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Enhanced lattice polarization in $SrTiO_3/LaAlO_3$ superlattices measured using optical second-harmonic generation

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Lattice polarization at the $SrTiO_3/LaAlO_3$ interface was investigated by optical second harmonic generation. Superlattices with varying periodicity were employed to study the evolution of interface polarization, while separating substrate contributions. We observed large perpendicular optical nonlinearity, which abruptly increases when the sublattice thickness goes above 3 unit cells. The polarization is primarily in $SrTiO_3$ and develops up to 8 unit cells from the interface.

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Although well developed in conventional semiconductors, engineering of oxide interfaces through the control of atomic termination has led to a new strategy to create novel electronic phases confined at the nanoscale. As an example, the emergence of an electron gas[1] at the interface between two band insulators $SrTiO_3$ (LAO) and $LaAlO_3$ (STO) has been a subject of intense debate. The contributions from the polar discontinuity, oxygen vacancies, interdiffusion, and concomitant lattice distortions were studied both experimentally[2–10] and theoretically.[11–16] Two types of heteropolar interfaces can be prepared in this system: $(TiO_2)^0/(LaO)^+$ (n-type) and $(AlO_2)^-/(SrO)^0$ (p-type), where $\mp 0.5e$ charge is nominally expected to be transferred at the interfaces to avoid the potential divergence due to the polar discontinuity.[2] Recently, it has been theoretically proposed that strong lattice polarization plays a central role in screening the interface,[13–16] in addition to screening by induced free carriers. Similar *ab initio* results were obtained for $LaTiO_3/SrTiO_3$ superlattices.[17,18] For the case of STO/LAO, the lattice polarization is predicted to occur mostly in the STO, extend up to several nanometers from the interface, and have substantial effects on the charge and orbital reconstruction.[8,15] Here we use optical second harmonic generation (SHG) to show experimentally the existence of this lattice polarization, and that it is intimately related to the reconstruction of the interface.

One useful feature to isolate and address the interface lattice polarization is the "critical thickness effect;" the metallic state only emerges for LAO films on STO substrates with thickness more than 3 unit cells (uc),[4] and a similar but gradual threshold was reported for the case of complementary interfaces.[5] This thickness has been suggested to be the threshold dipole shift above which it is energetically favorable to drive an electronic reconstruction,[19] or the threshold for charge transfer from the top of the LAO valence band near the surface to the STO conduction band at the interface.[14,16] In either case, this criticality involves both electronic and lattice instabilities, and probing this transition can provide fundamental insight. SHG is a versatile and nondestructive probe to study buried interfaces with atomic-layer sensitivity.[20] Since SHG is forbidden in a centrosymmetric material in the electric dipole approximation, slight structural distortion, or lattice polarization, of such materials, even with free carriers, can be selectively detected. It has also been utilized for the interfaces of oxides, with a scale down to a single interface.[21] Thus SHG is a powerful probe of the electronic structure of the STO/LAO interface.[22]

When probed with nonlinear optics, great care is needed for STO. Bulk STO is paraelectric at all temperatures due to quantum fluctuations.[23] However, with compressive or tensile strain,[24,25] under external electric field,[26] or at surfaces,[27] STO undergoes a ferroelectric transition at finite temperatures. In addition, any defects in STO have substantial contributions to SHG.[28] In practice, a single n-type interface shows relatively large SHG, which highly depends on the substrates and annealing conditions as will be discussed later. To avoid this large variable contribution from STO substrates, we have employed superlattice structures, in which the numerically evaluated SH coherence length is close to the total thickness of the SLs (>55 nm). Thus the SH from each layer accumulates with constructive interference, and the contributions from the substrate and the SL/substrate interface have enough relative phase shift to be distinguished, as will be shown below.

