Reflection High-Energy Electron Diffraction Oscillations Modulated by Laser-Pulse Deposited $YBa_2Cu_3O_{7-x}$

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Reflection high-energy electron diffraction oscillations during pulsed laser ablation of $YBa_2Cu_3O_{7-x}$ on $SrTiO_3(100)$ substrates were measured. We have found for the first time that the oscillations are modulated by the laser-pulse repetition frequency. Each laser pulse deposits 0.14 nm of material. This causes the specularly reflected intensity to decrease instantaneously, but then it increases exponentially due to crystallization. An activation energy of 0.7 ± 0.1 eV and a diffusion constant of 1.4×10^{-12} cm^2/sec at 720°C for the formation of c-axis oriented films was determined.

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Reflection high-energy electron diffraction (RHEED) oscillations during thin-film growth of ionic oxides and especially $YBa_2Cu_3O_{7-x}$ (YBCO) have been observed by other groups during reactive coevaporation [1] of the metals, molecular laser-beam epitaxy [2-4], and pulsed laser deposition [5]. However, the amount of material deposited per laser pulse was too small for modulation of the specularly reflected intensity to be observed during each pulse. The major result of these measurements was that the growth unit is a full unit cell due to requirements of charge neutrality and chemical stoichiometry. In the case of c-axis oriented YBCO, a full oscillation period indicates a complete unit cell layer 1.17 nm thick [1].

Pulsed laser deposition of thin ceramic films has attracted much attention. It is a fast, flexible, and reproducible technique different in important ways from deposition techniques like molecular beam epitaxy (MBE), coevaporation [6,7], and molecular laser-beam epitaxy [2-4] which are characterized by low background pressures and low continuous deposition rates. Pulsed laser ablation produces periodic high momentary deposition rates of 10^5 to 10^4 nm/sec for about 1 to 10 μs (0.1 nm/laser pulse) at background pressures of 10^{-3} to 1 mbar [8-10]. The laser pulse impinging on the YBCO target produces ions and atoms with initial kinetic energies of 40-70 eV. Collisions between the ejectants and the ambient oxygen results in a strongly forward peaked velocity distribution away from the target. Ablation into high pressure oxygen results in shock waves and causes the above-mentioned high rates. Moreover, there is no deposition between the laser pulses.

We measured for the first time RHEED oscillations modulated by the laser-pulse repetition frequency. The laser ablation of YBCO was performed on $SrTiO_3$.

Homogeneous YBCO deposition onto 10×10-mm^2 $SrTiO_3$ substrates was carried out using a cylindrical YBCO target and a KrF excimer laser line focus (20 mm long, wavelength 248 nm, pulse duration 30 ns, energy density 2 J/cm^2) aligned parallel to the YBCO cylinder axis. The substrates were set at a distance of 50 mm from the YBCO target to get 0.14 nm of material thickness per laser pulse. All depositions were performed on $SrTiO_3$ substrates at a molecular oxygen pressure of 1×10^{-2} mbar. Film preparation with a similar setup is described in more detail in Ref. [11]. The surface topography of the resulting YBCO film was imaged by scanning tunneling microscopy (STM) in air.

In order to perform *in situ* RHEED measurements with an ambient molecular oxygen pressure of 10^{-2} mbar, we used a differentially pumped electron gun and a short distance between the substrate and the fluorescent screen (150 mm). The pressure at the filament of the electron gun is 10^4 times smaller than the pressure within the deposition chamber. Although these high pressures increased the diffuse scattering of the electrons, the diffraction patterns were clearly observable. A charge-coupled-device (CCD) camera attached to the fluorescent screen (0.25 ms decay time) was used to record the RHEED diffraction patterns. The specularly reflected electron intensity was measured by integration of the corresponding pixels of the CCD chip with a sampling frequency of 12.5 or 25 Hz. In all measurements, the angle of incidence of the 30-keV electrons was 2° and the azimuth direction was $SrTiO_3[100]$.

Figure 1(a) shows the RHEED intensity oscillation of the specularly reflected electron beam. The laser-pulse repetition frequency was 1 Hz, consistent with the fine scale signal period (1 s) shown in a magnified scale in Fig. 2. A YBCO film thickness of 40 ± 2 nm was mechanically measured with a stage profiler after deposition by 300 laser pulses, yielding a deposition of 0.133 nm per laser pulse. From this we calculate that a full period of oscillation in Fig. 1(a) corresponds to the deposition of 1.2 nm of YBCO, which agrees quite well with the c-axis lattice constant of YBCO (1.17 nm).

