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Photoconductivity and non-exponential relaxation at insulating $LaAlO_3/SrTiO_3$ interfaces

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Abstract

$LaAlO_3$ is grown on SrO terminated (100) $SrTiO_3$, and (110) $SrTiO_3$, producing insulating heterointerfaces without light. Photocurrent spectroscopy at low temperatures reveals a broad distribution of interface states between 2 eV and 2.7 eV at both interfaces, with a higher density in the (110) case concomitant with relatively shallow traps. The photocurrent relaxation can be well fitted by a stretched exponential form, confirming energetically distributed electron traps. Photo-carrier lifetimes are larger than a few hundred seconds for optical excitation approaching the $SrTiO_3$ band-gap energy, providing the opportunity to study transient light-induced properties at low temperatures.

Keywords: A. Surfaces and interfaces, D. Photoconductivity and photovoltaics, D. Electronic states (localized), E. Photoelectron spectroscopies

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1. Introduction

The conducting interface formed when $LaAlO_3$ (LAO) is grown on the TiO_2-terminated surface of (100) $SrTiO_3$ (STO), the so-called "n-type" structure, has been the focus of intense research efforts [1, 2, 3, 4]. Far less attention has been paid to the insulating "p-type" interface, which can be formed by growing one unit cell of SrO on TiO_2-terminated STO, before the LAO layers. However, important insights can be afforded by comparing these rather similar interfaces, which possess dramatically different transport properties [5, 6]. In the context of interface engineering, it is also intriguing to consider LAO/STO heterointerfaces with different crystallographic orientations, such as the (110) interface, where there is no polar discontinuity in a simple ionic picture [7], and insulating interfaces are obtained. Despite the absence of free carriers at the p-type and (110) interfaces, microscopically we can expect significant differences in the electronic structure, disorder landscape and density of trap states, due to defects, interdiffusion, or oxygen vacancies [5].

Photocurrent spectroscopy can be used as a convenient characterization tool to investigate the electronic states at insulating interfaces [8, 9]. STO is a band insulator, (band gap $E_g \sim 3.2$ eV) known to show giant photoconductivity at low temperatures when illuminated above E_g [10, 11]. Recently, the photoconducting properties of STO have been utilized to study low dimensional transport [12], in the quantum limit [13], and to investigate the electronic structure of the n-type LAO/STO interface [14, 15]. In this work, we study two different insulating LAO/STO interfaces: the p-type and (110) systems. The photoconducting response to light from the infrared to ultraviolet region at low temperatures provides an ideal tool to probe the in-gap states.

2. Material and methods

The LAO/STO interfaces were fabricated by pulsed laser deposition with a KrF excimer laser. For the p-type interface, a commercial STO (100) substrate with a TiO_2-terminated surface was pre-annealed at 950 °C in an oxygen environment of 5×10^{-6} Torr for 30 minutes. One unit cell of SrO was grown, followed by 32 unit cells of LAO, as monitored using *in-situ* reflection high-energy electron diffraction. The growth temperature was $T_g = 800$ °C and oxygen partial pressure $P_g = 1 \times 10^{-5}$ Torr. For the case of the LAO/STO grown on STO (110), the substrate was prepared using a

previously reported two-step anneal procedure [7], and 32 unit cells of LAO were grown at $T_g = 600$ °C and $P_g = 2 \times 10^{-3}$ Torr. The laser fluence was fixed at 1.6 J/cm^2 with a repetition rate of 2 Hz for both interfaces. As a reference, a bare TiO_2-terminated STO (100) substrate was prepared using the same pre-annealing conditions of the p-type interface, but without LAO growth.

The photocurrent dynamics were investigated from the infrared to ultraviolet region using apparatus described elsewhere [16]. The samples were ultrasonically wirebonded with Al wire, and the two-probe photocurrent $I_{\rm photo}$ was measured with an electrometer at intervals of 0.25 s, using a d.c. bias voltage of 5 V. The distance between the voltage contacts was $\sim$1 mm, and the temperature was fixed at $T = 10$ K. The sample resistance was in the range 10^{12}-$10^{15}\,\Omega$ before irradiation. The photocurrent was measured as a function of time with monochromatic light (< 1 nm spread in wavelength), from low to high photon energies. At each photon energy, the light was illuminated for 100 s and then removed for 100 s, before increasing the energy. This procedure was utilized to avoid prohibitively long measurement times associated with the slow carrier relaxations in the samples. The normalized photocurrent (NPC) was defined as the value of $I_{\rm photo}$ 60 s after an electromagnetic shutter opened, (shutter opening time = 8 ms) normalized by the intensity at a calibrated Si-photodiode simultaneously monitoring a parallel optical fiber from the monochromator. The typical intensity was 1×10^{13} photons/mm^{2}s.

