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Depositions of YBCO Thin Films by Ion Beam Sputtering: a-c Orientations, Crystallinities and In-plane Orientations

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$YBa_2Cu_3O_x$ (YBCO) thin films were grown on MgO by ion beam sputtering at various substrate temperatures (T_S) and oxygen partial pressures (P_O) with a supply of either oxygen molecules (ML) or plasma (PL). At low P_O the single c-axis oriented phase (c-phase) can be grown at 650°C and the c-phase decreases while the a-axis oriented phase (a-phase) increases with increasing P_O both for ML and PL. This is explained in terms of enhancement of surface migration by the sputtered particle kinetic energy after collisions with the oxygen species. The intragrain crystallinity can be improved by PL at 650°C. The intergrain crystallinity can be improved by PL at 650°C but it is improved by ML at 700°C due to excess total energy for PL. In-plane orientation and vicinal axis alignment are improved with increasing the a-phase ratio both for ML and PL at 600°C. We can obtain the pure single c-phase which has the complete in-plain orientation at 650°C at 0.2 mTorr.
Keywords: Ion beam sputtering, YBCO thin films, a-c orientations, Intragrain and intergrain crystallinities, In-plane orientation, Oxygen plasma

1. INTRODUCTION

High temperature superconducting (HTS) microwave filter devices must be widely used at base stations of mobile telecommunication system in the near future [1-3]. The HTS microwave filters have less insertion loss of center-frequency microwave and sharper skirt characteristics compared to conventional microwave filter devices. In order to improve the HTS filter performances, it is necessary to develop large-area thin film fabrication but we should return back to basic research of thin film fabrication of $YBa_2Cu_3O_x$ (YBCO) as well.

It is critically important to reduce surface resistance of the superconducting thin films to obtain high efficient and low insertion loss filters [4-7]. The surface resistance is enhanced by various kinds of crystalline defects such as point defects, 2D dislocations, 3D grains, grain boundaries and so on [8]. In the case of YBCO, amounts of two sorts of phase boundaries must be especially reduced, i.e., phase boundaries between c-axis oriented phase (c-phase) and a-axis oriented phase (a-phase), and twin boundaries between 45° tilted grains [5,9-13]. In addition to these defects and boundaries, intragrain and intergrain crystallinities, in-plane orientation crystallinity and film surface roughness must also be crucial factors affecting the surface resistance [11,14].

In this work, we deposited YBCO thin films using ion beam sputtering. The thin film crystallinities were characterized in terms of the a-c orientation growths, intragrain and intergrain crystalllinities and in-plane orientation. Effects of oxygen plasma supply on these crystalline qualities were clarified.

2. EXPERIMENTAL

Thin films of $YBa_2Cu_3O_x$ (YBCO) were deposited by ion beam sputtering (IBS). The IBS system is shown in Fig. 1. A target (T) of $YBa_{1.5}Cu_{2.3}O_x$ was sputtered by 4 keV Ar^+ ion beam generated by sputter-ion-gun (SIG), and sputtered particles (SP) were deposited on MgO (100) substrate (S) attached on stainless steel (SUS) holder (H). The substrate was heated using two lamp heaters (LH). During the deposition, oxygen plasma (PL) was supplied from a plasma source (PS) located 11 mm above the substrate at various oxygen partial pressures (P_O). The plasma was produced by discharging oxygen gas in PS at around 1 kV and 9.6 mA. To clarify effects of oxygen plasma, a part of the films were deposited with a supply of oxygen molecules which were emitted from the same nozzles of PS without the discharge. The substrate temperatures (T_S) were monitored during the film growth using a thermocouple pressed onto the substrate surface. In this experiment, T_S was fixed at 600°C, 650°C and 700°C.

