Multiple conducting carriers generated in $LaAlO_3/SrTiO_3$ heterostructures

S. S. A. Seo,[1,a)] Z. Marton,[1,2] W. S. Choi,[3] G. W. J. Hassink,[4,5] D. H. A. Blank,[4] H. Y. Hwang,[5,6] T. W. Noh,[3] T. Egami,[1,7] and H. N. Lee[1,b)]
[1]*Materials Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831, USA*
[2]*Department of Materials Science and Engineering, University of Pennsylvania, Philadelphia, Pennsylvania 19104, USA*
[3]*Department of Physics and Astronomy, ReCOE & FPRD, Seoul National University, Seoul 151-747, Republic of Korea*
[4]*MESA+Institute for Nanotechnology, University of Twente, Enschede NL-7500 AE, The Netherlands*
[5]*Department of Advanced Materials Science, University of Tokyo, Kashiwa, Chiba 277-8561, Japan*
[6]*Japan Science and Technology Agency, Kawaguchi 332-0012, Japan*
[7]*Department of Physics and Astronomy, University of Tennessee, Knoxville, Tennessee 37996, USA*

(Received 1 July 2009; accepted 6 August 2009; published online 27 August 2009)

We have found that there is more than one type of conducting carriers generated in $LaAlO_3/SrTiO_3$ heterostructures by comparing the sheet carrier density and mobility from optical transmission spectroscopy with those from dc-transport measurements. When multiple types of carriers exist, optical characterization dominantly reflects the contribution from the high-density carriers whereas dc-transport measurements may exaggerate the contribution of the high-mobility carriers even though they are present at low density. Since the low-temperature mobility determined by dc-transport in the $LaAlO_3/SrTiO_3$ heterostructures is much higher than that extracted by optical method, we attribute the origin of high-mobility transport to the low-density conducting carriers. © *2009 American Institute of Physics*. [DOI: 10.1063/1.3213390]

Interfacial conductance with high mobility is a scientifically fascinating phenomenon with the potential in many technical applications. Recently, observation of metallic transport in a heterointerface between two insulators of $LaAlO_3$ (LAO) and $SrTiO_3$ (STO) has attracted a lot of attention due to its high mobility ($\sim 10^4$ cm^2 V^{-1} s^{-1}) at low temperature.[1] Following studies have revealed a number of additional features such as interfacial magnetic ordering and electric field controlled superconductivity at the LAO/STO heterointerface.[2,3] At the same time, concerns about the oxygen off-stoichiometry have been raised.[4,5] Thus, characterizing the nature of the high-mobility carriers will be an important step toward advancing oxide electronic materials and devices.

In this letter, by optical transmission spectroscopy and dc-Hall measurements, we report that there are at least two different kinds of conducting carriers with different mobilities in the LAO/STO heterostructure. Since optical transmission spectroscopy is an ac-transport measurement technique, its spectral analysis can provide us with not only qualitative but also quantitative information on the nature of conducting carriers. By comparing the physical quantities extracted from the optical spectroscopic data with the results of conventional dc-transport, we suggest that only a fraction of the carriers is responsible for the high-mobility ($>10^3$ cm^2 V^{-1} s^{-1}) observed in the LAO/STO heterostructure while the majority of conducting carriers have low-mobility (~ 10 cm^2 V^{-1} s^{-1}).

We grew 125-unit-cell-thick LAO thin films on TiO_2-terminated STO (001) substrates by pulsed laser deposition (PLD).[6] Figure 1(a) shows the metallic sheet resistance, R_{xx}, of an as-grown sample as a function of temperature. Another sample, which was prepared under the identical condition followed by *in situ* postannealing in a higher oxygen partial pressure (P_{O_2}=50 mTorr) for 10 min at the growth temperature, shows a highly resistive and insulating behavior, which is consistent with the previous reports.[4,5] The difference in optical transmission of the LAO/STO samples is also distinguishable by eye. The metallic as-grown sample has a dark bluish color while the postannealed sample is as transparent as an insulating STO substrate [see the inset of Fig. 1(a)].

