Tuning the Interface Conductivity of LaAlO₃/SrTiO₃ Using Ion Beams: Implications for Patterning

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ABSTRACT Patterning of the two-dimensional electron gas formed at the interface of two band insulators such as LaAlO₃/SrTiO₃ is one of the key challenges in oxide electronics. The use of energetic ion beam exposure for engineering the interface conductivity has been investigated. We found that this method can be utilized to manipulate the conductivity at the LaAlO₃/SrTiO₃ interface by carrier localization, arising from the defects created by the ion beam exposure, eventually producing an insulating ground state. This process of ion-beam-induced defect creation results in structural changes in SrTiO₃ as revealed by the appearance of first-order polar TO₂ and TO₄ vibrational modes which are associated with Ti—O bonds in the Raman spectra of the irradiated samples. Furthermore, significant observation drawn from the magnetotransport measurements is that the irradiated (unirradiated) samples showed a negative (positive) magnetoresistance along with simultaneous emergence of first-order (only second order) Raman modes. In spectroscopic ellipsometry measurements, the optical conductivity features of the irradiated interface are broadened because of the localization effects, along with a decrease of spectral weight from 4.2 to 5.4 eV. These experiments allow us to conclude that the interface ground state (metallic/insulating) at the LaAlO₃/SrTiO₃ can be controlled by tailoring the defect structure of the SrTiO₃ with ion beam exposure. A resist-free, single-step direct patterning of a conducting LaAlO₃/SrTiO₃ interface has been demonstrated. Patterns with a spatial resolution of 5 μm have been fabricated using a stencil mask, while nanometer scale patterns may be possible with direct focused ion beam writing.
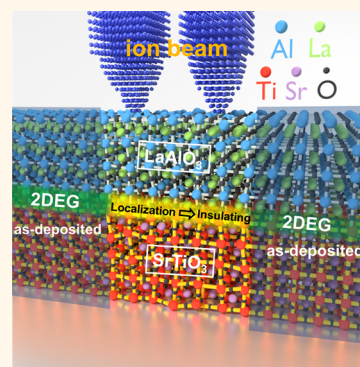
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The two-dimensional electron gas (2DEG) formed at the interface between two insulators LaAlO₃ (LAO) and SrTiO₃ (STO) is one of the most fascinating systems in the field of oxide electronics.[1] This interface 2DEG is shown to host novel phenomena such as superconductivity,[2] magnetism,[3−6] tunable metal—insulator ground state,[7,8] strong spin—orbit coupling,[9,10] and crystallographic anisotropy.[11] Further, unconventional interfacial superconductivity along with magnetic order has been proposed in one-dimensional electron gas formed at this interface.[12] Room-temperature electronic devices,[7,8] sensors, and nanophotodetectors[13,14] have

been demonstrated in these interfaces. Very recently, scaling violation of fundamental Ohm's law have been reported in this material system when the 2DEG is confined to nano dimensions.[15] The above device concepts have been realized by reducing the dimensionality of 2DEG at this interface. Lithography with multiple steps such as resist coating, beam exposure, hard mask of amorphous LaAlO₃ or AlOₓ deposition and etching, or surface engineering of SrTiO₃, combined with pulsed laser deposition (PLD) were utilized for patterning LaAlO₃/SrTiO₃.[16−18] Nanostructures of interface 2DEG were also achieved by writing charges

using conducting atomic force microscopy.[8] However, in all these approaches either the presence of residual hard mask in the film along with the number of sophisticated process steps, or the stability of the pattern in ambient conditions is an issue of concern. Lithography along with reactive ion etching (RIE) has been used extensively to fabricate controlled structures of various materials. However, heavy ions present in the commonly used RIE plasma transforms insulating $SrTiO_3$ to a conductor.[19] Thus, RIE cannot be applied in patterning oxide interfaces such as $LaAlO_3/SrTiO_3$. To achieve high quality devices and also to investigate the above-mentioned exotic phases from these unique interfaces, a reliable and simple patterning process is essential, but has not yet been realized. The important factor in patterning these conducting interfaces is to create a spatially insulating state. In this report, we demonstrate a novel way to create an insulating state and also to tailor the conductivity of the 2DEG at the $LaAlO_3/SrTiO_3$ interface using an ion beam exposure-based single-step strategy.

In recent years, ion beam exposure has emerged as a novel way to tailor the structural, mechanical, electronic, and even magnetic properties of materials by inducing atomic defects in a controlled manner.[20−23] Recent experiments with ion/electron beam exposure to various nanomaterials and devices have proven to create beneficial effects in providing devices with desired functionalities,[21,24,25] which has further found applications in nanoelectronics,[20−25] energy,[21] nanobiotechnology, etc.[26] Ion irradiation of oxide materials has been utilized for both device fabrication and material modification.[21,27] In particular, energetic proton beams were found to be most useful for pattering and device fabrication.[28,29] Very recently, coupled wave guides on a silicon-on-insulator platform have been fabricated by combining electrochemical etching with proton irradiation of a few tens of keV energy,[30] while low energy (less than 1 keV) ions were found to be useful in the patterning of complex magnetic nanoparticles to nanoscale dimensions.[31] Significantly, in a recent report, Hong et al.[32] reported the tunability of the electronic characteristics of ZnO field effect transistors by proton beam irradiation (few tens of MeV), which further enhanced the potential use of high energy proton irradiation for tailoring the material properties.

