Recent Advances of Quantum Conductance in Memristors

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Memristors with the filamentary switching mechanism have been acknowledged as a leading candidate for next-generation nonvolatile memory applications, primarily due to their excellent downscaling potential, fast operation speed, low power consumption, and high switching endurance. In particular, room-temperature quantum conductance effect can emerge as the size of the conducting filaments is reduced down to atomic scale, offering great opportunities for the physical understanding of memristive switching phenomena and the realization of ultrahigh-density storage, logic-in-memory circuits, atomic scale photodetectors, and etc. This review presents a timely and comprehensive summary of the recent advances in quantum conductance in memristors. After a brief description on the evolution of conducting filaments, the experimental phenomena, theoretical understanding, effective control, and promising applications of quantum conductance in memristors are summarized and discussed in detail. Finally, current challenges and future prospects concerning quantum conductance in memristors are presented.

1. Introduction

Memristor, a two-terminal resistor with memory function, was first proposed by Chua[1] from University of California, Berkeley in 1971 to link the charge and flux of a circuit (Figure 1a). In this sense, memristor has every right to be the forth basic circuit element, in parallel with the existing resistor, inductor, and capacitor. It was not until 2008 that Williams and co-workers[2] from HP Labs announced the physical realization of memristor based on a resistive switching Pt/TiO2-x/TiO2/Pt device (Figure 1b), since when the long-standing resistive switching devices over the past half century were all regarded as memristors[3] and aroused ever increasing research interest all over the world for promising nonvolatile memory, logic-in-memory as well as neuromorphic computing applications.[4–8]

Memristors usually consist of a simple “metal/insulator/metal” sandwich structure and can be reversibly switched between a high resistance state (HRS, or off state) and a low resistance state (LRS, or on state) under external electrical stimuli.[5] Despite various switching mechanisms have been proposed and solidly confirmed,[7,8] of particular interest and importance is the ion migration-based filamentary mechanism that can ensure an enhanced performance as the device scaling down (Figure 1c). Excellent device miniaturization of <10 nm,[9,10] ultrafast operation speed of <1 ns[11,12] and extreme switching endurance of >1012 cycles[13] have been demonstrated in memristors with filamentary mechanism, in addition to their abundant storage media including oxides, nitrides, chalcogenides, polymers, and etc.[7,8] Room-temperature quantum conductance has also been found in these memristors when the size of conducting filaments is reduced down to atomic scale,[14–16] as schematically shown by the panels (ii) and (iii) in Figure 1c. In this scenario, the device conductance G is able to be expressed as

\[ G = n \cdot 2e^2/h = nG_0 (n = 1, 2, 3,...) \]

(1)

where \( e \) is the electron charge, \( h \) is the Planck’s constant, the factor 2 accounts for spin degeneracy, and \( G_0 = 2e^2/h \) represents the fundamental quantum of conductance with the value of 77.5 \( \mu \text{S}.[17] \) Theoretically, \( G_0 \) results from the contact resistance when a ballistic conductor with single transverse mode is sandwiched between two conductive pads.[18] Assuming that the pads have infinitely many transverse modes, a redistribution of the current among the current-carrying modes at the pad/conductor interface is necessary. This will naturally result in the existence of some contact resistance, though the ballistic conductor itself has zero resistance.

Historically, quantum conductance was first discovered in the 2D electron gas system of a GaAs-AlGaAs heterostructure at 0.6 K by van Wees et al. in 1988,[19] and then in various metal nanowires[20–22] or quantum point contacts constructed by scanning tunneling microscope,[23–25] mechanically controllable break junction technique,[26,27] electrochemical deposition,[28,29] and etc. While quantum conductance in memristors was already...
reported in the early 1990s,[30,31] relatively less attention was paid to such effect which is partially due to the huge success of silicon-based Flash memories. As Flash memories are reaching the physical scaling limitations in the 21st century,[32] research interest on quantum conductance in memristors started to rise since 2005 when Aono and co-workers[33] demonstrated highly controllable quantum conductance using the atomic switch concept. Later on, distinct quantum conductance phenomena were reported in several oxide memristors[34–41] with unparallel CMOS compatibility, thus arousing increasingly high attention not only to understand such effect but also to explore its novel applications. It should be noted that, unlike the 2D electron gas system under extremely low temperature,[42] memristors at room temperature or even higher can still exhibit quantum conductance.[43] This is reasonable when considering the fact that the thinnest part of a conducting filament has only one to several atoms. For such small-area contacts, the energy spacing between the transverse modes is in the order of 1 eV or even higher,[43,44] thus making the temperature effect negligible.

In this work, we provide a comprehensive review on the recent advances of quantum conductance in memristors. After a brief description on the evolution dynamics of conducting filaments in Section 2, the experimental phenomena, theoretical understanding, effective control, and promising applications of quantum conductance in memristive devices are discussed in detail in Section 3. Finally, current challenges and future prospects in this field are presented.