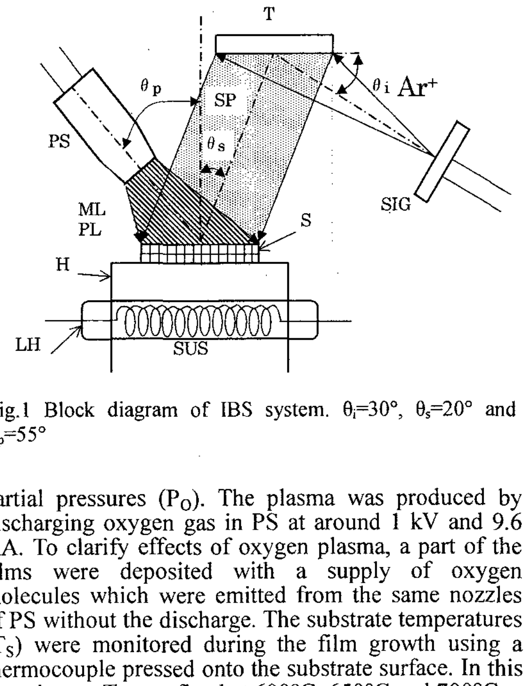

Fig.1 Block diagram of IBS system. θ_i=30°, θ_s=20° and θ_p=55°

The deposited YBCO thin films were characterized by X-ray diffraction (XRD) on θ-2θ scan using Cu Kα line. Phase ratios of γ_a (a-phase ratio) and γ_c (c-phase ratio) in a film were evaluated using XRD peak intensities of the corresponding a-phase and c-phase. "Intragrain crystallinity" of the films was estimated by full width at half maximum of θ-2θ XRD peaks (Av.Δ_θ), averaging over (100) and (200) peaks for the a-phase, and (003) and (006) peaks for the c-phase. "Intergrain crystallinity" of the films was estimated by full width at half maximum of XRD rocking curves (Av.Δ_ω) averaging over (100)+(003) peak and (200)+(006) peak. These two peaks of (100) and (003), and (200) and (006) cannot be separated in the rocking curves because they are very closely located. Then we cannot estimate the intergrain crystallinity independently for each a/c phase. The intragrain

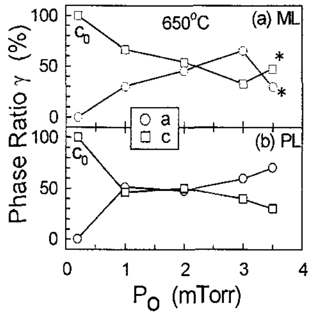

Fig.2 Phase ratios of γ_a and γ_c as a function of P_O for (a) ML and

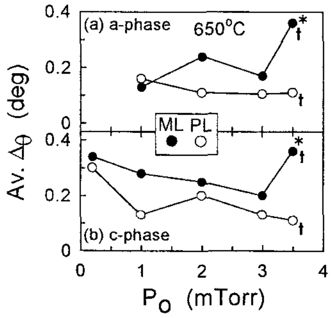

Fig.3 Av.Δ_θ vs P_O at T_S=650°C for (a) a-phase and (b) c-phase. Asterisks (*) indicate very poor crystallinity, and daggers (†) indicate that the a-phase peaks and c-phase peaks are not separated.

crystallinity is a measure of distribution of crystallographic plane-distance in the grains which have parallel planes to the substrate plane. The intergrain crystallinity is a measure of distribution of crystallographic plane-direction in the grains deflected from the substrate plane. This is frequently called "mosaicity".

Even in the pure single c-phase, sometimes the a/b axes in the film-plane are aligned to the substrate crystallographic axes, but sometimes they are deflected from the substrate axes. We call such axis-alignment as "in-plane orientation". There are two level of axis deflections. One is large deflections such as 45° tilt. In this case, we can clearly distinguish two different oriented phases, and these must be 45° tilted twins or diagonal grains in a film. The in-plane orientation was estimated by ϕ-scan XRD peaks, the in-plane orientation ratio (η) was defined as the sum ratio of axis-oriented peak intensities over the of sum of all peak intensities. The other is vicinal deflections around the substrate axes. This can be evaluated by full width at half maximum of the ϕ-scan XRD peaks (Δ_ϕ). It is called "vicinal axis alignment" henceforth.

Film surface roughness was measured by atomic force microscopy (AFM), and it is evaluated by average roughness R_Z.

3. RESULTS ANT DISCUSSION

3.1 Phase ratios

The YBCO thin films were deposited at T_S=650°C at various P_O ranging from 0.2 to 3.5 mTorr, and the calculated phase ratios of γ_a and γ_c are plotted in Fig.2 as a function of P_O both for (a) ML and (b) PL. In the both cases of ML and PL, the single c-phase grows at 0.2 mTorr, and the amount of c-phase decreases and that of a-phase increases with increasing P_O. This result can be explained as follows. Basically

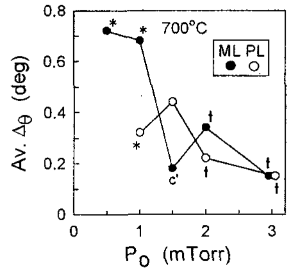

Fig.4 Av.Δ_θ vs P_O at T_S=700°C for ML and PL. A symbol c' indicates "quasi-single c-phase".

the particles to be deposited are activated by the thermal energy supplied from the substrate heat to get "surface migration" on the film surface. At low P_O, the sputtered particles have less collisions with the supplied low density of oxygen species in the gas phase above the substrate. Then they have higher kinetic energy, and can assist the surface migration. The c-phase need the long-distance surface migration of the deposited particles to be formed. This is a reason why the single c-phase grows at the low P_O. With increasing P_O, the sputtered particles get more frequent collisions with the denser oxygen species, then they lose more kinetic energy. The lower energy particles cannot assist the surface migration, then the c-phase cannot be grown, instead the a-phase grows. The a-phase does not need the long surface migration to be formed, because all of the sites of Y, Ba and Cu elements are exposed on the topmost surface of a-phase crystal structure.

