Resonant tunnelling in a quantum oxide superlattice

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Resonant tunnelling is a quantum mechanical process that has long been attracting both scientific and technological attention owing to its intriguing underlying physics and unique applications for high-speed electronics. The materials system exhibiting resonant tunnelling, however, has been largely limited to the conventional semiconductors, partially due to their excellent crystalline quality. Here we show that a deliberately designed transition metal oxide superlattice exhibits a resonant tunnelling behaviour with a clear negative differential resistance. The tunnelling occurred through an atomically thin, lanthanum δ-doped SrTiO₃ layer, and the negative differential resistance was realized on top of the bipolar resistance switching typically observed for perovskite oxide junctions. This combined process resulted in an extremely large resistance ratio (~10⁵) between the high and low-resistance states. The unprecedentedly large control found in atomically thin δ-doped oxide superlattices can open a door to novel oxide-based high-frequency logic devices.

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In quantum well (QW) heterostructures, the probability of quantum mechanical tunnelling depends on the available quantized states at both the originating and the receiving sides of the junction. Therefore, the tunnelling current is usually not a monotonically increasing function with respect to the external bias. In particular, quantized resonant states can form in a QW between the two barriers, and can give rise to an interesting tunnelling behaviour, so called, resonant tunnelling (RT). Here, the energy of the wavefunctions with discrete levels can shift and align by applying an external bias (Fig. 1)\(^1\)-\(^2\). When properly aligned, the tunnelling current peaks, exhibiting a negative differential resistance (NDR) just above the resonant bias \((V_R)\). Such an intriguing NDR behaviour can be exploited in various devices such as tunnel diodes and RT transistors. More importantly, the RT phenomena offer unique insight into electrical transport properties of materials, such as localized defect states, collective electronic excitations and QW band structures. Up to date, NDR and accompanying RT behaviours have been studied mostly in Si-based or III-V compound semiconductors\(^1\)-\(^3\). Excellent crystalline quality of the conventional semiconductors and actual realization of two-dimensional (2D) heterostructures with nanometre thick barrier layers enabled the observation of the RT behaviour. On the basis of recent advances in oxide thin-film synthesis, precision design of complex oxide thin films and heterostructures by pulsed laser epitaxy (PLE) or molecular beam epitaxy at the atomic scale has become available\(^6\)-\(^8\). Indeed, many previous studies demonstrated emergent physical phenomena in conjunction with the quantum mechanical tunnelling in transition metal oxide (TMO)-based tunnel junctions, utilizing the exotic properties, including superconductivity\(^9\), magnetoresistance\(^10\),\(^11\), electroresistance\(^12\),\(^13\) and multiferroicity\(^14\). The strong coupling among charge, spin, lattice and orbital degrees of freedom has been investigated in terms of the various tunnelling behaviours, such as Josephson effect and spin-polarized tunnelling. More recently, a large electroresistance was also observed in ferroelectric tunnel junctions\(^1\).\(^2\). The tunnelling current across the ferroelectric layer is found to be efficiently controlled by not only the polarization direction, but also, more importantly, the interfacial electronic phase of the electrode layers\(^1\).\(^2\). Unfortunately, however, a clear RT behaviour has not been experimentally realized in TMO heterostructures. Although a clear RT behaviour has not been widely explored with TMOs, the NDR behaviour itself has been reported in various complex oxide junction structures\(^15\)-\(^18\). In particular, non-volatile resistance switching (RS) in TMO-based heterostructures has attracted scientific attention for developing next-generation memory devices based on memristors\(^19\)-\(^21\). In typical RS devices, the electric resistance of a junction can be modulated by applying external bias, and the device can have two (or more) resistance states, that is, a high-resistance state (HRS) and a low-resistance state (LRS). The switching from a LRS to a HRS usually accompanies a NDR behaviour, as the amount of current decreases on increasing the bias above the switching voltage.

In the following, we investigate the junction transport property of a QW superlattice (SL) precisely designed by inserting atomically thin LaTiO\(_3\) (LTO) between SrTiO\(_3\) (STO) barrier layers. A clear RT behaviour with NDR is observed. Moreover, as oxide heterostructures can reveal RS, we further propose that the combination of RS with NDR is an efficient way to maximize the resistance ratio between the HRS and LRS in oxide QW heterostructures.

