Preparation of epitaxial $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ films by magnetron sputtering

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Abstract. Thin films of high T_c superconductor $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ were obtained by magnetron sputtering. MgO , YSZ , YSH and Al_2O_3 single crystals were used as substrates. Epitaxial films with tetragonal structure having T_c 55–60 K grow at substrate temperatures T_s between 930 K and 980 K. Orientation of the films in this T_s range was (100) and (001) for (100) MgO substrate, (111) and (001) for (1012) Al_2O_3 and (111) YSH and (113) or (103) on (110) YSZ and (111) YSH . Single crystalline films with orthorhombic structure and (001) orientation were grown on all the substrates when T_s exceeded 980 K. They have $T_c > 80$ K.

Keywords. High T_c superconductor; $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ films; magnetron sputtering.

1. Introduction

Two principal ways of preparing $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ films by magnetron sputtering are now known. The first one includes amorphous film deposition on warm (< 700 K) substrate and subsequent annealing in oxygen-containing atmosphere (see, for instance, Gulyaev *et al* 1988). The crystal structure of the film forms during the annealing process. The second one consists of film deposition in oxygen-containing atmosphere on substrate heated up to 850–1100 K (for instance, Adachi *et al* 1987). In this case formation of the film crystal structure takes place directly during deposition.

The purpose of this work was to investigate $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ films having tetragonal and orthorhombic structures obtained using the second method.

2. Experimental

2.1 Film composition control

Targets up to 100 mm in diameter were prepared by pressing of Y–Ba–Cu–O powdered ceramics samples with component ratio from 1:2:3 to 1:2:2:4:5. One of the most important problems to be solved to obtain $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ films with high T_c value is deposition of stoichiometric film composition on the substrate.

It is clear that material transport process from target to substrate at magnetron sputtering depends on a number of factors including target-substrate distance, magnetron design, substrate orientation with reference to target and flow of transported particles, substrate temperature T_s , composition and pressure of vapour phase and so on. One must investigate influence of all those factors to develop a method of preparation of film of reproducible predetermined composition.

Investigations included chemical analysis of the films deposited at different conditions. Analysis was made using two methods—electron probe X-ray microanalysis and chemical methods of composition analysis after complete dissolution of the film in nitric acid. The chemical composition of the film sputtered in argon at substrate

temperature $T_s < 700$ K does not differ from the target composition within the limits of determination accuracy (~ 5 wt%). Increase of T_s leads to change of the deposited film composition: relative concentration of barium and especially copper decreases. By that the copper concentration decrease is considerably higher than the calculated one using its temperature dependence of condensation coefficient.

Addition of oxygen to Ar in reactive vapour atmosphere also decreases considerably relative barium and copper concentrations in the films deposited. It is connected with selective sputtering of the components of the film by negative ions and atoms of oxygen bombarding its surface (Dikaev *et al* 1988). Energy and density of flow of oxygen ions and atoms bombarding the substrate are determined by target potential, by dark cathode region value, i.e. by a given magnetron design as well as by working pressure and vapour phase composition. One can considerably decrease bombardment intensity by increase of working pressure up to ~ 10 Pa instead of ~ 1 Pa and lower which are normally used. But this leads to deterioration of film electrophysical parameters resulting in film density decrease and increase of their contamination.

We have studied two methods to eliminate stoichiometry deviations. One is connected with considerable decrease of the target-substrate distance and the second is connected with using the gas baffle: argon is blown to the plasma region and oxygen to the substrate. Oxide formation probability is increased in both cases resulting in significant reduction of film metallic component reevaporation because the oxide vapour pressure at substrate temperature is less than metal vapour pressure. The smaller the substrate-target distance the poorer the film thickness uniformity, so we preferred the second method.

RF sputtering of ceramic target did not lead to chemical composition changes during a long (more than 200 h) time. In DC sputtering gradual copper concentration decrease was observed.