However, the surface energy is higher for the a-phase than the c-phase, then the a-phase needs some other energy to be grown in addition to the fundamental thermal energy and sputtered particle kinetic energy. A possible energy is activated energies of oxygen and sputtered particles after the gas-phase collisions. The particle kinetic energy is reduced but it can be transferred into the activated energy. In the case of PL, the plasma has originally the activated energy. This plasma energy can be utilized to form the a-phase with the higher surface energy. This presumption can be verified by an experimental result that the a-phase growth is enhanced by PL in a P_O region around 1 mTorr. However, this PL effect of the a-phase growth enhancement at 650°C is not so much prominent compared to that in low temperature depositions we have reported previously [11,13], because the thermal energy effect dominates over the plasma energy effect [12]. It must be mentioned that the pure single a-phase can be grown at lower T_S because the thermal surface migration is not activated by the low thermal energy resulting in the suppression of the c-phase growth. Thus the "total energy" and "energy balance" are crucial factors which determine the a-c orientation growth of YBCO thin films in this IBS system.

3.2 Intragrain and intergrain crystallinities

The values of Av.Δ_θ are plotted in Fig.3 as a function of P_O for the (a) a-phase and (b) c-phase in the films deposited at 650°C with ML and PL. The film with ML at 3.5 mTorr has very poor crystallinity both for the a-phase and c-phase. This is caused by the excess reduction of sputtered particle energy due to the heaviest collisions with the highest density of oxygen molecules. It implies that the particle kinetic energy is necessary for the growths of both a-phase and c-phase for ML. While the a-phase and c-phase can be grown by PL at the same P_O of 3.5 mTorr. The kinetic energy is also reduced much but the plasma energy can be utilized for the crystal formation for PL.

Except for this film, the films with ML (ML-films) have rather good intragrain crystallinity, and the best a-phase can be grown at 1 mTorr whereas the best c-phase can be grown at 3 mTorr. Probably the a-phase can release its internal strain energy to ambient larger amount of the c-phase grains while the c-phase can release its internal strain energy to ambient larger amount of the a-phase grains (see Fig.2). This results in the poorer intragrain crystallinity of the c-phase at the lower P_O and of the a-phase at the higher P_O, respectively, as observed in Fig.3.

The most striking features are that both of the a-phase and c-phase intragrain crystallinities can be improved by PL in almost all P_O regions. It is proposed that wrong-sited Y and Ba atoms at the topmost surface of growing a-phase can be exchanged into right-sites by utilizing the plasma energy, resulting in higher crystalline order. Therefore the a-phase crystallinity can be improved by PL. On the other hand, some wrong-sited atoms on the growing c-phase surface might be corrected by the same exchange effect by PL, resulting in the improvement of crystallinity of the c-phase. Then the plasma has good influences both on the a-phase and c-phase crystallinities at 650°C.

The values of Av.Δ_θ are plotted in Fig.4 as a function of P_O for the films deposited at 700°C with ML and PL. The a-phase and c-phase cannot be separated in most of the films, then this figure indicates the averaged intragrain crystallinity of the ML-films and PL-films with mixed phases. However, the film at 1.5 mTorr is near single c-phase (we call "quasi-single c-phase) denoted by c'. In general the crystallinity becomes better with increasing P_O. The total energy, the sum of thermal energy and sputtered particle kinetic energy, is higher because of the higher substrate temperature, then the total energy is too high for the crystal growth at low P_O due to the higher kinetic energy caused by the less collisions. This is the reason for the poorer crystallinity at the lower P_O. With