**Figure 1** | Resonant tunnelling from a quantum oxide superlattice. (a) Schematic diagram of a \(\delta\)-doped quantum oxide superlattice. The \(\delta\)-doped La layer creates a 2D electron gas within the layer forming a quantum well structure. (b,c) Calculated potential wells (thin black lines) and probability functions of finding electrons (thick lines), i.e., absolute square of wavefunction, at their corresponding energy levels. At \(V = 0\) \((b)\) the wavefunctions with the same energy levels are aligned for each quantum well. When \(V > 0\) the position of wavefunctions are shifted and no longer aligned. At \(V = V_R\) \((c)\) the ground state wavefunction of a quantum well becomes aligned with the first excited state wavefunction in the adjacent quantum well, allowing a large tunnelling current to flow across the superlattice junction. The dotted line indicates the electric field, which corresponds to \(V_R = 1.23\) V for the whole superlattice.
Nonlinear current–voltage characteristics. Figure 2 shows the junction current–voltage characteristics of the TMO QWs at various temperatures. At room temperature, a weak hysteresis curve, which manifests the typical bipolar RS behaviour, was observed. The two different resistance states could be achieved by switching the polarity of the bias voltage. Indeed, the memory characteristics have been confirmed to show a typical RS behaviour. In general, understanding the switching mechanisms is a major challenge in achieving better non-volatile memory performance. To explain the bipolar RS phenomenon, various electric field polarity-dependent models, including ion migration, Mott transition and formation of Schottky barrier, have been suggested. In particular, the Schottky barrier formed at the interface has been identified to trigger the RS behaviour for Nb:STO-based junctions. More specifically, changes in the Schottky barrier by either a charge trap at the defect states or oxygen migration due to applied bias voltage has been frequently attributed for the bipolar RS behaviour. Similar mechanism, if not the same, seems to play a major role in our SL as well. As a qualitatively similar bipolar RS behaviour was also observed for a Pt/Nb:STO junction (inset of Fig. 2a), we believe that the RS behaviour originates mainly from the interface between the SL and Nb:STO.

As temperature decreases, the overall current level increases for both voltage polarities, and the RS becomes more distinct with a larger discrepancy between the LRS and HRS. Such temperature-dependent increase of the current level can be attributed to the largely enhanced carrier mobility and dielectric constant of STO at low temperatures. In particular, similar temperature-dependence of the current level for the Pt/Nb:STO junction (inset of Fig. 2a) suggests that the bottom electrode Nb:STO is largely responsible for the increasing current level with decreasing temperature. At T<~220 K, an interesting transport behaviour starts to develop at ~1.2 V while maintaining the overall bipolar RS feature of our SL. A clear and smooth NDR behaviour is then observed by further ramping up the voltage to the positive bias direction. It should be noted that such a smooth peak in I(V) curve is significantly different from the usual abrupt NDR features observed for conventional RS in TMOs. For general RS (for both bipolar and unipolar), the current level drops immediately when the switching occurs from a LRS to a HRS, in stark contrast to what we observe here. Moreover, a further increase in the current above the clear peak feature in I(V) curve was observed, which has never been reported for conventional RS, to the best of our knowledge. These characteristic features signify that the origin of NDR in our QW SLs is fundamentally different from that of the conventional RS often observed in oxide thin films.

It is also important to point out that the NDR behaviour uniquely originates from the TMO QW structure. I(V) curves for a Pt/Nb:STO junction as a function of temperature shown in the inset of Fig. 2a represent only a typical bipolar RS behaviour of Nb:STO junctions. While similar RS behaviours have been observed for various Nb:STO-based junctions as discussed previously, the smooth peak feature and clear NDR behaviour were absent, indicating that the deliberately designed TMO SL with QWs is indeed responsible for the unique feature. Moreover, on differentiating the I(V) curves of the SLs as shown in Fig. 2b, we indeed find two clear zero-crossing points for T<200 K. This result again indicates that the NDR is a consequence of the resonant states formed inside the QWs, rather than associated with the conventional RS. Observation of NDR only at lower temperature possibly due to the reduced phonon scattering further confirms the RT behaviour.