2.2 Film preparation

Sputtering was done using substrates of different orientations made of MgO , $\text{ZrO}_2\text{:Y}_2\text{O}_3$ (YSZ), $\text{HfO}_2\text{:Y}_2\text{O}_3$ (YSH) and Al_2O_3 single crystals. Substrate temperature T_s varied from 900 to 1150 K. Target chemical composition was changed in accordance with data on film composition for different sputtering conditions. Gas baffle system was used: argon was blown to plasma region, and the oxygen to substrate. Vapour phase pressure was 0.2–1 Pa, partial oxygen pressure was equal to 3–10%. Target-substrate distance was 5–7 cm, film deposition rate was 3–5 $\mu\text{m/h}$ thickness of the films 2–10 μm . Films were cooled at the rate of ~ 5 K/h in oxygen. Films were studied using X-ray diffractometer and Reflection High Energy Electron Diffraction (RHEED) methods.

3. Results and discussion

Amorphous films were obtained at T_s lower than 800 K. T_s increase induced small grain polycrystal film condensation. Single crystalline films were obtained for T_s above 930 K, at T_s lower than 980 K film orientation depends strongly on the substrate used. $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ films with (100) and (001) orientations were obtained on (100)-

Figure 1. X-ray diagrams for some tetragonal $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ films. Substrate orientation is indicated in the figure. $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ films have orientation (001) (a, c), (100) (b) and (113) (d) $\text{CoK}\alpha_1$ radiation.

oriented MgO plates, films with (110) and (001) orientations grew on $(10\bar{1}2)$ Al_2O_3 and (111) YSH, with (113) or (103) orientation on (110) YSZ and (111) YSH. X-ray diagrams and RHEED patterns are given in figures 1 and 2. All these films have a tetragonal structure with $c = 11.81 \text{ \AA}$ and the end of superconducting transition temperature $T_c = 50\text{--}60 \text{ K}$. Typical resistivity-temperature dependence curve for such films is shown in figure 3 (curve 1). Films on MgO substrate are epitaxial, i.e. axes orientation in the film plane is fixed in response to the substrate and $[010]$ MgO axes coincides with $[010]$ $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$. Axes orientation for other films with reference to substrate axes is more difficult to establish although it is also fixed. The orientational correlations for (113) or (103) $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ films on (110) YSZ are not clear at present. (110) YSZ plane has parameters close to doubled a, b parameters of tetragonal $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ phase (Voronov *et al* 1989), and it would be natural to expect epitaxial growth of (001) $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ films on (110) YSZ. But this was not observed in the T_s range. It seems that formation of specific $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ film orientation is determined in this case to a considerable extent not only by simple geometrical correlations although they are important as in MgO case but mainly by crystallization conditions, i.e. by supersaturation value, deposited film chemical composition, oxygen pressure etc. Thermal stresses connected with difference in cell dimensions and thermal expansion coefficients between film and substrate seem also to be important (Hashimoto *et al* 1988). Our attempts to induce transformation of the tetragonal modification to the orthorhombic

Figure 2. RHEED pattern for tetragonal $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ films, (a) (113) Y–Ba–Cu–O/(111) HfO_2 , electron beam along a -axis; (b) (113) Y–Ba–Cu–O/(111) HfO_2 , 90° unit references to (a); (c) (100) Y–Ba–Cu–O/(100) MgO ; (d) (103) Y–Ba–Cu–O/(110) ZrO_2 .

Figure 3. Resistivity temperature dependence for $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$, (1) tetragonal phase, (2) orthorhombic phase.

one using annealing in oxygen at different pressures and during different time intervals did not give positive results till now. It is in strong contrast to the $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ ceramic samples where this transition is performed easily and reversibly (for instance, Shi and Capone 1988).

(001)-oriented single crystalline $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ films with orthorhombic structure and $c = 11.70 \text{ \AA}$ were obtained on all the substrates for T_s above 980 K. Transition temperature for these films exceeds 80 K (figure 3, curve 2).

It is necessary to note that no special efforts were made to discover weak additional reflections in RHEED patterns due to oxygen ordering so that the films obtained at $T_s < 980 \text{ K}$ may belong to the so called "orthorhombic II" phase as well.

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