Several series of $SrTiO_3/LaAlO_3$ SLs were grown on TiO_2-terminated STO(001) substrates by pulsed laser deposition with oxygen pressure of 1.0×10^{-5} Torr and substrate temperature at 973–1023 K. The thickness of each layer was controlled by reflection high-energy electron diffraction, which was confirmed by x-ray diffraction [Fig. 1(a)]. The fabricated SLs are denoted by $[STO(k)/LAO(l)]m$, or simply $[k/l]m$, where k and l refer to the thickness in uc, and m indicates the number of periods. We show the results for one series of SLs with total thickness of 144 uc with the ratio of STO:LAO=1:1, i.e., [1/1]72, [2/2]36 to [24/24]3. The motivation was to keep the total thickness of thin film STO, LAO, and the growth conditions the same. This allows us to keep growth kinetic effects such as possible oxygen vacancies constant, and quantitatively compare the optical response purely as a function of interface separation. Single interface n-type and p-type samples, LAO(16 uc)/STO and LAO(16 uc)/SrO/STO, were also prepared for reference. Transport measurements of the SLs show a sudden increase in sheet resistance around 3 uc. All fabricated samples were

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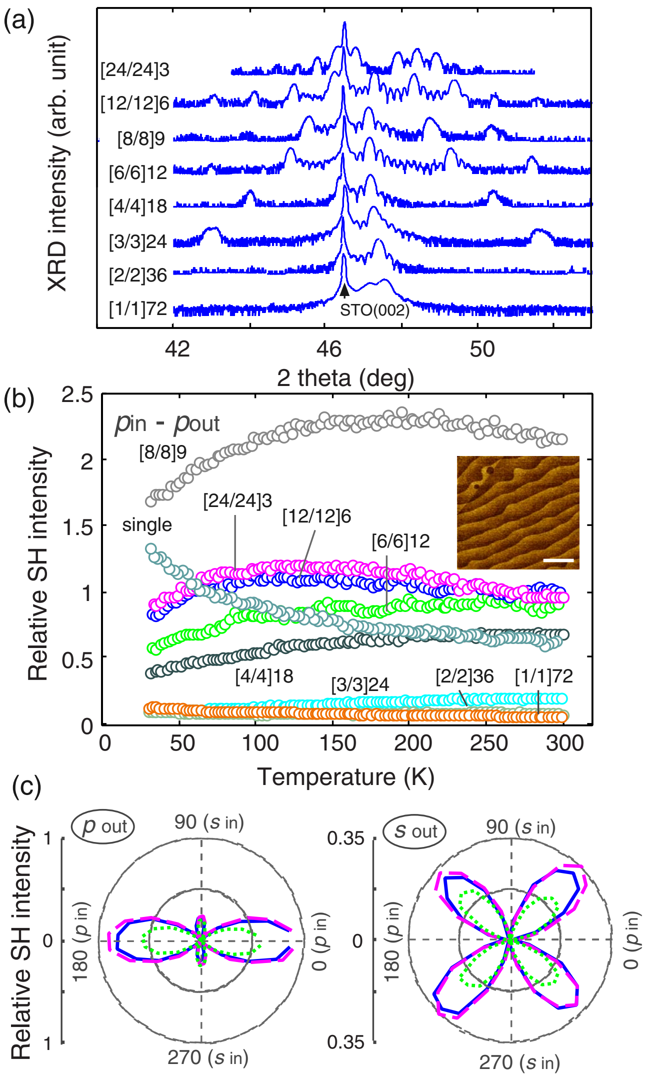

FIG. 1. (Color online) (a) Superlattice profiles in x-ray diffraction. (b) Temperature dependence of the SH intensity in p_{in}-p_{out} geometry, together with that for a single *n*-type interface. The inset shows a representative topographic AFM image for the [STO(6)/LAO(6)]12 sample (a scale bar of 1 μm is indicated). (c) Polar plots of the relative SH intensity for [STO(24)/LAO(24)]3 (dashed lines), [STO(12)/LAO(12)]6 (solid lines), and [STO(6)/LAO(6)]12 (dotted lines) in *p*-out and *s*-out geometry at 30 K.

carefully checked with atomic force microscopy (AFM), and we confirmed that their surfaces are terminated with clear step-terrace structures with step height of ~0.4 nm [Fig. 1(b) inset]. Since the surface quality is similar for all films, the differences in nonlinear optical signals arise from the internal or interface electronic states of the SLs.