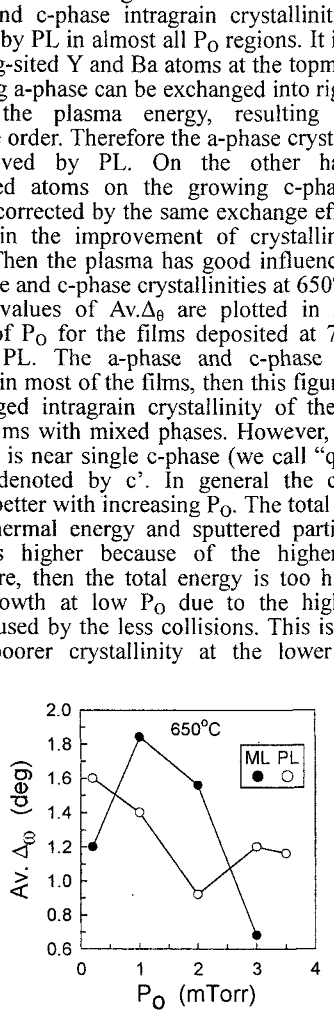

Fig.5 Av.Δ_ω vs P_O at T_S=650°C for ML and PL.

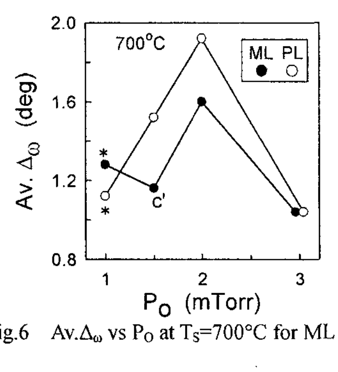

Fig.6 Av.Δ_ω vs P_O at T_S=700°C for ML and PL.

increasing P_O, the crystallinity is improved because of soft landing of the sputtered particles due to the heavier collisions. This must also be one of the reasons for the gradual improvements of crystallinity of the c-phases in the higher P_O region at 650°C (Fig.3). The values of Av.Δ_ω are plotted in Fig.5 as a function of P_O for the films at 650°C with ML and PL. In lower and higher P_O regions, the intergrain crystallinity is better for ML and the best film is grown at 3 mTorr. Whereas the crystallinity is improved by PL in middle P_O region and the best film is grown at 2 mTorr. Grossly the crystallinity becomes better with increasing P_O due to the appropriate loss of kinetic energy by the collisions. This tendency is nearly the same with that of Av.Δ_θ at 650°C shown in Fig.3. Thus the intragrain and intergrain crystallities have "regular correlation".

The values of Av.Δ_ω are plotted in Fig.6 as a function of P_O for the films at 700°C with ML and PL. The both of ML-films and PL-films show the same tendency, i.e., the intergrain crystallity is better at lower and higher P_O. The reason is not known. A notable result is that the crystallinity is improved by ML. This indicates that the total energy of thermal energy, particle energy and plasma energy is too high for the good mosaicity. At the higher P_O of 3 mTorr, the crystallity for PL approaches that for ML because the kinetic energy is more reduced by the plasma due to larger collision cross section for PL induced by Coulombic interactions. While at the lower P_O, the kinetic energy is higher but the plasma energy is lower, then the good crystalline films can be grown. However, at the lowest P_O of 1 mTorr, the kinetic energy is too high then the poor crystalline films grow which are marked by asterisks even though the values of Av.Δ_ω are small.

3.3 In-plane orientations

The ϕ-scan XRD patterns using (103) plane are shown in Figs.7 for (a) the ML-films deposited at 600°C at 2 mTorr and 3 mTorr, and (b) the PL-films deposited at 600°C at 2.5 mTorr and 2 mTorr. The two ML-films show 8-fold symmetry peaks, strong 4-fold symmetry peaks and weak 4-fold symmetry peaks. The ML-film at 2 mTorr has γ_a=81.5%, η=97.4% and Δ_ϕ=2.35. The ML-film at 3 mTorr has γ_a=75.1%, η=97.2% and Δ_ϕ=2.50. Therefore these films are a-phase dominant films. The stronger peaks correspond to grains with their axes oriented to the substrate axes which is called "in-plane oriented grain" henceforth (sometimes called "cube-on-cube" growth). The weaker peaks correspond to small amount of 45° tilted grains with respect to the in-plane oriented grains which is called "diagonal grain" henceforth. Then there are small number of 45° tilted twins. The most of strong 4-fold peaks come from the a-phase grains which are lying with their c-axes perpendicular with each other on the substrate because the films are dominant a-phase [14]. The in-plane orientation ratios η are very high, then the films are highly in-plane oriented.

The PL-film at 2.5 mTorr has γ_a=96.7%, η=99.7% and Δ_ϕ=2.07. The PL-film at 2 mTorr has γ_a=91.85%, η=98.54% and Δ_ϕ=3.10. The films are almost single a-phase (called "quasi-single a-phase" which is denoted by a'). The diagonal grain is almost eliminated. Then we have two notable effects by the plasma. The a-phase growth is prominently enhanced by the plasma. The in-plane orientation growth is extremely improved by the plasma.