Figure 1(b) shows optical transmittance spectra [$T(\omega)$] of the LAO/STO samples. The as-grown (metallic) sample has low transmittance in the photon energy region of 0.5–3.3 eV. On the other hand, the postannealed (insulating) sample has high transmittance reaching 80% below 3.2 eV. The common steep drop in the transmittance at 3.2 eV originates from the $O_{2p} \rightarrow Ti_{3d}$ charge-transfer transition of the STO sub-

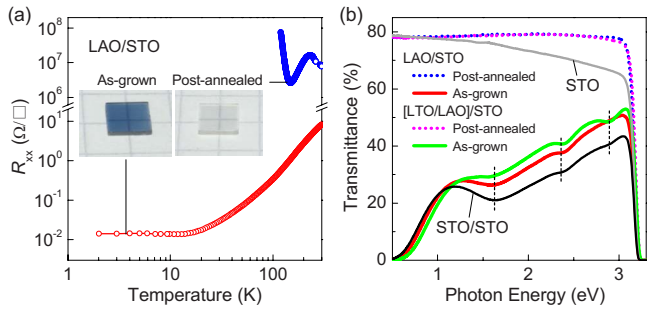

FIG. 1. (Color online) (a) Sheet resistance of LAO (125 unit cells) films on STO substrates. Inset: photographs of as-grown and postannealed LAO/STO samples on 5×5 mm^2 mesh paper. (b) Room temperature $T(\omega)$ of LAO films on STO, [LTO/LAO] superlattices on STO, a STO film on STO, and a bare STO substrate.

a)Electronic mail: seos@ornl.gov.
b)Electronic mail: hnlee@ornl.gov.

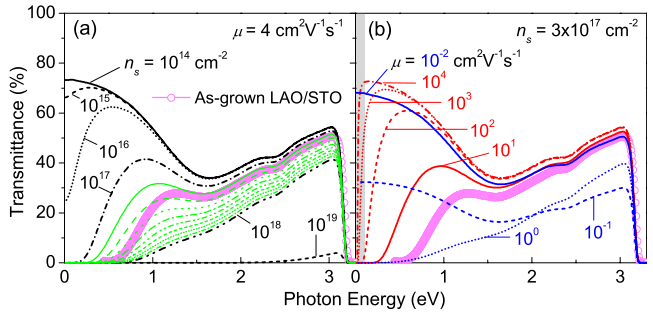

FIG. 2. (Color online) Simulated $T(\omega)$ of a LAO (50 nm) thin film ona STO substrate. (The experimental data of the LAO/STO sample is also shown for comparison.) (a) Simulated spectra with n_s from 1×10^{14} to 1×10^{19} cm^{-2} at μ=4 cm^2 V^{-1} s^{-1} and $m^*=1.8m_e$ (Ref. 15). Green lines are calculated spectra for n_s from 2×10^{17} to 9×10^{17} cm^{-2}. (b) Simulated spectra with various mobility values $\mu=10^{-2}-10^4$ cm^2 V^{-1} s^{-1} at $n_s=3\times10^{17}$ cm^{-2}. Transmittance measurement at very low photon energy <120 meV (shaded region) is practically hindered by the Restrahlen band of infrared-active phonons of the STO substrate.

