Preparation *in situ* and properties of thin films HTSC $\text{YBa}_2\text{Cu}_3\text{O}_x$

M I FALEY and M E GERSHENSON

Institute of Radio Engineering and Electronics of the Academy of Sciences of the USSR, Marx av. 18, GSP-3, Moscow 103907, USSR

Abstract. We describe the technique of *in situ* preparation of thin ($d = 0, 1\text{--}1\ \mu\text{m}$) YBCO films by the RF magnetron sputtering of the ceramic target in the argon-oxygen atmosphere on the heated substrates, and report the preliminary results of investigation of the multilayer structure based on such films.

Keywords. High temperature superconductivity; films; RF sputtering.

1. Introduction

One of the most promising methods of preparation of thin films of high- T_c superconductors (HTSC), which avoids high-temperature (up to 900°C) annealing, is the deposition (by RF sputtering, thermal or laser evaporation, etc.) of the constituent elements on the heated substrate in the oxygen atmosphere (see, e.g. Miura *et al* 1988). This method gives an opportunity to eliminate the diffusion between the film and the substrate, and therefore enables one to obtain thin (thickness $d < 0.1\ \mu\text{m}$) HTSC films with very high critical parameters. It is very important that the films with mirror-like surface can be prepared in such a way. These films are desirable for deposition of multilayer structures.

2. Technology

We have used the high vacuum plant Z-400 ("Leybold AG", FRG) with turbomolecular pump and residual pressure 10^{-6} mbar; the sputtering was carried out in a mixture of oxygen and argon at total pressure $P = (1\text{--}2) \cdot 10^{-2}$ mbar. The deposition rate was $\approx 50\ \text{\AA}/\text{min}$ at the discharge power $\approx 130\ \text{W}$ for the target 75 mm in diameter. The stoichiometry of the film grown in front of the magnetron erosion zone was disturbed by the oxygen ion bombardment, therefore the best superconducting films were prepared within the circle 30 mm in diameter situated opposite to the inner part of the erosion zone. Ion bombardment is also the reason for dependence of the content and properties of the film on the substrate-target distance S ; in our case the optimal S value was 25 mm. The substrate materials were SrTiO_3 and Al_2O_3 covered by a buffer film. The buffer layer $100\ \text{\AA}$ thick was deposited by RF magnetron sputtering at the substrate heated up to 300°C . The materials of the buffer layer were Y_2O_3 , SrTiO_3 or MgO . The best results were obtained with MgO and SrTiO_3 buffer layers (Gershenson *et al* 1989a).

The optimal interval for the substrate temperature T_s during deposition was $600\text{--}750^\circ\text{C}$ and the partial oxygen pressure was $10^{-3}\text{--}10^{-2}$ mbar. At such conditions the main mechanism of heat transfer between the heater and the substrate is the emission and absorption of IR radiation. Therefore the heater temperature should be higher than the desired T_s for $150\text{--}200^\circ\text{C}$. The usual heaters, except the platinum one, have a very limited lifetime at such conditions. We developed (Gershenson *et al* 1989b) a

heater with prolonged working time in oxygen atmosphere at temperatures up to 900°C. Its main feature is the use of heavily-doped Si as the heating element material.

There are two stages of the *in-situ* YBCO film preparation: (i) deposition in oxygen-argon atmosphere at hot ($T_s > 600^\circ\text{C}$) substrate to obtain an orthorhombic crystal structure; (ii) low-temperature (400°C) annealing at $P_{\text{O}_2} = 1$ bar in the vacuum chamber to saturate the film by oxygen and to obtain the high critical temperature. In our case the substrates were heated up to the desired T_s in 10 min (to prevent the cracking of the brittle single crystal SrTiO_3 substrate) the sputtering was carried out at $T_s = 650 \div 700^\circ\text{C}$ and $P_{\text{O}_2} = 1 \times 10^{-3}$ mbar, then P_{O_2} was increased to 1 bar (it results in rapid T_s fall to 500°C) followed by slow (15 min) cooling of the substrate in oxygen atmosphere.

The Cu concentration in films decreases (in comparison with the target material) with increase of P_{O_2} and (or) T_s (Miura *et al* 1988). With the use of $\text{YBa}_2\text{Cu}_3\text{O}_x \div \text{YBa}_2\text{Cu}_{7-x}\text{O}_x$ targets we have achieved the relative Cu concentration $C_{\text{Cu/Y}} = 2.4 \div 5$ in film at $T_s < 700^\circ\text{C}$. Therefore the optimal set of parameters T_s , P_{O_2} and P_{Ar} depends on the target content. The stoichiometric films with high T_c and J_c values were obtained for $\text{YBa}_2\text{Cu}_{4.2}\text{O}_x$ target at $T_s \approx 700^\circ\text{C}$, $P_{\text{Ar}} = 2 \times 10^{-2}$ mbar, $P_{\text{O}_2} = 1 \times 10^{-3}$ mbar.

