Large electropositive cations as surfactants for the growth of polar epitaxial films

Alfred K. C. Cheung,[1] Ilya Elfimov,[1,2] Mona Berciu,[1,2] and George A. Sawatzky[1,2]
[1]*Department of Physics and Astronomy, University of British Columbia, Vancouver, British Columbia, V6T 1Z1, Canada*
[2]*Quantum Matter Institute, University of British Columbia, Vancouver, British Columbia, Canada V6T 1Z4*
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Using density functional theory (DFT) we demonstrate that the adsorption of large cations such as potassium or cesium facilitates the epitaxial growth of polar $LaAlO_3$ (LAO) on $SrTiO_3$ (STO). The low ionization potential of K favors efficient electron transfer to the STO conduction band and results in a two-dimensional electron gas which exactly compensates for the diverging potential with increasing layer thickness. For large cations like K or Cs, DFT total energy considerations show that they remain adsorbed on the LAO surface and do not enter substitutionally into LAO. These results suggest a scheme for growing clean LAO/STO interface systems, and polar systems in general, by performing the growth process in the presence of large, low ionization potential alkali-metal ions.

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I. INTRODUCTION

Since the discovery of the high-mobility quasi-two-dimensional electron gas (q-2DEG) at the *n*-type interface between $LaAlO_3$ (LAO) and $SrTiO_3$ (STO) [1], enormous efforts have been made to understand its origins and its relation to the polar, crystallographic orientation induced electric potential which diverges with film thickness [2–4] Although the issue is still under debate, there is now consensus that compensation of this diverging electric potential (the polar catastrophe) is achieved through a combination of pure electronic reconstruction [3–5], interface defects [6,7], lattice distortions [8,9], and oxygen vacancies [7,10–23]. The latter is particularly noteworthy as recent studies [7,23] argue that the formation of oxygen vacancies on the AlO_2 surface provides a comprehensive explanation for the observed critical thickness of four LAO layers required for the q-2DEG to appear.

The relative contributions of these mechanisms to removing the polar catastrophe is expected to depend critically on the specific details of the growth conditions. This explains why samples grown by different groups can show widely dissimilar properties [24]. The important role played by defects and vacancies [3] also explains why the growth of clean LAO/STO interfaces, necessary for device applications, has proven to be such a challenge.

In this article we propose a solution for this challenge. We use DFT to show that a coverage of 1/2 K per unit cell of the AlO_2 surface acts like a surfactant that stabilizes the epitaxial growth of the polar LAO. Each K donates an electron to the LAO/STO interface, generating a q-2DEG while keeping the top LAO surface insulating. This compensates for the polar catastrophe for any LAO film thickness, removing the reason for the appearance of defects, vacancies, or distortions. Moreover, substitution of the large K ions into the LAO film is unlikely for epitaxial type growth. As a result, after the deposition of half a monolayer of K, the LAO film will grow cleanly under this surfactant.

We emphasize that we use the term *surfactant* as is customary in the crystal growth community [25,26]: a surfactant facilitates the growth of the film while "floating" on its surface [25–29]. An effective surfactant is energetically most favored on the film's surface [27]: when an adatom (La, Al, and O) arrives onto the surface, the adatom and a surfactant atom (K) exchange positions such that the surfactant re-emerges on the surface and the adatom is buried underneath. The process is then repeated [25–30].

Our proposal is supported by past successes in using surfactants to stabilize crystal surfaces [25–33]. For example, (111)-terminated MnS, otherwise impossible to grow due to the polar problem, was stabilized by adsorption of I^- on its surface [31]. The use of alkali metals as electron donors is also common: K deposition onto $YBa_2Cu_3O_{6+x}$ was used to tune its doping level [34,35]. Indeed, although we focus here on LAO/STO, this method should work successfully for many other polar materials. We believe that, in general, the use of low ionization energy surfactants can facilitate the growth of ionic materials with strongly polar orientations.

The article is organized as follows. After introducing our method in Sec. II, we present our results in Sec. III for K coverages of both 1/2 per unit cell, and for higher values. We conclude in Sec. IV with our summary and further discussions.

II. METHOD

All DFT calculations reported here are performed with the Vienna *ab initio* simulation package (VASP) [36] using the projector augmented plane-wave method. [37,38] The Perdew-Burke-Ernzerhof (PBE) functional [39] is used for the exchange-correlation energy. The energy cutoff for the plane-wave basis functions is 400 eV. For structural optimization calculations, a Γ-centered (7,7,1) *k*-point mesh is used. For density of states (DOS) calculations on the optimized structures, a Γ-centered (17,17,1) *k*-point mesh is used.

