Imposed layer-by-layer growth by pulsed laser interval deposition

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Pulsed laser deposition has become an important technique to fabricate novel materials. Although there is the general impression that, due to the pulsed deposition, the growth mechanism differs partially from continuous physical and chemical deposition techniques, it has hardly been used. Here, we will introduce a growth method, based on a periodic sequence: fast deposition of the amount of material needed to complete one monolayer followed by an interval in which no deposition takes place and the film can reorganize. This makes it possible to grow in a layer-by-layer fashion in a growth regime (temperature, pressure) where otherwise island formation would dominate the growth. © *1999 American Institute of Physics.* [S0003-6951(99)02424-9]

New developments in thin-film techniques have opened the possibility for atomic engineering of oxide materials. In order to be able to create a crystal structure by depositing consecutive unit cell layers of different materials, a layer-by-layer growth mode[1] is a prerequisite: nucleation of each next layer may only occur after the previous layer is completed. Occasionally, the deposition conditions such as the substrate temperature and ambient gas pressure (oxygen in the case of oxide materials) can be optimized for true two-dimensional (2D) growth, e.g., homoepitaxy on $SrTiO_3$ (001). True 2D reflection high-energy electron diffraction (RHEED) intensity oscillations are observed depositing $SrTiO_3$ with pulsed laser deposition (PLD) at a temperature of 850 °C and an oxygen pressure of 0.04 mbar.[2] The relatively high temperature in combination with a low oxygen pressure enhances the mobility of the adatoms on the surface and, therefore, the probability of nucleation on top of a 2D island is minimized. The as-deposited adatoms can migrate to the step edges of 2D islands and nucleation only takes place on fully completed layers.

In general, during deposition of different kinds of materials, i.e., metals, semiconductors, and insulators, by different deposition techniques, a roughening of the surface is observed. Assuming only 2D nucleation, determined by the supersaturation,[3] limited interlayer mass transport results in nucleation on top of 2D islands before completion of a unit-cell layer. Still, one can speak of a 2D growth mode. However, nucleation and incorporation of adatoms at step edges is proceeding on an increasing number of unit-cell levels, which is exhibited by damping of the RHEED intensity oscillations. In fact, an exponential decay of the amplitude is predicted assuming conventional molecular beam epitaxy (MBE) deposition conditions.[4]

Several groups have investigated the possibility of applying a form of growth manipulation to promote interlayer mass transport.[5] They suggest to apply two different temperatures, two different growth rates, or periodic ion bombardment to increase the number of nucleation sites, and thus, decrease the average island size. This will enhance the transport of material from an island to a lower-lying level. Usually, for epitaxy of complex oxide materials, the regime of temperatures and pressures is limited by the stability of the desired phases, e.g., $YBa_2Cu_3O_7$ can only be grown in a specific temperature and pressure regime.[6] At low temperatures *a*-axis-oriented films are formed whereas at high temperatures the material decomposes. Periodic, ion bombardment is very difficult to realize in view of the stoichiometry of oxide materials. Especially in artificial layered structures mixing of succeeding layers is undesirable. Growth rate manipulation to impose layer-by-layer growth could be a possibility to overcome this problem. A different approach is the use of surfactants.[7] However, a suitable candidate for complex oxides has, to our knowledge, not yet been found.

In the case of PLD, a typical value for the deposition rate within one pulse is of the order of 10 μm/s.[8] Therefore, a high supersaturation is expected when the plume is on, and thus, the number of 2D nuclei can be very high. Subsequently, when the plume is off, larger islands are formed through recrystallization, exhibited by the typical relaxation of the RHEED intensity of the specular spot during PLD.[9] Since small islands promote interlayer mass transport, one can utilize the high supersaturation achieved by PLD by maintaining it for a longer time interval and suppress subsequent coarsening.