3. Results and discussion

A typical result of $I_{\rm photo}$ vs. time (t) is shown in Fig. 1, where the energy of the irradiated light was 1.8 eV ($\sim$ 680 nm), smaller than the band gap of STO. The magnitude of the photocurrent is significantly larger for the heterointerfaces compared with the STO (100) substrate, namely four orders of magnitude larger for the (110) interface and one order of magnitude larger for the p-type interface. The transient behavior of $I_{\rm photo}$ also shows distinct difference between these samples. $I_{\rm photo}(t)$ of the STO (100) substrate is stabilized on a timescale comparable to the measurement resolution of 0.25 s, whereas for the heterointerfaces, $I_{\rm photo}$ does not saturate within the measurement duration. The appearance of $I_{\rm photo}$ below E_g excitation for the heterointerfaces suggests formation of filled interface states which simltaneously modifies the recombination processes leading to longer photo-carrier

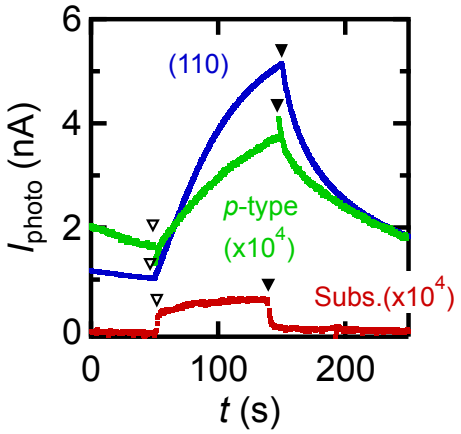

Figure 1: (color online) Typical photocurrent dynamics of the p-type and (110) heterointerfaces, and an annealed STO (100) substrate reference (Subs.) measured at $T = 10$ K. The incident photon energy was 1.8 eV. Open triangles show when irradiation of the samples started, and closed triangles indicate when the irradiation stopped.

lifetimes.

In order to investigate the spectral distribution of the interface states causing these long scale relaxations, photocurrent spectra as a function of photon energy have been measured. NPC as a function of photon energy $E_{\rm photon}$ is depicted in Fig. 2. An abrupt increase above 3.2 eV originating from the band-gap absorption of STO is clear for all three samples. For the reference STO (100) substrate, the NPC ($E_{\rm photon}$) is very small with little energy dependence below $E_{\rm g}$, consistent with previous reports [17]. However, both the p-type and (110) interfaces show considerable variation of NPC as a function of the photon energy, with the magnitude of NPC of the p-type being relatively smaller than that of the (110) interface. Below 2 eV, NPC for the p-type interface is rather similar to the reference STO (100) substrate (corresponding to $I_{\rm photo} < 10^{-14}$ A). NPC increases significantly as $E_{\rm photon}$ increases above 2 eV, showing saturation above 2.7 eV until the band-gap. In contrast, the (110) interface shows an increase of the NPC almost exponentially with $E_{\rm photon}$ up to $E_{\rm photon} \sim 2.5$ eV before saturating around 2.7 eV, similar to the p-type case.

From these results, it can be concluded that the two heterointerfaces have notable interface states from which electrons are excited into the conduction band (CB) and contribute to the photoconductivity. The possibility

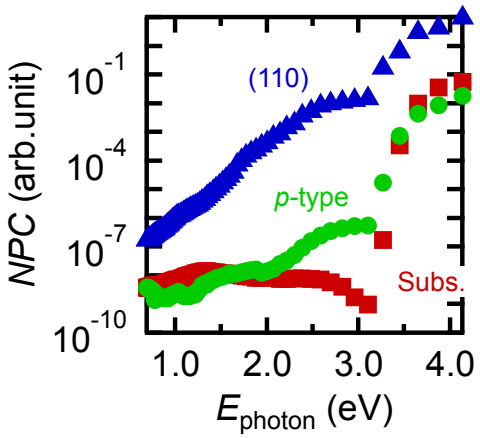

Figure 2: (color online) Photocurrent spectroscopy of the p-type and (110) heterointerfaces, and an annealed STO substrate reference (Subs.). Normalized photocurrent (NPC) refers to the photocurrent normalized by the relative intensity. $T = 10$ K.

