Artificial Nanostructures Formed on Si(111)-(7×7) Surfaces with Ultrahigh Vacuum Scanning Tunneling Microscopy and their Electron Transport Characteristics

D. Fujita, Z.-C. Dong, H.-Y. Sheng and H. Nejoh

National Research Institute for Metals, 1-2-1 Sengen, Tsukuba 305, Japan

(Received: 21 January 1998; accepted: 15 March 1998)

Abstract

Nanometer-scale gold dots have been fabricated reproducibly on an n-type Si(111)-(7×7) surface in ultrahigh vacuum by applying pulses to a piezo z-axis actuator of a scanning tunneling microscope (STM), that is, a so-called *z-pulse method*. The nanodot formation by the z-pulse method can be attributed to the spontaneous formation of a nanometer-scale point contact between a gold tip apex and the Si(111) surface. Even atomically resolved images of the reconstructed structure are still observable after point contact formations. Measurement of current-voltage characteristics with the STM tip located above a single gold nanodot showed equidistantly spaced steps with a spacing of about 200 mV, which can be attributed to a manifestation of single electron tunneling effect (Coulomb staircase).

* Corresponding author:
Dr. D. Fujita, National Research Institute for Metals, 1-2-1 Sengen, Tsukuba 305, Japan
Tel: +81-298-59-2737 Fax: +81-298-59-2701
E-mail: fujitad@nrim.go.jp

1. Introduction

Significant efforts have been made to fabricate artificial nanometer-scale structures since the middle 1980s, not only from scientific interests [1,2], but also for the potential technological applications in nanoelectronics [3]. The development of this new interdisciplinary field has been accelerated by the almost simultaneous advents of a scanning tunneling microscope (STM) and related scanning probe microscopes (SPM)[4,5]. Nowadays the SPM-based techniques have already proved themselves to be extremely powerful tools for the nanotechnology [6]. A number of SPM nanofabrication methods have been developed since then, for example, atom or molecule manipulation [7,8], local chemical-vapor deposition [9,10], nanoscale selective oxidation [11], nanoscale lithography [12], field induced transfer of tip material [13-16], and so on. Using the above nanofabrication techniques, some interesting prototypes of nanodevices such as single electron tunneling (SET) circuits have been realized by the STM nano-oxidation processes performed in air [17,18].

In our previous articles, we have reported that gold nanodots can be deposited on an atomically clean Si(111)-(7×7) surface in ultrahigh vacuum by applying negative voltage pulses to gold-coated tungsten or pure gold STM tips using field induced tip-material transfer [19,20]. The tip-material transfer method has been selected among the various nanofabrication methods because of its potential versatility in positioning the nanodots. Although the so-called *voltage pulse method* is found to be a suitable technique for fabricating various dimensions of nanodots, it should be pointed out that fabrication of a continuous nanoline is still difficult by this method because of its relatively low deposition probability in ultrahigh vacuum [19]. In the present article we report a new fabrication method for gold nanodots on a Si(111)-(7×7) surface. Instead of applying voltage pulses, this technique uses a controlled approach of the tip to the surface to form an atomic point contact. The electron-transport characteristics observed for a double barrier tunnel junction geometry with a STM tip/Au nanodot/Si(111)-(7×7) substrate arrangement are also demonstrated.

2. Experimental

The experiments were performed using a variable temperature STM (Omicron Ltd., VT-STM) operated in ultra-high vacuum with a base pressure of 1×10^{-9} Pa. The details of the total system for nanofabrication and transport measurement have been described elsewhere [20]. The sample was a sheet of 2×9×0.3 mm, cut from an n-type Si(111) wafer (P-doped, ca. 0.01 Ω cm). The Si(111)-(7×7) reconstructed