In this study, $LaAlO_3/SrTiO_3(100)$ interfaces were exposed to a 2 MeV proton beam, and the electrical transport, vibrational and optical properties of the samples were investigated as a function of ion fluence. We found that the metallic behavior of the 2DEG changes significantly with proton beam exposure, at a fluence of 2×10^{17} ions·cm^{-2} strong localization appeared in the 2DEG, and eventually at a fluence of 6×10^{17} ions·cm^{-2} the interface became insulating. This process of metal to insulator transition occurs through localization of mobile electrons via ion-induced defects, which results in structural changes in $SrTiO_3$ as revealed by Raman spectroscopy. Raman spectra showed the appearance of first-order modes of $SrTiO_3$, which indicate the presence of polar regions in the irradiated samples. Spectroscopic ellipsometry analysis of the ion exposed samples displays the appearance of increased scattering centers at the interface compared to the as-deposited case. The creation of a spatially selective insulating ground state by tuning the process parameters of an energetic ion beam-based single-step approach enable us to both pattern and also tune the electronic properties of the 2DEG.

RESULTS AND DISCUSSION

The $LaAlO_3/SrTiO_3(100)$ samples were prepared by pulsed laser deposition by ablating a $LaAlO_3$ target onto TiO_2 terminated $SrTiO_3(100)$ substrates. Samples were prepared in a range of oxygen pressure (PO$_2$) of $1-5 \times 10^{-3}$ Torr at 750 °C. Proton irradiation experiments and measurements were performed on the eight unit cells of $LaAlO_3$ on $SrTiO_3$ [(8 uc)$LaAlO_3/SrTiO_3$] sample deposited at PO$_2$ of 1×10^{-3} Torr. To make a systematic comparison, ion irradiation experiments were carried out as a function of ion fluence on a single $LaAlO_3/SrTiO_3$ sample (5 × 5 mm^2) consisting of four identical sections (2 × 2 mm^2) that are electrically isolated from each other (see Experimental Methods for details). Three out of the four sections of the same sample were exposed to proton beam, and the fourth region was kept unirradiated (defined as "as-deposited" in the following discussions). The ion fluences used were 1×10^{15}, 1×10^{16}, and 2×10^{17} ions·cm^{-2}, respectively. The details of the sample preparation are given in Supporting Information S1.

The electrical transport properties of the as-deposited and irradiated (8 uc)$LaAlO_3/SrTiO_3$ sections of the same sample were analyzed. The temperature dependence of the resistance $R(T)$ for the as-deposited and irradiated sections is shown in Figure 1a. The as-deposited section of the sample exhibits a typical metallic behavior similar to the conventional $LaAlO_3/SrTiO_3$ interfaces at this 8 uc $LaAlO_3$ thickness,[33−35] whereas for the irradiated sections, a gradual change in the resistance at 300 K is observed with ion fluence. As the proton fluence is increased, clear localization behavior in transport starts to emerge at low temperatures with the signature of increase in base resistance at 2 K. The resistance of the sample section irradiated with 2×10^{17} ions·cm^{-2} became 0.1 MΩ at 2 K and the resistance minimum in the $R(T)$ curve is found to shift towards higher temperature with an increase in ion fluence. The above $R(T)$ behavior gives adequate indication that ion exposure effects have created a high resistive state for the 2DEG through localization of the mobile electrons. The drastic upturns
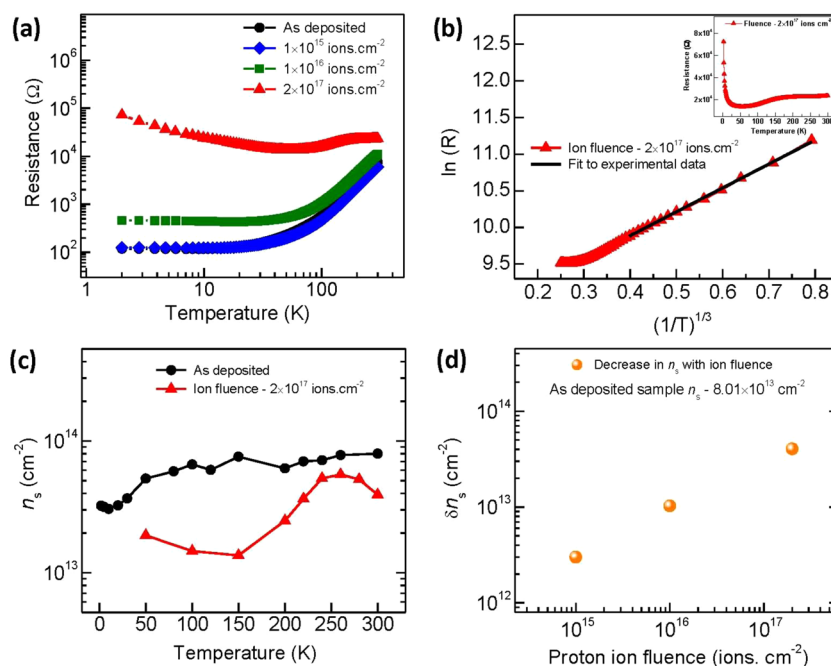
Figure 1. Electrical transport data of as-deposited and 2 MeV proton-beam-exposed (8 uc)LaAlO$_3$/SrTiO$_3$ sample sections. (a) Temperature-dependent resistance of as-deposited and ion beam exposed sample sections at different proton fluences. (b) Variable range hopping fit to transport data of ion irradiated with 2×10^{17} ions·cm^{-2} fluence; inset shows the nonsaturating behavior of the corresponding sample section. (c) Temperature dependence of carrier density (n_s) of as-deposited and ion-irradiated sample at a fluence of 2×10^{17} ions·cm^{-2}. (d) Reduction in carrier density δn_s with ion fluence at 300 K; here δn_s is defined as the difference in n_s of as-deposited and irradiated sample sections (($\delta n_s = n_{s(\text{as-deposited})} - n_{s(\text{irradiated})}$).