2. Evolution Dynamics of Conducting Filaments

2.1. Cation Migration-Based Conducting Filaments

In memristors with an electrochemically active electrode (typically, Ag or Cu) and an electrochemically inert counter electrode (e.g., Pt, Au, or W), the formation and reversible evolution of cation migration-based conducting filaments are usually the dominating resistive switching mechanism.[7,45,46] When the active electrode is positively biased, anodic dissolution will occur to generate metal ions, which is balanced by the reduction of moisture from the ambient environment at the counter electrode.[47] Being driven by the external electric field, the metal ions migrate toward the counter electrode, preferentially along the fast diffusion channels of the grain boundaries in polycrystalline films and the surfaces of nanowires. After capturing electrons, the metal ions will be reduced back to metal atoms, the accumulation of which leads finally to the growth of metal filaments connecting the anode and cathode, and thus the switching of memristors from the off to the on state. In contrast, when the active electrode is negatively biased, the existing metal filaments will be electrochemically dissolved with the help of Joule heating at their thinnest parts, thereby switching the memristors back to the initial off state.

By referring to the classical electrochemical deposition process in solutions, metal filaments had been considered and also confirmed to grow from inert to active electrode for a very long time.[48–50] In this scenario, the metal ions can only be reduced after reaching the inert electrode, thus leading naturally to the initial nucleation of metal filaments near cathode, such as in the Ag/SiO₂/Pt device (Figure 2a).[51] In 2012, a totally opposite growth mode of metal filaments, i.e., from active to inert electrode, has been theoretically proposed and experimentally demonstrated.[51–54] Such growth mode is
featured by the initial nucleation of metal filaments near anode, such as in the Ag/a-Si/Pt device (Figure 2c), and is attributed to the relatively low mobility of metal ions in comparison to that of electrons in the storage media. Later on, a more interesting growth mode of metal filaments with initial nucleation in-between anode and cathode has also been confirmed in the Ag/poly(3,4-ethylene dioxythiophene):poly(styrenesulfonate) (PEDOT:PSS)/Pt device (Figure 2b). To provide a universal model for all the confirmed growth modes of metal filaments, Pan et al. conducted a detailed 2D simulation on the initial nucleation site of metal filaments using the kinetic Monte Carlo (KMC) method. The obtained results suggest that the growth mode of metal filaments is codominated by cation migration and filament nucleation, as schematically shown in Figure 2d. If cation migration is the rate-limiting process, the metal ions can only migrate a very small distance before being first reduced. As such, the metal filaments will initially nucleate near anode and then grow towards cathode, just as in the Ag/a-Si/Pt device. On the contrary, for a given storage medium, the detailed composition of active electrode is decisive to the morphology of metal filaments. For instance, Goux et al. reported that the Cu filaments will become weak to strong as the increase of Cu content in the Cu$_x$Te$_{1-x}$ electrode, thus resulting in the transition of resistive switching from volatile to nonvolatile. Very recently, Liu and co-workers pioneered the modulation of cation injecting path by inserting a structure-defective graphene at the active electrode/storage medium interface (Figure 2f). With such method, well control of the metal filament quantity and size has been successfully realized, enabling a low operating current ($\approx 1$ µA) memory and a high driving current ($\approx 1$ mA) selector in the same material system and thus addressing the current-retention dilemma of cation migration-based memristors to some extent.

Besides their growth mode, the morphology of metal filaments is another key point of concern because it affects significantly the stability and consequent dissolution process of metal filaments. Based on detailed transmission electron microscope (TEM) observations, Yang et al. found that even with the same growth mode, the morphology of metal filaments depends critically on the redox rate. For example, both growing from cathode to anode, high and low redox rates tend to cause continuous and branched metal filaments, respectively (Figure 2e). In this scenario, the difference in redox rate is solely caused by the adoption of various storage media, since the used active electrode is identical. On the contrary, for a given storage medium, the detailed composition of active electrode is decisive to the morphology of metal filaments. For instance, Goux et al. reported that the Cu filaments will become weak to strong as the increase of Cu content in the Cu$_x$Te$_{1-x}$ electrode, thus resulting in the transition of resistive switching from volatile to nonvolatile. Very recently, Liu and co-workers pioneered the modulation of cation injecting path by inserting a structure-defective graphene at the active electrode/storage medium interface (Figure 2f). With such method, well control of the metal filament quantity and size has been successfully realized, enabling a low operating current ($\approx 1$ µA) memory and a high driving current ($\approx 1$ mA) selector in the same material system and thus addressing the current-retention dilemma of cation migration-based memristors to some extent.

Figure 1. Concept of quantum conductance in memristors. a,b) Theoretical propose and physical realization of the memristor. Reproduced with permission. Copyright 2008, Springer Nature. c) Schematic evolution of conducting filaments in memristor operation and the consequent quantum conductance effect. The orange pellets represent metal atoms or oxygen vacancies.
2.2. Anion Migration-Based Conducting Filaments