The structures simulated are comprised of *m* unit layers of LAO on top of four unit layers of STO substrate. The interface is *n* type (TiO_2/LaO). We begin by assuming that K atoms are adsorbed on the surface AlO_2 layer of LAO at a concentration of 1 atom per 2 lateral AlO_2 unit cells, i.e., the concentration needed for exact compensation of the polar problem. We refer to this as $K_{ads}\,(LAO)_m\,(STO)_4$. (We also consider coverages of 3 K per 4 lateral unit cells, and 1 K per lateral unit cell afterward). The $m = 2$ structure is shown in Fig. 1(a). We placed the K atoms above the center of squares formed by the oxygen atoms in the surface AlO_2 layer, as shown in Fig. 1(b).

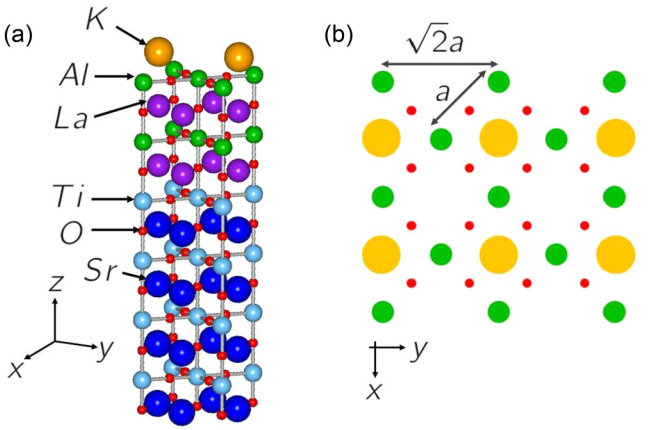

FIG. 1. (Color online) (a) K_{ads} $(LAO)_m$ $(STO)_4$ for $m = 2$ (initial structure). K atoms are placed on the surface AlO_2 layer in the middle of the squares formed by oxygen atoms. This is illustrated in panel (b) which shows a top view of the K adsorption sites on the surface AlO_2 layer. The simulated square unit cell has a side length of $\sqrt{2}a$, where $a = 3.913$ Å is the lattice constant of bulk STO obtained from DFT.

This is expected to be the most stable configuration because a K^+ cation is attracted to each O^{2-} anion. Indeed, other positions were found to be unstable to relaxing back into this position, thus validating our choice.

The lateral lattice constant is fixed at $\sqrt{2}a$, where $a = 3.913$ Å is the calculated DFT-PBE lattice constant for bulk STO. Atoms of the bottom-most STO unit layer are kept fixed so as to simulate the effect of the infinitely thick substrate. All other atoms are allowed to relax along the z direction until the force on each atom is less than 0.02 eV/Å. A 15 Å vacuum slab is placed above each slab to minimize interactions between periodic copies of the slab. Dipole corrections to the total energy and electric potential are used to remove any remaining spurious contributions due to periodic boundary conditions [40].

III. RESULTS

A. Compensation by potassium electron donation

Layer and element projected partial densities of states (PDOSs) are shown in Fig. 2(a) for $m = 3$. Upon K adsorption, electrons are donated into the Ti $3d$ conduction bands. The electron density is greatest for the titanate layer near the interface and decays for layers farther away, forming a q-2DEG as in pure electronic reconstruction.

In both cases, the extent of the electron transfer is limited by an associated energy cost. For pure electronic reconstruction, this is the band gap between the valence band of LAO and the conduction band of STO. In the present case, this is the binding energy of the $4s$ electron of the adsorbed K. This parameter controls how much of the diverging potential across LAO is compensated. To evaluate their efficiency, we look for residual potential buildup across the LAO film. We plot the xy-planar average potential and its macroscopic average over a unit cell [41] within the LAO region for the system without and with adsorbed K in Figs. 2(b) and 2(c), respectively. No potential buildup is observed in the latter, whereas a potential buildup of ~2 eV is present in the former.

