UDK 621.3:(53+54+621+66), ISSN 0352-9045 Informacije MIDEM 22(1992)3, Ljubljana

THERMALLY TREATED COLD SPUTTERED YBaCuO FILMS BY TRIODE SPUTTERING

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KEY WORDS: superconductive films, YBaCuO films, MgO substrates, amorphous films, cold sputtering, triode sputtering, thermal treatment, experimental research, experimental results

ABSTRACT: Superconductive YBaCuO films were sputtered onto (100) MgO substrates in a triode system. Stoichiometric target was used in reactive DC mode. Low temperature depositions were followed by various heat treatments in nitrogen and/or oxygen atmosphere. In the as deposited state the films were amorphous. Fast heating in nitrogen caused grains to grow up to 2 μm while oxygen would reduce the grain growth to average size below 0.4 μm. Raman spectra as well as XRD confirm the presence of orthorombic $YBa_2Cu_3O_7$ phase but indicate also traces of $BaCuO_2$. The transition temperature to superconducting state (R=0) was 80 K. Films annealed in nitrogen were porous.

TOPLOTNO OBDELANE HLADNO TRIODNO NAPRŠENE YBaCuO PLASTI

KLJUČNE BESEDE: superprevodne plasti, YBaCuO plasti, MgO substrati, amorfne plasti, hladno naprševanje, triodno naprševanje, toplotna obdelava, eksperimentalne raziskave, eksperimentalni rezultati

POVZETEK: Superprevodne YBaCuO plasti smo napršili na (100) MgO podlage v triodnem sistemu. Uporabili smo stehiometrično tarčo in enosmeren način naprševanja. Nizkotemperaturni depoziciji se sledile različne toplotne obdelave v dušiku in/ali kisiku. Napršene plasti so bile amorfne. Hitro segrevanje v dušiku je povzročilo rast zrn do velikosti 2μm, v kisiku pa je znašala povprečna velikost zrn le do 0.4μm. Ramanski spektri, kot tudi rentgenski spektri potrjujejo prisotnost ortorombske $YBa_2Cu_3O_7$ faze ob sledovih $BaCuO_2$. Temperatura prehoda v superprevodno stanje (R=O) je znašala 80 K. Plasti pregrete v dušiku, so bile porozne.

INTRODUCTION

Since the discovery of the superconductivity at temperatures above liquid nitrogen boiling point in some ceramic materials in 1986 /1/ an enormous amount of research efforts was put into both the scientific understanding and application of the phenomenon. Several thin film deposition methods for high temperature superconducting (HTSC) materials have been established, including PVD techniques (sputtering, evaporation, laser ablation), all giving films with superconductive transition temperature around 90 K. The superconducting quality of films made by different methods is similar because the postdepositional annealings are usually similar. However, the significance of annealing details (temperature, time, heating and cooling rates, atmosphere, etc.) has been generally accepted although not well understood. Usually, the deposition method is chosen depending on the available facility and then optimized.

The triode sputtering system is known for its ability of transferring multicomponent materials from the target to the substrate without changing the composition. Therefore it should be adequate for sputtering from the stoichiometric $YBa_2Cu_3O_7$ target. Additionally, due to large target to substrate distance, such arrangement is efficient when one wants to avoid the detrimental effect of negative ions during the deposition of YBaCuO films. Triode sputtering system has already been used by the Phillips group /2,3/ who successfully prepared Hall structures with 0.25 μm $YBa_2Cu_3O_7$ thin films on $SrTiO_3$, while their films on other substrates were reported to be of inferior quality.

Several materials have been considered for potential use as a substrate. The most important properties include the structure (lattice constants), temperature coefficient of expansion, dielectric constant and the sensitivity to film-substrate interface reactions. So far, the best results have been obtained on expensive substrates such as $SrTiO_3$ or $LaAlO_3$. Somewhat less succesful were films on cheaper MgO substrates. Regarding the temperature expansion, MgO substrate may be an appropriate choice with its temperature coefficient of $13*10^{-6}$ K^{-1} while $YBa_2Cu_3O_7$ is anisotropic having the corresponding temperature coefficients between 10 and $15*10^{-6}$ K^{-1} for a and b directions of the unit cell, respectively /4/.

