Quasiparticle Interference on Cubic Perovskite Oxide Surfaces

Yoshinori Okada,1,* Shiue-Yuan Shiau,2,3 Tay-Rong Chang,4,5 Guoqing Chang,2,3 Masaki Kobayashi,6 Ryota Shimizu,1 Horng-Tay Jeng,1,7 Susumu Shiraki,1 Hiroshi Kumigashira,6 Arun Bansil,8 Hsin Lin,2,3 and Taro Hitosugi1,9

1Advanced Institute for Materials Research (AIMR), Tohoku University, Sendai 980-8577, Japan
2Centre for Advanced 2D Materials and Graphene Research Centre, National University of Singapore, Singapore 117546, Singapore
3Department of Physics, National University of Singapore, Singapore 117542, Singapore
4Department of Physics, National Tsing Hua University, Hsinchu 30013, Taiwan
5Department of Physics, National Cheng Kung University, Tainan 701, Taiwan
6Photon Factory, Institute of Materials Structure Science, High Energy Accelerator Research Organization (KEK), 1-1 Oho, Tsukuba 305-0801, Japan
7Institute of Physics, Academia Sinica, Taipei 11529, Taiwan
8Department of Physics, Northeastern University, Boston, Massachusetts 02115, USA
9Department of Applied Chemistry, Tokyo Institute of Technology, Tokyo 152-8552, Japan

(Received 25 April 2016; revised manuscript received 10 December 2016; published 22 August 2017)

We report the observation of coherent surface states on cubic perovskite oxide SrVO3(001) thin films through spectroscopic-imaging scanning tunneling microscopy. A direct link between the observed quasiparticle interference patterns and the formation of a dxy-derived surface state is supported by first-principles calculations. We show that the apical oxygens on the topmost VO2 plane play a critical role in controlling the coherent surface state via modulating orbital state.

DOI: 10.1103/PhysRevLett.119.086801

Establishing a microscopic understanding of the mechanism leading to coherent two-dimensional (2D) electronic states at surfaces or interfaces of transition metal perovskite oxides is a key step for further exploration of exotic quantum states in various systems [1–5]. Despite an extensive investigation of transition metal perovskite oxides using angle-resolved photoemission spectroscopy (ARPES) [6–10], the underlying microscopic mechanism that leads to the formation of coherent electronic 2D states has remained elusive. In this connection, unraveling the link between the emergence of coherent surface states and atomic reconstruction constitutes an important step forward. Scanning tunneling microscopy (STM) and scanning tunneling spectroscopy (STS) allow us to observe the surface interference pattern with well-defined wave vectors [11–14], and to reveal the microscopic mechanism giving rise to coherent electronic 2D states. However, perovskite materials are intrinsically threedimensional (3D) crystals, and obtaining atomically well-aligned surfaces has been difficult.

In this Letter, we report the first STM/STS observation of quasiparticle interference (QPI) patterns on the epitaxial film surfaces of perovskite oxide SrVO3(001). The SrVO3 bulk has simple cubic symmetry with one electron in the 3d state, and hence it has been used as a prototype for understanding correlated transition metal perovskite oxides [15–29]. We interpret our experimental STM/STS results through parallel first-principles calculations to establish a microscopic understanding of the appearance and disappearance of the observed coherent surface states.

The epitaxial SrVO3(001) thin films were grown on a buffered-HF-etched Nb-doped (0.05 wt. %) SrTiO3(001) substrate by using pulsed laser deposition (PLD). In the three samples (thicknesses: 20, 40, and 110 nm) prepared for this study [30], the x-ray diffraction patterns showed negligible epitaxial strain. We used a scanning tunneling microscope equipped with a PLD system to transfer the as-deposited thin films to a low-temperature (4 K) STM head under ultrahigh vacuum conditions [45]. Figure 1(a) presents a STM topographic image of the SrVO3(001) surface showing a square lattice of protrusions along with randomly distributed defects. The periodicity of the protrusions is approximately 5.5 Å and exhibits a (\(\sqrt{2} \times \sqrt{2}\))-R45° surface reconstruction everywhere on the scanned surfaces.