in resistance toward low temperatures would be expected in transport mechanisms such as variable range hopping (VRH) in a strong localization regime or a magnetic Kondo scattering, which operates at this interface.[3,35] The $R(T)$ curve for the case of 2×10^{17} ions·cm^{-2} does not show any saturation even up to 2 K (inset of Figure 1b) inferring that Kondo scattering may not be the governing mechanism. The low temperature resistance behavior is further analyzed to the VRH mechanism: in the VRH regime R follows a $(1/T)^{1/n+1}$ (n = dimensionality of the system) dependence. A VRH fitting (with $n = 2$) of the experimental data for a fluence of 2×10^{17} ions·cm^{-2} case is shown in Figure 2b, and a clear $(1/T)^{1/3}$ dependence is observed below 30 K. The 2D nature of the VRH mechanism is further confirmed using a self-consistent analysis (Supporting Information S2). The hopping radius is estimated (Supporting Information S2) to be about 14−30 nm, which is relatively larger than the typical dimensionality (5−10 nm) of the 2DEG. Thus, the hopping mechanism must be most likely 2D in nature.

The other important quantity that can give further insight to the localization behavior is the carrier density (n_s). The n_s for as-deposited and each irradiated section of (8 uc)LaAlO$_3$/SrTiO$_3$ sample were extracted from Hall effect measurements. Figure 1c shows the temperature dependence of the n_s for the as-deposited and irradiated at a fluence of 2×10^{17} ions·cm^{-2}. The n_s for the as-deposited section of the sample is about 8×10^{13} cm^{-2} at 300 K. In comparison, the irradiated

section shows a significant decrease in n_s with about 4×10^{13} cm^{-2} at 300 K. The as-deposited and irradiated samples show similar temperature dependence of carrier density. The percentage change in both cases is of the same order. However, in the irradiated case the defects created can trap the charges and decrease the effective mobile electrons and enhance the localization. Figure 1d shows the decrease in carrier density (δn_s) with proton fluence at 300 K. Here δn_s is defined as the difference in the n_s of as-deposited and n_s of irradiated sections ($\delta n_s = n_{s(\text{as-deposited})} - n_{s(\text{irradiated})}$). From Figure 1d it is clear that δn_s increases with the proton fluence, and at fluence of 2×10^{17} ions·cm^{-2} δn_s became 4×10^{13} cm^{-2}. The above data clearly indicate that the proton beam exposure with a fluence of 2×10^{17} ions·cm^{-2} can reduce as many as 3−4 $\times$ 10^{13} cm^{-2} mobile carriers of the 2DEG at the interface, which is most possibly accomplished by localization of carriers within the lattice of SrTiO$_3$. From the above conclusion one can expect that the interface samples having initial $n_s \leq 4 \times 10^{13}$ cm^{-2} become insulating at these ion fluences because of the complete localization of carriers. In order to validate this possibility, a conducting LaAlO$_3$/SrTiO$_3$ sample having an initial carrier density of 1.9×10^{13} cm^{-2} (achieved by controlling the oxygen pressure during the growth) has turned to became insulating with the exposure of proton beam at a fluence of 2×10^{17} ions·cm^{-2} (see Supporting Information S3). A table showing the decrease of carrier density with ion irradiation on various samples is given in Supporting Information S1.
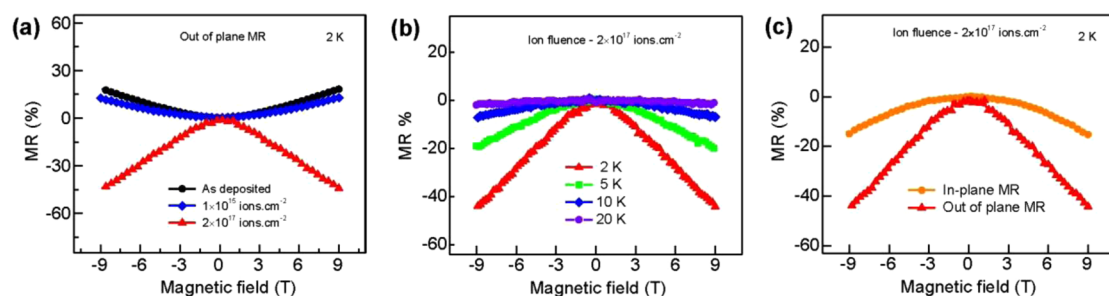
Figure 2. Magnetoresistance (MR) of the (8 uc)LaAlO$_3$/SrTiO$_3$ sample sections with different proton fluences: (a) out of plane MR at 2 K, (b) out of plane MR at 2, 5, 10, and 20 K, and (c) in-plane and out of plane MR for the sample section irradiated with 2×10^{17} ions·cm^{-2}.

