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Evidence for surface melting during the growth of high T_c thin films

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We present reflection high energy electron diffraction (RHEED) spot profile analyses, which show anomalous broadening over very short time scales. Our data can only be interpreted in terms of surface melting. The conclusions are consistent with the thermodynamic phase diagrams and with the vapor-liquid- solid (VLS) mechanism of crystal growth.

1. Introduction

Lower oxygen pressures allow the formation of YBCO films at lower temperatures, thereby minimizing interdiffusion and reaction with the substrate and improving film morphology. The quaternary phase relations in YBCO in reduced oxygen pressures has been determined [1].

2. EXPERIMENTAL

All RHEED data during the growth of YBCO thin films by molecular beam epitaxy (MBE) were obtained at 10 kV and a grazing angle of 28 mrad (1.5°). The RHEED patterns were photographed with high sensitivity film (1000 ASA) and the RHEED intensity oscillations of selected spots monitored.

We study the (11) spot. The intensity oscillations of the specular spot have been published [2, 3]. A computer controlled densitometer was used to analyse the spot profiles[4].

3. RESULTS

Figure 1 shows the oscillations in the intensity of the (11) diffracted spot as a function of time. We draw attention to the precipitous drop in the intensity immediately following the first maximum, caused by a surface process with a very small time constant. Fig. 2 is a plot of the intensity profile across the (11) diffracted spot which probes extent of ordering in the plane of the surface. There are two sets of data in this figure, with the closed circles indicating the profile at the point A (the point of the first maximum in the RHEED intensity oscillations of Fig. 1) and the triangles indicating the intensity profile at the point B (the first minimum immediately following point A). The spot profile is substantially broader at B than at A, and accompanied by a concomitant drop in the intensity. There is substantial Lorentzian broadening. One would ideally expect disorder to induce Gaussian broadening. The increase of the FWHM by a factor of 5 is hard to explain in terms of the birth-death model [5].

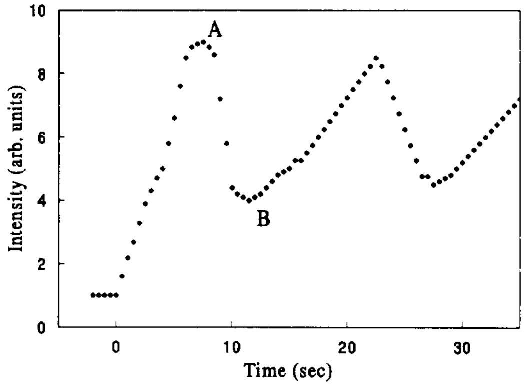

Figure 1. Intensity oscillations of (11) spot.

Activation energies may be deduced from RHEED intensity oscillation recovery profiles. We obtain a value of 0.8 eV, which is consis-

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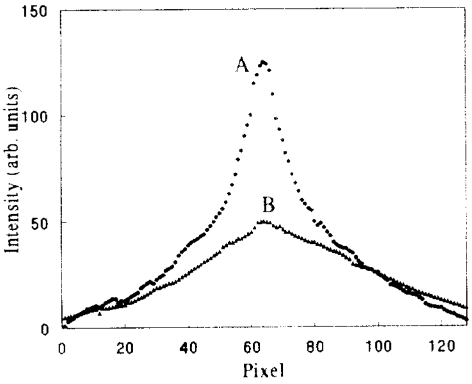

Figure 2. (11) spot profile *(see text)*.

tent with that reported in the literature by various groups. All the cation fluxes are turned off, with only the oxygen being on. Hence, if some species is being incorporated in the film it can be nothing but oxygen. We also note here that this activation energy is independent of the process used, i.e. MBE, sputtering and laser ablation all yield the same number, a remarkable independence of the process energy and fluence. Further, surface diffusion coefficients are in the range of 10^{-12} cm^2s^{-1}. These values are comparable to those for oxygen.

4. DISCUSSION

Wagner *et al.* [7] have proposed a vapor-liquid-solid (VLS) mechanism of crystal growth. In this mechanism, a liquid solution coexists with the crystalline material to be grown from the vapor. Crystal growth occurs by precipitation from the supersaturated liquid at the liquid-solid interface. A crystalline defect such as a screw dislocation is not essential for the VLS mechanism to operate. Deposition may be directly on a solid substrate in a vapor-solid system. An example is the epitaxial deposition of thin films [8].

Since the oxygen flux is always on during any measurement of RHEED relaxation profiles, it is not surprising that the activation energy measured is of the same order as that of oxygen diffusion and is independent of the process. This also explains the coincidence of the diffusion coefficient. Since the slowest process in this case is the diffusion of oxygen, it is reasonable to conclude that there is a lower activation energy for all the cationic species present on the surface along with some oxygen, which is a must for charge neutrality of the ionic compounds considered in this work.

Despite the problems associated with the measurements of p and T in vacuum, it is reasonable to assert that the p is between 0.1 to 0.3 atmospheres and that T is known to accuracies of at least 10 to 20%. Comparing with the published thermodynamic data, the substrate temperatures that are encountered in thin film growth are consistently higher than those for bulk material. This suggests that there may be a liquid phase present during the growth of thin films of these materials

5. CONCLUSIONS

In summary, we have presented data that confirm the existence of a liquid phase on the surface during the growth of YBCO thin films. These observations seem to indicate that the operative mechanism for the growth of high T_c thin films is the VLS mechanism of growth [7]. These observations mandate extreme caution in interpreting layer-by-layer growth in these materials.

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