At present the majority of research groups are dealing with in situ PVD thin film preparation methods. These methods give better film quality (controlled orientation, epitaxy, high J_C and T_{CO} , weaker film-substrate reaction) and are faster than two step ex situ methods. Their

drawback is, on the other hand, that they are limited to rather small areas with homogenous temperature. Ex situ methods will offer potentially larger deposition areas and larger substrates if adequate deposition and annealing conditions are defined and fulfilled.

In 1989 Nagata and his group /5/ have noticed that rapid heating of YBCO thin film in nitrogen atmosphere acts in favour of crystal grain growth. The aim of this study was to confirm this occurance and determine the influence of the atmosphere, heating rate and temperature during film annealing and oxidation after deposition onto (100) MgO substrates.

EXPERIMENTAL DETAILS

All depositions were performed in a plasma beam apparatus Sputron (Balzers, Liechtenstein) which permits DC as well as RF operation in inert or reactive atmosphere. The system geometry with its 15 cm target to substrate distance is similar to that during evaporation and minimizes the detrimental effects of negative oxygen ions /6/.

Both home made /7/ and original Balzers targets with nominal stoichiometric composition were used in our experiments. According to Balzers specification, the source contains 99.9% of the superconducting phase and very little impurities (less than 250 ppm Sr, 30 ppm Na, 25 ppm K, 10 ppm Ca; Al, Fe, As, Ni, Zn below 5 ppm). Control Raman spectra revealed excellent target homogeneity and possible presence of $BaCuO_2$ phase. Fig.1 shows Raman spectra from Balzers and home made targets. The oscillations are due to surface roughness, nevertheless clear peaks at 342 and 505 cm^{-1} can be found. The home made target was less homogeneous than Balzers target and gave poorer deposition repeatability. Its Raman spectrum is presented on figure 1b.

Stoichiometric targets were sputtered in argon DC plasma (800 V, 0.65 A, $5*10^{-3}$ mbar). To obtain reproducible results, we cleaned the targets through presputtering for 10 min before each deposition. One possible source of compositional changes in the film can be in the segregation on the target surface. To stabilize the target surface, $5*10^{-5}$ mbar of oxygen was introduced into the working chamber. This can hardly be considered as reactive deposition since "ordinary" reactive process would require about ten times higher oxygen partial pressure /8/. 1 μm thick films were sputtered at 2.5 nm/min deposition rate onto 100°C substrates.

Sapphire, ZrO_2, $SrTiO_3$ and MgO substrates were used. However, we present here only the results obtained with (100) MgO crystals. Both polished and air cleaved surfaces were used. After polishing the substrates were cleaned in mild detergent, distilled water and etanol.

Several postdepositional annealing procedures were tested. The samples were treated in 1 atm flowing nitrogen and/or oxygen following the experience of Nagata et al. /5/. The treatment can be divided into three (or four) stages: heating up, annealing at high temperature and cooling down (with or without additional oxidation above 450°C).In the warm up stage, heating rates between 1 and 10°C/min were used. Annealing temperature was varied between 750 and 850°C. Tests were made with annealing times between 1 and 60 min and 10 min annealing was chosen as optimum. Slow cooling down rates of 1°C/min in oxygen were used to improve the oxidation process and the transition from tetragonal to orthorombic phase. In early runs the cool down stage included also the 7 h oxidation at 450°C, whereas later this step was omitted.

Gold contacts were sputter deposited onto the heat treated films and wired with the conductive paste (Epotek, Poliscience AG). Conventional DC four point probe was used for measuring electrical characteristics. The temperature was measured with platinum thermometer in the range 300 to 25 K and varied slowly (0.5 to 1