In oxide memristors without electrochemically active electrodes, the migration of oxygen ions from storage media can be activated under an external electric field, which leads finally to the formation of oxygen-deficient filaments.\[7\] It has been demonstrated that the detailed composition of oxygen-deficient filaments depends critically on the adopted oxides as well as programming conditions. By combining high-resolution TEM and low-temperature conductivity measurements, Hwang and co-workers\[61\] confirmed the formation of Ti\(_2\)O\(_4\) filaments in TiO\(_2\) memristors (Figure 3a). Similarly, the filaments in V\(_2\)O\(_5\) memristors were recently affirmed by Xue et al.\[62\] to be VO\(_2\) nanochannels (Figure 3b). In contrast, based on oxygen electron-energy-loss spectroscopy (EELS) and temperature coefficient of resistance measurements, Miao et al.\[63\] argued that the filaments in TaO\(_x\) memristors should consist of an amorphous Ta(O) solid solution with a decreasing oxygen content as the programming current increases (Figure 3c). Such point of view was further verified very recently by Gao et al.\[64\]
using energy-dispersive X-ray spectroscopy (EDX) line scan analysis (Figure 3d). As for HfO$_x$ memristors, oxygen vacancy (VO) filaments have been normally suggested, as supported by spectroscopy analysis as well as numerical simulation.\[65,66\] Although the evolution dynamics of cation migration-based filaments can be readily and well understood through real-time and in situ TEM observations, the migration of oxygen ions and consequent growth/dissolution of oxygen-deficient filaments are hard to be captured due to the low atomic number of oxygen element and easy adsorption of oxygen contaminations from the ambient atmosphere. Remarkable breakthroughs were made very recently by exploiting the charge attribute of ions, instead of the normally used mass counterpart in previous works. Kang and co-workers\[67\] pioneered the electron holography in in situ TEM for analyzing the evolution dynamics of oxygen vacancy filaments (Figure 4a). The positive and negative potentials herein could be related to the oxygen vacancies in the film and the transport electrons residual in the migration path, respectively. As such, the negative potential can be used to track the evolution process of oxygen vacancy filaments. In contrast, Yang et al.\[68\] introduced a dual-pass electrostatic force microscopy (EFM) method into this field, where the first pass is to acquire surface morphology of the previously stimulated areas in tapping mode (Figure 4b), followed by the second pass in noncontact mode to measure the 1$\omega$ and 2$\omega$ components (Figure 4c,d) of the electrostatic force gradient between the probe and the switching regions. The 1$\omega$ and 2$\omega$ patterns are considered to be caused by the accumulated charges (i.e., oxygen ions) near the surface and the stoichiometry variation as well as structural deformation (i.e., oxygen-deficient filaments), respectively. The results obtained by these two groups coincide with each other, suggesting the evolution dynamics of oxygen-deficient filaments in Figure 4e.\[68\] External electric field can attract oxygen ions to the anodic interface, making oxygen vacancies accumulated initially at the cathodic interface. As the stressing time increases, more vacancies are accumulated, thus leading to the growth of oxygen-deficient filaments from cathode to
Once a complete filament is formed, the device will be switched to the on state. A subsequent reverse field can drive the originally attracted oxygen ions back into the oxide, resulting in the rupture of the existing filament and thereby the switching of the device back to the off state.

It is noted that the original amount of oxygen vacancies in oxide storage media is normally not enough for the formation of filaments. Additional vacancies are thus needed via oxidation of oxygen ions, accompanied by the eruption of oxygen gas to the ambient, as consolidated by the appearance of gas bubbles on the electrode surface.[69] This will certainly lead to the destruction of device structure and consequently the deterioration in device performance. To solve this issue, an oxygen reservoir is highly necessary, either by using a chemically active electrode (such as Ti or Ta)[63,65] or by inserting a highly oxygen-deficient oxide layer like TaO$_{2-x}$.[13] The reservoir layer can reversibly exchange oxygen ions with the storage media, i.e., storing oxygen ions during the formation of filaments and releasing oxygen ions to rupture the existing filaments, and thus make the memristor highly reliable. The record high switching endurance of $>10^{12}$ cycles was actually realized in a bilayer memristor with Ta$_2$O$_{5-x}$ and TaO$_{2-x}$ as the active switching layer and the oxygen reservoir layer, respectively.[13]

### 3. Quantum Conductance in Memristors

#### 3.1. Experimental Phenomena

The extreme downscaling of conducting filaments in memristors is atomic point contacts, whose lateral dimension is comparable to the Fermi wavelength and even smaller than the mean free path of electrons.[14,13,70] In this case, charge carriers can move through these quasi-1D systems ballistically without any scattering, which makes the device conductance to closely depend on the size of the atomic point contacts and thus to be quantized in the unit of $G_0 = 2e^2/h$ (where $e$ is the electron charge and $h$ is the Planck’s constant). For example, at the initial formation stage of a Nb filament in the Nb/ZnO/Pt memristor, an abrupt jump in the device conductance from 1 to 3$G_0$ was observed at 0.8 V, followed by the appearance of 4, 5, 6, 7, and 8$G_0$ in sequence as the increase in device voltage (Figure 5a).[14] To avoid randomness and to tolerate fluctuation in practical materials, quantum conductance in memristors is often confirmed by the peaks at integer multiples of $G_0$ in statistical analysis on plenty of experimental data (Figure 5b).[14] Similarly, quantum conductance can also occur at the final dissolution stage of an existing filament, such as the oxygen vacancy filament in the Pt/HfO$_2$/Pt memristor (Figure 5c,d).[71]
These results indicate that the size evolution of conducting filaments at their thinnest part is in the unit of single-atom point contact. Besides the normal integer multiples of $G_0$, discrete conductance plateaus with half-integer multiples of $G_0$ have also been reported in some memristors. Among them, one representative is the n-Si/SiO$_x$/p-Si memristor with statistical conductance peaks from 0.5 to 4.5$G_0$ with the interval of 0.5$G_0$ (Figure 5e). Such phenomenon may be caused by contamination or distortion of conducting filaments and can theoretically double the device storage density. Moreover, it is noteworthy that a low voltage sweeping rate to slow down the size evolution process of conducting filaments is usually necessary to observe quantum conductance in memristors.

