Mesoscopic phenomena in Au nanocrystal floating gate memory structure

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A resonant tunneling process is demonstrated in the HfAlO/Au nanocrystals/HfAlO trilayer nonvolatile memory (NVM) structure on Si, where the electrons tunnel back and forth to the Au nanocrystals due to the various mesoscopic behaviors. The electron tunneling behavior in this trilayer structure exhibits dissimilar resemblance to those in double-barrier tunnel junctions taking into account of the correlation of Coulomb blockade effect. The observed specific tunneling process is beneficial in studying the interplays of various mesoscopic physics and application of single electron devices into NVM. © *2009 American Institute of Physics*. [doi:10.1063/1.3229885]

Recently, extensive work has been carried out to realize the nonvolatile memory devices using metal nanoclusters due to their quantum confined structures having potentials to fulfill the demands for small size, low current, and enough on/off voltage gap.[1,2] Undoubtedly, metal nanocluster embedded in high-*k* materials could work as promising floating gate memory. Apart from this application, metal nanocrystals (NC) could also be used as well-controlled test laboratories to study the interplay between different types of order.[3] One could study the tunneling behavior via metal NCs as they provide zero-dimension states of microscopic dimensions, which is not accessible by conventional conductance experiments.[4] For instance, the discrete charges stored in the isolated metal nanoclusters could make it possible as single electron device, in which a number of electrons stored in one single NC tunnel in and out coherently.[5] This device retains its scalability from nanoscale down to atomic scale.

Since these structures permit the measurements of the energy required for adding successive charge carriers, they can be used to understand the energy-level spectra of small electronic systems, which can be considered as a convolution of consequence of random matrix theory and Coulomb blockade effect.[6–8] Though such measurements are effective means for verifying the Coulomb Blockade effect and providing spectroscopic measurement of electronic eigenstates in nanometer-scale metal particles, the application on large scale application in flash memory by single electron device is being hindered.

Inside a tunnel junction, or from electron tubes and tunnel junctions, there always exists time-dependent fluctuations in the electrical current due to the discreteness of the charge *e*, and is commonly known as shot noise.[9] This has been studied long time ago, as this tells that the electrons are transmitted through the conductor as uncorrelated current pulses.[10] Recent studies showed that shot noise in mesoscopic conductors could be greatly suppressed by the correlations in the electron transmission due to Coulomb interactions. There have been theoretical studies on the noise properties of double-barrier tunnel junctions taking into account the charging energy of the intermediate electrode.[11] However, the resonant tunneling and its convolution with Coulomb blockade effect in this kind of nonvolatile memory structure has not been reported before. Previously, single electron tunneling and Coulomb blockade effect have been observed in similar trilayer floating gate memory structure.[12] In this paper, we reported a phenomenal current-voltage characteristic which believed to be the convolution of these effects.

Au NCs embedded HfAlO/Au NCs /HfAlO trilayer structure on Si substrate was fabricated by pulsed-laser deposition at 550 °C with 2 Pa of O_2. Different gases have been tried for Au NCs growth besides high vacuum condition, in including N_2, Ar, and O_2 ambient. The Au NCs size is the smallest under vacuum condition, and there is no big difference between other gases. The gas molecules help Au NCs formation due to collision with Au atoms. Since the dielectric layer was deposited in vacuum with O_2 gas, it would be convenient to keep the same gas ambient during the deposition of Au NCs, and in fact, the oxidation effect to Au NCs is not obvious. After deposition of the three layers, the memory structure was annealed in N_2 ambient at 850 °C for 30 min. Structural characteristics of this trilayer structure were characterized by means of high-resolution transmission electron microscopy (HRTEM). Apart from conventional electrical characterization of floating gate memory, this structure has also been put into low temperature for electron tunneling charterization.[2] The low temperature experiments were performed in a ^{4}He bath cryostat with a variable temperature insert. The bias voltage is applied directly to the trilayer structure.

The cross-section and plane-view HRTEM images of HfAlO/Au NCs/HfAlO trilayer structure is shown in Fig. 1. The plane-view TEM image of the trilayer structure shows the Au NCs are uniformly distributed between the two HfAlO layers and the diameters of the Au NCs are ranged from 3 to 8 nm. The density of the Au NCs is estimated to be about 2×10^{12} cm^{-2}.

