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High mobility 2-dimensional electron gas at $LaAlO_3/SrTiO_3$ interface prepared by spin coating chemical methods

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Abstract

Highly mobile 2-dimensional electron gases (2DEGs) at the (001), (011) and (111)-oriented $LaAlO_3/SrTiO_3$ (LAO/STO) interfaces are obtained using spin coating chemical method, which is a gentle technique without plasma bombardment of the pulsed laser deposition. As revealed by x-ray diffraction spectrum and x-ray reflectivity analysis, the LAO over layer is epitaxially grown, and has a uniform thickness of ~15 nm, ~20 nm and ~26 nm for (001), (011) and (111) orientations, respectively. The interfaces are well metallic down to 2 K. The carrier mobilities are ~28 000 $cm^2 V^{-1} s^{-1}$, ~22 000 $cm^2 V^{-1} s^{-1}$ and ~8300 $cm^2 V^{-1} s^{-1}$ at 2 K for the (001), (011) and (111) LAO/STO interfaces, respectively, and ~8 $cm^2 V^{-1} s^{-1}$, ~4 $cm^2 V^{-1} s^{-1}$ and ~4 $cm^2 V^{-1} s^{-1}$ at room temperature. The present work shows that the spin coating chemical method is a feasible approach to get high quality 2DEG at both the polar/non-polar and polar/polar interfaces.

Keywords: 2DEG, $LaAlO_3/SrTiO_3$, chemical methods

(Some figures may appear in colour only in the online journal)

Introduction

Almost a decade ago, a highly conductive interface between two band insulators $LaAlO_3$ (LAO) and $SrTiO_3$ (STO) was discovered [1]. This historical discovery opened new horizons for researchers to study. Later on it was found that the interface is not only metallic in nature but also exhibits a number of interesting characteristics like superconductivity, ferromagnetism and the coexistence of these two phenomenon that is scarcely found in nature [2–5]. These properties make LAO/STO a promising candidate for oxide electronics.

LAO and STO are ABO_3 type perovskite oxides. The polar/non-polar LAO/STO (001) interface is considered to be containing of alternate stacks of $[SrO]^0/[TiO_2]^0$ for substrate and $[LaO]^{1+}/[AlO_2]^{1-}$ for film. But for polar/polar LAO/STO (111) interface the alternate stacking is comprising of polar $[Ti]^{4+}$ and $[SrO_3]^{4-}$ for substrate and $[LaO_3]^{3+}$ and $[Al]^{3-}$ for the LAO over layer, forming honeycomb lattice that resembles graphene. Despite of different stacking layers and charge attached with each stacking for (001) and (111) LAO/STO bilayers, the interface contains polar discontinuity with a mismatch of e/2 for each cation. But LAO/STO (011) contains alternate stacks of $[LaAlO]^{4+}$ and $[O_2]^{4-}$ for LAO and $[SrTiO]^{4+}$ and $[O_2]^{4-}$ for STO, thereby leaving interface without any polar discontinuity that could be unable to support any metallicity at interface as shown by some initial reports on (011)-oriented interfaces [6–8].

Extensive experimental and theoretical studies have been performed since the first report on 2-dimensional electron gas (2DEG) at the LAO/STO (001) interface regarding critical LAO layer thickness for the formation of metallic 2DEG at

interface with the high carrier mobility, the origin of superconductivity and ferromagnetism for epitaxial crystalline LAO as well as amorphous LAO (a-LAO) films grown at TiO_2-terminated (001) STO, and the effect of buffer layers and other factors such as charge writing on mobility [2–5, 9–15]. Most of these works focused on the (001) LAO/STO interfaces. Investigations on the (011) and (111) LAO/STO interfaces are very limited [16–18]. Particularly, for the (111) 2DEG only a few reports can be found, simply reported the temperature dependence of sheet resistance without further information on the Hall Effect and magnetoresistance effect. Even there is no report on carrier mobility which is an important characterization of the quality 2DEG.