The samples were mounted in an ultrahigh vacuum cryostat, and SHG was measured with 1.55 eV fundamental light (150 fs duration at 1 kHz repetition rate) incident through a $\lambda/2$ plate and a lens with 90° reflection geometry (0.5–1.5 mW on ~80 μm spot). The generated SH was directed to a Glan prism, color filters, and a monochromator, and detected with a photomultiplier tube. The signal was normalized by that of a reference potassium dihydrogen phosphate (KDP) crystal, and accumulated more than 10^4 times at each polarization configuration. The SH energy is below the band gaps of both STO (3.2 eV) and LAO (5.6 eV). We note that the SHG from a LAO film on $(LaAlO_3)_{0.3}(SrAl_{0.5}Ta_{0.5}O_3)_{0.7}$(LSAT)(001) substrate was negligibly small. Commercial STO(001) substrates also typically show smaller SHG compared to those of the SLs, with relatively large sample to sample dependence. At the interface of SLs, where inversion symmetry is broken, or under tetragonal distortion, STO has three independent elements in the nonlinear susceptibility tensor, $\chi_{xzx}=\chi_{yzy}$, $\chi_{zxx}=\chi_{zyy}$, and χ_{zzz} (4 mm symmetry). The SH intensity is roughly proportional to χ^2, and p_{in}-p_{out} optical geometry contains SHG from all these elements.

Figure 1(b) shows the temperature dependence of the relative SH intensity in p_{in}-p_{out} geometry. Most of the SLs, except for [1/1]72 and [2/2]36 which had very low intensity, show a decrease in SH intensity at low temperature, while the single *n*-type interface shows relatively large signal, which increases at low temperature. This behavior can be ascribed to the difference in the growth kinetics, and the increase in the SH intensity at low temperature has contributions from defects in the substrate.[28] We note that similar trends can be observed in pristine and Nb-doped STO substrates. To confirm this, we postannealed the single *n*-type sample in 1 atm of oxygen at 773 K for 10 min, and found that the SH intensity decreased by about 50% at 300 K, and became almost temperature independent (not shown). The single *p*-type interface as grown has approximately six times smaller SH intensity compared to that of the single *n*-type interface at 300 K, and showed little change with temperature or oxygen annealing. This difference is consistent with the fundamental asymmetry of *n*- and *p*-type interfaces.[2] However, it is difficult to exclude the bulk substrate contributions in single interfaces, and to isolate whether annealing has changed the bulk state, filled oxygen vacancies, or otherwise affected the interface (diffusion or relaxation). We therefore concentrate on the SL samples hereafter, in which *n*-type interfaces and their spacing dominate the evolution of the SHG, and fluctuations in the substrate contributions can be negligible. In practice, we can separate the substrate contributions by utilizing a phase shift of the SH field from SLs and substrates, as will be shown below.

Since STO is easily polarized by external perturbation, the dominant source of SHG from SLs is the lattice polarization induced by electronic reconstruction at the interface. Experiments[3,8,29] and theoretical calculations[13,15] reported the elongation of the unit cell at the interface. This induces polarization primarily in the STO associated with displacements of the central Ti atom extending several uc from the interface. The polarization analysis of the SH field pattern [Fig. 1(c)] revealed that all SLs show 4 mm symmetry at the interface as expected. For each SL, χ_{zzz} is several times larger than the other independent elements, which indicates a large asymmetry normal to the interface. We note that these three elements have similar amplitudes for bulk $BaTiO_3$ (Ref. 20) and STO under external electric field.[26]

The SH amplitude [Fig. 2(a)] is not proportional to the number of interfaces, suggesting that the SH is generated in the STO layer with bulk-like contributions rather than at the symmetry breaking interfaces. Note that LAO is far less po-