These in-plane orientation parameters of η and Δ_ϕ for 600°C deposited films are plotted in Fig.8 as a function of γ_a, and Fig.9 is plotted for 650°C deposited films are plotted in Fig.9 as a function of γ_c. First we discuss the results for 600°C (Fig.8). The in-plane

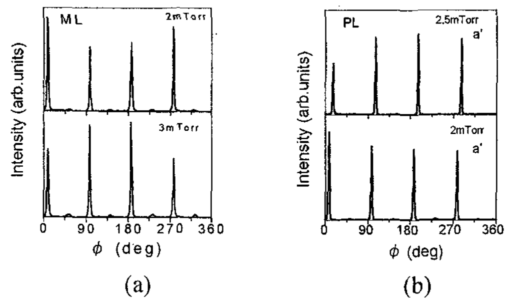

Fig.7 ϕ-scan XRD patterns at T_S=600°C for (a) ML and (b) PL. Values of P_O are indicated. A symbol a' indicates "quasi-single a-phase".

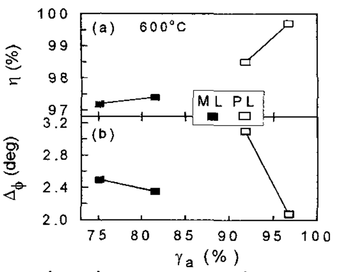

Fig.8 In-plane orientation parameters of (a) η and (b) Δ_ϕ as a function of γ_a at T_S=600°C.

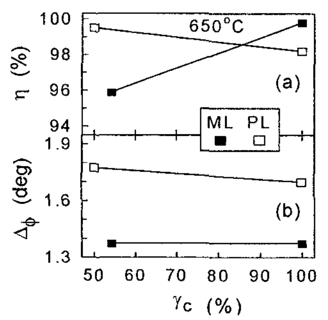

Fig.9 In-plane orientation parameters of (a) η and (b) Δ_ϕ as a function of γ_c at T_S=650°C.

orientation (η) is improved with increasing the a-phase ratio both for ML and PL. Contrary, this means that the in-plane orientation becomes poor with increasing the c-phase ratio. These two indicate that the a-phase has better in-plane orientation nature than the c-phase. Then the diagonal grain can be attributed to the c-phase and not the a-phase. The vicinal axis alignment (Δ_ϕ) is improved with increasing the a-phase ratio, indicating that the a-phase has better vicinal axis alignment than the c-phase. The value of Δ_ϕ is much larger for PL at γ_a=91.8% than for ML but it is absolutely small at γ_a=96.7%. This implies that the plasma does not always improve the vicinal axis alignment, rather it depends on particular deposition conditions.

Next we discuss the results for 650°C (Fig.9). The in-plane orientation becomes poor with increasing the c-phase ratio (it is improved with increasing the a-phase ratio) for PL. This is the same tendency with that for 600°C, so that it is explained in the same manner. However, the in-plane orientation is improved with increasing the c-phase ratio for ML. This is clearly opposite to the 600°C case but is very important. We can obtain the pure single c-phase (γ_c=100%) besides it has almost 100% in-plane orientation at 650°C with ML at P_O=0.2 mTorr. Furthermore this sample has very small Δ_ϕ as 1.37° indicating excellent vicinal axis alignment. Thus we can obtain the pure in-plane oriented single c-phase by controlling the deposition conditions in this IBS system. The vicinal axis alignment does not depend on γ_c so much for ML, but it is improved with increasing γ_c for PL at 650°C.

4. SUMMERY

YBCO thin films were grown by IBS at various T_S and P_O with the supply of either ML or PL on MgO. Their intragrain and intergrain crystallinities were investigated as well as a-c orientation growths as a function of P_O. At the low P_O the single c-phase can be grown at 650°C and the c-phase decreases while the a-phase increases with increasing P_O both for ML and PL. The intragrain crystallinity can be improved by PL at 650°C owing to the plasma energy, but it cannot be improved by PL at 700°C because the effect of thermal energy dominates over the effect of plasma energy. The intergrain crystallinity can be improved by PL in the middle P_O region at 650°C but it is improved by ML at 700°C due to excess total energy for PL. The in-plane orientation is improved with increasing the a-phase ratio both for ML and PL at 600°C, at the same time the vicinal axis alignment is improved with increasing the a-phase ratio. We can obtain the pure single c-phase which has the complete in-plain orientation at 650°C at 0.2 mTorr.

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