To evaluate the localized transport behavior at low temperature in the above ion exposed samples, a detailed magnetoresistance (MR) study was carried out. MR is a useful tool to investigate the transport mechanisms such as localization and magnetic scattering. MR measurements were performed in in-plane and out of plane modes. Figure 2a shows the out of plane MR (magnetic field H perpendicular to the interface) measured for different ion fluences and as-deposited sections at 2 K with H up to 9 T. Both as-deposited and low fluence (1×10^{15} ions·cm^{-2}) sections display a positive MR behavior. The positive MR is a characteristic of orbital scattering in the presence of a magnetic field due to the change in electron transit paths. On the other hand the section exposed with 2×10^{17} ions·cm^{-2} fluence shows a negative MR behavior. Comparison of the MR with respect to ion fluence infers that the MR slowly changes sign from positive to negative with increasing ion fluence. The large negative and nonsaturating MR observed in the irradiated case is an additional indication of the localization behavior discussed earlier (in Figure 1). The electron transport in the strongly localized regime can exhibit a negative MR, which is a consequence of the magnetic field disrupting the self-interference of the electrons undergoing localization. The temperature dependence of the out of plane MR measured for a fluence of 2×10^{17} ions·cm^{-2} is shown in Figure 2b. The magnitude of MR gradually decreases with increase in temperature, which can be understood as the effect of enhanced thermal fluctuations in the scattering process. Figure 2c shows the comparison of in-plane (H applied parallel to the interface) and out of plane MR for the 2×10^{17} ions·cm^{-2} case where both display a negative MR, however with a difference in MR magnitude. The orbital scattering is excluded in this in-plane geometry due to the absence of Lorenz forces on carriers. This MR dependence is consistent with the previous reports.[35]

The detailed electron transport and MR analysis discussed above clearly indicates a dependence on ion fluence for carrier localization and point towards the possibility of creating insulating regions in 2DEG. It is known that the 2DEG is accumulated on the Ti orbitals of SrTiO$_3$ for LaAlO$_3$/SrTiO$_3$ interfaces.[36] Since the ion irradiation produces dramatic changes in the transport of the 2DEG that resides in SrTiO$_3$, it is necessary to understand the effects of ion irradiation on SrTiO$_3$. Recent reports on SrTiO$_3$-based interfaces reveal that an atomic distortion of the SrTiO$_3$ lattice and defects in SrTiO$_3$ at the interface can manipulate the transport properties of 2DEG significantly.[37−41] The ion beam exposure process is expected to influence the structural and electronic properties of the material by inducing atomic defects. In order to investigate the ion irradiation effects on structural and electronic properties of the LaAlO$_3$/SrTiO$_3$ samples, Raman spectroscopy and spectroscopic ellipsometry experiments were carried out.

The nature of the induced defects and resultant possible microscopic structural changes in LaAlO$_3$/SrTiO$_3$ samples due to ion irradiation can be gained using Raman spectroscopy, which was performed on as-deposited and irradiated sections of the sample. The probing depth of Raman scattering signal was 2 μm from the top surface of the sample. Since the thickness of LaAlO$_3$ is 8 uc (3.2 nm) and also the interference enhancement of the Raman signal is negligible in this system, the Raman spectrum of the sample is dominated by the modes from the substrate SrTiO$_3$. SrTiO$_3$ at room temperature has an ideal cubic perovskite structure with a space group $Pm3m$ (O_h^1).[42] There are five atoms per unit cell, each of which is located at a point of inversion symmetry. The optical phonons in the cubic phase are of odd parity, which accounts for the absence of first-order Raman scattering in SrTiO$_3$ single crystals.[43−45] Even though the first-order modes are Raman inactive, SrTiO$_3$ shows a Raman spectrum with broad peaks that arise from higher-order modes which involve the creation or destruction of two or more first-order modes. Raman spectra for the irradiated and as-deposited sections of the sample are shown in Figure 3. As expected, the spectra are dominated by SrTiO$_3$ modes. In the spectrum of the as-deposited case, broad second-order peaks are clearly visible at 75, 200−500, and 600−800 cm^{-1}. Significantly, for the ion beam exposed portions, additional peaks emerge at 175, 540, and 795 cm^{-1} along with

increasing fluence (additional peak positions are indicated with dotted lines). These peaks are identified as symmetry-forbidden first-order modes arising from transverse optic TO_2, TO_4, and longitudinal optic LO_1, LO_4 phonons as indicated in Figure 3.[46−48] The appearance of first-order modes in the irradiated sections of the sample clearly indicates a lowering of crystal symmetry for the $SrTiO_3$ and thus the loss of the inversion center.[46−48] First-order Raman scattering has been observed in thin films, nanostructures of $SrTiO_3$, and also single crystals with lifted center-of-symmetry by the application of an external electric field.[46−49] The line shape of the TO_2 peak is strongly asymmetric; i.e., the scattering intensity increases at the high-energy side and is depressed at the low-energy side of the peak- and displays a Fano profile. The Fano effect occurs whenever discrete excitations and a broad continuum interfere coherently.[46−48] We speculate that the ion damaged regions in $SrTiO_3$ result
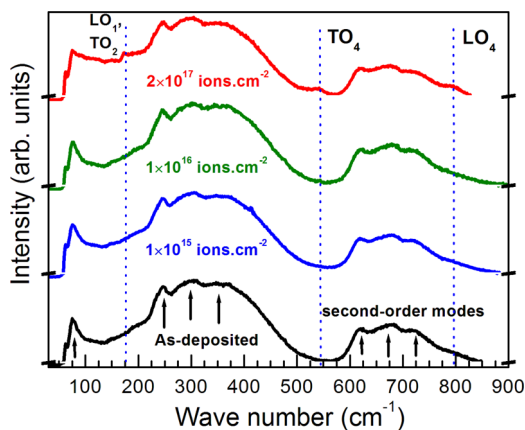
in a polar material with a continuum that interacts with the polar TO phonons. Such asymmetric line shapes have been observed for polar TO_2 modes in $SrTiO_3$ thin films and have been ascribed to the interaction of the phonon with a continuum arising from rapid polarization fluctuations.[46−48] Although TO_4 is also a polar phonon, its energy is much higher, the density of states for continuum most likely vanishes at this frequency, and thus, Fano asymmetry has not been observed in the case TO_4 mode.[47] The origin of the TO_2 and TO_4 modes is associated with Ti−O bonding in the $SrTiO_3$.[46−48] In our recent report on $LaAlO_3/SrTiO_3(110)$ interfaces it is shown that the electron transport of the 2DEG is highly anisotropic,[11] and it is critically linked to the Ti−O crystallographic arrangement, which further emphasizes the significance of this Ti−O bonding. Raman spectra analysis of an irradiated bare STO substrate has also shown the appearance of first-order modes, which supports the above discussion (Supporting Information S4).