Besides the common voltage sweeping mode, some researchers have also utilized current sweeping mode to study the quantum conductance in memristors. Unexpectedly,
more distinct quantum conductance levels have been observed, which is attributed to the negative feedback of device voltage caused by the abrupt decrease in device resistance. For example, Nandakumar et al. [70] tested the Cu/SiO$_2$/W memristor by using a current sweep from 0 to 100 µA with a fixed, small sweeping rate of 200 nA/10 ms. The obtained results in Figure 6 reveal clear quantum conductance levels from 0.5 to 4.5$G_0$ with the interval of 0.5$G_0$. Meanwhile, each quantum conductance jump is indeed accompanied by a sudden drop in device voltage, as can be seen by comparing the voltage and conductance curves in Figure 6a. Similarly, Tappertzhofen et al. [74] measured the Ag/AgI/Pt memristor using a current sweep from 0 to 20 µA with 100 nA and 2 s per step. Clear quantum conductance levels of 2, 3, 4, 6, and 7$G_0$ in single sweep and of 1, 3, 4, 5, 7, and 12$G_0$ in statistical histogram were obtained. In contrast, no more than two quantum conductance levels were able to be found by conventional voltage sweeping operation in the same device, thus highlighting the superiority of current sweeping mode to study the quantum conductance in memristors. It should be noted that at even higher currents, the device conductance will change so fast that quantum conductance becomes invisible. Also, current sweeping mode is certainly not suitable to study the conductance quantum in memristors during reset process due to the positive feedback of device voltage.

For practical applications, pulse operation is certainly necessary, which calls for the study of quantum conductance in memristors under short voltage pulses. In this scenario, three parameters could be tuned, i.e., pulse amplitude, pulse width as well as the time interval between two adjacent voltage pulses. Using voltage pulses with increasing amplitude but fixed width and interval, Tsuruoka et al. [38] observed distinct integer quantum conductance levels in the Ag/Ta$_2$O$_5$/Pt memristor with Ag filaments. More importantly, they concluded based on detailed comparative studies that the application of voltage pulses with increasing amplitude is crucial to obtain quantum conductance, while voltage pulses with constant amplitude can only affect the device conductance at the initial stage of voltage application. Following this rule, Chen et al. [75] successfully observed clear integer quantum conductance levels in a Ti/Ta$_2$O$_5$/Pt memristor with oxygen vacancy filaments, where the widths for positive and negative voltage pulses are 100 ns and 1 µs, respectively (Figure 7). Besides integer ones, half-integer quantum conductance levels under voltage pulses have also been reported by Gao et al. [39] in a Ag/poly(3-hexylthiophene):[6,6]-phenyl-C61-butyric acid methyl ester (P3HT:PCBM)/indium–tin oxide (ITO) memristor with Ag filaments. These results demonstrate the feasibility of modulating quantum conductance in memristors by voltage pulses. Moreover, it is noteworthy that the interval time between two adjacent voltage pulses is also an important factor to affect the quantum conductance behaviors. Short interval time tends to cause fluctuation in quantum conductance, which is due to the structural and electrochemical instabilities of newly formed filaments in a small period after the voltage pulse is removed.

A detailed summary of the reported memristors with quantum conductance up to date is presented in Figure 8. [14–16,31,33,34,36–39,41,42,70,72,73,75–85] It is clear that memristors with oxygen vacancy filament tend to show quantum conductance with both integer and half-integer multiples of $G_0$. In contrast, memristors with metal filaments are more likely to exhibit quantum conductance with only integer multiples of $G_0$. This is possibly caused by the difference in intrinsic conductivity between metal and oxygen vacancy filaments, which will be discussed in detail in the next section. On the other hand, for the same filament type, the quantum conductance has a tendency to be affected by the detailed composition of storage media. That is, quantum conductance with only integer multiples of $G_0$ is found for Ag filaments in classical ionic conductors such as GeS$_2$ [14], AgI [37] and AgInSbTe [76] but half-integer multiples of $G_0$ will occur once organic storage media like polyethylene oxide (PEO) [16] and P3HT:PCBM [39] are used. One possible explanation is the strong interaction between the Ag filaments and the hydrogen component from organic storage media, which needs to be further confirmed in future works.
Figure 7. Quantum conductance under short a) positive and b) negative voltage pulses with increasing amplitude in the Ti/Ta$_2$O$_5$/Pt memristor. a,b) Reproduced with permission.[75] Copyright 2013, AIP Publishing.

