Pulsed laser deposition of SrTiO$_3$/LaGaO$_3$ and SrTiO$_3$/LaAlO$_3$: plasma plume effects

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Pulsed laser deposition of SrTiO$_3$/LaGaO$_3$ and SrTiO$_3$/LaAlO$_3$ interfaces has been analyzed with a focus on the kinetic energy of the ablated species. LaGaO$_3$ and LaAlO$_3$ plasma plumes were studied by fast photography and space-resolved optical emission spectroscopy. Reflection high energy electron diffraction was performed proving a layer-by-layer growth up to $10^{-1}$ mbar oxygen pressure. The role of the energetic plasma plume on the two-dimensional growth and the presence of interfacial defects at different oxygen growth pressure has been discussed in view of the conducting properties developing at such polar/non-polar interfaces.

The recent discovery of a 2-dimensional electron gas (2DEG) at the interface between two insulators, e.g. the polar LaAlO$_3$ (LAO) and the non-polar SrTiO$_3$ (STO), raised great interest for both fundamental and applicative perspectives. The well known interpretation in terms of the so-called polar catastrophe has certainly some significance, but other mechanisms may as well contribute to the observed phenomenology. Since pulsed laser deposition (PLD) is the most used technique for the growth of these interfaces, an analysis of the growth process can be helpful in trying to better elucidate features related to the 2DEG formation and to pose some constraints to the various physical mechanisms involved. While the polar catastrophe scenario applies to perfect interfaces, alternative mechanisms are based on the possible doping role of point defects. A first mechanisms is related to the creation of oxygen vacancies in the STO crystal used as substrate during PLD. Oxygen vacancies are known to result in an electron doping, leading to bulk conductivity, and even superconductivity below 400 mK. The possible role of such defects in the 2DEG formation

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at the SrTiO$_3$/LaAlO$_3$ (STO/LAO) interface was already addressed in the seminal paper of Ohtomo and Hwang[1]. Several following papers [2–4] discussed the dependence of the electrical transport properties on the oxygen pressure during PLD of the LAO overlayer, typically in the range $10^{-6}$ and $10^{-3}$ mbar. Kalabukhov et al. [2] demonstrated that at $10^{-6}$ mbar a large number of dislocations and of oxygen vacancies is generated. It was also suggested that this may be connected with the impact of high kinetic energy species. This leads to the second possible source of point defects: if energetic La ions hit the STO surface, some cation intermixing may also take place, resulting in a chemical doping of the STO surface with potential effect on the 2DEG formation [4]. It is tempting to increase the oxygen pressure during LAO growth, in order to slow down the impinging species; however, this modifies the growth mode. Huijben et al. found a crossover from 2D layer-by-layer to the island growth mode at $10^{-2}$ mbar [4]. Maurice et al. [5] also showed that above $10^{-1}$ mbar STO/LAO had a rough surface and poor structure. In spite of the relevance of the issues, an analysis of the PLD plume and an exact determination of the species kinetic energies during the fabrication of STO/LAO interfaces is still lacking.

In this letter we report a study of the PLD process of SrTiO$_3$/LaGaO$_3$ (STO/LGO) and STO/LAO, carried out simultaneously with high energy electron diffraction (RHEED) on the growing samples, at different oxygen background pressures. 2DEG formation in STO/LGO was very recently reported [7], and the analysis of both systems could help elucidating possible differences related to their specific composition.

Films of LGO[7] and LAO[6] were deposited on single TiO$_2$-terminated STO substrates. The ablation was carried out by irradiating LGO or LAO rotating targets with laser pulses of 25 ns duration (full width half maximum) delivered by a KrF excimer laser at a repetition rate of 1 Hz at different oxygen pressures in the range from high vacuum (HV) up to $10^{-1}$ mbar. The substrate was positioned at a distance of 3.5 cm from the target surface and its temperature was fixed at 800°C. This procedure enables the achievement of a conducting 2DEG in both STO/LGO and STO/LAO, provided the film thickness reaches the 4 unit cells (u.c.) threshold. The full electrical transport characterization, together with a detailed analysis of the microstructural properties of the interfaces, is reported in ref.[7]. Conducting interfaces are routinely achieved in the samples grown in the range $10^{-4}$ - $10^{-2}$ mbar, with no clear dependence of the transport properties on the oxygen pressure.
During the growth process, the plasma plume was investigated by fast photography and space-resolved optical emission spectroscopy, following the plume expansion from the target to the substrate and identifying plume composition [8].