Figure 2 shows the *I-V* characteristics of the multilayer NVM structure under low bias voltage at 20 K. It can be seen that nonperiodic tunneling current peaks appear in both forward [Fig. 2(a)] and backward [Fig. 2(b)] bias voltages. Since the current peaks in the *I-V* curves are very large compared to the very low background (−100 to +130 fA), the likelihood to be the random noise can be eliminated. The Coulomb staircase was observed when the bias voltage was

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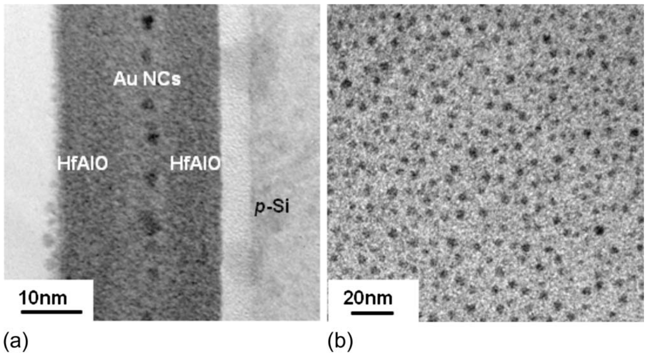

FIG. 1. (a) Cross-sectional HRTEM image of the trilayer quantum well structure, where Au NCs are evenly distributed in HfAlO matrix; (b) the plane-view HRTEM image of the Au NCs.

further increased, in which the Coulomb staircase is well described by the "orthodox theory," which assumes inelastic scattering of the electrons on the particle.[10,12,13] The tunneling current peaks in Fig. 2 can be attributed to resonant tunneling, and previously, Adams *et al.*[7] suggested that the peaks instead of steps were the transportation of electrons via resonant tunneling and were assumed to be the *signatures* of discrete energy levels of the NCs. To further understand this phenomenon, a similar analytical calculation is carried out based on a near-free electron model.[8] The mean spacing of independent-electron spin-degenerate energy levels was estimated by

$$\delta E \sim \frac{2\pi^2\hbar^2}{mk_F V},$$

where m is the electron mass, V is the mean volume of the NC, and k_F is the Fermi wavevector (1.20×10^8 cm^{-1} for

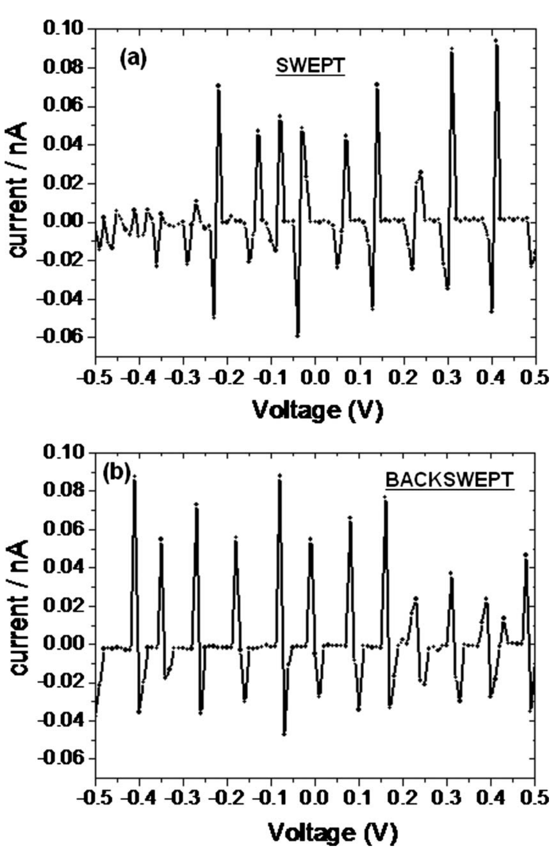

FIG. 2. *I-V* curve measured at 20 K, with (a) SWEPT, and (b) BACKSWEPT, voltages within −0.5 to 0.5 V.