To further understand the effects of the irradiation on the electronic band structure of the $LaAlO_3/SrTiO_3$ interface, spectroscopic ellipsometry measurements were performed on pristine and ion exposed (fluence of 2×10^{17} ions·cm^{-2}) portions of the substrate $SrTiO_3$ and 8 uc $LaAlO_3/SrTiO_3$ sample. Figure 4a,b shows the complex dielectric function $\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega)$ of the samples as extracted from the ellipsometry data as a function of incident photon energy ω. The details of the data analysis is given in Supporting Information S5. From Figure 4b, it can be seen that the ε_2 spectra of both $SrTiO_3$ and the $LaAlO_3/SrTiO_3$ interface have two main peaks centered at 4.2 and 5.0 eV, respectively. These two peaks are assigned to the optical transition from O-2p state (the valence band) to Ti-3d-t_{2g} state (the conduction band).[50−52] The peak at 4.2 eV arises
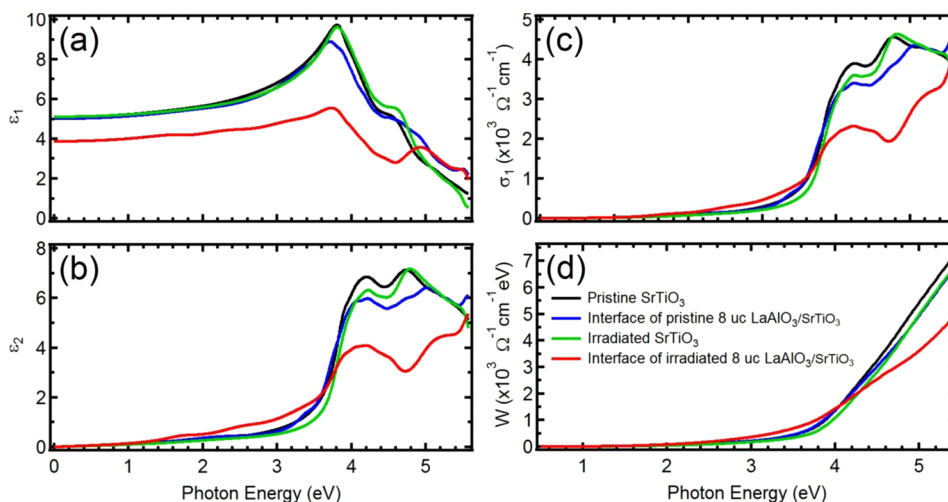

Figure 3. Raman spectra of as-deposited and proton-beam-exposed sample sections of (8 uc)$LaAlO_3/SrTiO_3$.

Figure 4. Complex dielectric function, optical conductivity, and spectral weight of pristine $SrTiO_3$, irradiated $SrTiO_3$, pristine (8 uc)$LaAlO_3/SrTiO_3$ and irradiated (8 uc)$LaAlO_3/SrTiO_3$ as extracted from the spectroscopic ellipsometry data. The irradiated sample mentioned above corresponds to 2 MeV protons at a fluence of 2×10^{17} ions·cm^{-2}. (a) Real part of dielectric function ε_1. (b) Imaginary part of dielectric function ε_2. (c) Optical conductivity σ_1. (d) Spectral weight W.

from the transition at the center of the Brillouin zone (Γ-point) of $SrTiO_3$, while the peak at 5.0 eV is due to the transition at the M-point of $SrTiO_3$. Thus, by analyzing the differences of $\varepsilon(\omega)$ between the as-deposited and irradiated portions, one can study the effect of ion beam exposure on the band structure around the O-2p and Ti-3d-t_{2g} states of $LaAlO_3/SrTiO_3$. From Figure 4a,b the $\varepsilon(\omega)$ of irradiated $LaAlO_3/SrTiO_3$ portion changes dramatically in comparison with the bare STO and as-deposited $LaAlO_3/SrTiO_3$ portion. For ε_2, the overall shape of the features between 0.5−5.4 eV is broadened; ε_2 decreases between 3.6−5.4 eV (*i.e.*, around the two peak centers), while it increases below 3.6 eV (*i.e.*, the peak tail region). According to the Drude−Lorentz model of the dielectric function used to fit the ellipsometry data (Supporting Information S5), the peak line width is controlled by the scattering rate parameter $\Gamma_k \sim 1/\tau$, where τ is the electron relaxation time. In this case, the peak broadening suggests an increase of Γ_k and correspondingly a decrease in τ. The decrease of τ indicates that the irradiated interface contains more scattering centers that can impede the motion of the electrons and thus point toward the presence of increased localization effects at the interface. Another important point is the fact that the M-point peak shifts into higher energy, from 5 to 5.3 eV from ε_2 plot in (b), which means that the irradiation also changes the band structure by further separating the valence band and the conduction band at the M-point. We have analyzed the second derivatives of $\varepsilon(\omega)$ to identify the van Hove singularities of the $LaAlO_3/SrTiO_3$ interface and thus distinguish the various optical interband transitions from the highest valence bands to the lowest conduction bands at various regions in the Brillouin zone.[53] The above analysis given in the Supporting Information S5 also supports this observation of the shift of the M point to higher energy. Furthermore, the overall intensity ε_1 of the irradiated $LaAlO_3/SrTiO_3$ interface is also found to be decreased compared to that of as-deposited $LaAlO_3/SrTiO_3$ interface.