RHEED analysis was performed during the growth. Intensity oscillations were observed up to $10^{-1}$ mbar, as shown in Figs. 1 (a) and (c). However, while the oscillations are not regular at such a high pressure, very good oscillations are obtained at lower oxygen pressure [7]. The oscillations indicate the two-dimensional (2D) layer-by-layer growth mode. In both LGO and LAO, the initial intensity drop is partially related to an extrinsic factor, i.e. the slight variation of the optimal diffraction conditions with respect to the STO substrate. In the case of LGO, an increase of the RHEED background is superimposed on the oscillations for deposition time between about 50 and 150 s. This is due to the progressive formation of the LGO layers characterized by a larger scattering efficiency. After completing the deposition, the RHEED signal increases (not shown here), as expected when an ordering process takes place at the surface. Our key result, in view of the following discussion, was the capability to achieve flat LGO and LAO surfaces even at $10^{-1}$ mbar, as qualified by the streaky RHEED patterns shown in Figs. 1(b, d), recorded at the end of the growth of 12 u.c. thick films. This pushes to a much higher pressure the limit for the 2D growth, previously reported as $10^{-3}$ mbar [4]. However, the samples grown at $10^{-1}$ mbar are insulating.

Fig. 2(a) reports typical images of the LGO plume emission at three different delays after the laser pulse, while spatially resolved emission spectra (in the range 370 - 630nm), collected at 1.6 $\mu$s delay at $10^{-3}$ - $10^{-1}$ mbar, are shown as an example in Fig. 2(b). The spectra show intense emissions from both La and Ga (Al in the case of LAO) neutrals, and from the Lanthanum oxide LaO. Qualitatively similar pictures are obtained for the LAO plume. The image at low pressure shows that the region of maximum emission is located at the rear part of the plume (free expansion regime), while it is shifted toward the front at increasing pressure (shock wave regime), similarly to what has been observed earlier [8]. Sequences of images as in Fig. 2 allow one to follow the plume propagation and henceforth to determine the maximum kinetic energy of the various species at the substrate position (see Table I). The data show that a crossover from free to braked expansion takes place at about $10^{-2}$ mbar, as indicated by the progressive changes of the plume shape in Fig.
2(a). In particular, at $10^{-2}$ mbar the interaction with the background gas starts promoting plume excitation and oxidation of the ablated species at the plume front, while only slightly influencing the maximum kinetic energy of the species finally impacting the substrate. By further increasing the oxygen pressure to $10^{-1}$ mbar, the plume is more braked and the kinetic energy of the impinging particles is strongly reduced. Moreover, as a consequence of the interaction with the background oxygen, emission from LaO at the plume front appears at $10^{-2}$ mbar, and becomes significantly enhanced at the larger pressure of $10^{-1}$ mbar. On the contrary, neither Ga nor Al oxides are observed.

On the basis of the data, we can now comment on the main issues of the paper. First we discuss La/Sr intermixing at the STO surface possibly induced by the impact of the energetic species. The ablated species lose their kinetic energy when impinging on the growing surface by elastic and inelastic collisions. The typical loss rate for this process is of $\approx 100$ eV/nm [9]. Then, the maximum kinetic energies of Table I fix a limit to the maximum subplantation depth, thus to the possible intermixing region close to the interface. Accordingly, below $10^{-2}$ mbar oxygen pressure, the maximum La-subplantation depth is less than 0.6 nm (about 1.5 u.c.), while at $10^{-1}$ mbar the kinetic energy is too low to give any La-subplantation. Considering that below $10^{-2}$ mbar the kinetic energy distribution within the ablation plume (not shown) indicates a most probable kinetic energy of $\approx 10$ eV, which rapidly decreases at larger kinetic energies values, the most energetic species constitute only a minor fraction of the plume. We therefore conclude that at usual growth conditions the impact dynamics may provide a low or null surface cation intermixing. These findings are compatible with the high-resolution scanning transmission electron microscopy images and electron energy loss spectroscopy profiles across the STO/LGO and STO/LAO interfaces reported in ref. [7], showing interfaces that are sharp at the limit of instrumental resolution.