We envisage the growth as follows. Each laser pulse effectively adds 0.14 nm of initially disordered YBCO to the substrate surface, decreasing the specular intensity. Atomic redistributions on the surface cause an intensity increase when another full layer of YBCO is formed, and the cycle repeats as more YBCO is deposited. The corresponding RHEED oscillation pattern indicates that the step density varies during growth. We speculate that two-dimensional nucleation on the terraces and subse-

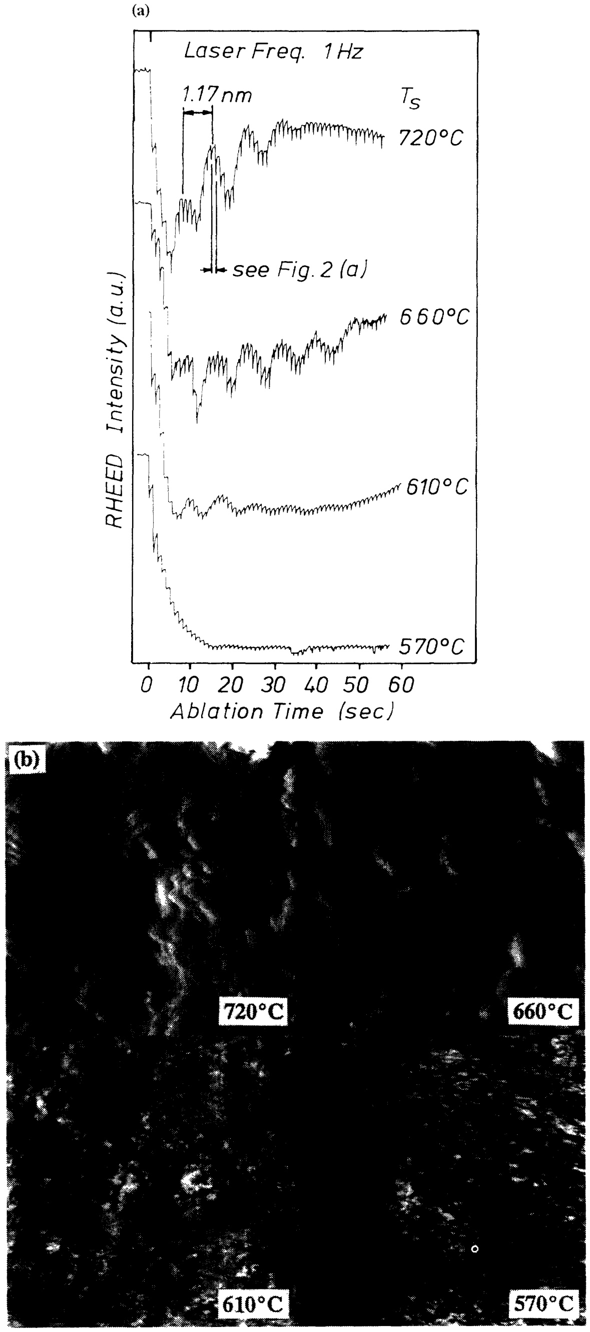

FIG. 1. (a) RHEED oscillations of the specularly reflected electron beam from films grown at different substrate temperatures. (b) Scanning tunneling microscopy images of the YBCO surface for deposition temperatures as indicated. The full image size is 505 nm×505 nm.

quent coalescence of the islands occurs. As seen in Fig. 1(a), at 660 °C the oscillations are damped, presumably due to the decreased mobility of the material at this temperature, so that the step density increases. At 610 and 570 °C damping increases still more; the films are evidently becoming increasingly more rough due to enhanced three-dimensional growth. At the lowest temperature the specular intensity simply decreases continuously without oscillations.