Probably, the easy preparation of appropriate TiO_2-terminated (001) STO surfaces for epitaxial growth, polar catastrophe-based explanations for some features between polar LAO and non-polar STO have attracted the interest of researchers. However, the (011), particularly the (111) 2DEG appeared at the polar/polar interface has distinct characteristics, such as honeycomb lattice and different symmetry from the (001) 2DEG, thus deserves special attention.

Most of the LAO/STO interfaces were prepared by pulsed laser deposition (PLD) or sometimes atomic layer deposition (ALD). In this case, high energy plume produced by laser pulse bombards the STO surface, which will inevitably lead to the formation of extrinsic defects that act as scattering centers for the 2DEG, the interlayer diffusion, and less smooth interface. All these will result in a degeneration of the sample quality, particularly for the (011) and (111) samples with complex crystal plane indices. This explains why the 2DEG usually exhibits a resistive upturn or a reduction in carrier mobility at low temperatures when the LAO over layer is thicker than ∼8 nm [19, 20].

In our work, we have utilized a spin coating chemical method for the fabrication of the 2DEGs at the LAO/STO interfaces of different crystal orientations and performed a systematic investigation on its transport behaviors. In spin coating method, a drop of the precursor solution is dropped at the surface of the substrate followed by spinning in order to get film with uniform thickness. The thickness of the film depends on the spinning speed and the concentration of the precursor solutions and volatility of the solution. This technique has been widely used for the preparation of metal oxides thin films for the study of optical applications and in the field of the transistors fabrication. Using this technique films with thickness from 15 nm to several micro-meters can be achieved. For the spin coating technique, high energy plume is not used so the interface could be free from extrinsic defects and a perfect interface is expected. Indeed, high quality 2DEGs are successfully obtained using this technique, which exhibit not only well metallic behavior but also a high carrier mobility. The highest mobilities are $\sim 28\,000\ cm^2\ V^{-1}\ s^{-1}$, $\sim 22\,000\ cm^2\ V^{-1}\ s^{-1}$ and $\sim 8300\ cm^2\ V^{-1}\ s^{-1}$ at 2 K for the (001), (011) and (111) LAO/STO interfaces, respectively.

Methods

The precursor is a 0.01 mole solution containing appropriate amounts of lanthanum nitrate hydrate $La(NO_3)_3 \cdot 9H_2O$, aluminum nitrate nano-hydrate $Al(NO_3)_3 \cdot 9H_2O$, N,N-dimethylformamide, polyvinylpyrorolidone and deionized water, which was constantly stirred for 14 h. A droplet of the precursor solution was dripped on a STO substrate ($5 \times 5 \times 0.5\ mm^3$), where (001) and (111) STO have been processed by buffered royal water and a followed post annealing at 900 °C in oxygen atmosphere for 0.5 h, and then was spread smoothly by first a spinning at 300 revolutions per minute for 15 s and a following spinning at 6000 revolutions per minute for 60 s to form homogeneous film on substrate surface. The film thus obtained was subsequently annealed in air for 3 h at 450 °C to crystalize the LAO film and then at 700 °C for 20 min in a high vacuum atmosphere of 10^{-4} Pa to form conducting interface accommodating 2DEG. As a reference, a (001) STO substrate without the LAO over layer was also treated following exactly the same procedures to confirm the formation of the 2DEG at the LAO/STO interface rather than the bare STO surface.

Surface morphology of the film was measured by atomic force microscopy (AFM, SPI 3800N, Seiko). Film thickness was determined by x-ray reflectivity (XRR). The crystal structure of the film was determined by x-ray diffraction (XRD) conducted by the Bruker diffractometer (D8 Discover with Cu Kα radiation). Ultrasonic aluminum wire bonding was adopted for electrical contacts. As will be shown later, the layer thickness of LAO is between ∼15 and ∼26 nm, which is thin enough to be penetrated through by wire bonding. Transport measurements were performed in Quantum Designed physical property measurement system with an applied current of 1 μA adopting the Van der Pauw geometry with standard four-terminal method.

