MOCVD-grown homoepitaxial $\text{YBa}_2\text{Cu}_3\text{O}_x$ thin films and its multilayers

H ZAMA*, N TANAKA and T MORISHITA

Superconductivity Research Laboratory, International Superconductivity Technology Centre, 10–13 Shinonome 1-Chome, Koto-ku, Tokyo 135-0062, Japan

Abstract. $\text{YBa}_2\text{Cu}_3\text{O}_x$ (YBCO) films, Zn-doped YBCO (YBCO:Zn) films, and their bilayers have been epitaxially grown on $\text{SrTiO}_3(100)$ and single-crystal YBCO(001) substrates by metalorganic chemical vapour deposition. The YBCO(001) films homoepitaxially grown on YBCO(001) substrates have flat surfaces on an atomic scale, and interfaces free from crystalline defects. We can systematically reduce the superconducting transition temperature (T_c) of YBCO:Zn films from 90 K to 37 K by increasing Zn concentration. The bilayers have a sharp distribution of Zn as evaluated from T_c measurements of the upper YBCO films and depth profiles of secondary ion mass spectrometer, suggesting the possibility to form the homoepitaxial SNS (S, superconductor; N, normal metal) junction operatable between 40 K and 90 K.

Keywords. Homoepitaxial growth; $\text{YBa}_2\text{Cu}_3\text{O}_x$ (YBCO); Zn-doped $\text{YBa}_2\text{Cu}_3\text{O}_x$ (YBCO:Zn); YBCO/YBCO:Zn bilayer; SNS junction.

1. Introduction

In thin film and multilayer growth processes for applications to electron devices, it is important to reduce lattice mismatch and a difference in thermal expansion coefficients between substrate and film, or adjacent films, which affect the growth mechanism and eventually the crystalline qualities of films through stress and strain at the interfaces.

$\text{YBa}_2\text{Cu}_3\text{O}_x$ (YBCO) thin films are usually grown on $\text{MgO}(100)$ and $\text{SrTiO}_3(100)$ (STO) substrates, which have mismatch of $\sim 10\%$ and 1% , respectively. Therefore, we observe islands and spirals on the film surface, where the crystallinity is necessarily limited. We have adopted YBCO(001) single crystal substrates expecting to improve surface morphology and crystallinity of films due to a release from lattice mismatch and the difference in thermal expansion coefficients.

For growing the multilayer aiming at the SNS or SIS junction (S, superconductor; N, normal metal; I, insulator), usually the barrier layer is doped with 123-structure materials such as Co-doped YBCO and Co-doped $\text{PrBa}_2\text{Cu}_3\text{O}_x$ for N type, and insulating perovskites like STO for I type, which have larger mismatch than 1% and/or the different crystal structure. We have adopted Zn-doped YBCO (YBCO:Zn) for N layer, which has lattice mismatch below 0.16% for YBCO(001) and the same crystal structure, orthorhombic, as undoped YBCO (Tarascon *et al* 1988).

In this paper, we investigate the homoepitaxial growth of YBCO films and YBCO/YBCO:Zn bilayer films grown on YBCO(001) single crystal substrates.

2. Homoepitaxial YBCO film growth

We used YBCO(001) single crystal substrates prepared by slicing from crystal-pulling-made single crystals (Yamada *et al* 1993) with a diamond blade and polishing them mechanically with colloidal silica solution. Surface morphology of the as-polished substrate is shown in figure 1. One-unit-cell (~ 1.2 nm) height steps were clearly observed using an atomic force microscope (AFM). We used both as-polished substrates and those chemically etched by HCl-methanol solution (Tanaka *et al* 1998) in order to remove a surface degradation layer.

We prepared YBCO films by metalorganic chemical vapour deposition (MOCVD), using a horizontal and cold-wall type MOCVD system. Y and Cu sources used were β -diketonate complexes of $\text{Y}(\text{DPM})_3$ and $\text{Cu}(\text{DPM})_2$ respectively, where DPM stands for dipivaloylmethane, $\text{C}_{11}\text{H}_{20}\text{O}_2$. Ba source was the normal-chain-amine adduct material, such as $\text{Ba}(\text{DPM})_2$ -2tetraen (Zama *et al* 1996) and $\text{Ba}(\text{DPM})_2$ -2pentaen (tetraen = tetraethylenepentamine, $\text{NH}_2(\text{CH}_2\text{CH}_2\text{NH})_3\text{CH}_2\text{CH}_2\text{NH}_2$; pentaen = pentaethylenehexamine, $\text{NH}_2(\text{CH}_2\text{CH}_2\text{NH})_4\text{CH}_2\text{CH}_2\text{NH}_2$), which is more volatile and stable than a conventional Ba source, $\text{Ba}(\text{DPM})_2$. The supply rate of Ba was kept stable within a standard deviation of 1.6% for 300 h, using $\text{Ba}(\text{DPM})_2$ -2pentaen under optimal conditions. The vapourizing temperature ranged from 90 – 140°C : i.e. $\text{Y}(\text{DPM})_3$; 90 – 120°C , $\text{Cu}(\text{DPM})_2$; 90 – 120°C , $\text{Ba}(\text{DPM})_2$ -

*Author for correspondence

Figure 1. $2 \times 2 \mu\text{m}^2$ area AFM image of as-polished YBCO(001) substrate surface.

2tetraen; 110–120°C, Ba(DPM)₂pentaen; 130–140°C. The reaction pressure and oxygen partial pressure were 10 Torr and 0.5 to 0.6 Torr, respectively. The temperature of the substrate susceptor was from 750 to 850°C. The temperature at the substrate surface was estimated to be ~ 100 –150°C lower than the susceptor temperature. The deposition rate was 20–40 nm/h under these conditions.