Theoretical calculations on resonant tunnelling. To verify that the NDR behaviour indeed originates from RT, we have performed a theoretical analysis by taking into account the band gap, effective mass and dielectric constant of the TMO heterostructure (see Methods section for detail). Among these parameters, εr of an oxide heterostructure with 2DEGs has not been widely studied. However, it is expected that the creation of interfacial charges would drastically reduce the εr value of the highly dielectric STO. As this change leads to a significant modification in the dielectric screening of the conducting carriers, we focus here on the effect of εr. Figure 3 shows the evolution of energy levels of the quantized states and Vr for [LTO1/STO6]10 SL as a function of εr. The quantized energy levels show the values in the absence of external electric field. The actual potential wells and wavefunctions within the well with corresponding energy levels are represented in Fig. 1b for εr = 100. As εr increases, the well becomes shallower, weakening the quantum confinement—that is, both the energy difference between the states and the number of confined states are reduced upon the increase of εr. For εr ≤100, the well is deep enough to accommodate three confined states (ground, first and second excited states) within the QW, while only two confined states are possible for εr > 100 (Fig. 3a). On the basis of the energy level separation and the QW geometry, we can calculate Vr as a function of εr (Fig. 3b). As εr increases, a smaller Vr is expected because of the smaller energy difference between the ground and first excited states. For εr = 100, Vr = 1.23 V is needed to induce RT between the ground and first excited states in the deliberately designed oxide SL, as shown in Fig. 1c. The theoretical calculation implies that it would be rather
The observation of RT behaviour further provides quantitative information useful for understanding the physics of RT phenomena and insight for technological applications. We note that such a quantitative analysis could not be conducted on TMO QWs, as RT behaviour has never been observed previously. As the RT lifetime ($\tau_{RT}$) is important to understand the tunnelling behaviour of electrons through the TMO QW, we have computed $\tau_{RT}$ using the energy uncertainty at the energy corresponding to the RT, that is, $\tau_{RT} = h/2AE$, where $h = h/2\pi$, $h$ is the Planck’s constant and $AE$ is the half width at half maximum of the resonant peak. Due to the broad feature of the resonance peak ($\sim 1\, \text{eV}$) for our TMO QW, we obtain a rather small $\tau_{RT}$ value ($\sim 0.7\, \text{fs}$), which is orders of magnitude smaller than that obtained in semiconductor QWs. This value is also rather small compared with the traverse lifetime across the tunnelling barrier, and therefore, strong coherence is not expected in the complex oxide QWs. In fact, the small $\tau_{RT}$ in our QW SL is expected as such a heterostructure has a rather small relaxation time ($\tau_{\mu} = 42.4\, \text{fs}$) of the charge carriers, which is also orders of magnitude smaller than those obtained from conventional semiconductors, due possibly to strong correlation. In addition, the peak-to-valley current ratio (PVCR) and the peak current density (PCD) of our TMO-based RT diode are about 1.3 and 120 A cm$^{-2}$, respectively, at the lowest temperature (4 K). PVCR is rather small compared with that of conventional semiconductor RT diodes where the typical value is $>3$ at room temperature. On the other hand, PCD of semiconductor RT diodes span seven orders of magnitude from tens of mA cm$^{-2}$ to hundreds of kA cm$^{-2}$. Therefore, the PCD value we have measured from our TMO RT device is within the range of the semiconductor-based RT diodes.