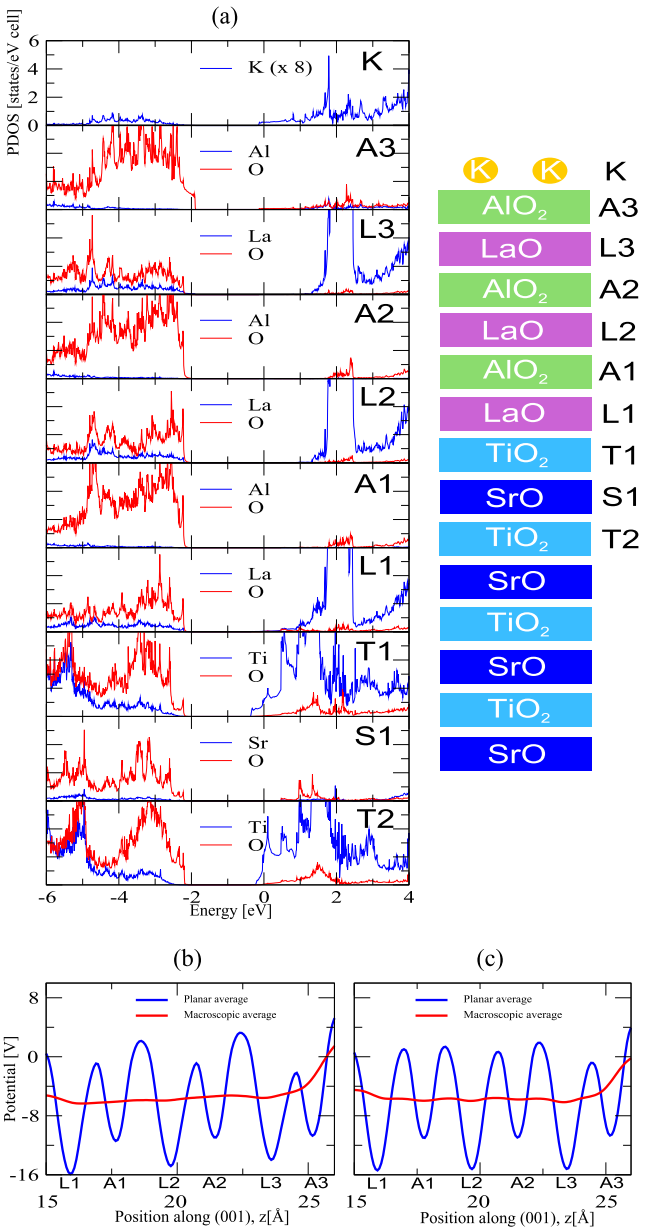

FIG. 2. (Color online) (a) Layer and element projected DOS for K_{ads} $(LAO)_3$ $(STO)_4$. The Fermi energy is at 0. The scale is the same for all panels. Upon adsorption of K, the TiO_2 layers become conducting. The conduction electron density is greatest for the TiO_2 layer closest to the interface. The xy-planar average and macroscopic average electric potentials are plotted versus the z position along the (001) direction of the supercell, within the LAO region, for the system (b) without and (c) with K. A potential buildup of the order of 2 eV exists for the bare system without K. This is eliminated in the system with the K surfactant.

In an effort to explain why no residual potential is actually observed experimentally, investigators [42] simulated the placement of metallic overlayers on top of LAO/STO *after growth*; this has subsequently been done with Co [43]. The main conclusion was that the presence of metallic contacts used for measurements explains why residual potential is absent in experiment. One might consider these results of

Ref. [42] as another way to remove the potential buildup. However, in this case the top layer is metallic and separating its conductivity from that of the q-2DEG is difficult. This is not an issue for our proposal, where the K surfactant layer is insulating after donating its electrons to the interface. More importantly, since the metal capping is done after growth, the tendency for defects and vacancies to form during growth is not mitigated. In contrast, as we argue below, the crystal grows underneath the K surfactant layer free of such defects.

It has been shown that in the absence of O vacancies or other defects, the onset of electronic reconstruction is delayed through formation of polar distortions within the LaO layers [8], which create internal compensating dipoles that screen the electric potential. Below a critical thickness of 4–5 unit LAO layers, this suffices to partially compensate the polar potential. In thicker films with larger potential buildup, the compensation requires electronic reconstruction, which in turn removes the need for these polar distortions. It is thus worthwhile to consider whether for similar reasons, a critical thickness exists for the transfer of the K 4*s* electron to the Ti 3*d* bands.

