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X-ray writing of metallic conductivity and oxygen vacancies at silicon/SrTiO₃ interfaces.

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Abstract

Tunable electronic properties of transition metal oxides and their interfaces offer remarkable functionalities for future devices. The interest of these materials has been boosted with the discovery of a two-dimensional electron gas (2DEG) at SrTiO₃-based interfaces. For the majority of these systems, oxygen vacancies play a crucial role in the emergence of interface conductivity, ferromagnetism, and high electron mobility. Despite its great importance, controlling the density and spatial distribution of oxygen vacancies in a dynamic way remains extremely challenging. The full potential of these systems can be achieved by stabilization of well-controlled metallic state over large areas and under ambient conditions. Here, we report lithography-like writing of a metallic state at the interface between SrTiO₃ and amorphous Si using X-ray irradiation. Using a combination of transport techniques and *in operando* photoemission spectroscopy, we reveal in real time that the X-ray radiation induces a transfer of oxygen across the interface leading to the on-demand formation of oxygen vacancies and a 2DEG in STO. The formed 2DEG stays stable in ambient conditions as the interface oxygen vacancies are stabilized by the capping of Si. Our study provides a fundamental understanding of X-ray induced redox reactions at the SrTiO₃-based interfaces and in addition show a potential of X-ray radiation for patterning stabile conductive pathways for future oxide-based electronic devices.

Introduction

Like silicon for the conventional electronic and semiconductor applications, STO is the workhorse in oxide electronics and thin-films growth technologies. The discovery of a high mobility two-dimensional electron gas (2DEG) at the $\text{LaAlO}_3/\text{SrTiO}_3$ (LAO/STO) interface has opened new perspectives for STO functionality. This finding has triggered intensive research on the STO-based heterostructure leading to the discovery of oftentimes coexisting phenomena including superconductivity,^[1-4] magnetism,^[5-7] resistance switching,^[8] and giant thermoelectric effect.^[9] However, from the perspective of electronic devices, the key issue is still to design cheap, and easy-tunable metallic interface stable at ambient conditions, which can be prepared on the large area.

The 2DEG can be induced by an electronic reconstruction induced by capping STO with a polar film, as in the case of LAO films on (001)-oriented STO.^[10,11] In the wake of the LAO/STO discovery, analogous STO-based systems displaying similar properties to LAO/STO were realized, including bare STO surfaces.^[12-18] Later on, formation of 2DEG has been realized by capping STO substrate with non-polar amorphous LAO, STO and yttria-stabilized zirconia.^[12,19,20] However, this approach requires the use of techniques, such as pulsed laser deposition or molecular beam epitaxy, which are expensive to be implemented on industrial scales. Despite that, previous studies showed that the atomic layer deposition method has already been used to create all-oxide transistors with outstanding high-frequency characteristics.^[21] A simpler approach to form the 2DEG was realized by capping the STO surface with metals such as an amorphous aluminum (Al) layer.^[22] In these alternatives to the benchmark LAO/STO, the 2DEG appears to be generated through a redox reaction that occurs across the interface between STO and the capping layer. The oxidation of the capping layer generates oxygen vacancies in STO that each provides two electrons to the system, and, consequently, a two-dimensional conductive region at the near-interface region of STO is formed.^[23,24] Oxygen vacancies in STO were proposed not only to produce conducting regions but also cause superconductivity,^[3,4] magnetism^[6,7] and memristive properties in STO.^[25] The control of the density and spatial extent of oxygen vacancies, however, remains a major challenge, which hampers the tuning of the properties exhibited by STO. Remarkably, it was proposed that a voltage-free control of the oxygen position was responsible for the mechanical nanoscale switching between insulating and conducting states observed at the LAO/STO interface.^[26] Moreover, it was shown that 2DEG can be formed and further tuned using X-ray irradiation in the case of bare STO surface.^[27] This approach constitutes an important step towards on-demand control of the STO properties and defect state, albeit it requires ultra-high vacuum (UHV) since the properties of 2DEG fabricated at bare STO under the light considerably depends on the environment, preparation conditions and surface cleaning procedure.^[28-30] In addition, the 2DEG formed in this way at the bare STO surface decays rapidly under ambient atmosphere.

Here we present a comprehensive study on a 2DEG formed at the interface between an amorphous silicon film deposited on a STO substrate (a-Si/STO). The main idea of the metallic-state-formation is based on a redox reaction at the a-Si/STO interface as in case of metal film deposition.^[31] However, in the presented case, we not only combine rich transition-metal-oxide physics with the well-established silicon industry^[32] but also provide the understanding and pathway to manipulate with the metal-insulator transition at the interface using light. The X-ray-induced redox reaction opens a wide perspective for writing on-demand patterns of conducting regions of any size and shape by variation of the beam dimension and irradiation time. The

generated metallic state survives after exposure to the ambient condition since naturally-formed SiO_2 capping layer blocks the further oxidation and protects the metallic interface state from surface adsorbates. Importantly, this approach also opens up the possibility of writing properties such as ferromagnetism and superconductivity in a versatile and simple manner.