The RT behaviour in our oxide QW SL enhances yet another advantageous functionality, which is unique to the TMOs. Indeed, the resistance ratio between the HRS and LRS is observed to be largely enhanced due to the RT feature. Figure 4 shows the junction resistance of the HRS and LRS measured at 0.5 and $-0.5\, \text{V}$, respectively, as a function of temperature. The inset shows the resistance plot as a function of applied bias voltage. The difference between the HRS and LRS resistance increased with decreasing temperature. Below 150 K, we observed the ON/OFF ratio to be larger than $10^5$, while it was slightly larger than 10 at room temperature. Typically, the ON/OFF ratio for bipolar RS is about $10^3$, much smaller than that for unipolar RS. The completely different temperature-dependent behaviour of the resistance (HRS shows insulating behaviour while LRS shows metallic temperature-dependent behaviour) mainly due to the RT feature greatly enhances the ON/OFF ratio. Below 120 K, the...
compliance current played a role, somewhat decreasing the HRS resistance value (empty symbols in red). Nevertheless, we could still observe a large resistance ratio (≈10^5) with an increasing trend towards the lowest temperature we employed. Undoubtedly, such a large enhancement in the resistance ratio stems from the RT behaviour of the QW SL. The drastically enhanced tunnelling probability near the resonant bias voltage substantially decreased the resistance of the LRS near V<sub>R</sub>. The dip feature for the resistance value at ~1 V for the LRS shown in the inset of Fig. 4 clearly signifies the enhanced tunnelling probability.

In summary, we have observed an intriguing NDR feature in a SrTiO<sub>3</sub>/LaTiO<sub>3</sub>/SrTiO<sub>3</sub> QW superlattice at low temperatures. The NDR behaviour is attributed to a resonant tunnelling occurring through the deliberately designed oxide QWs. In particular, because of the existence of the resonant tunnelling, a largely enhanced ON/OFF ratio has been achieved in the bipolar resistance switching, which occurs at the interface between the heterostucture and metallic substrate. Our study also demonstrates the potential of oxide heterostructures for a quantum mechanical behaviour that has been thought to be possible only in conventional semiconductor heterostructures. Thus, we believe that the discovery of resonant tunnelling through oxide-based QWs can lay down a stepping stone to oxide electronics.

**Methods**

**Sample fabrication.** A (LaTiO<sub>3</sub>)/SrTiO<sub>3</sub>/LaSTO SL sample was fabricated at 700°C in 10<sup>-5</sup> torr of oxygen partial pressure using pulsed laser epitaxy. A KrF excimer laser (λ = 248 nm) with a laser fluence of ~1 mJ cm<sup>-2</sup> was used for ablation of a single crystal STO and a sintered La<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> target. An atomically flat STO layer terminated (001) Nb-doped STO (0.05 wt%) single crystal buffer with 10 μc of STO was used as a substrate. The 10 μc STO buffer layer was used to ensure a good surface and interface quality of the oxide QW. The growth process was monitored using reflection high-energy electron diffraction (RHEED), ensuring the layer-by-layer growth. Supplementary Fig. 1a shows an oscillation of the RHEED specular spot intensity as a function of growth time. Six μc layers of STO and one μc layer of LTO were consecutively deposited. The 10 μc layers of STO formed an epitaxial Nb–SrTiO<sub>3</sub> Schottky interface.

**Electrical characterization.** The top electrode Pt (~300 μm in diameter) was patterned by RF sputtering on top of the surface using a shadow mask. External bias was applied to the Nb-STO interface, which served as the bottom electrode. The temperature-dependent current–voltage (I(V)) curve was measured using a physical property measurement system (Quantum Design Inc.) with a source measure unit (Keithley 236). The current compliance (0.1 A) and the maximum sweep voltage value (~2 to 4 V) were set to prevent the device from damaging.

**Theoretical calculation.** The shape of electrostatic potential (Fig. 1b) induced by La-doping in STO was obtained by solving the Poisson and the Schrödinger equation self-consistently, without any electric field applied. The self-consistent calculations were performed iteratively using Brodyen's second method until the convergence of the electrostatic potential is reached. An external electric field was then applied to obtain envelope wavefunctions and energy levels of electrons (Fig. 1c). We calculated ε<sub>c</sub> of STO in the range of 10<sup>-10</sup>–10<sup>-3</sup> (note, while ε<sub>c</sub> of bulk STO at low temperature is known to be very large, ε<sub>c</sub> strongly varies with the electric field, temperature and sample geometry) and effective mass of 4.4 (out-of-plane band effective mass of STO) was used for the calculations.

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