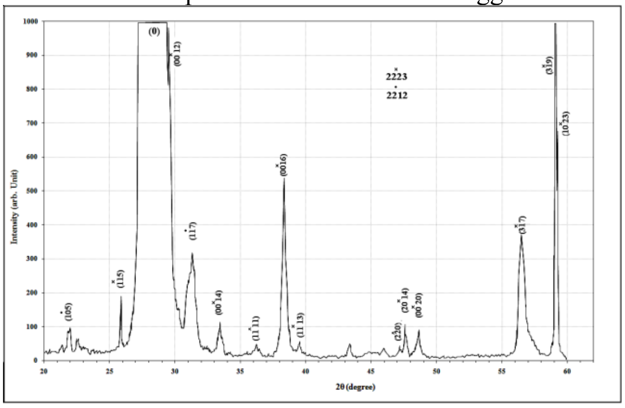
The lattice constant of thin films samples a= 4.8nm.,c=37.1 nm were calculated using d,h,k and l values of the strong peaks in the XRD patterns with the aid of Bragg's law .



Fig(3) XRD pattern of $Bi_{1.6}Pb_{0.4}Sr_2Ca_2Cu_3O_{10}$ film deposited by PLD and annealed at 820 °C

The critical temperature measurement performed by four-probe resistance measurement. The dimensions of film thickness(t) 184.2 nm, width of film(b) 1 cm and the distance between two probe points(d) 29.272×10^{-6} m. The value of the current flow in film is 0.25 mA. So the final equation for resistivity of film

$$\rho = \frac{bt}{d}\frac{V}{I} = 6.292\times10^{-5}\frac{V}{I} \qquad (1)$$

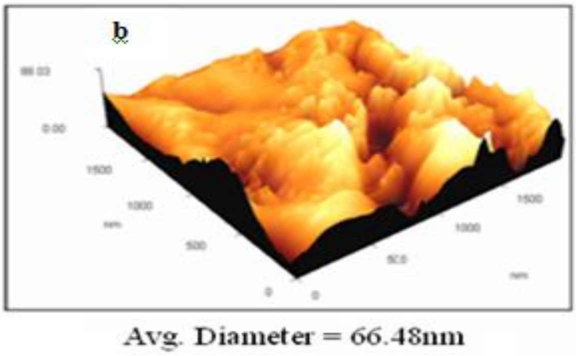


Fig.(4) ρ -T curve showing resistivity of $Bi_{1.6}Pb_{0.4}Sr_2Ca_2Cu_3O_{10}$ bulk and annealed thin films

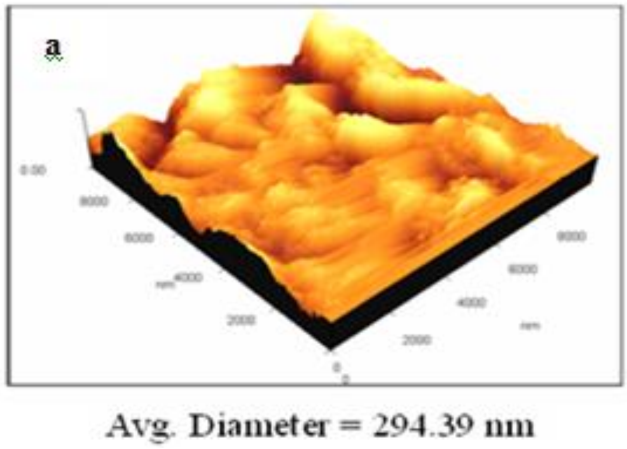
The transition temperature of the film deposited by PLD is about 97K. On the other side the sample deposited by sputtering, T_c is about 90K as shown in Fig.(4). In fact, the sputtering process in most cases it suffers from non-stoichiometric transfer of the elements from the target to the substrate. Also, spatial inhomogeneties and instabilities of the plasma lead to inhomogeneous film deposition. The difficulties apparent in the deposition of high T_c materials are related to the fact that they are complex, multi component materials; with a delicate sensitivity to film composition that significantly influences the electrical properties of the films [5].