The optical conductivity $\sigma_1(\omega) = \varepsilon_0 \varepsilon_2(\omega)\omega$ of the samples were calculated from the $\varepsilon(\omega)$ data and is shown in Figure 4c. The analysis of σ_1 is linked to the effective number of electrons excited by the photon, n_{eff}, *via* the f-sum rule[54]

$$\int_0^\infty \sigma_1(\omega)\, d\omega = \frac{he^2}{4mV} n_{\text{eff}} \qquad (1)$$

where e is the elementary charge, m is the electron mass, and V is the volume of the unit cell. Thus, by integrating σ_1 over a particular energy range (in this case 0.5−5.4 eV) the partial spectral weight W can be obtained, which is related to the total number of electrons being excited in that particular energy range. Figure 4d shows the W of each sample. From the plots it can be seen that the spectral weight at 5.4 eV (*i.e.*, the

measurement limit) of the irradiated $LaAlO_3/SrTiO_3$ interface is much less than the as-deposited $LaAlO_3/SrTiO_3$ interface. A more detailed quantitative analysis of W (Supporting Information S5) reveals that the number of charges related to the 5 eV transition in the irradiated $LaAlO_3/SrTiO_3$ interface is decreased by as much as ∼0.4e. However, it should be noted that this decrease may also be due to charge transfer into higher energy regions, which requires high-energy optical spectroscopy data.[55]

The conductivity of the same $LaAlO_3/SrTiO_3$ sample measured before and after irradiation showed an increase in 2DEG resistance with fluence. In a separate experiment, a $SrTiO_3$ substrate irradiated with a fluence of 2×10^{17} ions·cm^{-2} did not show any change in the insulating nature of the $SrTiO_3$ within the sensitivity of our measurements (10^8 ohms). This confirms that the current irradiation experiments do not simply create oxygen vacancies alone, but also generate compensating cationic vacancies, and at higher fluences other defect complexes that can trap charges efficiently. This is a benefit as the low Z ion beam will not produce a parallel conducting path in the $SrTiO_3$ as in the cases with low energy heavy ion irradiations.[19]

To explore the patterning capability of the interface using ion beam exposure technique, a sample of (8 uc)$LaAlO_3/SrTiO_3$ was grown under identical conditions and selectively exposed with 2 MeV protons in two regions (500 μm width and 2 mm in length) at fluences of 2×10^{17} and 6×10^{17} ions·cm^{-2}. Thus we have a (8 uc)$LaAlO_3/SrTiO_3$ sample encompassing two ion-irradiated rectangular sections with a pristine portion as shown in Figure 5a. Raman spectroscopy and imaging and electrical transport measurements were carried out on this sample. As shown in the Figure 5b the Raman spectrum displays similar behavior as in the previous case. The intensity of the polar modes was found to increase with ion fluence and is strongly reflected in the observation of a stronger intensity profile for the polar mode peaks in the spectrum. Furthermore, a Raman spectroscopy image produced using the integrated intensity of TO$_4$ mode at 540 cm^{-1} of the irradiated sample is shown in Figure 5c. The as-deposited and the irradiated regions at a fluence of 2×10^{17} and 6×10^{17} ions·cm^{-2} are clearly distinguishable in the intensity profile. Here for the as-deposited section (with an electrically conducting state, Figure 5d) the signal from the TO$_4$ mode is absent. However, the patterned line with 2×10^{17} ions·cm^{-2} (exhibiting strong localization, Figure 5(e)) shows a significant intensity of the TO$_4$ mode, indicating the emergence of structural changes in $SrTiO_3$ at this fluence. The highest intensity of the TO$_4$ mode is observed for the 6×10^{17} ions·cm^{-2} irradiated part and which is found to be electrically insulating. Raman imaging thus allows an indirect mapping of the interface conductivity of the ion-beam patterned $LaAlO_3/SrTiO_3$ system.
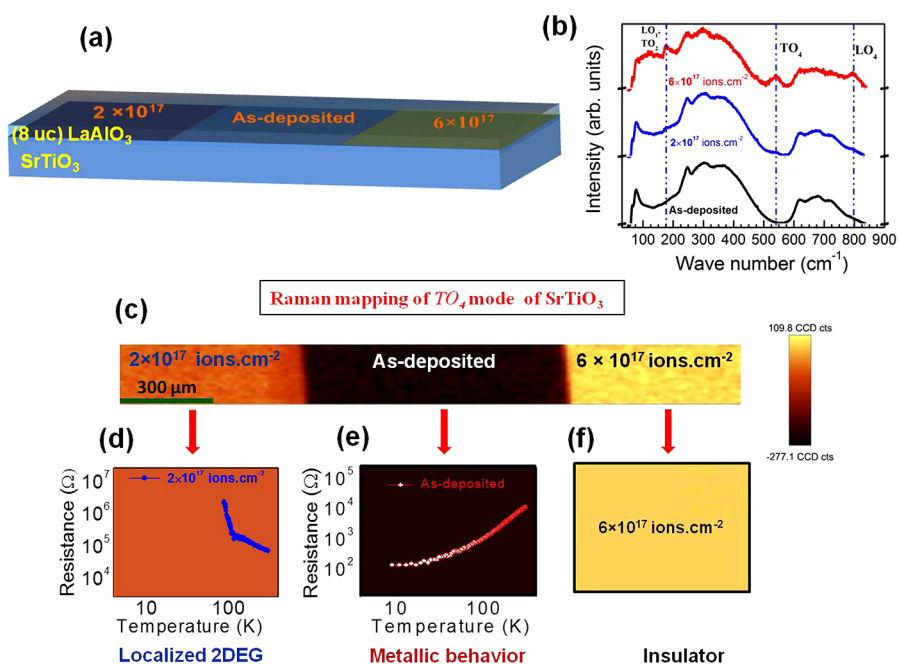
Figure 5. (a) A schematic representation of the ion-irradiated sample: lines having width 500 μm and length 2 mm made with different proton fluences on a (8 uc)LaAlO$_3$/SrTiO$_3$ sample. (b) Raman spectra obtained from the as-deposited and ion-beam-exposed at fluences of 2×10^{17} and 6×10^{17} ions·cm^{-2} in the rectangular sample regions. (c) Raman image created from the integrated intensity of the TO$_4$ mode at 540 cm^{-1} for as-deposited as well as patterned lines of LaAlO$_3$/SrTiO$_3$ sample sections. Temperature-dependent resistance of the corresponding patterned lines with (d) 2×10^{17} ions·cm^{-2} (strong localization), (e) as-deposited (metallic behavior), and (f) 6×10^{17} ions·cm^{-2} (insulator).