The \(\sqrt{2} \times \sqrt{2}\) superlattice surface structure [Fig. 1(c)] is formed by a VO2-terminated layer with apical oxygen adsorption [46,47]. Naively, we would expect the topmost V atoms to have similar valence as the bulk V\(^{4+}\) atoms because the bulk structure can be seen as stacked \((\text{Sr}^{2+}\text{O}^{2-})^0\) and \((\text{V}^{4+}\text{O}_{2-})^0\) layers. However, previous emission-angle-dependent photoemission studies show more V\(^{5+}\) atoms on the surface [22,48], which means that the V atoms near the surface are more oxidized than those in the bulk [49]. This observation excludes the possibility of a bare VO2 termination with \(\sqrt{2} \times \sqrt{2}\) buckling near the surface since such a surface structure is unlikely to accommodate substantially oxidized V atoms. A 50% coverage of the apical oxygen sites (forming a SrVO3.5 surface structure) is, however, allowed, which in turn would lead to the formation of the \(\sqrt{2} \times \sqrt{2}\)
superlattice. Similar $\sqrt{2} \times \sqrt{2}$ superstructures with 50% coverage of the apical oxygen sites have also been seen in manganite perovskites [50–52].

Figure 1(d) shows spatially averaged differential conductance ($dI/dV$) spectra. The metallic electronic properties observed on the surface are consistent with previous photoemission experiments [20,49]. The $dI/dV$ spectra show a large spectral weight at zero sample bias voltage $V_s$, a peak at $V_s = +400$ mV, and two minima at $V_s = -410$ and $+710$ mV. Right at the peak position ($V_s = +400$ mV), a shoulder structure has also been observed in angle-integrated inverse photoemission experiments [53]. The energy at $-410$ mV for the conductance minimum agrees quantitatively with the band-edge position at the $\bar{\Gamma}$ point in previous ARPES studies [20].

Figures 2(a) and 2(b) show the topographic and differential conductance images which were simultaneously measured at $V_s = -150$ mV. In order to extract the QPI pattern, which is present only in the conductance image, we compared the Fourier transforms (FTs) of the two images in Figs. 2(c) and 2(d). While both FT images show peaks at $\sqrt{2} \times \sqrt{2}$ spots [green circles in Fig. 2(c)], only the conductance FT image clearly exhibits an additional periodicity with respect to momentum [green dashed ellipses in Fig. 2(d)]. Figure 2(e) shows the energy-dependent intensity profile of the FT images along the $\bar{\Gamma} - \bar{\bar{X}}$ direction for the three samples. The clear energy dispersion seen in Fig. 2(e) provides indisputable evidence for the existence of coherent electronic states on the SrVO$_3$(001) surface. Hereafter, we will refer to this characteristic momentum dispersion along the $\bar{\Gamma} - \bar{\bar{X}}$ direction as $q^*$. In order to understand the energy dependence of the QPI pattern, we constructed a semi-infinite slab model using Wannier functions derived from first-principles density functional theory (DFT) (see Supplemental Material for...
computational details [30]). We refer to an O-adsorbed V-atom site as a “VO site” and to a bare V-atom site without apical oxygen as a “Vb site” [Fig. 3(a)]. Figure 3(b) shows the obtained orbital-dependent densities of states (DOS) and the total DOS averaged over VO and Vb sites [54]. Using a bandwidth renormalization factor of 0.4, which is close to the value obtained from previous ARPES experiments [20] and first principles calculations [21], the total surface DOS [bold black curve in Fig. 3(b)] captures the overall behavior of the experimental dI/dV spectrum [Fig. 1(d)] [55]. Such a renormalization of the DFT bands should reasonably describe the orbital information needed to model the emergent QPI pattern.

In order to establish that the QPI pattern is directly linked to the formation of the dxy-derived coherent 2D band on the surface, we project the spectral weight of dxz/dyz orbitals for VO (Vb) sites [see Fig. 3(k)]. Therefore, we conclude that the emergent QPI pattern on the surface originates from dxy-derived quasiparticle surface states, which are more or less isolated not only from the surface dxz/dyz states but also from the corresponding bulk states.