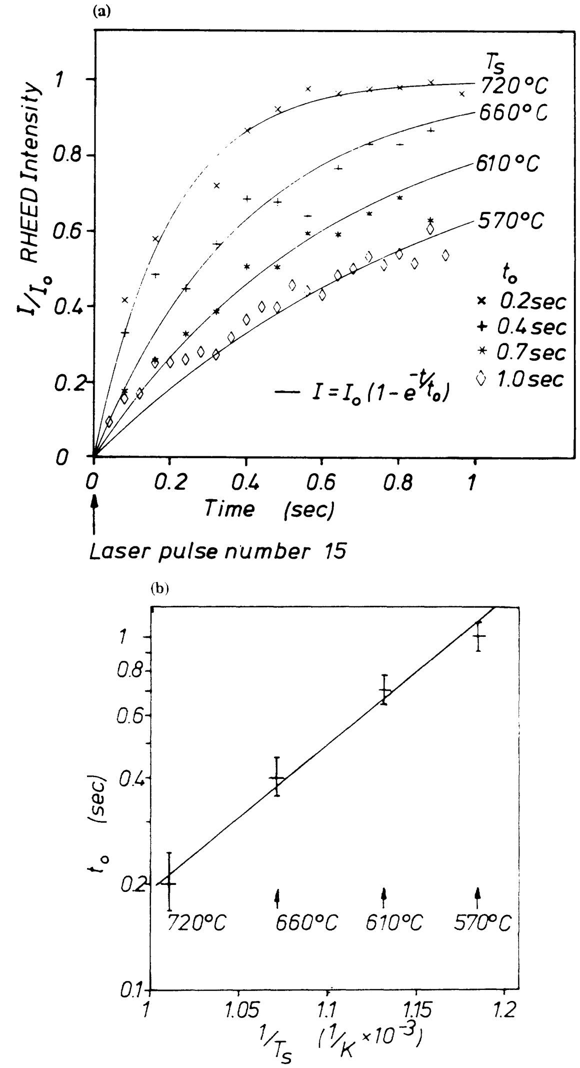

FIG. 2. (a) Time dependence of the normalized RHEED intensity near the second oscillation maximum [Fig. 1(a)] after laser-pulse number 15. The saturation intensity is normalized to 1. The solid lines are fits by an exponential function. (b) Arrhenius plot of the time constants t_0 of 2(a).

This picture is confirmed by STM images of the thin-film surfaces after the deposition of 40 nm in Fig. 1(b). The YBCO film growth at a substrate temperature of 720 °C exhibits widely spaced steps with large areas of two-dimensional growth. Films grown at 660 and at 610 °C show more smeared out steps, and those grown at 570 °C are increasingly more rough.

Figure 2(a) shows the RHEED signal between the fifteenth and sixteenth laser pulses of Fig. 1(a) on a magnified time scale. The intensities are fitted by $I = I_0[1 - \exp(t/t_0)]$ and are plotted normalized to I_0. The recovery of the RHEED signal after a laser pulse monitors the diffusion and formation of an epitaxial *c*-axis oriented YBCO layer. In order to understand the observed time dependence, we assume that the deposited disordered YBCO material initially homogeneously covers the substrate surface. Immediately after the deposition, crystallization begins to take place at already existing nucleation sites on the substrate surface. As the RHEED oscillations show, epitaxial *c*-axis oriented YBCO islands grow two dimensionally with a thickness of one unit cell. Since the deposited material is only 0.14 nm thick and the *c* axis of YBCO 1.17 nm long, as crystallization proceeds the thickness of the disordered material remaining around each crystallizing island must decrease. This establishes a gradient in the atomic surface density towards the nucleation sites and leads to a further transport of material from the remaining disordered YBCO to the growing islands. The process is completed when all the newly deposited YBCO material has crystallized into two-dimensional *c*-axis oriented epitaxial islands. There is no equilibrium between impinging flux and desorption rate during laser ablation, since the growth must be carried out at oxygen pressures and substrate temperatures at which the YBCO is stable.

This growth model is different from that applicable to MBE films, where there is an equilibrium between the impinging flux of atoms and the desorption rate. In this case, the deposited atoms experience only a small driving force toward nucleation sites, which depends on the supersaturation [12]. Each atom or molecule randomly walks across the surface until it comes to rest at a nucleation site.

The time constant t_0 versus the reciprocal substrate temperature is presented in a logarithmic plot in Fig. 2(b). From this Arrhenius plot we determined an activation energy of 0.7 ± 0.1 eV necessary for the different diffusion and growth processes involved. These measurements cannot separate contributions to the growth process from the internal energy or crystallization energy. It might be that there is a rate-limiting reaction during the YBCO film formation which determines the activation energy.