Figure 8. Detailed summary of the reported memristors with quantum conductance to date. The integer and half-integer quantum conductance effects are denoted by $G_0$ and $0.5G_0$, respectively.
3.2. Theoretical Understanding

3.2.1. Quantum Point Contact (QPC) Model

The thinnest part of a conducting filament, normally composed of a few atoms and exhibiting quantum conductance characteristics, can be reasonably considered as a QPC structure. Within it, electrons can transport ballistically without undergoing any collision as described by the Landauer theory.[17] Due to quantum size effect, the potential barrier herein lies in the bottom of limited discrete sub-bands, whose dispersion curves are expressed as:

\[ E(k_z, z) = \varepsilon_n(z) + \frac{\hbar^2 k_z^2}{2m} \]  

(2)

where \( k_z \), \( z \), \( m \), and \( \hbar \) are the \( k \) space coordinate, the real-space coordinate, the electron mass, and the Planck’s constant, respectively. The \( \varepsilon_n(z) \) relates closely to the filament thickness, with thinner filament leading to stronger spacing out of the sub-bands (Figure 9a).[16]

Within the Landauer theory, the current flowing through a QPC structure is calculated as:

\[ I = \frac{2e}{h} N_{ch} \int_{-\infty}^{\infty} T(E) \left[ f(E - \beta eV) - f(E + (1 - \beta) eV) \right] dE \]  

(3)

where \( N_{ch} \) is the total number of opened conducting channels, \( E \) is the energy, \( T \) is the transmission probability, \( f \) is the Fermi distribution function, and \( 0 \leq \beta \leq 1 \) is the fraction of the potential dropped on the source side of the constriction (Figure 9b). Assuming an inverted parabolic potential barrier, \( T \) is analytically expressed as:

\[ T(E) = \left[ 1 + \exp\left(-\frac{\pi^2 \hbar^2}{2m^2 \Phi_0} (E - \Phi_0)\right) \right]^{-1} \]  

(4)

Figure 9. Understanding of quantum conductance in memristors using QPC model. a) The dependence of sub-bands structure on filament size. Reproduced with permission.[36] Copyright 2012, AIP Publishing. b) The transmission probability of the bottom of ground quantized sub-band with a parabolic potential barrier. Reproduced under the terms of the Creative Commons Attribution 4.0 International License.[71] Copyright 2015, The authors, published by Springer. c) The dependence of quantum conductance type on the chemical potential difference. Reproduced under the terms of the Creative Commons Attribution 3.0 Unported License.[41] Copyright 2013, The authors, published by Elsevier. d) The dependence of quantum conductance type on the number of sub-bands between the contact Fermi levels. Reproduced with permission.[70] Copyright 2016, American Chemical Society.
where $\Phi_0$ is the height of the first sub-band and $t_0$ is the width of the first sub-band at $E = 0$. As such, the conductance for very narrow filaments is calculated to be

$$G \equiv N_0 \beta G_0$$  \hspace{1cm} (5)$$

indicating that $G$ is the integer multiples of $G_0$, when the voltage drop at two interfaces is asymmetric with $\beta = 1$. That is, each opened conducting channel will contribute a conductance unit of $2e^2/h$.

It is noteworthy that in addition to the integer ones, half-integer quantum conductance levels have also been frequently observed in many memristors. For example, Miranda et al.\cite{36} reported clear half-integer quantum conductance levels in the W/CeO$_2$/SiO$_2$/NiSi memristor and proposed a simple explanation with simulation results fitting well with the experimental data. In their model, the total current is expressed as

$$I = G_0 \{ BN^+ + (1 - \beta) N^- \} (V - V_0)$$  \hspace{1cm} (6)$$

where $N^+$ and $N^-$ are the numbers of right-going and left-going conducting channels (i.e., the numbers of sub-bands with $E_i \leq \beta(E - V_0)$ and $E_i \leq -(1 - \beta)(E - V_0)$), respectively, and $V_0$ represents any potential drop on the outside of analysis region. For simplicity, symmetrical potential drops at the two ends of the constriction are assumed, leading to $\beta = 1/2$ and thus the total current

$$I = 1/2G_0 \{ N^+ + N^- \} (V - V_0)$$  \hspace{1cm} (7)$$

In this case, half-integer quantum conductance levels emerge naturally when the difference between $N^+$ and $N^-$ is an odd number.

A similar model has also been proposed by Mehonic et al.\cite{41} which highlights the critical role of the chemical potential difference ($\Delta \mu$) between the left and right reservoirs (Figure 9c). Given that quantum conductance in the n-Si/SiO$_2$/p-Si memristor occurs at very high voltage region ($> 5$ V), half-integer quantum conductance levels are thus attributed to a large $\Delta \mu$ caused by the high voltage bias across the device. In this framework, half-integer quantum conductance levels should be hard to see in metal filaments because a large $\Delta \mu$ seems to be impossible due to their extremely high conductivity. However, half-integer quantum conductance levels have actually been reported in several memristors with metal filaments, such as Ag/P3HT:PCBM/ITO\cite{39} and Cu/SiO$_2$/W.\cite{70} To explain this, Nandakumar et al.\cite{70} described the current through the nano constriction to be

$$I = I_L - I_R = e \int_{E_1}^{E_2} dE n_{1D}v_g \left[ f(E - E_{\text{FL}}) - f(E - E_{\text{FR}}) \right]$$