Accordingly, to circumvent premature nucleation due to the limited mobility of the adatoms at a given pressure and temperature, causing a multilevel 2D growth mode, we introduce the possibility of interval deposition. Exactly one unit-cell layer is deposited in a very short-time interval, i.e., of the order of the characteristic relaxation times [typically, 0.5 s (Ref. 10)], followed by a much longer interval during which the deposited material can rearrange. During the short deposition intervals, only small islands will be formed due to the high supersaturation typical for PLD. The probability of nucleation on the islands increases with their average radius[3] and is, therefore, small in the case of fast deposition. The total amount of pulses needed to complete one unit-cell layer has to be as high as possible, to minimize the error introduced by the fact that only an integer number of pulses can

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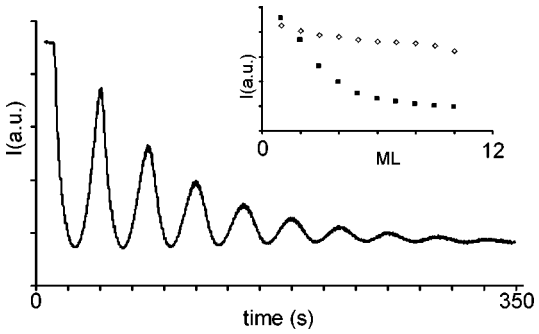

FIG. 1. The intensity changes of the specular beam during deposition of $SrTiO_3$ at 800 °C and 0.1 mbar O_2 using a repetition rate of 1 Hz. The number of pulses needed to complete one unit-cell layer (ML) is estimated to be 31. The inset shows the decay of the maxima, using this method ■, compared to the maxima using the interval method ◇.

be given. Both a high deposition rate and sufficiently accurate deposition of one unit-cell layer can be obtained by PLD using a high laser pulse frequency.

To prove this method of growth, we used $SrTiO_3$ as a model system. $SrTiO_3$ was deposited using a KrF excimer laser (248 nm) with a maximum repetition rate of 10 Hz as well as a XeCl excimer laser (308 nm) with a maximum repetition rate of 100 Hz. A single-crystalline $SrTiO_3$ target was used and the energy fluence on the target was 1.5 J/cm^2. During deposition, the growth was monitored using high-pressure RHEED.[11,12] The incident angle of the 20 keV electrons was set at 1°, while the intensity of the specular reflection was recorded with a charge-coupled device (CCD) camera. The $SrTiO_3$ substrates were specially prepared to obtain a single terminated surface with only unit-cell steps.[2] Wafers with the smallest miscut angles ($<0.2°$) were selected for this study to exclude step-flow-like growth behavior.

Depositing $SrTiO_3$ at a temperature of 800 °C and an oxygen pressure of 0.1 mbar, with a continuous pulse frequency of 1 Hz (referred to as standard deposition conditions) the surface is transiting from a single-level system to a multilevel system, as indicated by the damping of RHEED intensity oscillations in Fig. 1.

Figure 2 shows the RHEED intensity during ten cycles of deposition (at 10 Hz) and subsequently a period of no deposition, using the same oxygen pressure and substrate

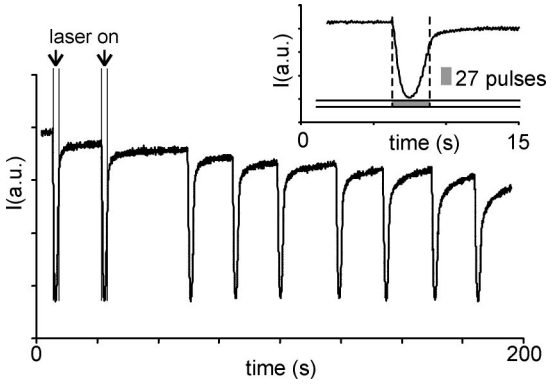

FIG. 2. The intensity changes of the specular beam during interval deposition of $SrTiO_3$; the repetition rate of the laser used here is 10 Hz. The number of pulses needed to complete one unit-cell layer is estimated to be 27. The inset gives the intensity change during one deposition interval.