surface was obtained with several cycles of thermal annealing and flashing up to about 1500 K in UHV ($<1\times10^{-7}$ Pa). The gold STM tips were prepared from a 400 μm diameter gold wire by electrochemical etching in concentrated hydrochloric acid (35%, +1.5 V DC). The tunneling voltage V_t was applied to the tip while the sample was grounded. In order to cause a point contact between the gold tip and the Si(111) surface, the voltage pulses were applied to the z-axis piezo actuator, by which the tip can reduce its gap distance by a certain distance for a certain period. Hereafter, this new method is named as *z-pulse method* so that we can distinguish it from the conventional voltage pulse method [13-16]. Using the STM control software, we can set the pulse conditions such as the tip position, the magnitude of the z-axis movement, and the duration of pulses. The z-position deviation Δz with an applied pulse was set within the gap distance. The period of a pulse t_p was fixed to 1 ms. The nanofabrication experiments were performed at room temperature (RT) and at about 50 K to check the temperature dependence of deposition. The sample cooling was performed with a liquid helium cryostat of the VT-STM. The spectroscopy measurement procedure is to first acquire a topographic image and then locate the tip above an isolated gold nanodot for the current-voltage (*I-V*) data.

3. Results and discussion

After the sample cleaning procedure, STM images of the Si(111)-(7×7) reconstructed surfaces were observed even with atomic resolution both at RT and 50K using the gold tip. By applying the z-pulses under certain conditions, gold nano mounds were found to be deposited on the Si(111) surface at both temperatures. The typical image of the gold nanodot after applying a single z-pulse (Δz = -0.3 nm) at 50K is shown as a three-dimensional plot in Fig. 1 (V_t = -2.0 V, I_t = 0.69 nA). The figure clearly shows a gold nano-mound protruding on the Si(111)-(7×7) surface. It should be noted that the reconstructed (7×7) structure of the Si(111) surface is still atomically resolved. Typical dimensions of the gold nano-mound are about 5-10 nm in width and 1.0 nm in height with the above conditions. Generally, a gold nano mound was not observed when the magnitude of z-pulse was smaller than 0.2 nm. The size of gold mounds tended to be larger when the z-pulse magnitude was increased