Figure 3 shows DOSs for $1 \leqslant m \leqslant 6$, with and without adsorbed K. The critical thickness at which the system without K becomes conducting is confirmed to be of four LAO unit layers, see Fig. 3(d). In contrast, the system with adsorbed K is metallic for all thicknesses: even at one unit layer of LAO, where the potential across the film is smallest, K gives up its 4*s* electron to the Ti 3*d* bands and the polar distortions within LAO are eliminated.

B. Cohesive energies

Figures 2 and 3 show that K adsorption negates the polar catastrophe and stabilizes the LAO/STO heterojunction. The energetic stability can be quantified by calculating the cohesive energy $E_{\mathrm{coh}}(m)$:

$$E_{\mathrm{coh}}(m) = E_{\mathrm{K_{ads}LAO}_m\mathrm{STO}_4} - E_{\mathrm{LAO}_m\mathrm{STO}_4} - E_{\mathrm{K}}, \qquad (1)$$

where m is the number of unit layers of LAO, $E_{\mathrm{K_{ads}LAO}_m\mathrm{STO}_4}$ is the total energy of the system with K adsorption, $E_{\mathrm{LAO}_m\mathrm{STO}_4}$ is the total energy of the system without K adsorption (using the same size of lateral unit cell), and E_{K} is the energy per atom of metallic K (body-centered cubic). Thus E_{coh} is the cohesive energy per adsorbed K with respect to metallic K. It is plotted as a function of m in Fig. 4.

Two observations can be made: (1) The K-adsorbed system becomes more stable relative to the original system as the number of LAO unit layers is increased. This is a trivial consequence of the potential buildup across LAO increasing with m—the greater the potential buildup, the greater the energy reduction when it is eliminated by electron transfer from adsorbed K; and (2) for the thicknesses considered, $|E_{\mathrm{coh}}|$ ranges from 1 eV to over 2 eV, which is a very substantial energetic stabilization.

C. Potassium coverage beyond 1/2 per unit cell

We also consider what happens if more potassium is adsorbed than the minimum of 1/2 per unit cell needed for compensation of the polar problem. In Fig. 5, we plot the K

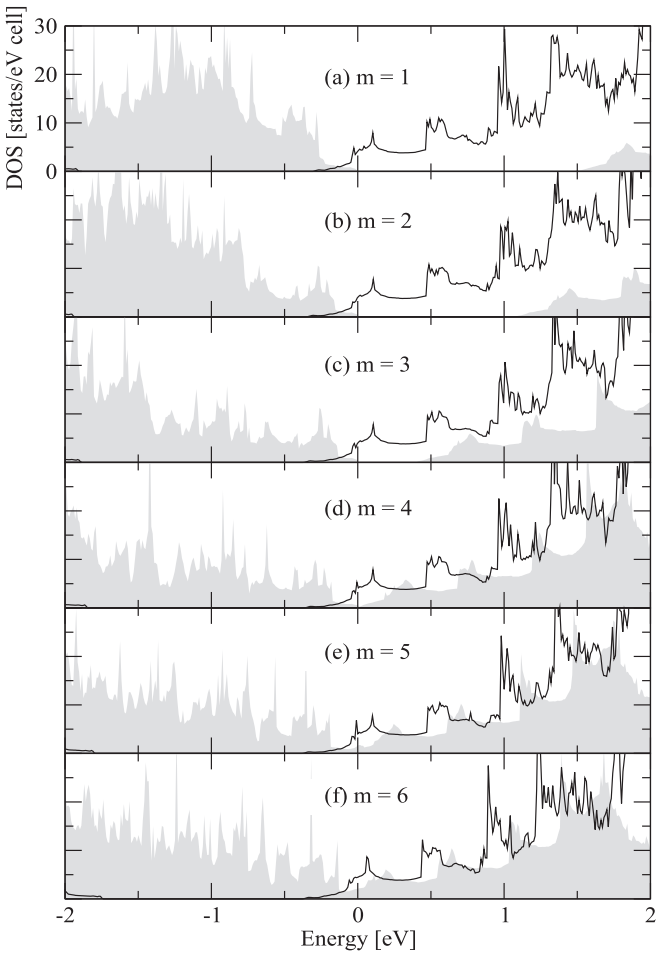

FIG. 3. Total DOS for $(\mathrm{LAO})_m(\mathrm{STO})_4$, $m = 1$–6, with (black line) and without (shaded gray) K adsorption. The Fermi energy is at 0. The scale is the same for all panels. The critical thickness at which the system without K undergoes electronic reconstruction and becomes conducting is four unit layers of LAO. In contrast, the system with K is conducting at all LAO thicknesses simulated.

