Anisotropy and scaling of $YBa_2Cu_3O_{7-x}$ thin films

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Abstract. Anisotropy and scaling properties of $YBa_2Cu_3O_{7-x}$ thin films grown on $SrTiO_3$ substrate by pulsed laser deposition are studied by using two-point, two-dimensional statistical functions. It is found that films whose deposition conditions differ by the pulse deposition rate and the chemical treatment of the substrate have significantly different anisotropies and scaling intervals. This is interpreted as branching of initially identical growth mechanisms into two modes. The branching occurs at lateral scales of about 80 nm and above.

In a recent paper [1], we reported an example of a detailed study of the morphology of $YBa_2Cu_3O_{7-x}$ (YBCO) thin films. The films of interest are grown on a vicinal $SrTiO_3$ (STO) substrate using the pulsed laser deposition system at Cambridge University. The methods we use for characterization of YBCO morphologies are statistical and incorporate both one-point and two-point statistical functions. Here we further extend and refine the analysis of YBCO thin films morphologies. The analyzed sample includes films obtained at different laser pulse repetition rate (PRR), however, keeping the total number of pulses the same – 2000. That is, the amount of material deposited was maintained approximately the same. The deposition temperature, i.e. the temperature of the substrate, was also kept identical at 765 °C. We also incorporate analysis of the substrates morphologies. The latter clearly plays an important role during the surface growth and especially at its early stages.

Important facets of the surface growth are encapsulated in the scaling properties of the morphology. The scaling for an anisotropic surface may, in principle, depend on the direction. To reckon with this, we employ a new, indirect, estimate of the mean square increment function (MSIF) as the main statistical tool to probe for scaling. Below we first focus on inferring the anisotropy of a STO vicinal substrate cut and YBCO morphologies grown on this substrate. On this basis and using the sample MSIF, we study next the scaling properties of the YBCO deposits along the major axes of anisotropy.

Examples of atomic force microscope (AFM) images of both the substrates and the films are shown in figure 1 and figure 2, respectively. The commercially available (STO) substrates used in this study were cut at $\alpha_{vic} = 2^\circ$; $\alpha_{vic}$ is the angle off the [001] plane and towards the [100] direction, i.e. [100] direction crosses the step edges, whereas the [010] direction is along the step edges. A chemical treatment procedure was performed in order to obtain a TiO$_2$ terminated layer. The procedure utilizes commercially available NH$_4$F buffered HF solution (pH≈ 4.5) for removal of SrO from the surface. A thermal treatment at 950° C and 1 atm of oxygen for
Figure 1. AFM image of a vicinal STO substrate: $\alpha_{\text{vic}} = 2$ deg. The estimated average direction, width and extent of the steps are given in the text.

approximately 2 hours finalized the substrate preparation. The AFM image was taken after the sample was rotated on $\sim 45$ degrees revealing an almost perfectly stepped surface, see figure 1.

Figure 2. AFM image of a YBCO thin film, deposited on the substrate similar to that shown in figure 1 at pulse repetition rate of 5Hz.

Figure 3. A contour level plot the two dimensional sample autocovariance function for the YBCO morphology shown in figure 2.

In order to estimate the average width and the longitudinal extent of the terraces we compute the sample, two-dimensional (2d) autocovariance function (AcF) [1] of the surface heights. We use the notation $A(u)$ for this function, where $u$ is a 2d lag vector, i.e. the vector representing the difference between two points in the image [1]. Using a method identical to that used to
quantify the anisotropy of YBCO deposits below, i.e., fitting an AcF horizontal slice with an ellipse, we estimated: the average direction of the steps is $\psi = 46.9^\circ$, the average terraces extent and width are: $a = 251.2 \, \text{nm}$ and $b = 4.99 \, \text{nm}$, respectively.

![Figure 4. Horizontal slice of the sample AcF shown in figure 3 (circles). The solid line represent the ellipse that best fits the points.](image)