of acceptor-like interface states can be ruled out because of the extremely low hole mobility in STO. In both heterointerfaces, it is clear that these states are not discrete but continuously distributed from 2.0 eV to 2.7 eV, below the CB minimum in the p-type case, and spread further down to below 1 eV in the (110) case. Above $E_{\rm photon} > E_{\rm g}$, the p-type sample and the STO substrate show similar order NPC, whereas the (110) interface shows two orders of magnitude larger NPC, suggesting larger quantum efficiency in the (110) heterointerface or substantially enhanced mobility along the [001] direction compared with [100] or [010].

We examined in detail the functional form of $I_{\rm photo}$ (t) for the two heterointerfaces. The relaxation after switching off the light in both cases could clearly not be fitted to a single exponential. Rather, we could obtain a good fit to the $I_{\rm photo}$ (t) data using a stretched exponential, as shown in Fig. 3(a). Here the theoretical fits are of the form

$$I_{\rm photo}(t) = I_{\rm photo}(0)\exp\left[-\left(\frac{t}{\tau}\right)^{\beta}\right], \qquad (1)$$

where τ is the characteristic relaxation time, and β is the stretching parameter in the range of $0 < \beta < 1$. This functional form can be derived from a sum of independent single exponential decays with relaxation times τ_i, with

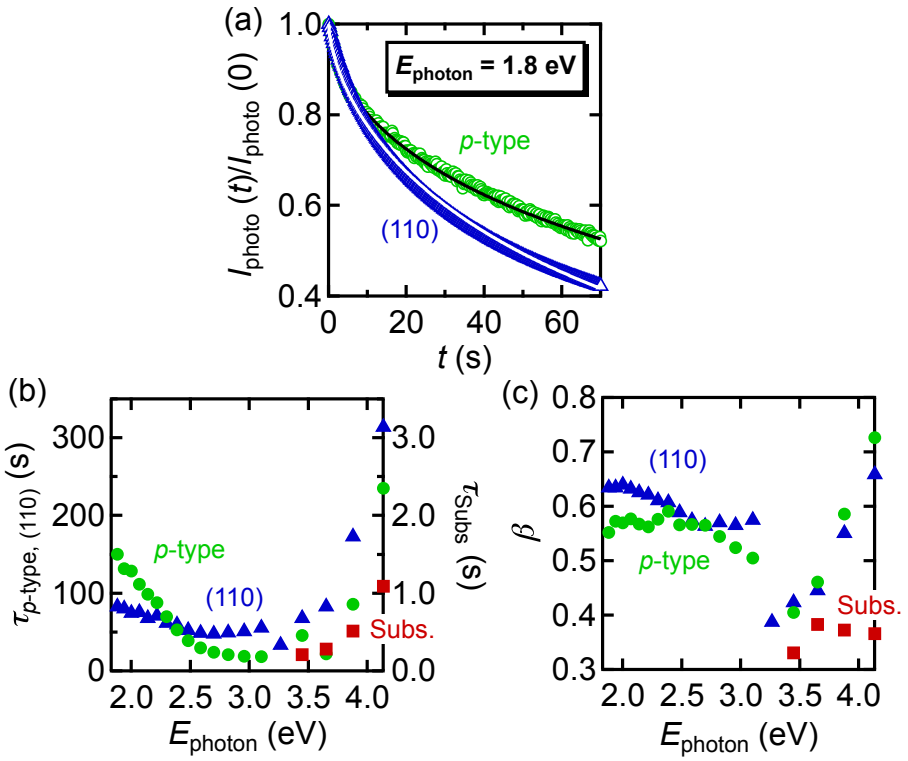

Figure 3: (color online) Stretched exponential fits for the p-type and (110) interfaces. (a) The relaxation of the normalized photocurrent at $E_{\text{photon}} = 1.8$ eV and $T = 10$ K. The black and white solid lines are best fits using Eq. 1. E_{photon} dependence of (b) τ, and (c) β obtained from the fits.

a particular probability distribution $P\ (\tau/\tau_i)$ for a given value of β, where β can be interpreted as a measure of the low relaxation rate cut-off of $P\ (\tau/\tau_i)$ [18]. Such stretched fits have been previously successfully used to model the dynamics of various disordered and quenched systems [19, 20, 21, 22].