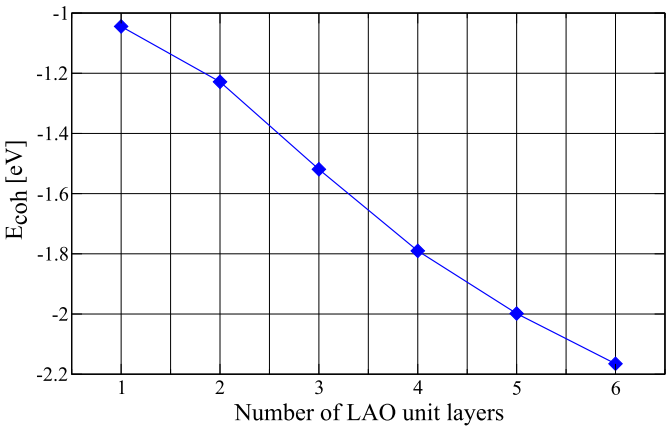

FIG. 4. (Color online) Cohesive energy per adsorbed K, defined in Eq. (1), as a function of the thickness of LAO. The system with adsorbed K becomes more stable as the thickness increases. The cohesive energy is approximately 1 eV for one unit layer of LAO, increasing to over 2 eV as the LAO thickness is increased.

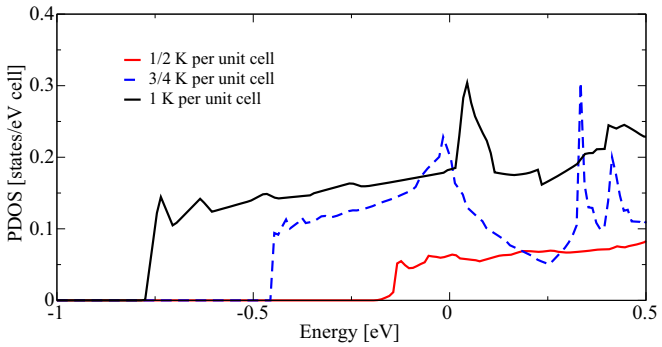

FIG. 5. (Color online) K PDOSs near the Fermi energy ($E = 0$), at three cases of K coverage, for LAO thickness of two unit layers. The density of conduction electrons retained by K increases significantly going from 1/2 to 3/4 per unit cell coverage, and then from 3/4 to 1 per unit cell coverage. Hence, K adsorption beyond the critical amount needed for the ideal exact compensation does not result in extra electrons being transferred to the interface; the extra electrons remain in the K overlayer.

projected densities of states (PDOSs) near E_F at three values of K coverage: the optimal value of 1/2 per unit cell, as well as 3/4 and 1 per unit cell, respectively. The thickness of the LAO layer is $m = 2$.

For the latter two coverages, Fig. 5 shows that although the K overlayer now has enough electrons to transfer more than 1/2 electron per unit cell to the interface, the extra electrons are retained in the K overlayer for the coverages beyond 1/2 K per unit cell. This confirms that K donates just enough electrons to compensate for the diverging potential. Anything beyond that would result in energetically expensive overcompensation.

The energetic favorability for further K adsorption can be quantified by calculating the additional cohesive energy upon adsorption of extra K atoms. In particular, we take as a reference four lateral unit cells of LAO/STO with two adsorbed K atoms (1/2 K per unit cell coverage), whose total energy we denote by $E_{K_2[LAO_2STO_4]_4}$. We then further adsorb one or two more K atoms onto this system to attain 3/4 and 1 per unit cell K coverage. We denote the total energies of these systems by $E_{K_3[LAO_2STO_4]_4}$ and $E_{K_4[LAO_2STO_4]_4}$, respectively. The extra cohesive energies upon adsorption of each additional K is defined as

$$E_{\mathrm{coh},3/4} = E_{K_3[LAO_2STO_4]_4} - E_{K_2[LAO_2STO_4]_4} - E_K,$$
$$E_{\mathrm{coh},4/4} = E_{K_4[LAO_2STO_4]_4} - E_{K_3[LAO_2STO_4]_4} - E_K.$$