$$= 2e \hbar \int_{E_1}^{E_2} \sum_{\nu} \theta(E - E_{\nu}) \frac{dE}{h}$$

$$= 2e \hbar \left( \sum_{\nu = 1}^{\nu_{1D}} \theta(E - E_{\nu}) dE + \sum_{\nu = 1}^{\nu_{1D}} \theta(E - E_{\nu}) dE \right)$$  \hspace{1cm} (8)$$

where $n_{1D}$ is the density of states obeying $n_{1D}v_g = (2/\hbar) \theta(E)$, $v_g$ is the electron velocity, $\theta(E)$ is the Heaviside step function of energy, and $E_i$ is the position of quantized energy levels for multimode ballistic transport. Assuming one energy level halfway between $E_{\text{FL}}$ and $E_{\text{FR}}$, the current will be

$$I = \frac{2e}{h} N_0 eV + \frac{2e}{h} N_0 eV = G_0 N_0 V + G_0 \frac{N}{2} V$$  \hspace{1cm} (9)$$

where $N_0$ is the number of sub-bands below $E_{\text{FR}}$ and $N (= 0$ or $1$) is the number of sub-bands between the contact Fermi levels. Hence, when $N = 1$, half-integer quantum conductance levels were observed (Figure 9d).\cite{70} They further suggests that a minimum Fermi level split limited only by the thermal energy of electrons is needed for a device to show half-integer quantum conductance levels and that the actual dielectric material may have an effect on the half-integer quantum conductance effect.\cite{70} Hence, further works are urgently needed to construct a universal QPC model for the quantum conductance in memristors.

### 3.2.2. First-Principle Calculations

Some attempts have been made to understand the quantum conductance in memristors by the use of first-principle calculations within the density-functional theory (DFT). For example, Krishnan et al.\cite{46} have performed detailed atomistic simulations to understand the correlation between the quantum conductance levels and the QPC structures in the Ag/PEO/Pt memristor. A 5 nm length channel was designed between two Ag electrodes to estimate the transmission eigenstates and calculate the corresponding eigenvalues and conductance values. The transmission eigenvalue herein represents the transport probability of electrons from one electrode into the counter electrode. When the transmission eigenvalue is “1,” electrons can transport from one electrode to another without being scattered. To understand the integer quantum conductance behaviors, optimized unit cells including in-line single, two, three, four, and nine atom chains were constructed (Figure 10a). As expected, maximum conductance values of 1, 2, 3, 4, and 9$G_0$ in the electron energy range of $-1$ to 1 eV have been obtained for the channels with single, two, three, four, and nine atom chains, respectively (Figure 10b). Further, to elucidate the half-integer quantum conductance levels, they constructed a more realistic Ag QPC configuration between two Ag electrodes. It is found that the conductance value will reduce in the heavily twisting configuration due to electrons suffering from heavy elastic scattering, which may be a possible origin of half-integer quantum conductance behaviors.

On the other hand, Long et al.\cite{83} have made detailed calculations to understand the quantum conductance behaviors of oxygen vacancy filaments in the Pt/HfO$_2$/Pt memristor, wherein the transmission $T(E)$ at the zero bias conditions is calculated through nonequilibrium Green’s functions and then the conductance is calculated using the Landauer formula as $G = T(E)G_0$. It is found that the removal of a single oxygen atom can bring a filled impurity state in the gap, but farther from the band edges (panel i) in Figure 10c). By reducing the distance between neighboring vacancies, the impurity band width will increase due to an enhanced overlap between
the impurity wavefunctions (panels (ii)–(iv) in Figure 10c). If a critical oxygen vacancy concentration (i.e., $1.5 \times 10^{21}$ cm$^{-3}$ for HfO$_{2-x}$ with $x = 0.05$) is reached, the carriers transport will change from hopping to band conduction, meaning the formation of oxygen vacancy filaments. After this, the conductance of filaments will increase significantly as their diameter changes, with each transmitting channel contributing one $G_0$ (Figure 10d).

### 3.3. Effective Control

The effective control of quantum conductance in memristors is a prerequisite for practical use. Since the quantum conductance values are determined by the constriction size of conducting filaments, they are possible to be effectively controlled by either programming current or stop voltage that can precisely modulate the filament strength in memristors. In 2012, Zhu et al.\[14\] first explored the control of quantum conductance in the Nb/ZnO/Pt memristor through various compliance currents ($I_{\text{comp}}$) in the set process and different stop voltages in the reset process. Started from 2.5$G_0$ realized by $I_{\text{comp}}$ of 100 µA, the quantum conductance can increase to 4.0$G_0$ with $I_{\text{comp}}$ of 250 µA, followed by 4.5, 6.5, and 8.5$G_0$ with further increased $I_{\text{comp}}$ values (Figure 11a). This is reasonable because a higher $I_{\text{comp}}$ tends to generate a stronger Nb filament that allows more sub-bands for electron transport. In contrast, a gradual increase in stop voltage can cause the existing Nb filament to be thinner, thus reducing the quantum conductance from the initial 14.5 to 8, 4, and 1$G_0$ in sequence (Figure 11b). They further found that by applying a suitable $I_{\text{comp}}$ in set process as well as a suitable stop voltage in reset process, the memristor can be switched between two stable quantum conductance states, such as 2 and 6$G_0$. Later on, Gao et al.\[39\] reported the realization of 1, 2, and 3$G_0$ quantum conductance states in the Ag/P3HT:PCBM/ITO memristor by using $I_{\text{comp}}$ of 50, 100, and 150 µA, respectively. Also, they observed stable memory operation between off state and 1$G_0$ quantum conductance state.