This clearly indicates the potential of this method to fabricate insulating regions in conducting LaAlO$_3$/SrTiO$_3$ samples. In addition, this also reveals the ability to tune the conductivity by simply adjusting the ion fluence.

An estimate of the defects created by the proton beam can be determined from Monte Carlo simulations (SRIM 2008)[56] using full damage cascade. Oxygen ions being the lightest in the SrTiO$_3$ lattice have maximum displacements compared to Ti and Sr under irradiation by energetic ions. If oxygen vacancies were the dominant defects in the MeV proton irradiated SrTiO$_3$, one would expect a reduction in resistance for the irradiated SrTiO$_3$ as observed by Kan et al.[19] The displacement per atom (dpa) for Sr and Ti is found to be half that of oxygen.[56] The oxidation states of O, Ti, and Sr in SrTiO$_3$ are -2, $+4$, and $+2$, respectively. Thus the cationic and anionic vacancies will have different charges. The ion range of the 2 MeV proton in (8 uc)LaAlO$_3$/SrTiO$_3$ sample is about 27 μm. The oxygen vacancies estimated at the surface is $\sim 10^{20}$ cm^{-3} and at the end of range it is about $\sim 10^{21}$ cm^{-3} at an ion fluence of 6×10^{17} ions·cm^{-2}. The sputtering yield of oxygen at the LaAlO$_3$ surface is 10^{-4} atoms/ion, which gives the fraction of oxygen atoms sputtered from the LAO surface is less than 0.2% at a fluence of 6×10^{17} ions·cm^{-2}. For SRIM simulations sample is treated as an amorphous matrix with homogeneous mass density, and the ion kinetic energy is transferred ballistically to the target atom. The above calculated values are an overestimate because the crystalline nature (ion

channeling) and the annealing of the defects have not been incorporated in this simulation.[21]

To investigate the elemental redistribution across the interface and probe the crystalline quality of the irradiated LaAlO$_3$/SrTiO$_3$ sample, we have performed high resolution Rutherford back scattering (HRRBS) on as-deposited and irradiated sample at a fluence of 6×10^{17} ions·cm^{-2} (details are given in Supporting Information S6). The analysis of HRRBS indicates that the irradiation effects on La redistribution and the variations in stoichiometry were very small and beyond the detection limit of HRRBS, which is about 4 Å. X-ray diffraction measurements (data not given here) on the above samples had shown broadening of SrTiO$_3$(200) peak, and the LaAlO$_3$(100) and (200) peaks were clearly visible in the spectra. Estimating the microscopic structural perturbations of the LaAlO$_3$ layer (top 3.2 nm in our samples) require techniques such as extended X-ray absorption fine structure (EXAFS).

Furthermore, to show the patterning capability for device applications, ion irradiation was carried out with the optimized parameters (fluence of 6×10^{17} ions·cm^{-2} for 2 MeV protons) on a LaAlO$_3$/SrTiO$_3$ sample covered by a stencil mask, which is thick enough to stop the ion beam to create spatially selective insulating regions at the interface 2DEG. Figure 6a shows a scanning electron microscopy (SEM) image of the patterned LaAlO$_3$/SrTiO$_3$ sample using a metal stencil mask (made from 0.5 mm thick brass) with a Hall bar geometry (channel width $\sim$150 μm). The Hall bar

(a)