Results and discussions

Figures 1(a)–(c) shows the AFM image and figures 1(d)–(f) shows step height of the (100), (011) and (111) STO substrate. Step-featured topography can be clearly seen. As shown in figures 1(d)–(f), the step height is about 3.54, 5.17 and 2.3 Å, corresponding to approximately one unit cell, and the step widths are ∼400, 250 and 80 nm for (001), (011) and (111) STO substrates. For (111) STO, the step height is corresponding to the distance between vicinal Ti layers, and the step width is not large due to miscutting of the substrate for (111) STO. The substrate quality is fairly good though its terrace structure is not as regular as the (001) or (011) STO, probably due to the strong polar nature of the Ti-terminated layer.

Figures 1(g)–(i) is the AFM image of the LAO film on the (001), (011) and (111) STO and figures 1(j)–(l) are line profile for the LAO films. Unexpectedly, the film is very smooth, and a direct statistics gives the root mean square (RMS) roughness of ∼1.4 Å for (001) and 2 Å for each of (011) and (111) LAO/STO. It is comparable to the RMS of

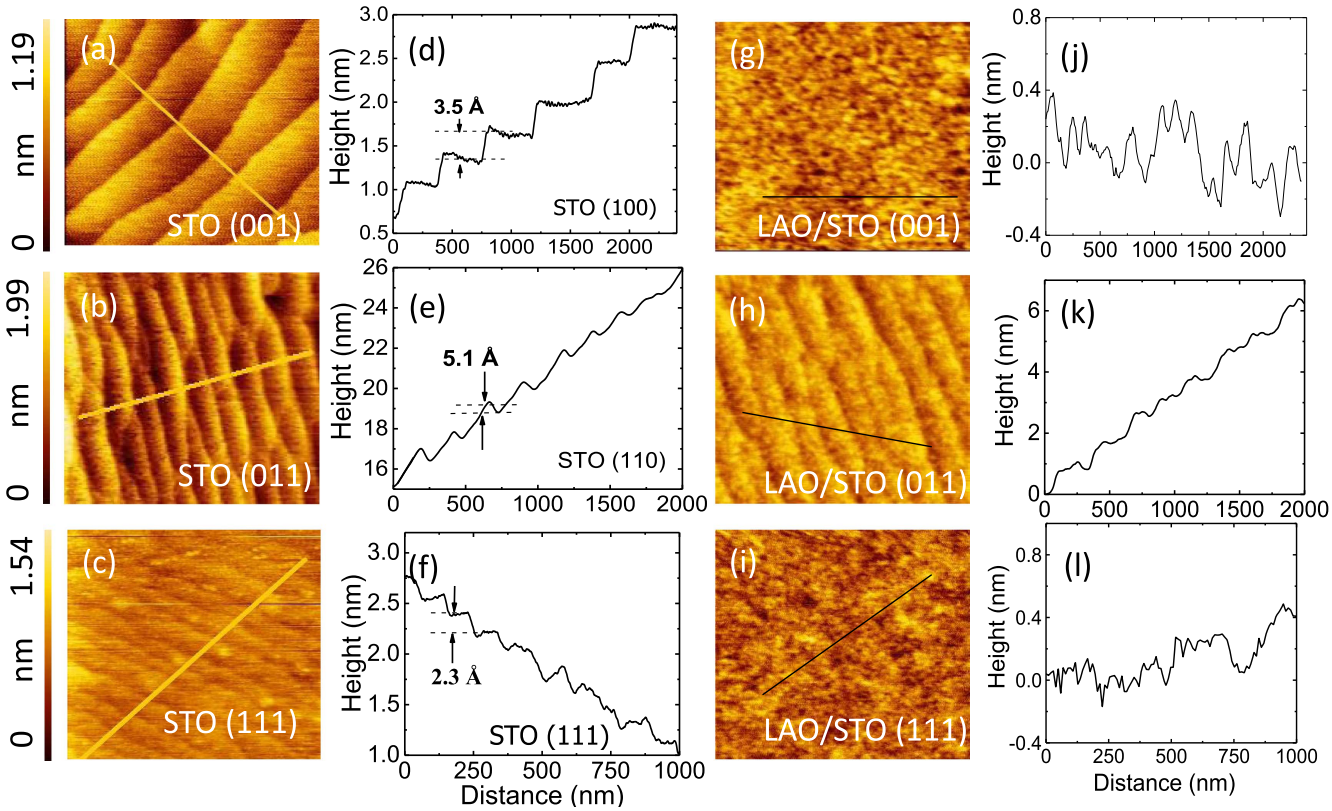

Figure 1. (a)–(c) AFM image of Ti-terminated (001), (011) and (111) STO. Surface steps can be clearly seen. (d)–(f) are the line profiles of the substrates and (g)–(i) are the AFM images for the films that indicates film smoothness with a root mean square roughness of ∼1.4 Å for (001) and 2 Å for each of (011) and (111). Slight lines in the images show the position where the line profile is recorded. (AFM images dimensions for (001) and (011) are 2.5 × 2.5 μm^2 and for (111) is 1 × 1 μm^2. Same scale bar should be used for (001) STO and (001) LAO/STO, similar is applied for other orientations.)

the film fabricated by PLD. The difference in height from peak to valley is almost 0.2 nm for (001) and (111) LAO/STO. However the steps height for (011) STO is 0.51 nm so after film deposition the steps are still observable with reduced steps height. The surface steps of STO are not visible after film deposition (figures 1(g), (i)). This is understandable since the RMS is in the same order as step height.