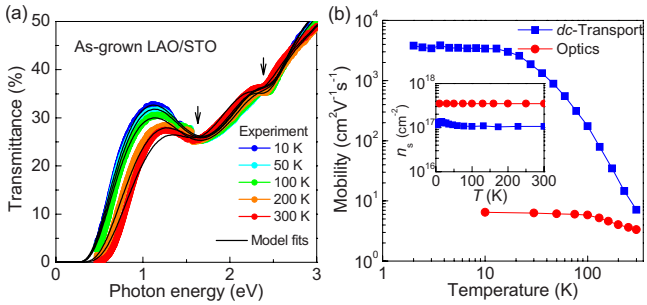

FIG. 3. (Color online) (a) Temperature-dependent $T(\omega)$ of LAO/STO and their model-fit curves at each temperature. The arrows point the weak absorption bands showing a blue-shift. (b) The mobility as a function of temperature extracted from dc-resistivity and Hall measurements as well as optical transmission spectroscopy. Inset shows n_s as a function of temperature.

strates. The low transmittance from the as-grown sample at lower photon energies is a signature of conducting carriers, which will be discussed below. Interestingly, the postannealed sample shows even higher transmittance than a bare STO substrate in the measured photon energy region due to the antireflection effect.[7] To identify the detailed spectral features of the as-grown sample, a superlattice of $[(LaTiO_3)_1/(LAO)_5]_{20}$ (a total of 120 unit cells in thickness) on a STO (001) substrate ([LTO/LAO]/STO) was also tested. Note that both as-grown LAO/STO and [LTO/LAO]/STO show a very similar spectral shape [Fig. 1(b)]. Transmittance decreasing to zero at ~0.5 eV and three weak absorption bands at 1.7, 2.4, and 2.9 eV (marked with dashed vertical lines) are observed for both samples. However, after postannealing under oxygenating conditions (flowing O_2, at 400 °C for 1 h), the [LTO/LAO]/STO sample also becomes transparent and shows quite flat $T(\omega)$ [Fig. 1(b)]. Interestingly, however, x-ray diffraction does not reveal any structural changes (data not shown here), suggesting that the spectral features of the as-grown samples come mainly from the STO substrate. To clarify this point, we grew a STO film (250 unit cells) on STO (001) in the same conditions as those for LAO/STO. By comparing its $T(\omega)$ with other heterostructures, it is now clear that the above-mentioned spectral features originate not from LAO but from STO [Fig. 1(b)]. Below we focus our discussion only on features of the absorption spectra that are directly correlated with the transport properties of conducting carriers, rather than the origins of the absorption bands[6] at the finite photon energies.

Figure 2 shows simulated $T(\omega)$ based on a model system with a LAO film on a metallic STO substrate.[6] Increasing the sheet carrier density (n_s) from 10^{14} to 10^{19} cm^{-2} while fixing the mobility (μ) at 4 cm^2 V^{-1} s^{-1} results in systematically decreased $T(\omega)$ and the variation becomes larger particularly at lower photon energies, as shown in Fig. 2(a). By comparing these simulated spectra with the experimental spectrum of LAO/STO, we can estimate that n_s is about 3×10^{17} cm^{-2}. In addition, the evolution of $T(\omega)$ as a function of μ at a fixed $n_s=3\times10^{17}$ cm^{-2} is shown in Fig. 2(b). At higher mobilities (μ=10–1000 cm^2 V^{-1} s^{-1}), there is a drastic change in the curvature of the spectra at lower photon energies while the spectra with lower mobilities (μ=0.01–1 cm^2 V^{-1} s^{-1}) exhibit a rather moderate change at the same energies. Thus, one can estimate n_s and μ of the conducting carriers with reasonable confidence. Interestingly, the simulated spectra at μ=10 000 and 0.01 cm^2 V^{-1} s^{-1} are very similar to each other for different reasons. The former has a very narrow Drude absorption feature with a small scattering rate, which lies below our photon energy range, and the latter has a rather broad featureless shape of the Drude absorption over a wide region of photon energies.

Since the high-mobility values of free carriers in LAO/STO at low temperatures are of interest, we measured temperature-dependent $T(\omega)$, as shown in Fig. 3(a). Note that the most pronounced change in transmittance is observed at lower photon energies (approximately 0.5–1.5 eV) while the weak absorption bands centered at 1.7 and 2.4 eV show subtle blue-shifts.

