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

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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 2D electron gas which exactly compensates for the diverging potential with increasing layer thickness. For large cations like K orCs, DFT total energy considerations show that they remain adsorbed on the LAO surface and do not enter substitutionally into LAO. These results suggest a novel 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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Since the discovery of the high mobility quasi-2-dimensional electron gas (q-2DEG) at the $n$-type interface between LaAlO$_3$ (LAO) and SrTiO$_3$ (STO) [1], enormous experimental and theoretical 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 a general 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 last mechanism 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 Letter we propose a solution for this challenge. We use DFT calculations 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, generates a q-2DEG while keeping the top surface of LAO insulating. This q-2DEG fully compensates for the polar catastrophe for any thickness of the LAO film, removing the reason for the appearance of defects, vacancies or distortions. Moreover, because of their large size, the K ions cannot enter substitutionally into LAO film. As a result, after the deposition of half a monolayer of K, the epitaxial 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]. In surfactant-mediated epitaxy, the surfactant facilitates the layer-by-layer growth of the film while always “floating” on its top surface [25–29]. An effective surfactant is energetically most favored on the film’s surface [27]; when an adatom (in this case, La, Al, and O) arrives onto the surfactant surface, the adatom and a surfactant atom (in this case, K) exchange positions such that the surfactant re-emerges on the surface and the adatom is buried underneath; this process is then repeated [25–30].

Our proposal is supported by past successes in using surfactants to stabilize crystal surfaces [25–33]. As a specific example, Heikens et al. [31] stabilized (111)-terminated MnS, otherwise impossible to grow due to the polar problem, by adsorption of I$^-$ on the (111) surfaces. Another example is the growth of GaN$_x$As$_{1-x}$ in the presence of Bi which was found to stabilize the semiconductor-vacuum interface, increase surface smoothness, and enhance nitrogen incorporation [32, 33]. The use of alkali metals as electron donors is also common. For instance, potassium deposition onto YBa$_2$Cu$_3$O$_{6.5}$ was used for tuning its level of doping [34, 35]. We believe that, in general, the use of low electron affinity surfactant layers of positive ions can facilitate the growth of ionic materials with strongly polar orientations.

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 4 unit layers of STO substrate. The interface is $n$-type (TiO$_2$/LaO). K atoms are adsorbed on the surface AlO$_2$ layer of LAO at a concentration of 1 adsorbed atom per 2 lateral AlO$_2$ unit cells, i.e. the theoretical concentration needed for exact compensation of the polar problem (other coverages are considered in the Supplemental Material [40]). We refer to this general structure as $K_{ads}$(LAO)$_m$(STO)$_4$. The structure for $m = 2$ is shown in Fig. 1a. We choose to place the K atoms...
attracted to each O upon donating its 4s electron, a K$^+$ cation should be attracted to each O$^{2-}$ anion. Indeed, alternate positions were found to be unstable towards relaxing back into this chosen position, thus validating our choice.

The lateral lattice constant is fixed at $\sqrt{2}a_0$ where $a_0 = 3.913$ 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. 15 Å of vacuum is put on top of 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 [41].

Compensation by potassium electron donation: Layer and element projected partial densities of states (PDOS) for the case of $m = 3$ are shown in Fig. 2a. Upon adsorption of K, electrons are donated into the Ti 3d conduction bands. The conduction electron density is greatest for the titanate layer closest to the interface and decays for layers further 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 penalty is the band gap between the valence band of LAO and the conduction band of STO. In the present case, this is given by 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 LAO along the z-direction. If $V(x, y, z)$ is the electric potential function, then the planar-average potential along z, $\bar{V}(z)$, is defined by:

$$\bar{V}(z) = \frac{1}{S} \int_S dx dy V(x, y, z),$$

where $S$ is area of the lateral unit cell. It is also useful to define the macroscopic average potential, $\bar{V}'(z)$ [42],

$$\bar{V}'(z) = \frac{1}{a_z} \int_{z-a_z/2}^{z+a_z/2} dz' \bar{V}(z').$$

Here, $a_z$ refers to the lattice constant of LAO in the z-direction. In other words, $\bar{V}(z)$ averages out oscillations within one unit cell. Because of relaxation, especially in the uncompensated film, a constant $a_z$ is actually ill-defined. For convenience, we take as $a_z$ the relaxed thickness of LAO divided by the number of unit cells. One can also generalize the notion of the macroscopic average to account for the interface with STO [42], but since we are only interested in the potential buildup across LAO, we use the definition in Eq. 2.

In Fig. 2b, we plot $\bar{V}(z)$ and $\bar{V}'(z)$ within the LAO region for the system without adsorbed K. The same is shown for the system with adsorbed K in Fig. 2c. No potential buildup is observed across LAO in the system with K, whereas a potential buildup of $\sim 2$ eV is present in the system without K. This is evident looking at the overall slopes in the macroscopic potentials, as well as the positions of the minima in the planar-average potentials.