In case of bulk the equation of

$$\rho = 4.532\frac{V}{I} \qquad (2)$$

where $4.532 = \frac{\pi r^2}{d}$

Where r is the radius of pellet, d=29.272×10^{-6}m, diameter of sample is 13mm and thickness of the pellet is 3mm. The T_c of bulk obtained here in four-probe measurement is about 102 K. The decreases of the critical temperature of films corresponding to T_c of bulk attributed to the existence of lead in grain boundaries improve weak link between grains, which lead to decrease in barrier between these boundaries [11]. The surface morphology of $Bi_{1.6}Pb_{0.4}Sr_2Ca_2Cu_3O_{10}$ thin films deposited on Si(111) substrates using sputtering and PLD methods was carried out by using AFM as shown in Fig.5.



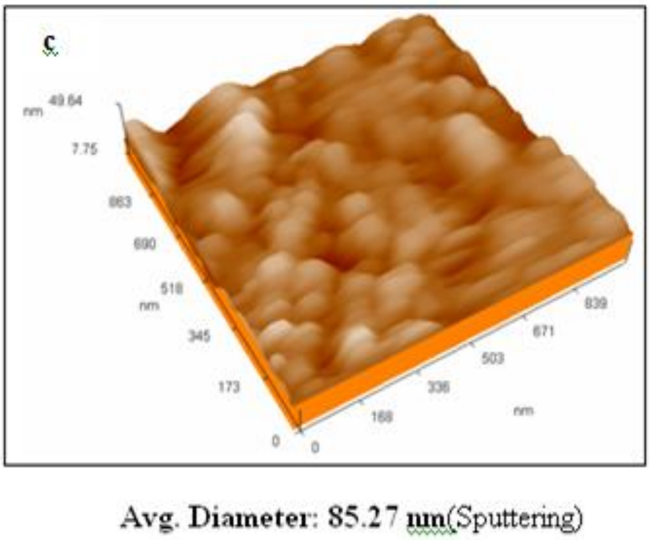


Fig.(5). AFM image of the $Bi_{1.6}Pb_{0.4}Sr_2Ca_2Cu_3O_{10}$ thin films (a) as deposited by PLD. (b) deposited by PLD annealed at 820ºC (c) deposited by sputtering annealed at 820ºC.

It is convenient to note the width of the surface pits (average diameter) of the samples prepared by the first method is 85.27nm, while films deposited by the second method have an average diameter of 66.48nm.The greater size of no oriented particles on the surface of the sputtering films can results from the higher overall nonstoichemetry of them. Indeed the small size of the average diameter for PLD films is due to the high mobility of atoms on the growing film surface which leading to decreases the terrace breadth as indicated by Latz et al [12] It is obvious that the width of the surface pits (average diameter) of samples annealed at 820 ºC is smaller than the as deposited films as shown in Table 1. the phenomenon is ascribe to the reduction of electronic density of state, which results from structural defects (twin boundaries and stacking faults)and chemical imperfections such as oxygen deficiencies inside the grains.

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Table (1): width of the surface pits (average diameter)of thin films

	Avg. Diameter(nm)
Sputtering films	85.27
PLD films (before annealing)	294.39
PLD films(T_a=820 ºC)	66.48

IV. CONCLUSIONS

PLD is a very useful technique to grow superconducting thin films of $Bi_{1.6}Pb_{0.4}Sr_2Ca_2Cu_3O_{10+\delta}$ as the temperature required to achieve the same are exorbitantly high, and there is a chance of contaminating the films with the material of substrate, for laser- deposited film can be explained by a lower deposition rate providing time recrystallization process. The re-evaporation becomes significant for dc sputtering at high deposition temperatures and results in bad efficient. The high mobility of atoms on the surface of growing film during laser deposition helps in the formation of smooth c- oriented areas of the film.

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