In order to determine the thickness of the LAO layer, XRR was measured. The XRR results in figures 2(a)–(c) show clear oscillations in reflectivity up to the 2θ angle of 4°–6°. The meanings of this result are two-fold, i.e., the layer surface is smooth and the layer thickness is uniform. Through data fitting of the XRR oscillations we obtained the layer thickness of ∼15 nm, ∼20 nm and ∼26 nm, corresponding to about 68, 90 and 118 monolayers (MLs) of LAO for the (001), (011), and (111) LAO/STO structures, respectively. This layer thickness is much greater than that of the 2DEG obtained by PLD, for which the optimal 2DEG usually has a LAO layer below 10 MLs. Sometimes one may require a thick cap layer to reduce leakage current when, for example, the top gating effect is studied. Moreover, to study the coupling between vertically piled 2DEGs in the structure of LAO/STO/LAO/STO, one may hope to tune the thickness of the intermediate LAO layer in a wide range.

Figures 2(d)–(f) shows the XRD pattern of the (001), (011) and (111) LAO/STO film. It confirms the epitaxial growth of the LAO film on STO. From each XRD pattern, the distance between adjacent planes can be determined. From the LAO peak, the distance is ∼3.791 Å, ∼2.68 Å, and ∼2.18 Å between adjacent (001), (011), and (111) planes, respectively. The deduced lattice parameter is 3.791, 3.777 and 3.790 Å assuming a cubic unit cell for the LAO film on STO (001) and (111) and tetragonal for (011). For all of these orientations, these values for lattice parameters are slightly smaller than the lattice parameter of bulk LAO (3.795 Å), which could be a consequence of in-plane lattice expansion of the LAO film. Hence using the technique of spin coating plus two-step post annealing, we are successful in fabricating an epitaxial LAO film on STO substrate, which is very smooth and uniform.

To get the information on transport properties, the resistance of the LAO/STO bilayer structure is further measured. Figure 3 shows sheet resistance (R_S) as a function of temperature (T). It displays a well metallic behavior for each orientation. The sheet resistance is ∼4.79 kΩ/□, 8.05 kΩ/□ and 6.80 kΩ/□ at 300 K, smoothly decreases with the decrease of temperature, and reaches a value as low as ∼2.46 Ω/□, 6.07 Ω/□ and 4.10 Ω/□ at 2 K for (001), (011) and (111) orientations respectively. The corresponding $R_S(300\,K)/R_S(2\,K)$ ratio is as high as 1948, 1326 and 1658. This is the typical behavior of high quality metallic 2DEG. To confirm that the metallic conduction stems exclusively from interface, we also measured LAO layer and the simultaneously processed STO