250 μm

(b)
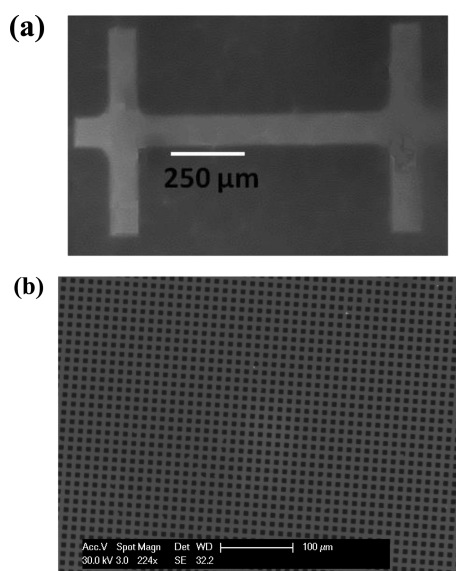
Acc.V Spot Magn Det WD |——————| 100 μm
30.0 kV 3.0 224x SE 32.2

Figure 6. (a) Scanning electron microscopy (SEM) images of the patterned LaAlO$_3$/SrTiO$_3$ sample using (a) 2 MeV proton beams at a fluence of 6×10^{17} ions·cm^{-2} with a hard mask of Hall bar geometry, (b) 500 keV helium ions at a fluence of 1×10^{16} ions·cm^{-2} with a mask (made of gold) of size 5 μm.

structure is found to be transferred to the sample with the expected dimensions. Significantly, the SEM image shows the contrast between the irradiated and as-deposited sections. The contrast for the secondary electrons at the conducting (as deposited) and insulating (irradiated) regimes is due to the difference in the number of secondary electrons reaching the Everhart—Thornley detector used in the SEM. We have also explored low energy helium ion irradiations (500 keV He) to create localization and insulating state in conducting LaAlO$_3$/SrTiO$_3$ interfaces as discussed earlier. An insulating state is found to be created at a fluence of 1×10^{16} ions·cm^{-2} and strong localization at 1×10^{15} ions·cm^{-2} in the case of helium ions (Supporting Information S7). A pattern was formed using a mask made of gold with 500 keV helium ion irradiation, and the corresponding image is shown in Figure 6b. Here, the 5 μm conducting regions (the bright contrast), which are clearly visible in SEM micrographs, demonstrate the capability to pattern the interface down to lower dimensions. With the development of helium ion microscope with focused ion beams having spatial resolutions of sub-0.5 nm, direct patterning of fine conducting lines may be possible on the nm scale. This demonstrates the ability to pattern the LaAlO$_3$/SrTiO$_3$ interfaces using low Z-ions without any intermediate deposition or etching techniques that were previously employed.

CONCLUSIONS

A resist-free, single-step direct patterning of the conducting oxide interface in LaAlO$_3$/SrTiO$_3$ utilizing energetic ion beam exposure has been demonstrated. It is shown that this method is tunable to engineer the conductivity of the two-dimensional electron gas at the LaAlO$_3$/SrTiO$_3$ interface by inducing localizations *via* defects, as evidenced by electrical transport, Raman spectroscopy, and spectroscopic ellipsometric measurements. The spectroscopic studies reveal that the induced defects/distortions in the SrTiO$_3$ lattice can significantly manipulate the electrical ground state of the 2DEG in these systems. The further practical advantage of such low Z ion beam exposure is the elimination of undesired ion-beam-induced substrate conductivity (as seen with Ar ions), thus allowing us to custom-tailor the 2DEG formed at the oxide interface. Considering the limits of conventional lithography to pattern these interfaces due to the buried nature of the 2DEG, this new strategy may open up a novel way to pattern the conducting oxide interfaces whose properties are sensitive to the metal—oxygen bonds and the local crystal structure.

EXPERIMENTAL METHODS

Sample Preparation and Electrical Characterization. Ion irradiation was carried out using a 3.5 MV Singletron accelerator at the Center for Ion Beam Applications at the National University of Singapore. A collimated ion beam was used to raster-scan under normal incidence with a current density of 50 nA/mm^2 for protons and 10 nA/mm^2 for Helium ions. The pressure in the chamber during the irradiation was 1×10^{-6} mbar. To produce a sample with four isolated equal sections, cross lines were made on the square SrTiO$_3$ substrate surface with a diamond cutter. Then, a LaAlO$_3$ film of 8 uc was deposited on to the partitioned SrTiO$_3$ substrate. Each section of the deposited LaAlO$_3$/SrTiO$_3$ sample had shown a conducting behavior, and the absence of conductivity between any two sections indicates good electrical isolation. The details of the sample preparation are given in Supporting Information S1. The electrical connections to the interface were made by Al wire bonding to the interface. The Al wire penetrates into the sample from the top surface and makes the connection across the interface that enables us to probe the LaAlO$_3$/SrTiO$_3$ interface conductivity. Hall measurements were performed to extract the carrier density in these samples with ±1.5 T, and the results fit well to a single carrier model in this low field regime.

Raman Spectroscopy. Visible Raman spectroscopy was carried out at room temperature using Renishaw Invia Raman system. The excitation wavelength used was 532 nm, and the laser power at the sample was below 1.0 mW/cm^2 to avoid any laser-induced damage. A 50× objective lens was used with a laser spot size of ~1 μm, and the scattered light from the sample was collected in the back scattering geometry. Raman imaging was carried out using WITec ALPHA300RAS system using 532 nm excitation wavelength with a motorized stage.

Spectroscopic Ellipsometry. The spectroscopic ellipsometry measurements were performed in the spectral range between 0.5 and 5.4 eV by using a Sentech SE 850 ellipsometer at room temperature. The incident angle was set at 70° from the sample normal, and the incident light was linearly polarized and 45° from the plane of incidence. Specially designed lenses were used to focus the incoming light to achieve a beam spot size of ~500 μm. The analysis method to extract the complex dielectric function of the materials from the raw spectroscopic ellipsometry data is explained in the Supporting Information S5.

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