Si/STO interface

The sample with 2 nm a-Si capping layer was transferred to the ARPES chamber without breaking UHV condition. Here, a $5 \times 3 \text{ mm}^2$ area of the sample was subsequently irradiated by raster scanning with a $70 \times 1400 \text{ }\mu\text{m}^2$ beam size (photon density $\sim 5 \times 10^9 \text{ ph/s/}\mu\text{m}^2$) for 15 min at room temperature (Figure 1a). Afterwards the sample was transferred back to the preparation chamber and capped with an additional $\sim 40 \text{ nm}$ thick a-Si film in UHV to protect the Si/STO interface when exposed to ambient conditions. The visual observation reveals that the irradiated part of the sample is darker than the non-irradiated part (Figure 1a). The transport properties of both irradiated and non-irradiated areas have been measured by a commercial Physical Property Measurement System (PPMS). Figure 1b displays the sheet resistance of the irradiated part showing a metallic temperature dependence with an upturn around 50 K. This saturating resistance upturn at low temperature is characteristic of the Kondo effect^[33,34] and agrees well with a simple Kondo model fit.^[33,34] From the fit, a Kondo temperature of $T_K \approx 53 \text{ K}$ is derived (Figure 1b), which is consistent with STO-based systems.^[33,34] The resistance of the non-irradiated area at room temperature is above the upper limit of the instrument ($1 \text{ G}\Omega$), which indicates very strong insulating behavior. Therefore, we conclude that the development of the metallic state in the a-Si/STO sample is triggered by the light irradiation. In the following, we further speculate that the conductivity arises from the light-induced transfer of oxygen from STO to Si as depicted in Figure 1a, and use photoemission to monitor this process.

Figure 1 a) A side view schematics (top) and top view photo of the sample (bottom) composed of three different regions: (i) Non-irradiated a-Si/STO capped with Si, (ii) irradiated a-Si/STO and (iii) bare STO. b) The resistivity of the irradiated amorphous Si/STO interface as a function of temperature (blue solid line) including a fit to a Kondo model (red dashed line).

Exposure of STO to the synchrotron light can result in inducing oxygen vacancies formation. This process is manifested as an appearance of an in-gap state which is related to the symmetry-breaking near an oxygen vacancy.^[35] Irradiating STO using photon energy over the insulation gap causes a population of antibonding O $2p$ state, weakening O-Ti bond and promoting the formation of oxygen vacancies. In order to get insight into the mechanism of creating metallic conductivity in the irradiated area of a-Si/STO, we subsequently prepared a-Si/STO systems with a 0.6, 1.0 and 2.0 nm thick a-Si overlayer. Since the X-ray light has a significant effect on core-level peak positions and the spectral weight, we, firstly, characterize as-grown samples by taking each XPS spectra at the fresh non-irradiated spots. Besides the Si⁰ $2p$ peak at 99 eV binding energy (BE) in Figure 2a, we found a broad shoulder, which corresponds to ~~Si¹⁺ silicon oxide~~. This shoulder becomes weaker when increasing the overlayer thickness indicating the presence of oxidized Si near the interface rather than at the surface. This is consistent with a strengthening of the shoulder as the photon energy increases (Figure 2c), which leads to the higher kinetic energy of the escaping electrons and, therefore, larger detecting depth (Figure 2d). Therefore, this finding suggests that although the non-irradiated area might be oxygen deficient, it is insufficient to cause metallic conductivity of the sample. This conclusion is supported by the darker color of non-irradiated a-Si/STO (area (i) in Figure 1a) relative to the bare, non-irradiated STO (area (iii)).

Figure 2. Spectra evolution of a) Si 2p spectra and b) O 1s spectra taken on bare STO and STO covered with a thin layer (0.6, 1 or 2.2 nm) of a-Si at 700 eV photon energy. c) Si 2p spectra of 1 nm thin a-Si/STO taken at varying photon energies corresponding to different kinetic energies of the photoemitted electrons (E_{kin}). The tendency of increase of SiO component as a function of photon energy (*i.e.* increased intensity of oxidized component with depth penetration) reveals the formation of oxidized layer away from the surface. d) The scheme of amorphous Si/STO interface illustrates the formation of SiO fraction near the interface.

Figure 2b shows the O 1s peak of bare STO and the three a-Si/STO systems. The component of the O 1s peak at 530 eV BE corresponds to oxygen bonding in STO as observed in the uncapped STO (O-STO). The peak can still be clearly identified in the spectra measured for 0.6 and 1.0 nm thick Si-film, but it becomes weaker for the 2.0 nm thick film. Upon Si deposition, the component at ~531 eV BE in O 1s peak corresponding to O-Si bonding appears and its intensity increases monotonously with the Si thickness. **The formation of discrete peaks supports the initial assumption of the redox reaction instead of charge transfer scenario.** Therefore, the components of Si 2p and O 1s peaks can be used to trace the oxidation process in real time as oxygen vacancies are formed in STO.