To get better insight into the relationship between programming conditions and quantum conductance values, statistical analyses based on huge experimental data are highly necessary. In this regard, Hu et al.\[84\] counted in detail the obtained...
3.4. Promising Applications

With numerous discrete conduction states in theory, quantum conductance in memristors is primary for ultra-high-density memory applications via multilevel storage in a single cell, as extensively explored in previous works. Recently, some interesting and promising applications beyond this basic aspect have also been explored to extend the application scope of quantum conductance in memristors.

3.4.1. Logic Circuits

Ideal logic circuits should possess high integration density, fast operation speed as well as low power consumption, all of which can be satisfied by quantum conductance in cation migration-based memristors with nanoscale device size, >GHz switching speed and sub-1 V operation voltage. Aono and co-workers\(^{[33]}\) pioneered the construction of AND, OR, and NOT logic gates by exploiting the bistable switch attribute of quantum conductance in Ag/Ag\(_2\)S/gap/Pt memristors (Figure 13a–c). For example, the AND gate was made using two Ag/Ag\(_2\)S/gap/Pt memristors and a resistor, where the two input signals (\(V_1\) and \(V_2\)) are applied to the Pt line, with the output signal \(V\) measured at one end of the Ag line. In this case, the output level becomes high only when both inputs are at the high level. Since AND, OR, and NOT gates can constitute one functionally complete logic combination, any logic gate is thus theoretically feasible to be configured with Ag/Ag\(_2\)S/gap/Pt memristors. Further, they succeeded in constructing an adder circuit by precisely controlling the conductance values of a \(1 \times 2\) Ag/Ag\(_2\)S/gap/Pt memristor array (Figure 13d).\(^{[33]}\) Using pulsed voltages to modulate the conductance values at each Ag bridge independently from \(N = 0\) to \(3\), the total conductance measured at the end of the silver line corresponds to the sum of the two conductance values, thus realizing the additive operation. Also, such circuit can be used as a multi-state memory with 16 states. Combining the intrinsic nonvolatility, quantum conductance in cation migration-based memristors thus shows great potential for developing area-, time-, and energy-efficient in-memory computing architecture to eliminate the latency and energy burdens faced by conventional von Neumann computers.

3.4.2. Neuromorphic Computing

Neuromorphic computing systems, inspired by the human brain, could bring about extremely cheap and efficient computing chips and have enormous advantages in dedicated machine learning applications. In neurobiology, the changes in the strength of synaptic connections (or weights) are called neuromplasticity and caused by memorization events, underlying the ability of the brain to learn and memorize. Ohno et al.\(^{[86]}\) first associated the quantum conductance in Ag/Ag\(_2\)S/gap/Pt memristors with biological neuromplasticity (Figure 14a). In this scenario, the memristor is considered as an inorganic synapse, with the input voltage pulse and Ag filament strength as the biological action potential and synaptic connection, respectively. Two basic types of synaptic plasticity, short-term plasticity (STP)
and long-term potentiation (LTP), have been well mimicked by precisely modulating the stimulation rate for the memristor (Figure 14b,c). When applying input voltage pulses with a longer repetition interval of 20 s, the approximately single-atom point contact conductance value (77.5 µS) is not maintained after removing pulses due to the deformation of an incomplete metallic atomic-sized bridge (Figure 14b). This resembles the STP in biological synapses that describes the temporal enhancement of a synaptic connection. In sharp contrast, the shorter repetition interval of 2 s can lead to a persistent conductance change for a long period of time due to the formation of a robust single atomic point contact (Figure 14c), similar to the permanent change in the synaptic connection known as LTP. Later on, Nayak et al.\(^\text{[81]}\) conducted a systematic synapse emulation study based on the quantum conductance in Cu/Cu$_2$S/gap/Pt memristors. The synaptic plasticity is found to be influenced not only by air but also by temperature. For instance, a long-term memory is achieved much faster at elevated temperatures with shorter or fewer number of input pulses, indicating a close analogy with a biological synapse where elevated temperature increases the degree of synaptic transmission. These results promise the great potential of quantum conductance in cation migration-based memristors for the development of artificial neural networks with high computing efficiency as well as smart air/temperature sensibility.

3.4.3. Atomic Scale Plasmonic Switch and Photodetector

The interactions between optical stimuli and electronic devices could open new doors to develop novel and superior optoelectronic nanodevices. In this regard, Emboras et al.\(^\text{[87]}\) first introduced an electrically controlled plasmonic switch operating at the atomic scale, which consists of a planar silicon photonic waveguide with a plasmonic Ag/a-Si/Pt slot waveguide on top (Figure 15a). The silicon waveguide is used to launch the optical signal into the Ag/a-Si/Pt slot, wherein the optical signal is converted into a gap plasmon. It is found

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Figure 12. Control of quantum conductance a,b) through various compliance currents in the single-crystal anatase-TiO$_2$ memristor and c,d) through different stop voltages in the Ag/PEO/Pt memristor. a,b) Reproduced with permission.\(^\text{[84]}\) Copyright 2014, American Chemical Society. c,d) Reproduced with permission.\(^\text{[16]}\) Copyright 2017, John Wiley & Sons, Inc.
Figure 13. Quantum conductance in memristors for logic circuits applications. a–c) The structures and operating results of AND, OR, and NOT gates. d) The structure and operating result of an adder circuit. All panels reproduced with permission.[33] Copyright 2005, Springer Nature.