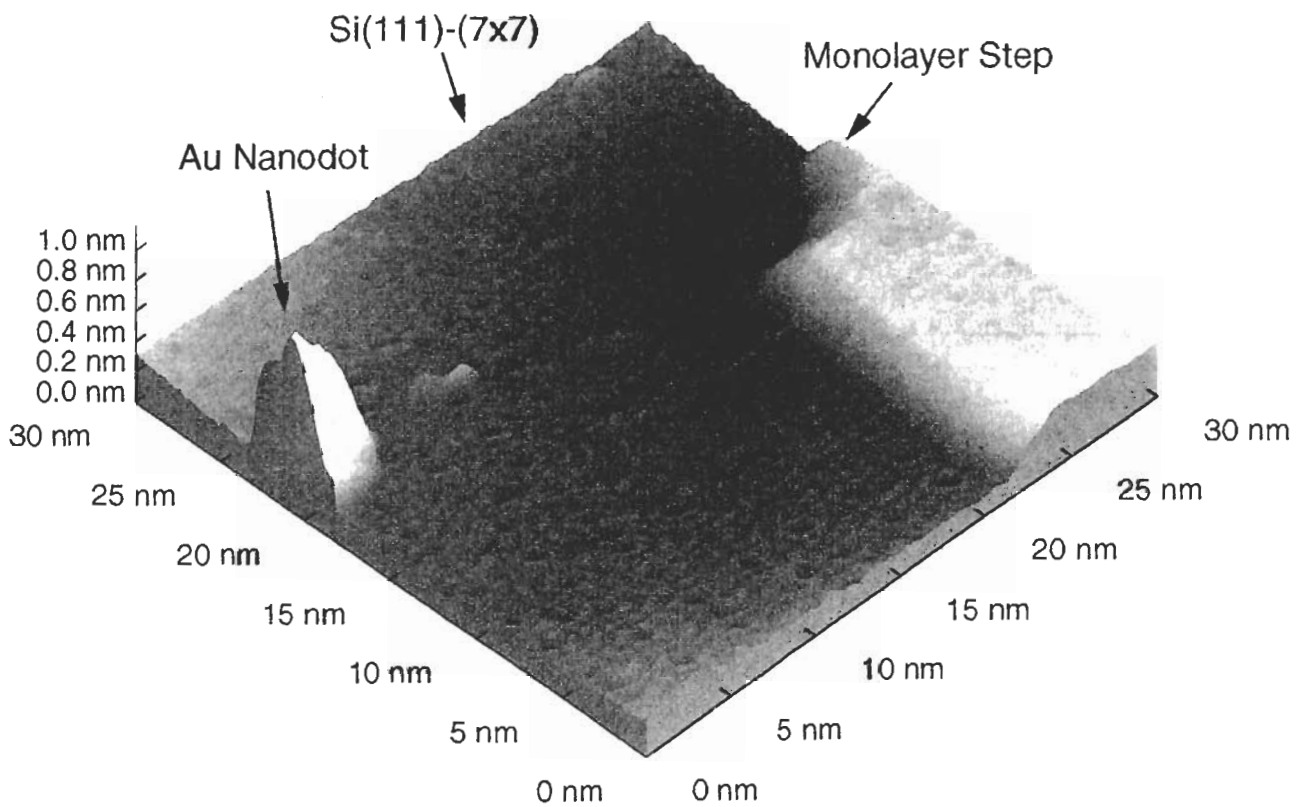

Fig.1 An STM image of a gold nanodot formed on a Si(111)-(7×7) surface after applying a single z-pulse (Δz = -0.3 nm, t_p = 1 ms) to a gold tip at 50 K. Imaging conditions: Vt = -2.0 V, I_t = 0.69 nA.

from 0.2 nm to 0.4 nm.

A qualitative model for the tip-material transfer from a gold tip to a Si(111) surface by the z-pulse method has been developed, which is schematically shown in Fig.2 (a) and (b). The mechanism of nanofabrication by z-pulse method has been described in detail elsewhere [21]. At the initial stage, the tip is located at the regulated height by feedback control. The gap distance is typically around 0.5-0.6 nm dependent on the tunneling conditions such as the applied gap voltage and the feedback tunnel current. By applying a single z-pulse, the gold tip approaches to the surface by typically 0.3-0.4 nm in our cases. When the gap distance becomes close to the atomic distance of about 0.2-0.3 nm, an atomic-sized point contact will be spontaneously formed as shown in Fig.2 (b) probably because of the following reasons. One possible reason is formation of an atomic-scale protrusion caused by field induced diffusion of gold atoms to the tip apex. It is well known that applied high electric field makes atoms at the tip shank diffuse to the tip apex by a field-gradient-induced surface diffusion [22]. The other explanation is a chemically induced diffusion or a formation of chemical bonds. According to the DAS model proposed by Takayanagi et al., the Si(111)-(7×7) surface has surface adatoms, which have dangling bonds protruding to vacuum [23]. Therefore, it is possible to form an atomic-sized point contact through chemical bonding with these dangling bonds, if the gap distance is close enough for both valence wavefunctions to overlap. After extracting the tip, a nanoscale gold dot should be left on the surface as shown in Fig.2 (b), because of the relatively strong chemical bonds between the gold and the silicon atoms.

Compared with the voltage pulse method, the advantage of the z-pulse method is its higher deposition probability. The deposition probability is defined as the number of deposition events divided by the number of applied pulses. In the previous paper we have reported that the maximum deposition probability with the voltage pulse method is about 50% [19]. In this case, if the tip condition such as the shape of the tip apex is suitable enough, a gold nanodot is formed after applying a single z-pulse (Δz= ~ -0.3 nm) with the deposition probability of about 90%. Using this property, we can deposit a gold dot very close to a previously deposited one, which means the high feasibility of forming a continuous line by sequential depositions. Figure 3 shows the STM image after the manual application of multiple z-pulses (Δz= -0.25 nm) at 50K. Along the line of applied pulses, gold mounds of the size ranging from ~3 nm to ~10 nm across were observed. Most of the dots were found to be connected with the neighboring dots, which suggests that it may be possible to form a continuous gold line by this method. The typical dimensions of a gold nanoline are ~5 nm wide and ~50 nm in length.