Turning to the YBCO morphology presented in figure 2 (film thickness approximately 140 nm; image taken with no rotation), we observe an array of a high-plateau structures with a typical size of 250 – 300 nm, distributed almost uniformly. No apparent anisotropy can be discerned in them or in the other surface corrugations. That such an anisotropy exists, however, is revealed by the contour plot of the sample AcF depicted in figure 3. It shows that the surface features in a direction of roughly 10 degrees with respect to the horizontal axis have a larger lateral extent compared to their extent in the transversal direction. The anisotropy takes place on all lateral scales roughly between 60 nm and 220 nm. We quantify the identified anisotropy in the following manner: Take a horizontal slice of the AcF centered at, say, level 0.1 from the max of $A(u)$. The AcF maximum is at $u = 0$, note that r.m.s. height is $\sigma = \sqrt{A(0)} = 9.0 \, \text{nm}$. The points of the AcF within the slice have an elliptical shape, see figure 4; hence, fitting them by an ellipse, we can quantify the anisotropy at these scales by the angle of the ellipse orientation with respect to the horizontal axis, $\psi$, and aspect ratio $\gamma$ (the ratio of the small to the large axes of the ellipse). The values of both $\psi$ and $\gamma$ are given in the legends of figure 4.

What could be the mechanism producing the observed relatively low degree of anisotropy? Note that the major axis is almost parallel to the direction of the substrate steps. One can argue that at this relatively high influx of YBCO species – see [2] for details of the YBCO nucleation on the STO surface – the sticking rate is high, certain terraces are quickly filled in, prompting across the steps flow at early times of the YBCO growth. Further studies are needed, however, to confirm such a scenario.

A different morphology is observed for the film deposited at PRR of 1 Hz, see figure 5. Instead of high-plateau areas, a great number of deep holes are seen. At about the same film thickness the r.m.s height is markedly lower, $\sigma = 4.92 \, \text{nm}$. Such porous YBCO films were obtained by...
various groups in the past, see e.g. [3]. Beneath each hole a precipitate of some secondary compound (usually $Y_2O_3$, $CuO$ and combinations of them) was found in [4]. On the other hand, the conditions favoring the formation of precipitates and consequently holes remains largely unknown, see also [5]. The comparison of the films grown at 1 Hz and 5 Hz PRRs suggests...
that precipitate/holes form when the system has enough time between two pulses for surface self-organization and relaxation, although it should be noted that this film was deposited onto a 2 degree vicinal substrate without the chemical treatment previously described. The different pulse rates lead to a somewhat different anisotropy properties of the YBCO morphology. The latter is seen from the 0.1 level of the AcF slice, shown in figure 6, which indicates that the YBCO morphology has aspect ratio close to unity, i.e. the film almost lost “memory” for the steps of the substrate.

Figure 7. Cross-section of the MSIF along the principle axis of anisotropy for the film shown in figure 2.

As stated earlier, we account for the fact that the scaling properties of an anisotropic surface could in principle depend on the direction by using for this purpose the 2d MSIF estimated in terms of the sample AcF by: \( B(v) = 2(A(0) - A(v)) \). The MSIF like \( A(v) \) involves two-point statistics but unlike AcF is strictly positive for all lags \( v \neq 0 \). If the morphology possess approximate scale-invariance, \( B(v) \) is expected to scale according to \( B(v) \sim \tau^{1-\alpha}|v|^{\alpha-2} \), where \( \tau \) and \( \alpha \) are called topothesy and spectral exponent, respectively [6]. In figures 7 and 8 we show cross-sections (in a log-log scale) of the MSIF along the major principle axis of anisotropy, for the films generated at 5 Hz and 1 Hz PRR, respectively. Scaling intervals are identified for both films, however, clearly with different lengths. For the 5 Hz morphology, the scaling interval spans between 40 and 120 nm, whereas for the 1 Hz morphology the scaling holds within 40 – 80 nm only. The spectral exponents inferred from the slopes of MSIFs are closely similar, see the legends. (The error bounds for \( \alpha \) are estimated by employing synthetic simulations of the sample MSIF points, details of which will be published elsewhere.) In a more popular terminology, we can say that the fractal dimensions, \( D \), of both films are the same. (There is a simple relationship between the spectral exponent and the fractal dimension: \( D = (8 - \alpha)/2 \).) This is an indication that at short distances the nucleation and the growth mechanisms of both films are the same. At lateral scales of about 80 nm, however, the growth of the 1 Hz morphology branches to a different mode, imprinted in the departure of its MSIF from the short distance scaling.

In conclusion, we found that the anisotropy properties of YBCO thin films grown at different pulse repetition rate, but otherwise under identical pulsed laser deposition conditions, differ by
both direction and aspect ratio. The scaling along the major axis of anisotropy, though having similar exponents, also differs by the extent of the scaling interval. This can be interpreted as branching of initially identical growth mechanisms into two modes. The branching occurs at lateral scales of about 80 nm and above.

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