The X-ray diffraction (XRD) $\theta - 2\theta$ scan of a 100 nm thick YBCO(001) film on the as-polished substrate showed absence of ($k00$) diffraction peaks ($k = 1 \sim 4$), showing thereby that the c -axis oriented film had grown along the orientation of single crystal substrate. In the case of YBCO(100) substrate, the orientation of YBCO film also followed the orientation of single crystal substrate (Zama *et al* 1997). This is one of the greatest advantages of homoepitaxial growth over heteroepitaxial growth. Figure 2 shows the cross section of the 100 nm thick homoepitaxially-grown YBCO(001) film by transmission electron microscope (TEM) images. It is very difficult to discern the interface in the TEM image (figure 2a). However, a stacking fault on the interface is confirmed, indicated by the arrows. In the low magnification image in figure 2b, the interface is observed as

Figure 2. Cross-sectional TEM images of the homoepitaxial YBCO(001) film: (a) atomic image around the interface and (b) large area image.

a dark line and twin structures are continuous throughout the interface. The channeling spectra of Rutherford backscattering spectrometry (RBS) showed the minimum yields of 1.8% and 1.9% for the substrate and homoepitaxial film, respectively. Thus all the measurements revealed that the growing films maintain the crystallinity and orientation of the substrate.

The AFM image of the surface of a 20 nm thick YBCO(001) film on the etched substrate is shown in figure 3. The film still reflects the step structure of the substrate surface with atomically flat terraces and unit cell (~ 1.2 nm) step height.

3. Zn-doped YBCO film growth

We prepared YBCO : Zn films by almost the same method as undoped YBCO films except for the doping source, which was Zn(DPM)_2 , and which had similar characteristics as other DPM complexes, especially Cu(DPM)_2 . The concentration of Zn was controlled by varying the vapourizing temperature of Zn(DPM)_2 . The 20 nm thick *c*-axis-oriented YBCO : Zn films were deposited on STO substrates by varying the Zn concentration. Their superconducting transition temperatures (T_c) change from 90 K to 37 K with the increase in the Zn concentration. The surface morphologies of these films were the same as those of the undoped films. It is difficult to determine the Zn concentration in YBCO films, because the Zn concentration is too low for our inductively-coupled plasma spectroscopic analysis system. We therefore estimated the Zn concentration, using the relationship for YBCO : Zn single crystal, between the doping concentration and T_c (Yao *et al* 1996). The results show that

the highest doping concentration is 4.6%-Zn substitution for the Cu-site, corresponding to the lowest T_c of 37 K. With the increase in the amount of Zn source supply, ZnO particles appeared. The relationship between the vapourizing temperature of Zn(DPM)_2 and Zn concentration in YBCO film is described by the Arrhenius' equation.

Since Zn is known to have a high diffusion coefficient in Si (Sze 1981), this could be a serious drawback for forming a multilayer. We grew the *c*-axis-oriented YBCO(30 nm)/YBCO : Zn(30 nm) bilayer on a STO substrate to evaluate the diffusion of Zn from YBCO : Zn to YBCO layer. As references, the 60 nm thick YBCO and YBCO : Zn films were also grown. T_c and zero-resistivity temperature (T_{c0}) are 90 K and 89 K for the YBCO film, 64 K and 62 K for the YBCO : Zn film, and 88 K and 86 K for the YBCO/YBCO : Zn bilayer, respectively. The T_c and T_{c0} of the YBCO/YBCO : Zn bilayer on the STO substrate are only a few degrees lower than those of the YBCO film. Considering that the T_c was measured on the YBCO layer of the YBCO/YBCO : Zn bilayer, we are convinced that there is little Zn diffusion between YBCO and YBCO : Zn layers during the deposition of the YBCO film. The YBCO/YBCO : Zn bilayer deposited on a MgO(100) substrate, however, showed that the T_{c0} decreased to 78 K for the same measurement, indicating that significant Zn diffusion had occurred. It seems that the island growth mode on MgO enhanced the Zn diffusion into the YBCO layer, while the two-dimensional growth mode on STO suppressed it. Therefore, the Zn diffusion is not a serious problem to affect the superconducting properties of the upper layer and a sharp doping profile.

Figure 3. $2 \times 2 \mu\text{m}^2$ area AFM image of homoepitaxial YBCO(001) film surface.

Figure 4. Time sequence of metal source supplies for growing the YBCO/YBCO : Zn bilayer by MOCVD.

Figure 5. SIMS depth profile of the YBCO/YBCO : Zn bilayer on YBCO(001) substrate.

4. Homoepitaxial SNS multilayer growth

We prepared the SNS structure, YBCO film/YBCO : Zn film/YBCO(001) substrate, using the sequential deposition of YBCO and YBCO : Zn by MOCVD. The sequence of deposition is presented for each element in figure 4. The depth profile of secondary ion mass spectrometer (SIMS) of a YBCO(60 nm)/YBCO : Zn(12 nm)/YBCO(001) substrate is shown in figure 5. A sharp distribution of ^{66}Zn in the film results in the modulation in T_c as YBCO(~ 90 K)/YBCO : Zn(~ 40 K)/YBCO(~ 90 K),

suggesting the possibility to fabricate the SNS junction operatable between 40 K and 90 K.

5. Conclusions

The YBCO homoepitaxial film grew on the (001)-oriented substrate with only a stacking fault at the interface and maintained crystallinity, orientation, and surface morphology of the substrate. The T_c (Zn concentration) of YBCO : Zn films were systematically controlled between 90 K(0%) and 37 K(4.6%). The YBCO/YBCO : Zn bilayers grown on STO and YBCO substrates have a sharp distribution of Zn, as evaluated by the T_c measurements and the SIMS depth profiles.

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