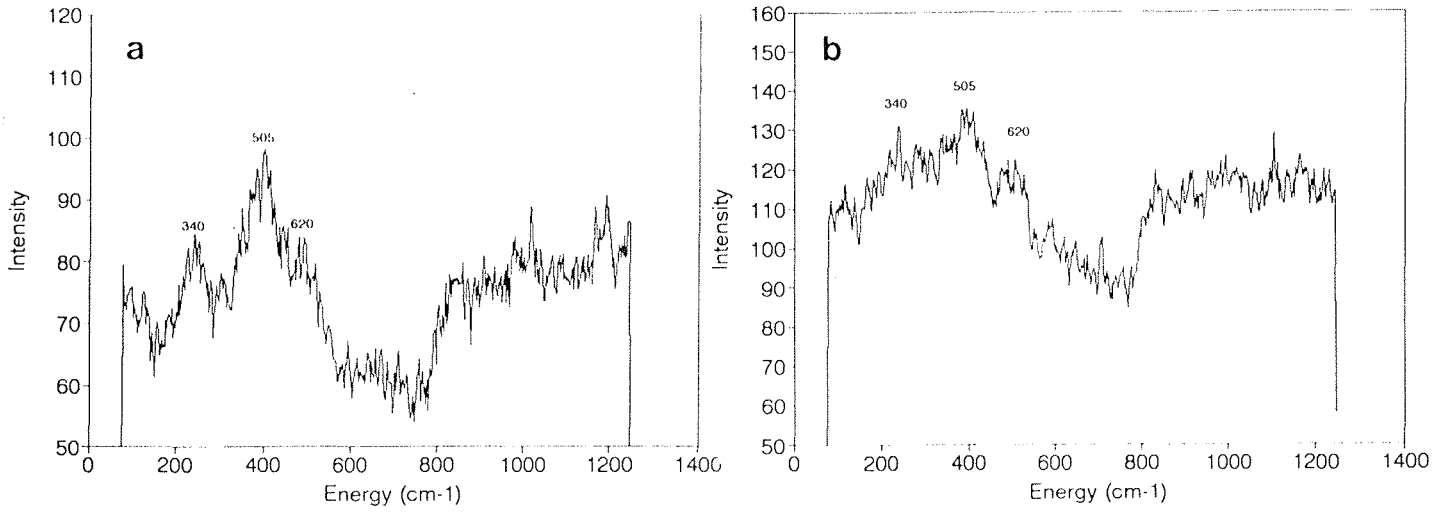


Fig. 1: Raman spectra of Balzers (a) and home made (b) target.

K/min) to compensate the influence of poor thermal contact between the sample and the thermometer and reduce the hysteresis around the critical temperature.

Films were analyzed before and after heat treatment using several techniques. Raman light scattering was measured in triple spectrometer with carefully normalized response of the detector. Argon ion laser (λ = 514.5 nm) was used with 40 mW beam (30 μm in diameter).

X-ray diffraction was made in the Enraf Nonius 591 apparatus with 40 kV / 26 mA generator and Huber thin film diffractometer having a Seemann-Bohlin geometry. The wavelength of the CuK_α source was 0.154 nm).

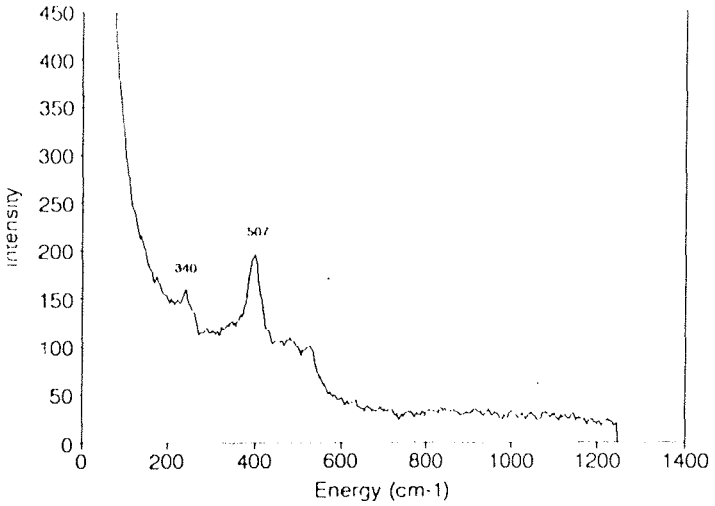


Fig. 2: Raman spectrum of 1 μm thin YBCO film on MgO, heated up and annealed for 10 minutes in nitrogen and cooled in oxygen at a rate 1°C/min.