3. Measurements

X-ray diffraction pattern of stoichiometric films (shown in figure 1) reveals the texture: C-axis is normal to the substrate surface. The highest T_c values of 2000 Å thick films were 93 K for SrTiO_3 substrates and 90 K for Al_2O_3 substrates. Figure 2 shows the temperature dependence of resistance of the sample with $d = 2000$ Å. The slope of the quasilinear dependence $R(T)$ at $T > T_c$ increases with increase of Cu concentration. The stoichiometric films have the resistivity $\rho \approx 0.2$ mohm·cm at 300°C. The surface of such films is mirror-like; the deviations from the stoichiometry result in the multiphase content of the film and the appearance of small ($< 1 \mu\text{m}$) inclusions of minor phase at the film surface (see figure 3).

To measure the critical currents J_c we made small microbridges (width 10 μm) with the aid of photolithography. Thin (100 Å) Ag film deposited on the YBCO film without

Figure 1. X-ray diffraction pattern of the stoichiometric $\text{YBa}_2\text{Cu}_3\text{O}_x$ films on the $\text{SrTiO}_3(100)$.

Figure 2. Temperature dependence of resistivity of the sample with $d = 2000 \text{ \AA}$.

Figure 3. Scanning electron micrograph of the surface of $\text{YBa}_2\text{Cu}_{2.5}\text{O}_x$ film.

the vacuum break was used as a protective layer during photolithography and a low-resistivity contact to the YBCO film in the J_c measurements. Ion etching was used to etch the film after photolithography. The T_c values were not influenced by this procedure (the resistive transition becomes even sharper if the film is not homogeneous). The critical current density was 10^6 A/cm^2 at 77 K and exceeds $3 \times 10^7 \text{ A/cm}^2$ at 4.2 K.

We have attempted to prepare tunnel junctions based on the YBCO films. For this purpose YBCO film was successively covered by Ag film $100 \text{ \AA}$ thick and Al film $50 \text{ \AA}$

Figure 4. Dependence of differential resistance R on the bias voltage obtained for YBCO/Ag/Al/Al-oxide/Al at different temperatures ($T_c \approx 40$ K).

thick (in single-vacuum cycle). Ag film protects the YBCO surface against the contact with Al; the superconductivity in the Ag film is induced by the proximity effect (Muzushima *et al* 1988). Ag film was annealed in $P_{O_2} = 1$ bar before deposition of Al. Then the 2000 Å thick SiO film with 0.5 mm² window in it was deposited on Al. The tunnel barrier was formed by oxidation of the Al film, and then the upper electrode—Al film 2000 Å thick—was deposited.

The characteristics of these tunnel contacts are very sensitive to the thermoprocessing of Ag layer. The optimum T_s for annealing of Ag film is about 350°C.

Figure 4 shows the dependence of differential resistance R on the bias voltage obtained for such structure at different temperatures. The main features of the low-temperature dependences $R(V)$ are the well-distinguishable zero-bias anomaly and symmetric anomalies at ≈ 25 mV similar to the gap structure of the traditional superconducting tunnel structures.

4. Conclusion

YBa₂Cu₃O_x thin films were prepared *in-situ* on SrTiO₃(100) and sapphire substrates by RF magnetron sputtering from sintered targets. Films with stoichiometric composition and mirror-like surfaces were fabricated. High critical parameters of the films were achieved. Tunnel structure YBCO/Ag/Al/Al-oxide/Al was fabricated and the gap structure was observed up to T_c of YBCO film.

Acknowledgements

This work was supported by the Scientific Council on the HTSC problem and performed in the framework of project N42 of the State Program "High temperature superconductivity".

References

- Gershenson M E, Nevelskaya Y A and Faley M I 1989a *Proceedings of the 2nd Soviet Conference on HTSC, Kiev* (in Russian) **2** 281
- Gershenson M E and Faley M I 1989b *Instrum. Exp. Tech.* (in Russian) 160
- Miura T, Terashima Y, Sagoi M and Kubo K 1988 *Jpn. J. Appl. Phys.* **27** L1260
- Mizushima K, Sagoi M, Miura T and Yoshida J 1988 *Jpn. J. Appl. Phys.* **27** L1489