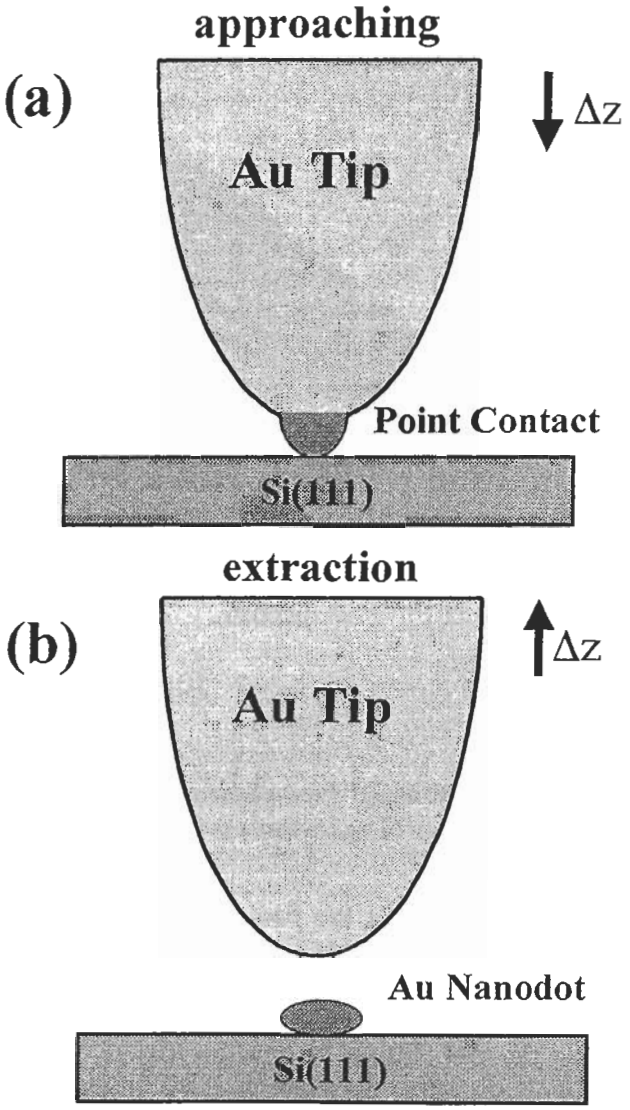

Fig.2 Schematic representations of tip material transfer mechanism from a gold STM tip to a Si(111)-(7×7) surface by the z-pulse method. (a) The gold tip makes a mechanical point contact spontaneously with the Si(111)-(7×7) surface by a controlled approach Δz. (b) After a fixed period, the tip is extracted by feedback control. A gold nanodot is formed on the surface because of the chemical bonds between gold and silicon atoms.