Figure 3. The development of a) O $1s$ and b) Si $2p$ and c) Ti $3d$ spectra with Ti^{3+} shoulder in the insert taken under the light illumination (during the first half of hour of measurements) in 1.0 nm thin a-Si/STO. The spectral weight transfer from Si to SiO shows the Si oxidation under the light. The spectral weight transfer from ~530 eV BE to ~532 eV BE of O1s peaks, corresponding to O-Ti and O-Si bond respectively, claim the oxygen transfer from STO to Si under the light.

In order to explore the oxygen transition from STO to a-Si capping layer, we will now focus on the core level peaks in real time under X-ray illumination. Figure 3a,b show O $1s$ and Si $2p$ spectra of 1 nm a-Si/STO collected at the non-irradiated spot under X-ray beam during measurements. Under the irradiation, we observe the spectral weight transfer of the O $1s$ component related to O-STO bonding to the component identifying O-Si bonding. At the same time, the Si $2p$ peak also shows the spectral weights transfer under illumination from Si^0 to SiO components. The illumination provides mobile electrons **at the near-interface region of STO** and results in an increase of the Ti^{3+} component (Figure 3c). We can, therefore, conclude that the X-ray light induces an interface redox process **where oxygen is transferred from STO to Si, resulting in oxygen vacancies and mobile electrons in the near-interface region of STO.**

The buried metallic state is also observed as electronic states near the Fermi level at a resonance photoemission map measured through the Ti $L_{2,3}$ absorption edges (Figure 4a). The intensity extending from 4.5 eV to 7.5 eV BE is the valence band formed mainly by the O $2p$ states hybridized with Ti $3d$ ones.^[36,37] The broad peak in the gap at ~1.3 eV BE corresponds to the oxygen-vacancy-induced in-gap state. Its BE position varies for different STO-based interfaces,^[38] however, in general, the resonance photoemission map of a-Si/STO is similar to other STO-based interfaces.^[35,39,40] It is important to note the absence of e_g-t_{2g} resonance as in case of bare STO surfaces.^[35] In Figure 4c,d, we present Fermi surface maps taken with linear horizontal (LH) polarized X-rays, where d_{xz} - and d_{xy} -derived bands selected at the L_3 and L_2 -edges. Circular polarization (C+) highlights all bands which are compared with a scheme in Figure 4b identifying $d_{xz,yz}$ - and d_{xz} -derived bands. The Si coverage does not affect the band topology or band occupation since a-Si/STO films have the Fermi surface topology similar to the STO surface^[27,41] and LAO/STO interfaces.^[13]

Figure 4. a) Resonance (angle-integrated) photoemission intensity map for 0.6 nm a-Si/STO across the $L_{2,3}$ resonances, identifying the valence band (VB), in-gap state (IGS) and 2DES states; b) Scheme of Fermi surface map shows a 2DEG typical for the STO surface and LAO/STO interfaces indicating Ti 3d-derived bands. c,d) Fermi surface maps taken at the L_3 and L_2 -absorption edges with linear horizontal polarization highlighted d_{xz} - and d_{xy} -derived bands, respectively. e) Fermi surface map at L_3 edge taken with circular polarized light selecting the $d_{xz,yz}$ - and d_{xy} -derived bands, schematically presented in Figure 4b.

Perspective

We have demonstrated lithography-like X-ray writing of a metallic state at the a-Si/STO interface stable under ambient conditions. The real-time monitoring reveals that X-ray radiation induces a transfer of oxygen ions across the a-Si/STO interface, which produces oxygen

vacancies as well as itinerant carriers in the near-interface region of STO. Oxygen vacancies are known to produce numerous other functionalities in STO beyond being the origin of conductivity. The on-demand X-ray formation of oxygen vacancies may therefore also open up for the spatial control of superconductivity,^[1-4] magnetism,^[5-7] light absorbance (Figure 1) and memristive behaviors.^[25,42] In addition, oxygen vacancies remain the most common dopant in oxides, and together with the non-epitaxial growth of Si that does not require lattice matching substrates, this approach may be applicable across a wide range of oxides, including TiO₂-based systems.^[43,44]

Methods

Amorphous silicon thin films with different thicknesses have been prepared on commercial SurfaceNet TiO₂-terminated STO(001) substrates by the sequential thermal evaporation at room temperature in UHV (5×10^{-10} mbar). After each a-Si coverages were completed, the sample was transferred into the analysis chamber without breaking the UHV and measured at 12 K. The thicknesses were defined by Ti 2p core level peak attenuation induced by the overlayer.

All measurements were performed at the SX-ARPES endstation of the Advanced Resonant Spectroscopies (ADRESS) beamline^[45] of the Swiss Light Source, Paul Scherrer Institute, Switzerland. The combined energy resolution was of the order of 60 meV.

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