From the best fits using Eq. 1, $\tau\ (E_{\text{photon}})$ and $\beta\ (E_{\text{photon}})$ are obtained, as shown in Figs. 3(b) and (c), respectively. For both interfaces $\tau\ (E_{\text{photon}})$ monotonically decreases for $E_{\text{photon}} \lesssim 3.2$ eV due to the interface states formed by LAO deposition, before a strong increase of τ above E_{g}. Given that the recombination time of the interface states to the CB is inversely proportional to the number of interface states, a systematic decrease in τ with E_{photon} indicates a substantial increase in the interface state density [23]. For the p-type sample, the states emerge ~ 2.0 eV below the CB, saturating

around 2.7 eV. For the (110) heterointerface, the number of interface states is more energy independent and hence the smaller variation in τ vs. E_{photon}.

Above the bandgap, τ increases for both heterointerfaces with increaseing E_{photon}. A similar trend is observed for STO (100) with τ smaller by two orders of magnitude. Typically, higher electron-hole pair (EHP) density leads to shorter average lifetimes because less time is required to travel to reach a recombination site. The counterintuitive trend observed here can be explained if the electron and hole capture cross sections are not equal and the recombination centers are positioned close to the intrinsic Fermi level of the semiconductor [23]. Therefore, the increase in τ with E_{photon} above E_{g} suggests a high density of recombination centers in the *bulk* of STO dominating these recombination processes. Furthermore, these states act as the intermediate centers in providing sub-gap photocurrent in a two-photon process in STO (100) [22].

The larger τ for the heterointerfaces compared to STO (100) suggests that the interface formation has induced a dramatic change in the recombination mechanism. As one such candidate, we consider the spatial separation of EHPs due to an internal electric field. In the presence of an internal electric field, the EHPs are spatially separated giving rise to longer lifetimes because the electrons need to diffuse against the electric field to find the holes to recombine. Such long τ of the order of 100 s has been observed in GaAs heterointerfaces in which the decay transient was well explained by the stretched exponential form [22]. In the present case, the positive fixed charges to screen the negatively charged interface states are the likely origin of the electric field. We note that in principle we must also consider other electron excitations from possible bulk trap states and surface states in the LAO layer into the STO. Such electrons are implicitly included in the above discussion.

The energy range in which the interface states are formed is similar to where green photoluminescence has been observed [11, 24, 25], and explained in terms of self-trapped excitons [26, 27], and more recently to oxygen vacancies, or their complexes with Ti, which trap electrons [28, 29]. The p-type interface is known to contain oxygen vacancies at the interface, which provide a route to compensate the polar discontinuity between the STO and LAO [5]. In the case of the (110) interface, however, the higher density of the interface states, as well as the lower background resistance ($\sim 10^{12}\,\Omega$, compared to $\sim 10^{15}\,\Omega$ for the p-type and the substrate) is less easily explained since there is no polar discontinuity in this case, and one would naively expect less atomic

or electronic reconstructions driven by the electrostatic boundary conditions. However, the initial polar surface of the (110) STO substrate, and the significantly higher pre-annealing temperature compared to the other two samples may play an important additional role [30] in the formation of interface states that strongly perturb the photoconducting response.

4. Conclusions

To summarize, we have studied the photoconductivity response in the visible to ultraviolet range for two LAO/STO interfaces at low temperatures, and found a wide range of energies below the band-gap where significant, and long lived, photoelectrons can be excited from interface states. These measurements give important insights into the electronic states found in these heterointerfaces, emphasizing their distinct character compared to bulk STO. We note the large τ, comparable to the 100's of seconds found in the ultraviolet region above the bandgap, suggest the possibility of persistent photoconductivity at even lower temperatures, providing a promising tool to control the two-dimensional electrons at the interface [31, 32].

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