Figure 14. Quantum conductance in memristors for neuromorphic computing applications. a) Schematics of a Ag$_2$S inorganic synapse and the signal transmission of a biological synapse. b) STP induced by a longer repetition interval of 20 s. c) LTP induced by a shorter repetition interval of 2 s. All panels reproduced with permission.[86] Copyright 2011, Springer Nature.
that the presence and absence of quantum conductance in the Ag/a-Si/Pt memristor can alter the plasmonic cavity properties to the extent that two distinct plasmonic resonances are supported. Remarkably, reversible digital optical switching with an extinction ratio of 9.2 dB and operation at room temperature up to MHz with femtojoule (fJ) power consumption for a single switch operation has been demonstrated. Later on, they proposed an optically controlled electronic switch based on the redistribution of a few atoms on the atomic scale for fast atomic photodetection (Figure 15b).[88] The photodetector consists of a silicon waveguide for input light propagating and a Ag quantum point contact constructed by applying voltage to the Ag/α-SiO$_2$/Pt memristor. When the light is input into the plasmonic Ag tip, a hot spot will be created with high optical field strengths and temperature, which leads to the dissolution of the Ag quantum point contact and thus the dramatical resistance increase to the order of $10^{10}$ Ω. Subsequently, after the light is turned off, the Ag quantum point contact is reformed, thereby decreasing abruptly the resistance by several orders of magnitude to the order of a few $G_0$. In such way, atomic photodetection with a digital electronic response, a high resistance extinction ratio (70 dB), and a low OFF-state current (10 pA) at room temperature is enabled. Combined together, these results could provide intriguing perspectives for a fully integrated and highly scalable chip platform, where optics, electronics, and memory may all be controlled at the single-atom level.

Noting that the above interesting and promising applications of quantum conductance are all demonstrated based on memristors with metal filaments. This is because quantum conductance in such memristors has been studied more intensively, as revealed in Figure 8. But theoretically, most of these applications are also feasible for quantum conductance in memristors with oxygen vacancy filaments.
4. Challenges and Outlook

Due to excellent downscaling potential, fast operation speed, low power consumption, and high switching endurance, memristors have been listed as a leading next-generation nonvolatile memory candidate for years by the International Technology Roadmap for Semiconductors (ITRS). More importantly, the quantum conductance effect of memristors, originating from the quantum size effect of the formed conducting filaments therein, promises great potential for ultrahigh-density storage and logic-in-memory circuits applications, which are highly desired in the nowadays Big Data era featured by a striking explosion in global digital information. As such, much attention has been paid to quantum conductance in memristors during the past dozen years, and significant advances have been made in consequence concerning both experimental observation and theoretical understanding of such effect. Meanwhile, its effective control and promising applications such as synapse emulating and photon detecting have been preliminarily explored.

Despite the above progress, some serious challenges have to be resolved before practical applications of quantum conductance in memristors. First, a thorough understanding on the physical origin of integer as well as half-integer quantum conductance is urgently required, which may serve as a guide for optimizing the performance of quantum conductance in memristors in future. To this point, the influence of storage media on quantum conductance is of particular importance because of the strong interaction between storage media and conducting filaments. Next, the stability of quantum conductance states, especially those related to metal filaments, needs to be significantly improved. The fast decay of quantum conductance states with retention time is certainly caused by the rapid diffusion of filament atoms into storage media, and thus proper combinations of filament composition and storage media could be a possible resolution. Since oxygen ions often have a higher diffusion barrier than silver and copper ions in oxide films, highly stable quantum conductance states are thus more likely to be obtained in memristors with oxygen vacancy filaments. Finally, the acquisition of any desired quantum conductance state on demand is a long desire in this field. To achieve this goal, the location variation of the dominating conducting filament during continuous operation cycles needs to be first settled, since it can lead to large fluctuation in memristor resistance. Possible solutions include electrode engineering (e.g., nanoparticle decorating and pyramid electrode), interface engineering (for example, inserting structure-defective graphene), and storage media optimization like dislocation design. On this basis, it still requires a more thorough understanding of the thinning and thickening dynamics of the dominating conducting filament. With all these challenges resolved, quantum conductance in memristors will certainly be a disruptive technology for wide applications including ultrahigh-density information storage, logic-in-memory circuits, neuromorphic networks, and so on. Moreover, close attention should also be given to other physical properties of the quantum conductance states in memristors, such as magnetoresistance, superconductivity, thermoelectricity, and photovoltaic effect. Advances in such studies may not only help to better understand the quantum conductance effect itself, but also open new doors for developing novel functionally integrated nanodevices.

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Conflict of Interest

The authors declare no conflict of interest.

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References