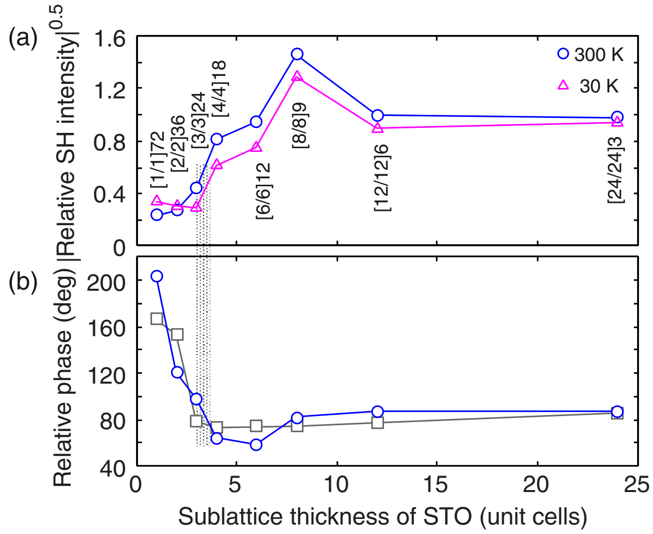

FIG. 2. (Color online) (a) Sublattice thickness dependence of the SH amplitude in p_{in}-p_{out} geometry. Circles and triangles show the data at 300 and 30 K, respectively. (b) Relative phase of the SH field in p_{in}-p_{out} geometry at 300 K (open circles) compared with that from the numerical calculation (open squares). A shaded thick line indicates the sublattice thickness between 3 and 4 uc.

larizable than STO. The SH amplitude shows a sudden increase for the sublattice thickness between [3/3] and [4/4] uc (shaded in Fig. 2), indicating a threshold; the transition is sharper at 30 K. The SH amplitude shows a peak at the sublattice thickness of 8 uc. The reduction in the amplitude for [12/12]6 and [24/24]3 indicates that in the thicker SLs, some STO layers are left unpolarized. We also measured the relative phase of the SH field with an interference technique[21,22] at 300 K [Fig. 2(b)]. The phase angle rotated continuously from [1/1]72 to [4/4]18, passed through a minimum, and then stabilized.

In order to understand quantitatively the physics behind this complex behavior, we performed model calculations solving nonlinear Maxwell equations[30] employing realistic parameters, i.e., the experimentally extracted c-axis length, 0.3905 nm and 0.375 nm for STO and LAO (strained on STO), respectively, and reported dielectric constants. The substrate contribution was incorporated as a 4 uc thick nonlinear layer just beneath the SL, which generates SH of comparable amplitude with that of real substrates.

Let us first assume that all STO layers in the SL have the same nonlinearity as that in a [8/8]9 sample. Naturally, the resulting SH amplitude is nearly independent of the structure [see Fig. 3(a)], because the total amount of STO within the coherence length is kept constant. This clearly contradicts the observed behavior. The optical nonlinearity of each STO layer is rather small at small sublattice thickness, develops rapidly to a maximum at a [8/8]9 sample, and gradually decreases beyond.

We therefore took the structure dependent nonlinearity into account empirically. We assigned an effective χ to STO layers such that the experimentally observed SH amplitude is reproduced in the calculated SH from the SL and the substrate combined. The calculated phase of the total SH is shown in Fig. 2(b) (open squares), which nicely reproduces the experimental phase evolution. The individual contribution of SH from SL and substrate is shown in Fig. 3(b) in the complex plane. Note that due to the designed thickness of the SL, the substrate component in the complex plane tends to be perpendicular to that from the SL. The substrate thus mainly contributes to the overall phase, a fact that facilitates separating the amplitude of the SL signal from the observed value (as noted above) by the simple geometrical construction shown in Fig. 3(b). Due to the small effective χ in the short period SLs, the SH phase is strongly influenced by that of the substrate for [1/1]72 to [3/3]24. As the SL contribution increases with increasing sublattice thickness, the SH phase rotates.