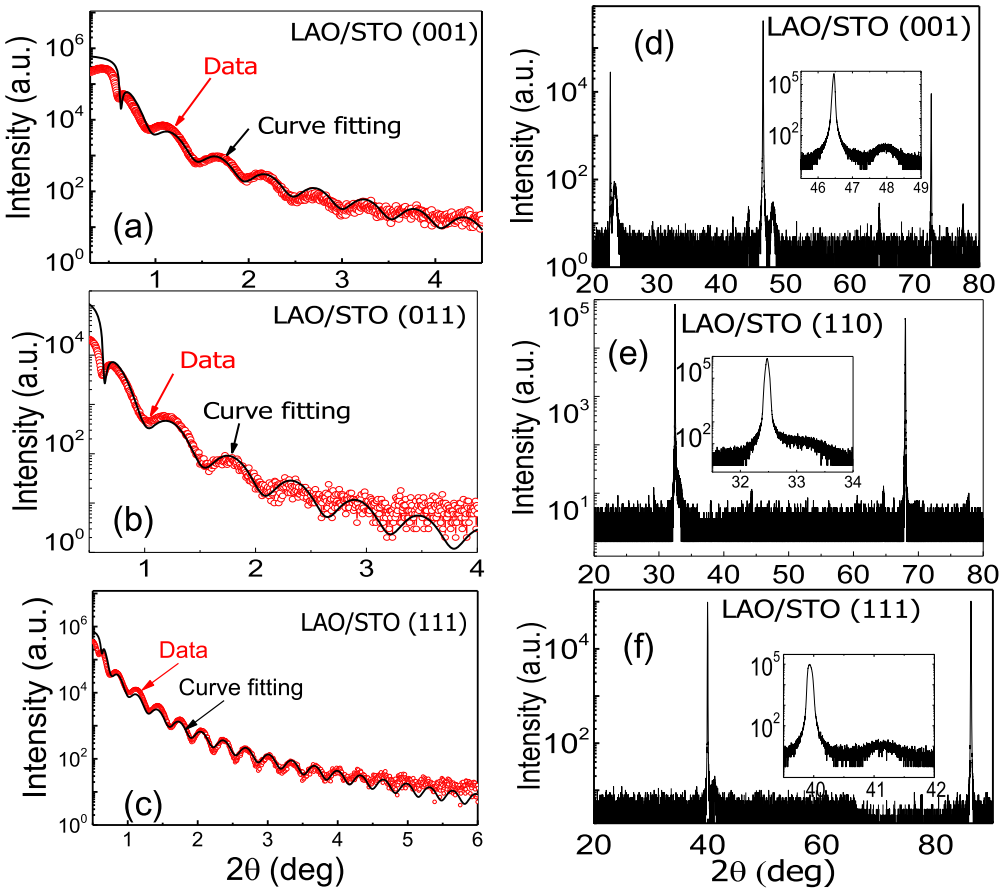

Figure 2. (a)–(c) X-ray reflectivity plots for LAO/STO (001), (011) and (111) that indicates oscillations (red symbols). The thickness of LAO film calculated by fitting curve is ∼15, 20 and 26 nm (black line). (d)–(f) are x-ray diffraction pattern of LAO/STO (001), (011) and (111). The inset shows clear peak for LAO (001), (011) and (111). It confirms the success of epitaxial growth of LAO film on STO by spin coating chemical method.

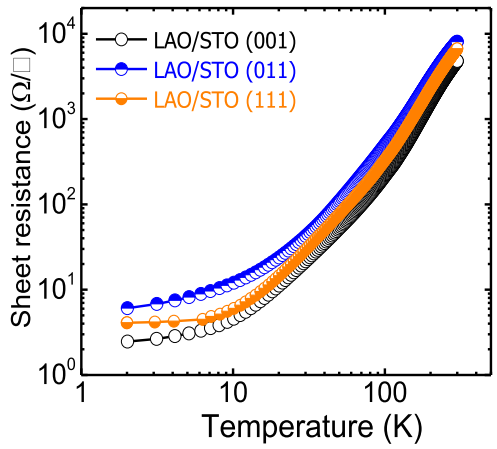

Figure 3. Sheet resistance as a function of temperature for (001), (011) and (111) LAO/STO interfaces.

substrate by connecting electrodes directly to LAO or STO using silver paste, and found that both LAO and STO are insulators. We therefore declared that a highly conducting 2DEG is formed at the LAO/STO interface.