We find that $|E_{\mathrm{coh},3/4}| = 0.39$ eV and $|E_{\mathrm{coh},4/4}| = 0.56$ eV. These are to be contrasted with the cohesive energy per adsorbed K for the first two adsorbed K atoms, which was calculated to be 1.2 eV (Fig. 4). The cohesive energy as defined is approximately 0.7–0.8 eV smaller for K atoms adsorbed beyond the critical 1/2 per unit cell coverage, i.e., it is much less energetically favorable for extra K atoms to be adsorbed onto the system. This observation is critical for preventing any undesired accumulation of K onto the surface. In particular, the large cohesive energy difference between K atoms adsorbed up to 1/2 coverage and K atoms adsorbed beyond 1/2 coverage suggests that if the substrate temperature is kept higher than some critical threshold, the extra K will evaporate off, preventing a thick layer of K metal from forming on the surface and hence fundamentally changing the system—the surfactant density will stabilize at exactly the density needed to compensate for the diverging potential.

D. Is potassium a surfactant?

Our proposal to use a K surfactant to stabilize the epitaxial growth of LAO/STO(001) hinges on K remaining on the AlO_2 surface instead of entering into LAO by substitution of La or Al ions. Substitution is highly unlikely given the large differences in ionic radii between K^+ (151 pm), La^{3+} (116 pm), and Al^{3+} (54 pm) [44]. We confirm this by calculating the total energy change if K exchanges position with a La or Al ion close to the surface, in a $m = 5$ film (this is expected to be representative for all m).

Consider first the exchange of K with a La ion in the top LaO layer. The energy cost per substituted K is found to be 1.93 eV if K exchanges positions with the La beneath it, and 2.27 eV for the other La (cf. Fig. 1). In a striking display of how energetically unfavorable is the substitution of K for Al, our relaxation of the substituted structure resulted in the K pushing its way back above the rest of the structure. Substitution into deeper layers of LaO/AlO_2 is expected to be just as, if not more, energetically costly. This proves that the energy cost for K substitution of La/Al within the bulk of LAO is indeed very large, and thus that K is a surfactant in this system.

IV. SUMMARY AND DISCUSSIONS

To summarize, we have shown that K adsorbed on the AlO_2 surface of an n-type LAO/STO(001) heterojunction compensates for the diverging electric potential across LAO by donating its 4s electron to the Ti 3d conduction band. The compensation is highly efficient, with very little residual potential buildup across LAO. Also, substitution of K into layers of LAO by exchange with La or Al is demonstrated to be extremely unfavorable.

Taken together, these results suggest an elegant scheme for growing clean LAO/STO heterojunctions and polar films in general. By executing the growth in the presence of alkali metals with low ionization energies, the diverging potential is eliminated without appealing to the myriad of other—often uncontrollable—compensation mechanisms. On a practical level, this requires only a small surface concentration of K, of $\sim 10^{14}/\mathrm{cm}^2$. The cohesive energy for K adsorbed beyond the 1/2 per unit cell (ideal) concentration is significantly smaller than for the ideal concentration. Hence, if the substrate temperature is sufficiently high, any extra K will evaporate, preventing the formation of an undesired thick metallic overlayer of K on the surface. The large size of K also prevents the alkali metal cations from being incorporated into the film during growth, guaranteeing their role as surfactants. In contrast, smaller 3d transition metal ions (TMs) would not be suitable because most of them form $LaTMO_3$ perovskite structures with similar lattice constants as LAO so it is reasonable to expect that they would substitute for Al during growth.

In principle, it is possible that K may undergo fast oxidation with the resulting oxide accumulating on the surface, impeding

further growth. Whether this really happens can only be ascertained through experiment. If it does, a potential solution is to grow the first two or three layers without K, allowing the internal buckling to compensate for the potential buildup [8]. The O, La, and Al sources are then shut off, after which K is absorbed onto the exposed AlO_2 surface. This will remove the buckling since the K will take over in compensating for the polar problem. The K source is then turned off and the growth of the LAO is restarted, with the film growing cleanly underneath the layer of K surfactant.

This proposal could become a new paradigm for growing clean LAO/STO(001) samples whose properties are no longer highly sensitive to growth conditions. The problem of electronic and structural properties being attributed to different defects in samples prepared differently has been identified as a major potential pitfall for the development of applications based on the LAO/STO interface [24]. We believe that the method proposed here solves this problem not just for LAO/STO, but also for many similar systems in which clean growth in a particular direction is impeded by the polar catastrophe.

ACKNOWLEDGMENT

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