Our observation can be explained as follows: (a) SHG is primarily from the polarization of STO, which develops toward the interface to screen the polar discontinuity, (b) for thinner sublattices, the presence of complementary interfaces close to each other reduces the polarization because of insufficient polar energy to cause the reconstruction,[4,5] (c) a transition occurs at the critical thickness (between 3 and 4 uc), which induces lattice polarization and its screening by the

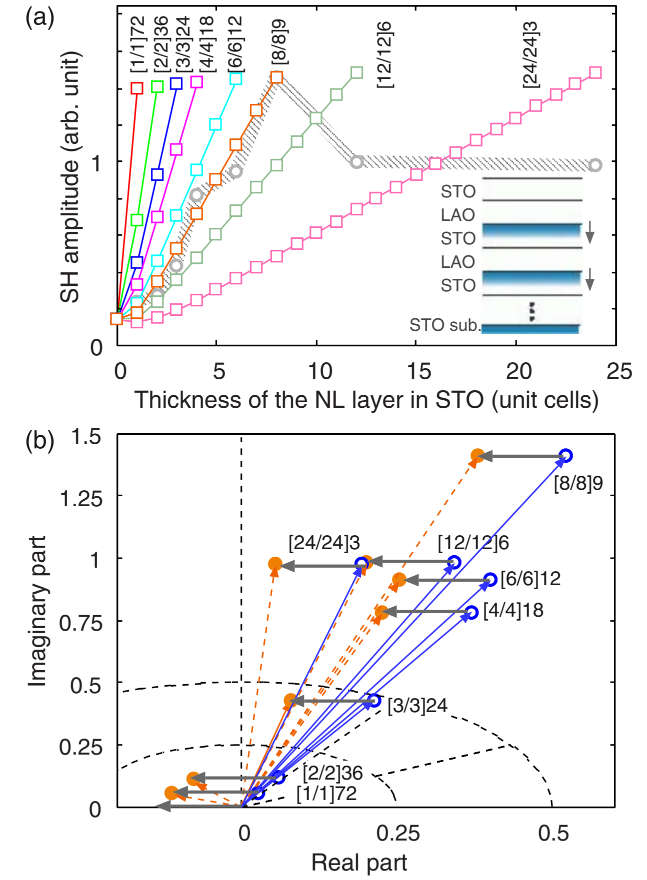

FIG. 3. (Color online) Numerical calculations assuming a constant χ for varying thickness of the STO in the SL with one nonlinear layer in the substrate (inset). (a) Dependence of the SH amplitude on the thickness of nonlinear region in the STO extending from n-type interfaces. The shaded line shows the normalized experimental data at 300 K. (b) Experimentally observed (filled circles) and retrieved (open circles) SH field in the complex plane. Transverse arrows indicate the contribution from the substrate.

free carriers, and (d) the polarization develops up to 8 uc in STO. The range of this primary lattice polarization from the interface (8 uc ~ 3.2 nm) is in good agreement with the theoretical prediction.[15] For thicker sublattices ([12/12]6 and [24/24]3), some portion of the STO is left unpolarized, which reduces the total SH yield.

In summary, we have studied the evolution of the optical nonlinearity in STO/LAO superlattices, and found that the amplitude of the SH field shows a threshold between 3 and 4 unit cells of the sublattice thickness. Quantitative analysis was enabled by the choice of SL structures, where the signals from the SL are accumulated with enough phase shift to distinguish from the inessential substrate signals. Comparison with numerical calculations showed that the SHG can be well described by the development of polarization, and also indicated that the growth kinetics were well maintained during film fabrication. The observed criticality is induced by the polar discontinuity and can be understood mainly as a lattice polarization under the influence of induced free carriers. The lattice polarization is found to develop rapidly up to ~8 uc from the interface, as has been predicted theoretically.

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