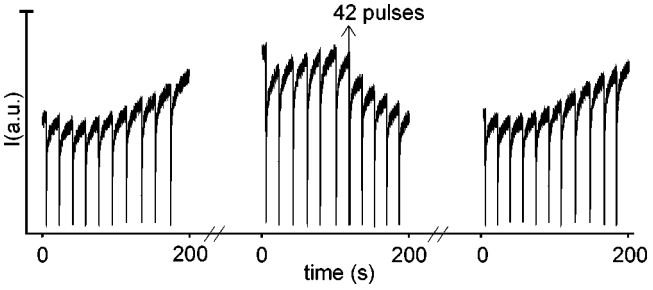

FIG. 3. The intensity changes of the specular beam during interval deposition of $SrTiO_3$; the repetition rate used here is 100 Hz. The number of pulses needed to complete one unit-cell layer is estimated to be 43. Sometimes, the number of pulses was changed by one, as indicated in the graph, to fine tune the amount of deposited material.

temperature, following our approach. In this case, the number of pulses needed per unit-cell layer was estimated to be about 27 pulses. The decay of the intensity after each unit-cell layer is significantly lower compared to the situation in Fig. 1. In the inset of Fig. 1 the intensities at each maximum of both methods are compared. The recovery of the intensity after each deposition interval will be fast when exactly one unit-cell layer is deposited. Note that, besides nucleation on the next level, the decrease in intensity also can be ascribed to the fact that only an integer number of pulses can be given to complete a unit-cell layer. A slightly lower or higher coverage causes a longer recovery time. This situation will deteriorate with every subsequent unit-cell layer, as follows from increasing relaxation times.

The intensity change during deposition of one unit-cell layer at 10 Hz is given in the inset in Fig. 2. The shape of the intensity curve at 10 Hz strongly resembles the parabola when calculating the intensity change of a two-level growth front with random distributed island and island sizes in the kinematical limit.[13] From the shape of the curve it can be seen that the time needed to deposit one unit-cell layer is still too long. This is because the deposition time interval of 2.7 s

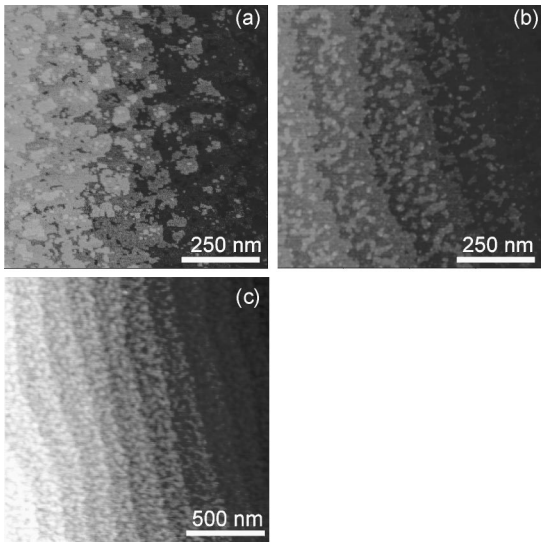

FIG. 4. (a) *Ex situ* AFM micrograph after deposition of 90 unit-cell layers of $SrTiO_3$ using standard deposition conditions; (b) *ex situ* AFM micrograph after interval deposition of 90 unit-cell layers of $SrTiO_3$ using a repetition rate of 100 Hz; and (c) *ex situ* AFM micrograph after interval deposition of 30 unit cells of the superlattice existing of two unit cells of $BaCuO_2$ and two unit cells of $SrCuO_2$.

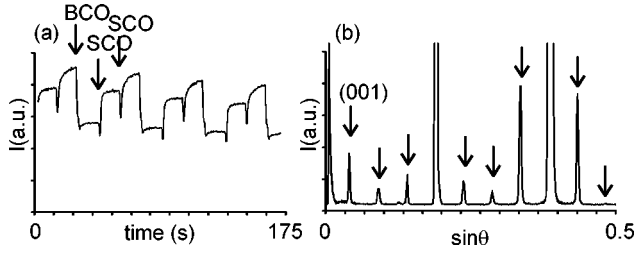

FIG. 5. (a) Fragment of the RHEED intensity during the growth of the superlattice of two unit cells of $BaCuO_2$ and two unit cells of $SrCuO_2$. The two unit cells of $BaCuO_2$ are deposited in one interval. (b) XRD profile of the superlattice. Arrows indicate the (001) reflections. The (004) and (008) reflections merge with those of the $SrTiO_3$ substrate.

is longer than the characteristic relaxation time ($\sim$0.5 s). However, a significant suppression of the formation of a multilevel system has already been achieved at this point.