Ref. [43] proposed a different way to remove this potential buildup, by placing metallic overlayers after growth; this has since been done with Co in Ref. [44]. However, in this case the top layer is also 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 at a concentration of 1/2 per unit cell remains insulating since it has donated its charge carriers to the interface. Furthermore, 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 oxygen 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 and electronic reconstruction does not occur. In thicker films with larger potential buildup, the compensation requires electronic reconstruction, which in turn removes the need for these polar distortions within the LaO layers. It is thus worthwhile to consider whether the donation of the K 4s electron to Ti...
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. This is due to the donation of the K 4s electron to the Ti 3d conduction bands. The conduction electron density is greatest for the TiO$_2$ layer closest to the interface. The planar-average and macroscopic average electric potentials (as defined in Eq. 1 and Eq. 2) 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. On the scale of the plot, no residual potential is observed for the K adsorbed system. In contrast, a potential buildup of the order of 2 eV exists for the bare system without K.

FIG. 3. Total DOS for (LAO)$_m$(STO)$_4$, $m$ = 1, 2, 3, 4, 5, and 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 4 unit layers of LAO. In contrast, the system with K is conducting at all LAO thicknesses simulated.

Cohesive energies: Figs. 2 and 3 show that K adsorption negates the polar catastrophe and stabilizes the LAO/STO heterojunction. The additional energetic sta-
We define the system with K becomes more stable as the thickness increases, reflecting the increasing electric potential across LAO as LAO thickness is increased in the bare system. The cohesive energy is approximately 1 eV for 1 unit layer of LAO, increasing to more than 2 eV as LAO thickness is increased, a significant energy reduction.

FIG. 4. (Color online) Cohesive energy per adsorbed K, defined in Eq. (3), as a function of the thickness of LAO. The system without K and in the absence of other defects. We define the LAO thickness dependent cohesive energy $E_{coh}(m)$ as:

$$E_{coh}(m) = E_{LAO,mSTO} - E_{LAO,mSTO} - E_K,$$

where $m$ is the number of unit layers of LAO, $E_{LAO,mSTO}$ is the total energy of the system with K adsorption, $E_{LAO,mSTO}$ 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 K crystal (body-centered cubic). Hence, $E_{coh}$ can be interpreted as 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 increasing potential buildup across LAO as more LAO layers are stacked—the greater the potential buildup, the more energetically unstable the original system becomes, and the greater the energy reduction when the potential difference is eliminated by electron transfer from adsorbed K; (2) The thicknesses considered, $|E_{coh}|$ ranges from 1 eV to more than 2 eV (1 eV ~ 12000 degrees Kelvin), a very substantial energetic stabilization.

Undesired substitutions of K into LAO: Our discussion above argues for K surfactant adsorption as an effective mechanism for removing the polar catastrophe in LAO/STO(001) to allow for the growth of clean heterostructures. This proposal hinges on K remaining on the AlO$_2$ surface instead of entering the bulk of the LAO by substitution of La or Al ions. This is highly unlikely given the large differences in ionic radii between K$^+$ (151 pm), and La$^{3+}$ (116 pm) and Al$^{3+}$ (54 pm) [45]. We confirm this by calculating the total energy difference between systems where K exchanges position with an La or Al ion close to the surface, and the system with K adsorbed on the surface. Calculations are done for $m = 5$ and are expected to be representative for all $m$.

Consider first the exchange of K with a La ion in the LAO layer closest to the surface. Two substitutions are possible: (1) K exchanges position with the La beneath it, or (2) with the other La (cf. Fig. 1). The corresponding energy cost per substituted K is 1.93 eV for the first case, and 2.27 eV for the second one. For the exchange of K with an Al ion in the surface layer, there is only one option possible. In a striking display of how energetically unfavorable this substitution is, our relaxation of the substituted structure resulted in the potassium cation 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 very large, confirming our hypothesis.

To summarize, we have shown that K adsorbed on the AlO$_2$ surface of an n-type LAO/STO(001) heterojunction compensates the diverging electric potential across LAO by donating its 4s electron to the Ti 3d conduction band. The electron transfer is found to occur at all thicknesses of LAO studied, below and above the critical thickness for electronic reconstruction in the system without K. Furthermore, the compensation is highly efficient, with very little residual potential buildup across LAO. The cohesive energy is calculated to be approximately 1 eV per adsorbed K for 1 unit layer of LAO, increasing to more than 2 eV as LAO thickness is increased, proving how energetically favorable K adsorption is. Finally, 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. By executing the growth process 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 very small surface concentration of K on the order of 10$^{14}$/cm$^2$. This can be obtained with an exposure to K after deposition of very few layers with the O source closed, and then removing the K source. This could also solve the issue of oxidation of K, if it occurs [46]. As we show in the Supplemental Material [40], the cohesive energy for K adsorbed beyond the 1/2 per unit cell (ideal) concentration is significantly smaller than for K adsorbed at 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. Their large size also prevents the alkali metal cations from being incorporated into the film during growth, guaranteeing their role as surfactants. Smaller 3d transition metal ions (TM) 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.

More importantly, our proposed scheme can become a new paradigm for growing LAO/STO(001) interfaces wherein the resulting samples will no longer have properties 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 we have proposed here is a solution to this problem, not just for LAO/STO, but for many systems in which clean growth in a particular direction is impeded by the polar catastrophe.

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[46] 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.