Our calculations also capture the appearance of the momentum q* selectively along the Γ − X direction. We computed the scattering probability I(q) in terms of the spectral weight A(k), using I(q) = ∫ A(k) × A(k + q) dk. Typical A(k) and I(q) results using E_re = −250 meV are shown in Figs. 3(h) and 3(i). Because the shape of A(k) deviates from a simple circle, the joint DOS is significantly

FIG. 3. Simulation of the electronic states on the surface of SrVO3(001). (a) Cross-sectional view of the calculated relaxed near-surface structure. VO and Vb denote the V-atom sites with and without apical oxygen, respectively. (b) Calculated density of states averaged over VO and Vb sites. (c) Schematic drawing of the surface Brillouin zone (BZ). Green lines mark the BZ of the (√2 × √2)-R45° structure. (d)–(g) Spectral weights of the dxy and dxz/dyz orbitals for VO (Vb) sites are shown in (d) and (e) [(f) and (g)], respectively. The top axis of (b) and right axes of (d)–(g) represent the renormalized energy scale E_re using a renormalization factor of 0.4 (i.e., E_re = 0.4E_r). (h)–(j) Simulated total spectral weight at E_re = −250 meV (h) and the associated scattering probability (i). The experimental Fourier transform image of conductance mapping at V+ = −250 mV is shown in (j) for comparison with (i). (k) The orbital and site dependence of onsite energies relative to the degenerate bulk t_2g states; see Table S2 in the Supplemental Material [30] for details. The onsite energy differences within our model mainly reflect local crystal field effects; these are not related to onsite Coulomb repulsion U. See Ref. [30] for details of our calculations.
enhanced along the $\Gamma - X$ direction in $I(q)$. The magnitude and direction of this enhanced joint DOS [Fig. 3(i)] is consistent with the $q^*$ value obtained from the experimental conductance image at the corresponding energy $eV_s = -250$ meV [Fig. 3(j)].

As the energy increases across the Fermi level $E_F$ (here $E_F$ is set to zero), the QPI signal gradually weakens in intensity and ultimately disappears altogether [Fig. 2(e)]. This fading of the QPI signal near $E_F$ contradicts the behavior of simple metallic surfaces in which, according to conventional Fermi liquid theory, quasiparticle states would have a longer lifetime near $E_F$, and as a result, the QPI patterns would be more prominent [56]. We consider three possible scenarios in this connection. (i) The suppression (decoherence) of the quasiparticle interference via inelastic electron-electron, electron-phonon, and/or electron-plasmon scatterings. However, the symmetric energy dependence on both sides of $E_F$ expected for these inelastic scattering processes contradicts the monotonic fading of the QPI signal observed across $E_F$. (ii) The effect of the shape of $A(k)$. This scenario, however, is also unlikely because the shape of the calculated $A(k)$ changes from circular-like (smaller joint DOS) to square-like (larger joint DOS) across $E_F$, which completely fails to explain the observed QPI signal fading. (iii) The suppression of the $d_{xy}$-derived spectral weight itself. Indeed, our numerical results show a suppression of the $d_{xy}$-derived spectral weight, especially at the VO site [dotted square in Fig. 3(f)]. This is driven by two mechanisms: (i) hybridization and (ii) sublattice formation.

The first mechanism, which involves hybridization between the $d_{xy}$- and $d_{xz}/d_{yz}$-derived states at the $V_b$ site, is illustrated schematically in Fig. 4(a) [57]. As the axially extended $d_{xz}/d_{yz}$-derived bulk bands have an intrinsically strong dispersion normal to the (001) surface, the projection of these bands onto the (001) surface BZ results in a broad spectral weight distribution in momentum space. The broad distribution of the spectral weight at the $V_b$ site [Fig. 3(g)] indicates the existence of a strong coupling between the $d_{xz}/d_{yz}$-derived surface and bulk bands. Such a strong mixing can be naturally understood from the smaller bulk-surface energy separation ($\sim 0.2$ eV) for $d_{xz}/d_{yz}$ orbital at the $V_b$ site compared to that for the VO site ($\sim 1.2$ eV) [Fig. 3(k)]. An important consequence is the possible coexistence of the $d_{xy}$- and $d_{xz}/d_{yz}$-derived bands at the same energy ($E$) and momentum ($k$) over a wide range across the Fermi level [dotted square in Fig. 3(f)]. The hybridization with the $d_{xz}/d_{yz}$-derived bands then leads to (i) the suppression of the $d_{xy}$-derived spectral weight through spectral weight transfer, and (ii) the enhancement of the scattering channel between the $d_{xy}$- and $d_{xz}/d_{yz}$-derived states at the $V_b$ site.