If we make a comparison among R_S–T curves in this study with those for relatively thick LAO layers provided in literature fabricated by either PLD or ALD [6, 9, 10, 14], it is found that the 2DEG with a thick LAO layer usually exhibits a resistive upturn when cooled down below ∼60 K, indicating the occurrence of electron localization. This feature is particularly obvious for the (011) and (111) 2DEGs [6], and sometimes electron localization takes place even when the layer thickness of LAO is only 12 MLs (corresponding to a LAO of ∼2.6 nm) [6]. According to the literature, the conducting properties of the (011) and (111) LAO/STO interfaces are very sensitive to the layer thickness of LAO, and usually a degeneration in conductivity appears when the LAO layer exceeds ∼10 MLs. Probably, the high fabrication energy of the PLD plume and temperature leads to interlayer atomic diffusion or interfacial reconstruction due to the strongly polar nature of the STO surface. The only metallic 2DEG in the whole temperature range below 300 K appears at the (001) a-LAO/STO interface with a thick LAO layer (20 nm), for which the LAO layer is deposited at room temperature [10]. However, its sheet resistance is much larger than ours. For (011) and (111)-oriented LAO/STO, in order to get high mobility electron gas, the thickness of LAO is controlled carefully by PLD but the sheet resistance in these cases is still larger than in our samples. Even for these samples, quality of 2DEGs is not as high as ours. Hence, the

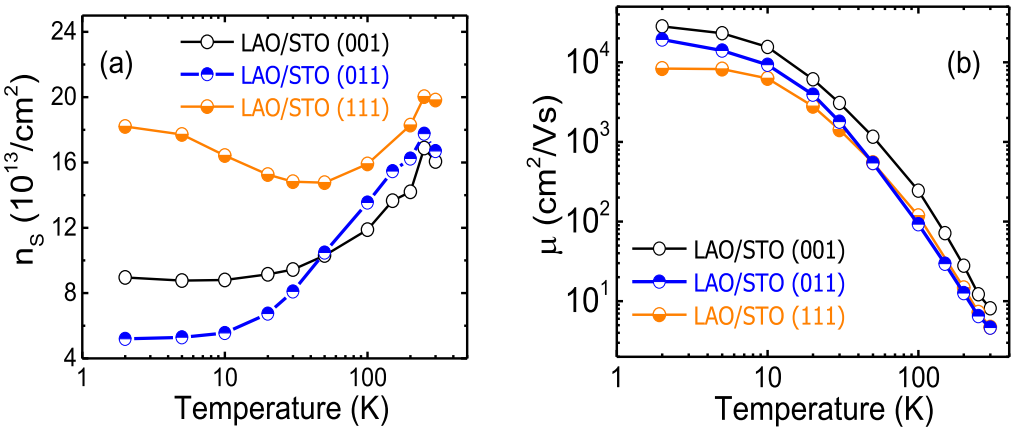

Figure 4. (a) Sheet carrier density as a function temperature and (b) Hall mobility versus temperature for the (001), (011) and (111) LAO/STO interface obtained by spin coating chemical methods.

present work demonstrates that the technique of spin coating plus post annealing is capable for achieving high quality (001), (011) and (111)-orientated interfaces without suffering from the limitation of LAO layer thickness.