In order to obtain films of good crystalline quality, the crystallization of material deposited by a given laser pulse should be completed before the next pulse deposits more material onto the surface. Therefore the time between pulses should be larger then the exponential time constant t_0. We observe that when the laser-pulse repetition frequency is reduced to 0.2 Hz, the RHEED intensity between pulses must be fitted by the sum of two exponential functions. The intensity does not saturate at 1 s but continues to increase slowly with a time constant of $\sim 10t_0$. This additional slow recovery of the intensity is commonly observed after stopping the flux of atoms during MBE or coevaporation [1], and is attributed to a decrease of the step density by rearrangement of islands. Large two-dimensional islands grow at the expense of small ones, decreasing the step density.

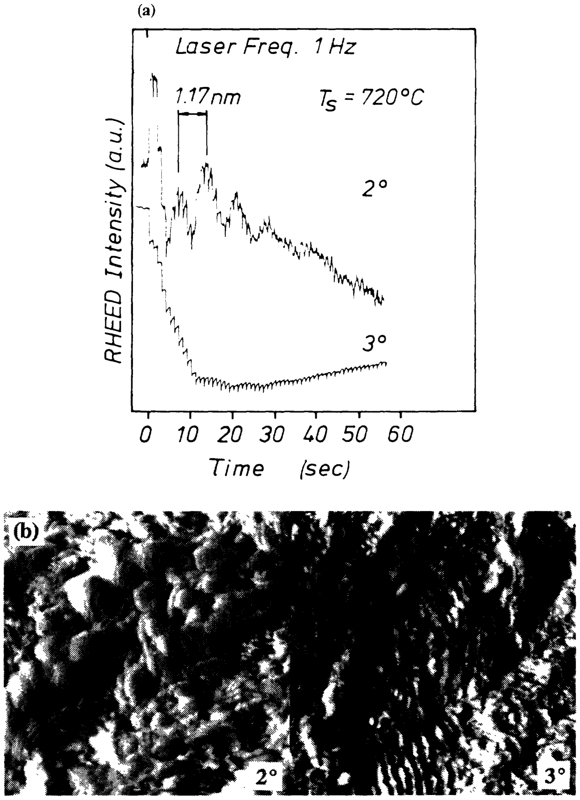

FIG. 3. (a) RHEED oscillations of the specularly reflected electron beam from a film grown at 720 °C on 2° and 3° misoriented $SrTiO_3(100)$ surface. (b) STM images of YBCO surface grown on the 2° and 3° misoriented $SrTiO_3(100)$ surface. Full image size is 505 nm × 505 nm.

Finally, an estimate of the terrace width at which step movement occurs was obtained by measuring RHEED oscillations during deposition on slightly misoriented $SrTiO_3(100)$ at a substrate temperature of 720 °C. In order to vary the terrace widths, $SrTiO_3(100)$ crystals misoriented by 2° and 3° towards (110) [13] were used; these have terrace widths of 11 and 7.5 nm and steps in the [100] direction. As shown in Fig. 3(a) the 2° vicinal surface leads to oscillations whereas the 3° vicinal surface does not. Corresponding STM images in Fig. 3(b) show that for 3° misorientation well-aligned steps parallel to the [100] direction exist due to growth by step movement. The step density remains constant and therefore no oscillations are observed [13]. Surface atoms and molecules move to the steps, which function as nucleation lines, and t_0 is the average time this nucleation process takes. This indicates a diffusion length between 7.5 and 11 nm at 720 °C. With $l = 7.5$ nm and $t_0 = 0.2$ sec [Fig. 2(a)] we obtain from $l^2 = t_0 2D$ a surface diffusion constant of $D = 1.4 \times 10^{-12}$ cm^2/sec.

In conclusion, we have measured for the first time RHEED oscillations on which are superimposed oscillations due to pulsed laser ablation. The process of crystallization after each laser pulse is directly monitored and shows an exponential increase with time. The characteristic time constant has an Arrhenius-like temperature dependence, and an activation energy of 0.7 ± 0.1 eV is derived. As each laser pulse deposits 0.14 nm of noncrystallized YBCO material, nucleation can instantaneously take place since disordered YBCO is already located at the nucleation sites, and two-dimensional *c*-axis oriented islands grow. A concentration gradient becomes established towards these 1.17-nm high two-dimensional islands, which leads to directed transport from the disordered thin layer to the growing islands.