Figure 3(b) summarizes n_s and μ extracted from the model fits in Fig. 3(a). For comparison, we also plot the data obtained by dc-Hall measurements. As shown in the inset, the values of n_s measured by both optical and dc techniques are in good agreement and remain almost unchanged [$(1-3)\times10^{17}$ cm^{-2}] with temperature. Although $n_s\approx10^{17}$ cm^{-2} are consistently observed in LAO/STO heterostructures,[1,4,5] it gives a very high carrier density if one assumes that the carriers are confined within a few hundreds nanometers or less.[8] Such a high carrier density has been attributed to the fact that the growth of oxide thin films under reducing conditions by highly energetic PLD can effectively generate a high concentration of electron donors, e.g., oxygen vacancies, in underlying STO as reported recently by Herranz *et al.*[9]

Note that the mobility at low temperature, μ (10 K), determined by spectral analyses is enhanced by about a factor of two as compared to the room-temperature value, while the dc-transport mobility is increased enormously by about three orders of magnitude, as shown in Fig. 3(b). In inhomogeneous materials, the dc-transport may show lower conductivity than the optically measured one since the dc-transport strongly depends on the connectivity of the conducting channels while the optical spectroscopic measurement does not.[10] However, what we have observed here strongly suggests that the carriers that contribute dominantly to the dc-transport and optical spectroscopy are not the same, and there exist at least two kinds of carriers.[6] One that contributes mostly to

the dc-transport has high mobility, low density, and strong temperature dependence. The other one that is dominantly seen by optical spectroscopy has low mobility, high density, and weak temperature dependence. If we assume that there exist multiple, parallel conducting channels within STO, the sheet conductivity can be expressed as $S_{xx}(\equiv 1/R_{xx}) = n_{s1}e\mu_1 + n_{s2}e\mu_2 + \cdots$, then both results from dc-transport and optical spectroscopy can be understood consistently. Thus dc-conductivity is dominated by high-mobility carriers. On the other hand, optical spectra are dominated by high-density carriers, regardless of their mobility.

At this moment, it is still unclear which part of STO, i.e., the region close to or far from the interface, has the carriers with higher mobility since both optical spectroscopy and dc-transport are macroscopic bulk-sensitive techniques. Nevertheless, the origin of low-density carriers with high mobility at low temperature seems to be related to the quantum paraelectric behavior of STO. It is well known that the dielectric permittivity of STO diverges as it approaches the incipient-ferroelectric transition at low temperature.[11] The increased dielectric permittivity can effectively screen the scattering sources such as defects from mobile electron carriers and thus their mobility can be enormously increased. Recently, Copie *et al.*[12] reported that carriers can be confined in a very narrow region near the interface even at low temperature by considering reduction of the dielectric permittivity of STO under a strong electric field. Hence, a reasonable picture might be that high-density low-mobility carriers are confined near the interface region while low-density high-mobility carriers can be distributed far from the interface. Since the low-density high-mobility carriers are distributed in a high dielectric permittivity region, the electric field control of the conductivity[2] might have been realized effectively in this type of heterostructures. To further clarify the spatial distribution and mobility profile of the conducting carriers, a microscopic transport measurement such as quadra-probe scanning tunneling microscopy at low temperature[13] on a cross-sectional heterointerface might be a useful approach. Regarding the origin of the multiple carriers, we also need further experimental investigations even though the finding reported here—the conduction in this heterostructure can be intrinsically associated with more than one type of carriers—has been previously proposed.[3,14]

In summary, transport properties of conducting carriers generated at the polar/nonpolar interface in LAO/STO heterostructures have been investigated by optical transmission spectroscopy and dc-transport. We demonstrate that $n_s \approx 10^{17}$ cm^{-2}, which is consistent with the result of dc-transport measurements, can be estimated by analyzing the temperature-dependent optical transmittance spectra. However, while the dc-transport mobility shows a huge increase by three orders of magnitude as temperature decreases, the optically probed mobility only approximately doubles. The discrepancy can be understood by the assumption that low-density high-mobility carriers are generated in the metallic LAO/STO heterostructures in addition to high-density low-mobility carriers.