To determine the carrier density and mobility of the 2DEG, Hall Effect is further studied. The Hall resistance displays a well linear variation with magnetic field for (001), (011) and (111) (not shown), irrespective of temperature. This is the typical behavior of the 2DEG of LAO/STO, indicating that only one species of charge carriers exist in the 2DEG. Meanwhile, the slope of the Hall resistance against magnetic field varies slightly with temperature, implying a weak temperature dependence of carrier density. Figure 4(a) shows the deduced carrier density as a function of temperature. The carrier density is $\sim 1.6 \times 10^{14}$ cm^{-2} at 300 K and achieves the minimal value of $\sim 8.9 \times 10^{13}$ cm^{-2} at $\sim$2 K for (001) LAO/STO, the carrier density is $\sim 1.6 \times 10^{14}$ cm^{-2} at 300 K, and $\sim 5.2 \times 10^{13}$ cm^{-2} at $\sim$2 K for (011) LAO/STO and the carrier density is $\sim 2 \times 10^{14}$ cm^{-2} at 300 K, and approaches the lowest value of $\sim 1.4 \times 10^{14}$ cm^{-2} at $\sim$45 K for (111) LAO/STO that displays a slight upturn upon further cooling, reaching a value of $\sim 1.8 \times 10^{14}$ cm^{-2} at 2 K. Generally speaking, the carrier density is in the order of $\sim 10^{13}$–10^{14} cm^{-2}, in good agreement with the expected value for an idealized 2DEG ($\sim 3 \times 10^{14}$ cm^{-2}). The slight increase in carrier density below 45 K for (111) is interesting. It could be associated with the distinct quantum para-electric properties of STO which are sensitive to external perturbations at low temperatures.

The fairly small variation of carrier density with temperature indicates the absence of strongly localized electrons, which is a lateral evidence for the perfect LAO/STO interface of our (111) sample. This is obviously different from the limitedly reported 2DEGs obtained by PLD or ALD, for which charge localization usually occurs at low temperatures when the LAO layer is thick, leading to considerable reductions in carrier density [6, 10].

Figure 4(b) displays the Hall mobility (μ) of 2DEG as a function of temperature, obtained based on sheet resistance and Hall resistance. The Hall mobility is ~ 8.12 cm^2 V^{-1} s^{-1} for (001) and ~ 4 cm^2 V^{-1} s^{-1} at the room temperature for each of (011) and (111) LAO/STO. This is a value similar to that of the most 2DEGs at the LAO/STO interfaces. With the decrease of temperature, μ undergoes a rapid increase, reaching a value as high as $\sim$28 000, and $\sim$22 000 and $\sim$8330 cm^2 V^{-1} s^{-1} at 2 K for (001), (011) and (111) LAO/STO. These results are comparable to or even better than, for the (011) and (111) 2DEGs, the best ones ever reported. Mostly, the reports on mobility are available for (001) oriented 2DEGs, ranging from $\sim$1000 to 60 000 cm^2 V^{-1} s^{-1} [12, 13, 15]. But good quality 2DEGs prepared by PLD with controlled over layer thickness have mobility about 10 000 cm^2 V^{-1} s^{-1} and our results for (001) are comparable with these reports. So our results indicate that spin coating chemical method is a feasible and cheaper approach for obtaining large scale and good quality 2DEGs for comparatively thicker over layers.

There are two possible origins for the 2DEG. The first one is charge transfer; electrons from the valence band of LAO are transferred to the LAO/STO interfacial potential well to overcome polar catastrophe, leaving electron holes in LAO. The second one is the outwards oxygen diffusion during vacuum annealing, which will introduce oxygen vacancies, thus mobile electrons into the interfacial layer of STO. Which mechanism dominates the formation of the 2DEG is still unobvious at present. We prefer to accept the explanation that the 2DEG forms after outwards oxygen diffusion since no polarity catastrophe occurs for the (011) interface.

Conclusions

In summary, high quality 2DEG at the polar/non-polar and polar/polar LAO/STO interface is obtained using spin coating chemical method. The LAO film thus fabricated is very smooth and uniform, showing an epitaxial growth above STO. The resulted 2DEG is metallic in the whole temperature range below 300 K. The highest Hall mobility is $\sim$28 000 cm^2 V^{-1} s^{-1} for (001), $\sim$22 000 cm^2 V^{-1} s^{-1} for (011) and $\sim$8330 cm^2 V^{-1} s^{-1} for (111), gained at 2 K. The carrier density is of the order of 10^{14} cm^{-2}, slightly varying with

temperature. The present work indicates that spin coating is a feasible approach to get high quality 2DEG, particularly the 2DEG at the (011) and (111) LAO/STO, for which the interface quality deteriorates when the LAO layer is thick adopting the PLD technique.

Acknowledgments

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