We next discuss the mechanism of sublattice formation, which involves transfer of the spectral weight from the $d_{xy}$ orbital at the $V_b$ site to the $d_{xz}$ orbital at the VO site, as shown schematically in Fig. 4(b). The calculated on-site energies for the $d_{xy}$ orbital at the VO and $V_b$ sites are $\sim 0.1$ and $\sim 0.3$ eV, respectively. In general, a difference in on-site energies will induce a spectral weight transfer between these inequivalent sites around the zone boundary [58]. We confirm this effect by focusing on the $d_{xy}$-derived lower energy-band branch near the $X$ point [dotted squares in Figs. 3(d) and 3(f)]. Our numerical results show that around the $X$ point, the $d_{xy}$-state spectral weight at the $V_b$ site (with higher potential) is more suppressed compared to the $d_{xy}$-state spectral weight at the VO site (with lower potential) around the same ($E, k$) region.

The preceding discussion of hybridization and sublattice formation mechanisms suggests that it is the nonuniformity of the $d_{xy}$-derived spectral weight [Fig. 4(c)] that principally causes the QPI signal on the $(\sqrt{2} \times \sqrt{2})$-R45$^\circ$ surface to fade monotonically with energy. At low energies, we obtain a rather uniform distribution of the $d_{xy}$-derived spectral weight [see Fig. 4(d)]. In contrast, at higher energies, this spectral weight is suppressed while interorbital scatterings are enhanced at the $V_b$ site [see Fig. 4(e)]. Both mechanisms act to disrupt the uniformity of the $d_{xy}$-derived spectral weight [see also Fig. S6].

Our results provide important insights for designing 2D quasiparticle states at surfaces and interfaces of perovskite oxides. We identify the pivotal role of apical oxygens in the formation of 2D electronic states via orbital modulation. Because of the large on-site energy difference at the VO site, the negatively charged apical oxygen strongly eliminates electrons selectively from the axially extended $d_{xz}$ and $d_{yz}$
states [see Fig. 3(k) (left)]. The apical oxygen thus plays a key role in isolating the in-plane $d_{xy}$ and out-of-the-plane $d_{xz}/d_{yz}$ orbitals on the (001) surface. Since apical oxygens are ubiquitous in perovskite oxides, these considerations would also be relevant for designing systems such as the cuprates, where the interplay between the $d_{xy}$ and out-of-the-plane orbitals including $d_{xz}$ is important [59], as well as for surfaces or interfaces involving sublattice formation more generally. We should keep in mind, however, that an obvious unique factor in SrVO$_3$ is its electron filling of one electron in the bulk 3d system. Interestingly, our results suggest that the SrVO$_3$(001) surface is similar to the 2D metallic state at SrTiO$_3$(001)-based surfaces or interfaces because in both systems the degeneracy of the $t_{2g}$ orbitals is lifted and the $d_{xy}$-derived band becomes dominant at low energies [60–72]. This similarity points out that the SrVO$_3$(001) surface would be an interesting playground for exploring emergent quantum functionalities such as magnetism and superconductivity.