To avoid the above-mentioned situation, a similar experiment was performed using the XeCl laser with a pulse frequency of 100 Hz. The number of pulses needed to complete one unit-cell layer was estimated to be 43 (i.e., deposition time of 0.43 s). Here, the increase of the RHEED intensity occurs after the deposition interval and recovers almost to the same level. The fact that the overall RHEED intensity slightly decreases is an indication that the number of 43 pulses is not exactly correct. Therefore, we periodically changed this number to 42 and observed, after an initial decrease of the interval maxima, that the intensity increased again, indicating that the surface becomes smoother. We repeated this procedure several times, and in Fig. 3 an example of this sequence is given. Only the intensity change during the final 30 intervals of a total of 90 intervals (each constituting one unit-cell layer) is depicted here. This led us to the possibility to, partly, correct for the error due to the integer number of pulses: adjusting the amount of deposited material, by changing the number of pulses by one just after a decrease in maximum intensity, we can maintain the level of RHEED intensity during deposition, suppressing the formation of a multilevel system. In fact, by doing this we proved the validity of this approach. In Fig. 4 the difference in surface morphology of a 90 unit-cell-thick sample with continuous [Fig. 4(a)] and interval [Fig. 4(b)] deposition is shown. In the latter case, the surface consists of terraces of about 200 nm width, originating from the miscut angle of the $SrTiO_3$ substrate. On these terraces, with height differences of only one unit cell, small islands can be seen with a height corresponding to one unit cell of $SrTiO_3$. This is in contrast to the surface properties obtained after continuous deposition, see Fig. 4(a) where at least four unit-cell levels are visible.

The applicability of interval deposition is not restricted to homoepitaxy, but can also be used for the fabrication of, e.g., superlattices. Here, we show results of a superlattice of two unit cells of $BaCuO_2$ and two unit cells of $SrCuO_2$, made by interval deposition. Here, we needed 26 pulses to obtain the double layer of $BaCuO_2$ and 16 pulses for one unit-cell layer of $SrCuO_2$. The pulse frequency was 10 Hz.[14] In Fig. 5(a) the RHEED intensity is given during deposition. The two unit-cell layers of $BaCuO_2$ are deposited in one interval. This is because $BaCuO_2$ has the tendency to grow in blocks of two.[15] The difference in RHEED intensity after the deposition of $BaCuO_2$ and $SrCuO_2$ is because of, e.g., the difference in growth or reflection properties. Figure 5(b) shows the x-ray diffraction (XRD) intensity profile of the superlattice, with a c-axis length of $\sim$1.58 nm. The arrows indicate the (00l) reflections originated from the superlattice, the $SrTiO_3$ substrate (004) and (008) reflections merge with the reflections of the superlattice. In Fig. 4(c) the corresponding atomic force microscope (AFM) image is given. As in the case of homoepitaxial growth of $SrTiO_3$, the terraces originate from the miscut of the $SrTiO_3$ substrate and are, even after a deposition of 48 nm, clearly visible. On the terraces only single unit-cell steps of $SrCuO_2$ can be seen.

In conclusion, we have shown that it is possible with PLD to impose a single-level 2D growth mode or layer-by-layer growth mode for $SrTiO_3$ despite unfavorable deposition conditions with respect to mobility. Depositing every unit-cell layer at a very high deposition rate followed by a relaxation interval, we extend the typical high supersaturation for PLD keeping the average island size as small as possible. Therefore, the interlayer mass transport is strongly enhanced and the formation of a multilevel growth front does not occur. This technique is unique for PLD, no other technique has the possibility to combine very high deposition rates with intervals of no deposition in a fast periodic sequence. We demonstrated the value of this method using homoepitaxy of $SrTiO_3$ and showed results on the infinite layer structure $SrCuO_2/BaCuO_2$, for which the choice of temperature and pressure is more critical, proving the importance of this growth method.

[1] A 2D growth mode can either be layer-by-layer growth or step-flow growth. However, in the case of step-flow growth, rate control with RHEED is not possible.
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