For Auger electron spectroscopy (AES) depth profile we have used a Perkin Elmer PHI SAM 745 A spectrometer.

RESULTS AND DISCUSSION

The as deposited films were amorphous and insulating with sheet resistivity in the MΩ range. During the cool down to 25 K they would not exhibit the transition to superconductive state. Sheet resistivity after annealing can be rough indication of film quality for selection and and detailed analysis. A 1μm films had room temperature sheet resistivities larger than 0.16 Ω. This corresponds to ρ above 18 $\mu\Omega$cm. Individual parameters of the thermal treatment and their influence on the film structure were tested. Heating rates between 1 and 10 C/min were tried, the latter giving best results. Although rapid heating may cause holes to appear in the films which were grown on sapphire, we had no such problems with MgO substrates. Films on MgO which had been annealed at 750°C had no transition to superconductive state. The best results on MgO were obtained when annealing at 850°C. It is known that slow cooling down improves the oxidation process and the transition from tetragonal to orthorombic phase. Also, it is often recommended to perform an additional oxidation at 450°C for several hours. Our experience shows that the oxidation at 450°C would not be necessary if the film was heated up in nitrogen.

After heat treatment the samples were analyzed at room temperature by Raman light scattering. Compared to Fig.2a spectrum from Fig.2b with its clear peak at 505 cm^{-1} indicates composition $YBa_2Cu_3O_{6.9}$ /9/. However, $BaCuO_2$ phase is probably present as indicated by the peaks at 600 cm^{-1} and confirmed by X- ray spectra (eg. Fig.3) and temperature dependence of resistivity. Ac-

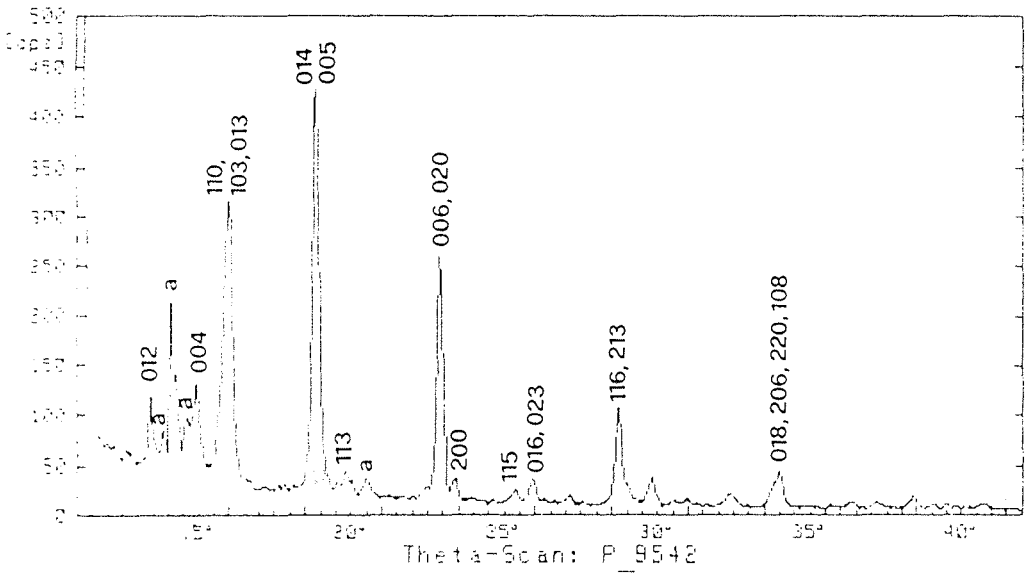


Fig. 3: X-ray diffraction of 1 μm thin YBCO film on MgO, heated up and annealed for 10 minutes in nitrogen and cooled in oxygen at a rate 1°C/min. Peaks marked by "a" are $BaCuO_2$ peaks.