Substrate surface steps act as nucleation lines. If the diffusion length is larger than the terrace width then the steps of the YBCO film are well aligned to the substrate surface steps. We then observe no RHEED oscillation, implying growth by step movement. From this growth on vicinal surfaces, we determine the diffusion length which, with the exponential rise time t_0, allowed an estimate of the surface diffusion constant.

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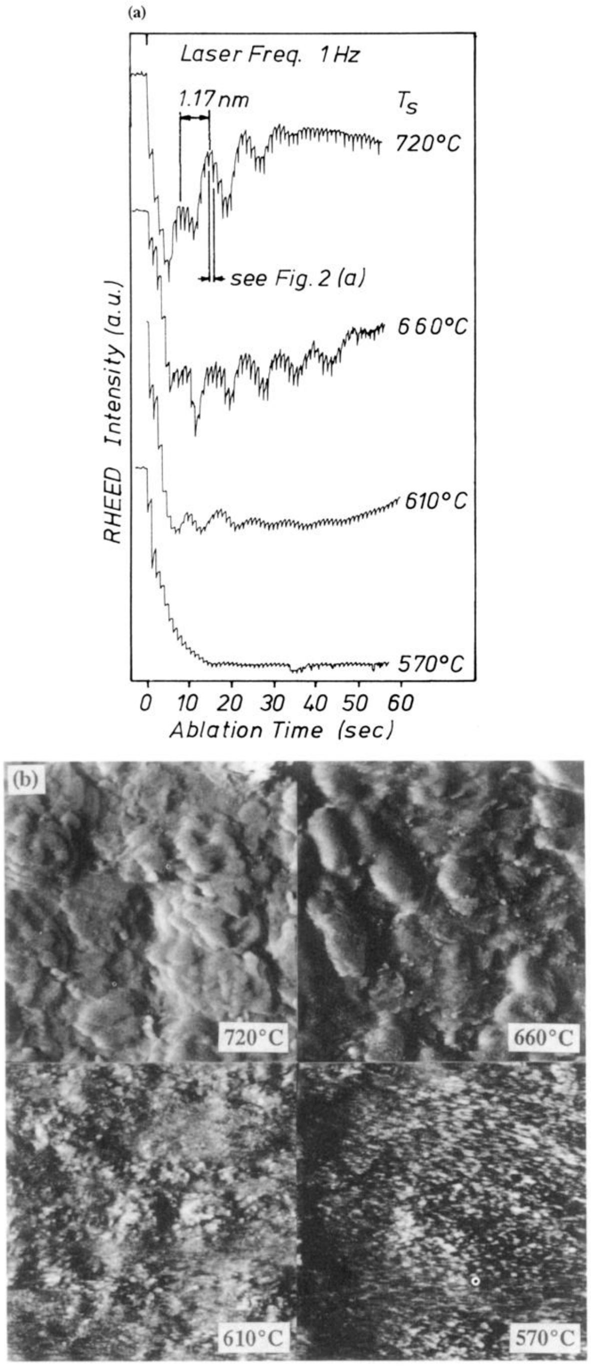

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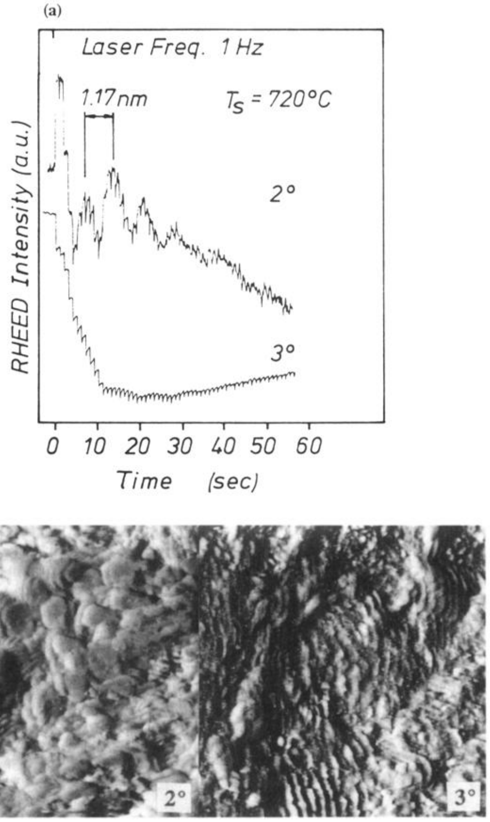

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