We thank I. Ivanov and H. M. Christen for useful discussions. This work was sponsored by the Division of Materials Sciences and Engineering, U. S. Department of Energy, a nanotechnology program of the Dutch Ministry of Economic Affairs (NanoNed), and National Science Foundation by Grant No. DMR04-04781.

[1] A. Ohtomo and H. Y. Hwang, Nature (London) **427**, 423 (2004).
[2] S. Thiel, G. Hammerl, A. Schmehl, C. W. Schneider, and J. Mannhart, Science **313**, 1942 (2006).
[3] A. Brinkman, M. Huijben, M. van Zalk, J. Huijben, U. Zeitler, J. C. Maan, W. G. van der Wiel, G. Rijnders, D. H. A. Blank, and H. Hilgenkamp, Nature Mater. **6**, 493 (2007).
[4] A. Kalabukhov, R. Gunnarsson, J. Borjesson, E. Olsson, T. Claeson, and D. Winkler, Phys. Rev. B **75**, 121404 (2007).
[5] G. Herranz, M. Basletic, M. Bibes, C. Carretero, E. Tafra, E. Jacquet, K. Bouzehouane, C. Deranlot, A. Hamzic, J.-M. Broto, A. Barthelemy, and A. Fert, Phys. Rev. Lett. **98**, 216803 (2007).
[6] See EPAPS supplementary material at http://dx.doi.org/10.1063/1.3213390 for experimental details.
[7] The refractive index of LAO is smaller than that of STO. For the antireflection effect, see G. R. Fowles, *Introduction to Modern Optics*, 2nd ed. (Dover, New York, 1989).
[8] If the effective thickness of the carriers is about 100 nm, then the carrier density becomes about 10^{22} cm^{-3}. One electron carrier per Ti ion gives 1.68×10^{22} cm^{-3} in carrier density. Also note that half-electron per interfacial unit-cell ($n_s \approx 3.3 \times 10^{14}$ cm^{-2}) is required to avoid the polar catastrophe.
[9] G. Herranz, M. Basletic, O. Copie, M. Bibes, A. N. Khodan, C. Carretero, E. Tafra, E. Jacquet, K. Bouzehouane, A. Hamzic, and A. Barthelemy, Appl. Phys. Lett. **94**, 012113 (2009).
[10] K. H. Kim, J. Y. Gu, H. S. Choi, D. J. Eom, J. H. Jung, and T. W. Noh, Phys. Rev. B **55**, 4023 (1997).
[11] T. Sakudo and H. Unoki, Phys. Rev. Lett. **26**, 851 (1971).
[12] O. Copie, V. Garcia, C. Bodefeld, C. Carretero, M. Bibes, G. Herranz, E. Jacquet, J.-L. Maurice, B. Vinter, S. Fusil, K. Bouzehouane, H. Jaffres, and A. Barthelemy, Phys. Rev. Lett. **102**, 216804 (2009).
[13] T.-H. Kim, Z. Wang, J. F. Wendelken, H. H. Weitering, W. Li, and A.-P. Li, Rev. Sci. Instrum. **78**, 123701 (2007).
[14] Z. S. Popovic, S. Satpathy, and R. M. Martin, Phys. Rev. Lett. **101**, 256801 (2008).
[15] Regarding m^* of STO-based conducting materials, see M. Ahrens, R. Merkle, B. Rahmati, and J. Maier, Physica B **393**, 239 (2007); S. S. A. Seo, W. S. Choi, H. N. Lee, L. Yu, K. W. Kim, C. Bernhard, and T. W. Noh, Phys. Rev. Lett. **99**, 266801 (2007).