We thank H. Ishida and K. Sato for helpful discussions, and D. Walkup and P. Han for critical reading of the manuscript. Y.O. acknowledges funding from the Japan Society for the Promotion of Science Grant-in-Aid No. 26707016 and No. 25886004. T.H. acknowledges funding from the Japan Society for the Promotion of Science Grant-in-Aid No. 16H02115. The work at Northeastern University was supported by the U.S. Department of Energy, Grant No. DE-FG02-07ER46352 (core research), and benefited from Northeastern University Grant No. DE-FG02-07ER46352 (core research), and benefited from Northeastern University Grant No. DE-FG02-07ER46352 (core research). The work at Northeastern University was supported by the U.S. Department of Energy, Grant No. DE-FG02-07ER46352 (core research), and benefited from Northeastern University Grant No. DE-FG02-07ER46352 (core research). The work at Northeastern University was supported by the U.S. Department of Energy, Grant No. DE-FG02-07ER46352 (core research), and benefited from Northeastern University Grant No. DE-FG02-07ER46352 (core research). The work at Northeastern University was supported by the U.S. Department of Energy, Grant No. DE-FG02-07ER46352 (core research), and benefited from Northeastern University Grant No. DE-FG02-07ER46352 (core research). The work at Northeastern University was supported by the U.S. Department of Energy, Grant No. DE-FG02-07ER46352 (core research), and benefited from Northeastern University Grant No. DE-FG02-07ER46352 (core research). The work at Northeastern University was supported by the U.S. Department of Energy, Grant No. DE-FG02-07ER46352 (core research), and benefited from Northeastern University Grant No. DE-FG02-07ER46352 (core research). The work at Northeastern University was supported by the U.S. Department of Energy, Grant No. DE-FG02-07ER46352 (core research), and benefited from Northeastern University Grant No. DE-FG02-07ER46352 (core research). The work at Northeastern University was supported by the U.S. Department of Energy, Grant No. DE-FG02-07ER46352 (core research), and benefited from Northeastern University Grant No. DE-FG02-07ER46352 (core research). The work at Northeastern University was supported by the U.S. Department of Energy, Grant No. DE-FG02-07ER46352 (core research), and benefited from Northeastern University Grant No. DE-FG02-07ER46352 (core research). The work at Northeastern University was supported by the U.S. Department of Energy, Grant No. DE-FG02-07ER46352 (core research), and benefited from Northeastern University Grant No. DE-FG02-07ER46352 (core research). The work at Northeastern University was supported by the U.S. Department of Energy, Grant No. D
We employed the same film growth conditions as in Ref. [30].

Since more oxygen is available in the Sr$_2$V$_2$O$_7$ target compared with that in SrVO$_3$, additional oxygen can be adsorbed on the topmost VO$_2$ layer during film growth in ultrahigh vacuum (see Ref. [30]).

Valence of the topmost V has more than 5+ components, as compared to the bulk value of 4+. Note that the topmost V state is not equal to 5+. We increased the electron filling on the pristine surface in our computation by raising the chemical potential to match the experimentally observed QPI dispersion. The origin of this electron doping to surface can be due to extra missing apical oxygens on $\sqrt{2} \times \sqrt{2}$ sublattice [see dark spots in Fig. 1(a)]. The density of these apical oxygen defects is at most 0.2 per V site.

Formation of the conductance minimum at $V_g = -410$ mV can be explained by the combined effects of the enhanced conductance of 3d states peaking at +400 mV, and the tail of the enhanced conductance due to incoherent spectral weight and/or oxygen 2p state, which peaks well below −1 V. While the overall experimental $dI/dV$ curve [Fig. 1(d)] is reasonably described by our calculated total DOS [Fig. 3(b)], the DOS also features additional peaks which do not appear in the $dI/dV$ curve. These extra peaks could be washed out by a number of effects that are not included in our modeling of the $dI/dV$, such as the effects of the tunneling matrix element, complications due to the tip DOS, and the broadening of electronic states due to finite lifetime and other effects.

Since the surface structure is not a cubic $Pm\overline{3}m$ space group, the $d_{xy}$ and $d_{yz}$ orbitals are not orthogonal on the surface, and hence are allowed to hybridize.

We increased the electron filling on the pristine surface in our computation by raising the chemical potential to match the experimentally observed QPI dispersion. The origin of this electron doping to surface can be due to extra missing apical oxygens on $\sqrt{2} \times \sqrt{2}$ sublattice [see dark spots in Fig. 1(a)]. The density of these apical oxygen defects is at most 0.2 per V site.

Formation of the conductance minimum at $V_g = -410$ mV can be explained by the combined effects of the enhanced conductance of 3d states peaking at +400 mV, and the tail of the enhanced conductance due to incoherent spectral weight and/or oxygen 2p state, which peaks well below −1 V. While the overall experimental $dI/dV$ curve [Fig. 1(d)] is reasonably described by our calculated total DOS [Fig. 3(b)], the DOS also features additional peaks which do not appear in the $dI/dV$ curve. These extra peaks could be washed out by a number of effects that are not included in our modeling of the $dI/dV$, such as the effects of the tunneling matrix element, complications due to the tip DOS, and the broadening of electronic states due to finite lifetime and other effects.