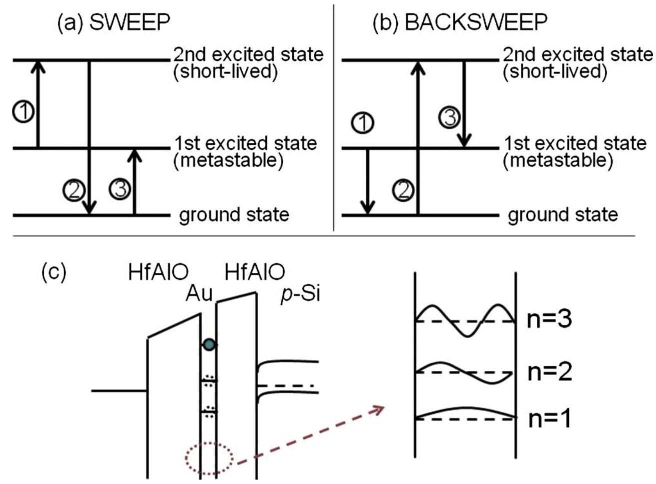

FIG. 3. (Color online) Schematic diagram of the two possible resonant tunneling processes are shown in (a) and (b), corresponding to the SWEPT and BACKSWEPT *I-V* curves obtained at 20 K (refer to Fig. 2). (c) Inside the quantum well, electron wave reflects back and forth to restore energy, until the threshold voltage is large enough to reach the threshold.

Au).[14] With the mean size of Au cluster of ~3.5 nm, the estimated mean level spacing is ~2.9 meV with the tunneling time $\sim3.0\times10^{-13}$ s and the number of atoms is in the order of 10^3. Individual levels should be resolvable by tunneling for $\delta E \geq k_B T$, or $T \leq 23$ K or even lower.

It is interesting to notice that the *I-V* characteristic, as shown in Fig. 2, shows dissimilar resemblance to the reported results.[6–8,15] Earlier reported results show that only peaks with current larger than zero were observed. In our study, the peaks exhibit both negative current and negative conductance. One can also see that the current peak values are much different under different resonant voltages. This is probably due to the nonuniform distribution in size of the Au NCs, as well as a shot noise effect. An explanation of the shot-noise suppression on resonant tunneling caused by charge tunneling and Coulomb blockade effect can be given by the two-state model.[11,16] The schematic diagram of two possible resonant tunneling processes are shown in Figs. 3(a) and 3(b), corresponding to the SWEPT and BACKSWEPT *I-V* curves obtained at 20 K as shown in Fig. 2. Excluding all the stray resistance, here, we assume that all the free electrons in Au NCs are at the same quantum state at low temperature during measurements (i.e., coherent transmission)[3] and only the two charge states with the energetically most probable number of the electrons on the NCs are considered. During the sweeping of voltage ΔV, the voltage increases at each time interval, the electrons are charged up to the excited state (a rather metastable state) by the constantly applied electric field; while resonance is set up by the increased electric field, as illustrated in Fig. 3(c). Once the resonance is set up, electrons in the Au NCs jump from the original metastable state to a higher excited state [refer to Fig. 3(a)] and a drop in current appears first due to the back tunneling of electrons from the Au NCs to the Si substrate. But the excited state is short-lived, so the electrons drop back to the ground state, resulted in a current up rise while electrons tunnel into the Au NCs from the Si substrate, as depicted in Fig. 2(a). Similar explanation can also be used to interpret the backswept process [Figs. 2(b) and 3(a)], where a negative current peak appears first, followed by a positive peak.

In summary, dissimilar resonant tunneling process of HfAlO/Au NCs/HfAlO trilayer structure has been demonstrated experimentally and the theoretical explanation has been discussed. This process may be due to the convolution of shot-noise suppression, Coulomb Blockade effect, and resonant tunneling, resulting in a different *I-V* characteristics from the ordinary resonant tunneling inside quantum well. However, as the temperature goes down, dopants freeze-out and thermal generation of minority carriers is minimal, resulting in gradual increases of resistance, and therefore, the memory effect is not obvious at cryogenic-temperature. Memory effect at low temperature deserves further study.

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