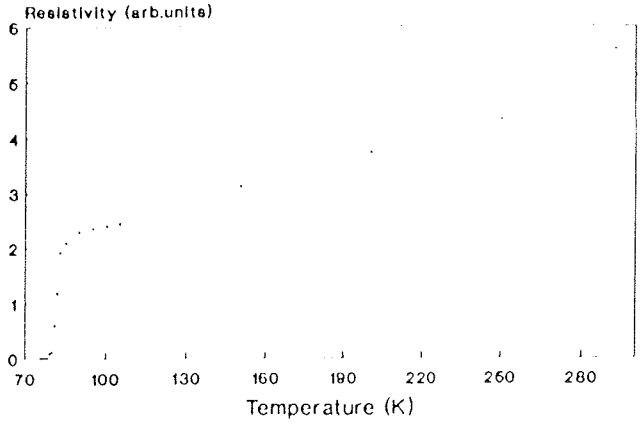


Fig. 4: Resistivity vs. temperature for 1 μm YBCO film on MgO

cording to X-ray diffraction peaks (013), (103) and (110) the films are randomly oriented. Peaks around $\vartheta = 13^{\circ}$ belong to $BaCuO_2$ phase. In some cases poor correlation was found between the Raman spectrum and the resistance characteristic. The reason for this lies in the difference of the signal origin. Light is scattered from the surface while the whole thickness is important for resistivity.

Various heat treatments result in very different temperature characteristics. Annealing in oxygen with additional oxidation at 450°C resulted in relatively broad transition as measured through temperature dependence of resistivity. The resistivity began to drop at 80 K with R = 0 below 25 K for the sample which was heated at 2°C/min in oxygen. Negative temperature coefficient of resistivity in the normal state indicated the presence of tetragonal phase. Rapid heating (10°C/min) of the sample in nitrogen moved the transition start point between 85 and 90 K and end point (R = 0) to 60 K. Also, the temperature coefficient became positive in the normal state. In contrast to many authors who reported the benefits of oxidation above 400°C for several hours, our experience

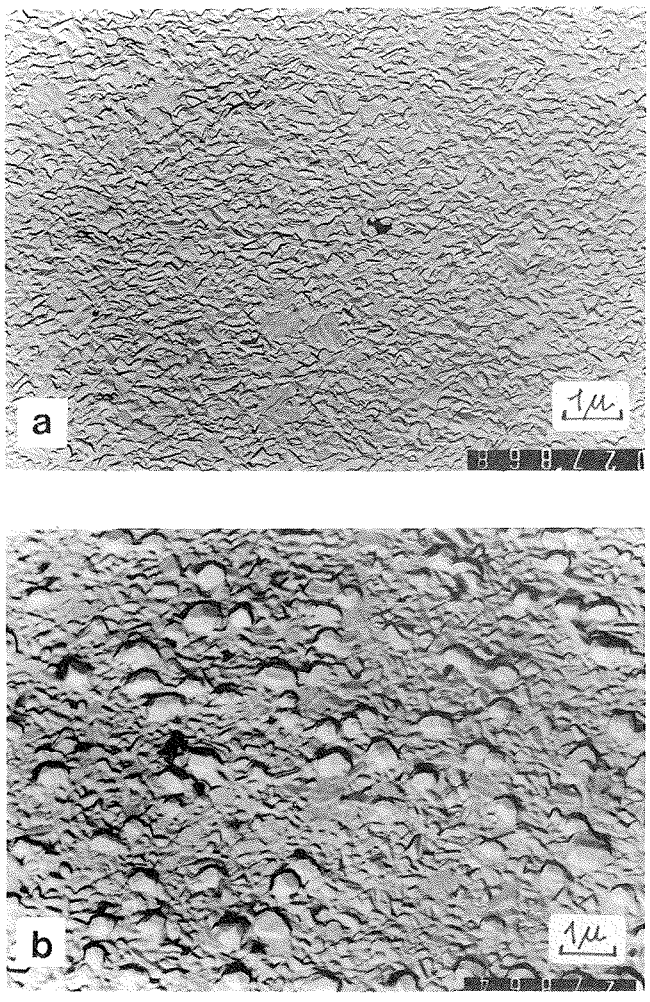


Fig. 5: Electron micrographs of surface replicas from 1 mm thick films completely treated in oxygen (a), and heated in nitrogen, then treated in oxygen (b).