As for the role of the oxygen vacancies, two issues are in order: (a) the impact of energetic species creating vacancies through oxygen sputtering at the STO surface, and (b) deposition of oxygen deficient LGO (LAO) overlayer which can get the lacking oxygen at expenses of the STO substrate through diffusion [10, 11]. As for mechanism (a), a simple evaluation can be based on elastic collisions between the impinging species and the oxygen
atoms at the STO surface. By resting on tabulated bond strengths of Ti-O and Sr-O [12], the energy required to break the oxygen bonds and kick it off the surface is $\approx 10 \text{ eV}$. This simple estimate is consistent with the values obtained by first principles methods [13]. The maximum kinetic energy of the impinging atoms of Table I can be therefore sufficient to kick off oxygen atoms for pressures up to $10^{-2} \text{ mbar}$. At larger pressure, this process is hindered by the significant reduction of the maximum kinetic energy. Nevertheless, the over-pressure due to the presence of the ablation plume at the substrate surface could further limit the efficacy of such a process. As for mechanism (b), our data suggest that La is the only cation acting as an oxygen getter (see Fig. 2(b)), and the direct deposition of plume’s LaO molecules is therefore one channel of incorporation of oxygen in the film. Below $10^{-2} \text{ mbar}$ LaO formation is rather ineffective, and only at $10^{-1} \text{ mbar}$ a significant amount of LaO at the plume front is formed as a consequence of shock wave [8] and molecular oxygen dissociation [14]. In this respect, we notice that distance-time plots of the plume front propagation (not shown) confirm that the plume follows a shock-wave-like propagation behavior close to the substrate surface at $10^{-1} \text{ mbar}$. This suggests that films deposited at lower pressure can be oxygen deficient, and could get the lacking oxygen at expenses of the STO substrate, which instead is not very likely at $10^{-1} \text{ mbar}$. These observations seem to correlate well with the variation of the conducting properties of the STO/LGO and STO/LAO, suggesting a possible role of these mechanisms on the properties of the interfaces. Nevertheless, it is worth noting that SrTiO$_3$/LaMnO$_3$ interfaces grown in similar conditions, at $10^{-4} - 10^{-2} \text{ mbar}$, show an insulating character [7]. This testifies the complexity of the 2DEG generation, where specific material issues may also play an important role.

Finally, we want to comment on the effects of the particles kinetic energy on the growth dynamics. As discussed in Ref. [15] kinetic energy can favor 2D growth through island breakup mechanism with prompt insertion, at very low coverage, and enhanced surface diffusion, above 50% monolayer coverage. Following the approach of ref.[15], the energy scale of the island break-up mechanism can be estimated by the binding energy between one island made by two unit cells and two separated single unit cells. On the basis of the tabulated bond strengths of La-O, Al-O and Ga-O [12], such energy is $\approx 20 \text{ eV}$ in the case of LGO and LAO. When comparing this figure with the data of Table I, one
realizes that the stable 2D growth is consistent with the growth mechanisms discussed above only below $10^{-2}$ mbar. However, while the kinetic energy strongly drops at the higher pressure, RHEED data still show a 2D growth (see Fig. 1). We propose that a further amount of energy is provided by the internal energy of the particles. Actually, the electronic transitions in the spectra of Fig. 2 are in the 2-3 eV range. Such values are comparable with the maximum surface diffusion barrier energy at high coverage reported in ref.[15]; therefore the higher plume internal energy at $10^{-1}$ mbar eventually favors surface diffusion resulting in the 2D growth. The differences in the growth dynamics at low and high pressure might finally also reflect on the different conducting properties of the interfaces.

In conclusion, we studied PLD of LGO and LAO on STO elucidating the effects of the background oxygen gas pressure on the ablation plume and deposited film interfaces. Analysis of oxygen pressure variation on ablated species kinetic energy and oxidation state allowed us to provide further insights on some of the mechanisms (e.g. oxygen vacancy creation, La subplantation, and growth dynamics) considered to contribute to conductivity of the interfaces, in addition to the polar catastrophe. Our results also indicate that 2D growth can be achieved up to $10^{-1}$ mbar, but a crossover exists at $10^{-2}$ mbar since the kinetic energy of the impinging species changes from tens of eV to tenths of eV as a consequence of the interaction with the background gas.

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TABLE I: Maximum kinetic energy (eV) of the ablated species from LGO and LAO impacting the substrate at different growth pressures (mbar).

| Species | 10^{-6}-10^{-3} | 10^{-2} | 10^{-1} |
|---------|----------------|---------|---------|
| Al      | 14±0.2         | 14±0.2  | 0.1±0.02|
| Ga      | 35±0.2         | 35±0.2  | 0.4±0.02|
| La      | 58±0.2         | 55±0.2  | 0.7±0.02|
| LaO     | 52±0.2         | 52±0.2  | 0.8±0.02|
FIG. 1: (Color online) RHEED oscillations during the initial phase of (a) LaAlO$_3$ and (c) LaGaO$_3$ film growth on a SrTiO$_3$ substrate at $10^{-1}$ mbar of oxygen. RHEED patterns after the growth of 12 u.c. of (b) LaAlO$_3$ and (d) LaGaO$_3$. 
FIG. 2: (Color online) (a) 2D single-shot images of LGO ablation plume at three different delays $\tau$ after the laser pulse for oxygen pressure from $10^{-3}$ (left) to $10^{-1}$ mbar (right). Each image is obtained from a different laser shot and shown in normalized false color scale. $z=0$ marks the position of the target surface. The images at $10^{-3}$ mbar are also representative of the plume propagation registered at lower pressure. (b) Emission spectra of the LGO plume at a delay $\tau=1.6\mu$s for three different oxygen pressures ($10^{-3}$, $10^{-2}$ and $10^{-1}$ mbar).