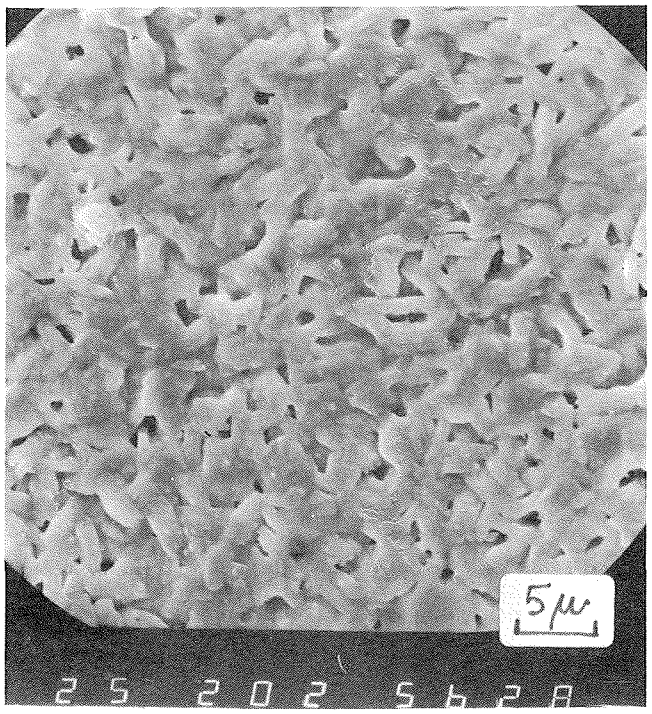
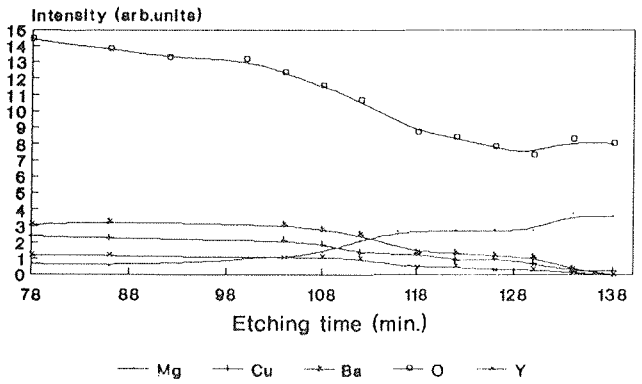


Fig. 6: SEM micrograph of YBCO film on MgO, annealed at 850°C in nitorogen and cooled down in oxygen.



Fig, 7: AES film depth profile of YBCO/MgO junction after 850°C annealing in nitrogen and cool down in oxygen.

suggests to abandon this step - the slow cooling (1°C/min in oxygen) alone moved the transition end point to 80 K. Fig.4 shows temperature dependence of resistivity for different annealing procedures.

Surface replicas were taken to look at the grain size. For the films that were heat treated in oxygen only the grain size was in the range around 0.4 μm, while fast heating in nitrogen caused the grains to grow up to 2 μm, on the average, as illustrated in Figs. 5a, 5b and 6.

Optical inspection of films uder microscope revealled, that films heated in nitrogen were porous. In some cases the nucleation process was so strong, that a 1μm film thickness was not satisfactory to enable full substrate coverage after the furnace annealing process. On the other hand, films full time annealed in oxygen were homogenous what is in agreement with above mentioned differencies in grain sizes.

CONCLUSIONS

Various heat treatments were tested for Y-Ba-Cu-O films sputter deposited onto (100) MgO substrates. Raman light scattering spectra and X-ray diffraction patterns were taken for heat treated films together with temperature dependence of resistivity. As deposited films were amorphous and insulating (at room temperature their resistivity was in MΩ range). Rapid heating (10°C/min) in nitrogen enhances the grain growth to about 2 μm compared to 0.4 μm when heated up in oxygen. The taken spectra indicate the dominance of orthorombic $YBa_2Cu_3O_{7\pm0,1}$ phase but also the presence of $BaCuO_2$ phase. The resulting resistivity characteristics were improved considerably. Our best films had critical temperature around 85 K and transition width of 5 K. The temperature coefficient of resistivity in normal state was positive.

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Prispelo: 02.09.92 ***Sprejeto: 21.09.92***