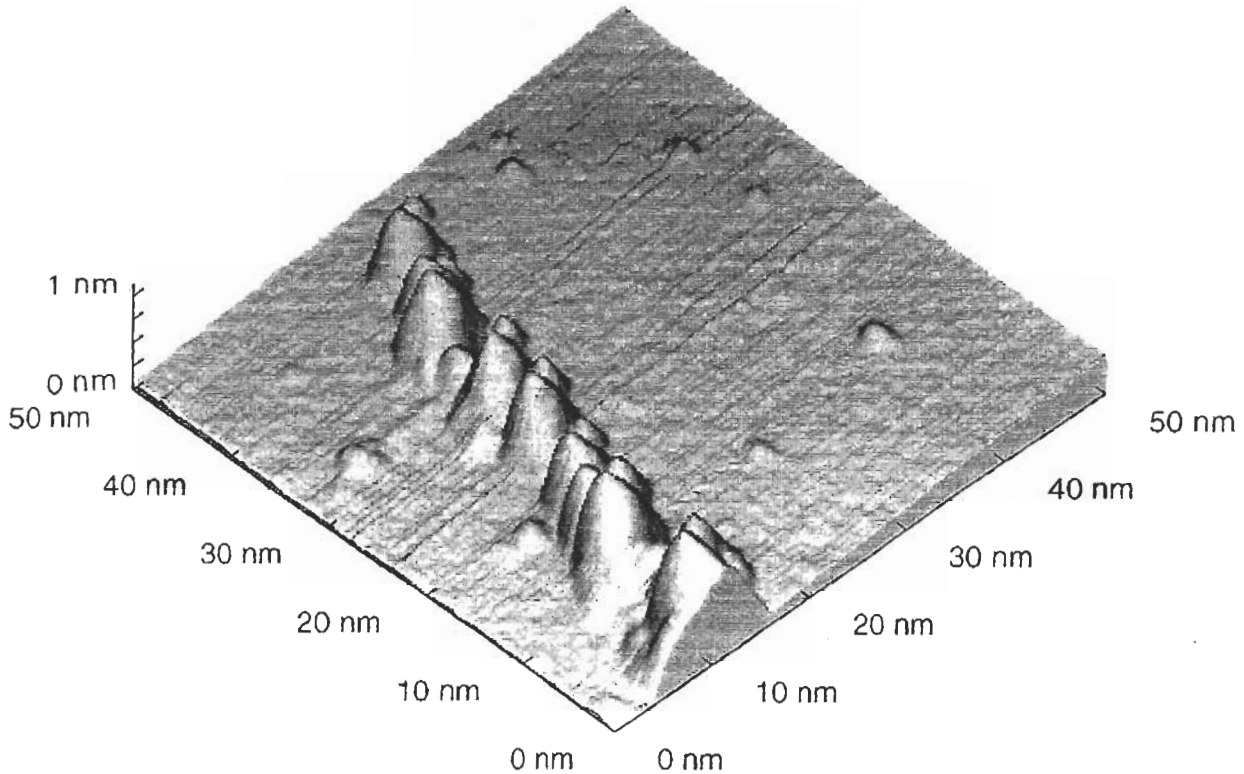

Fig.3 An STM image observed for a sequence of gold nanodots formed on a Si(111)-(7×7) surface after manual application of successive z-pulses (Δz = 0.25 nm) to a gold tip at 50 K. Imaging conditions: V_t = -2.0 V, I_t = 0.37 nA.

Immediately after the formation of the gold nanodot by the z-pulse method, tunneling current as a function of the z-position (*I-V* curve) was measured by positioning the tip just above the dot. Figure 4 depicts a typical *I-V* spectrum obtained for a single gold nanodot of about 10 nm in diameter and 1 nm in height at RT. A sequence of almost equidistantly spaced steps with a step width of $\Delta V \approx 200$ mV was observed in the *I-V* curve, which overlaps with a conventional *I-V* curve of n-type Si(111) surface. Possible origin of the equidistant step structure can be attributed to the SET effect occurred in double barrier tunnel junctions as shown schematically in Fig.5. One junction is specified by the vacuum gap between the tip and the gold nanodot with a resistance of R_1 and a capacitance of C_1. The second junction arises from a depletion region or a Schottky barrier formed just under the gold nanodot (R_2, C_2). If a high-work-function metal makes contact with an n-type semiconductor, electrons flow from the semiconductor to the metal after contact, depleting a characteristic surface region in the semiconductor of electrons [24]. The local electrical resistivity increases significantly near the surface with respect to its bulk value. The existence of a similar space-charge region under a nanoscale gold dot deposited on a p-Si(111) surface was previously pointed out by Radojkovic et al. [16]. SET effects, such as Coulomb blockade and Coulomb staircase can be observed under certain conditions. Firstly the charging energy $E_c=e^2/2C$ corresponding to

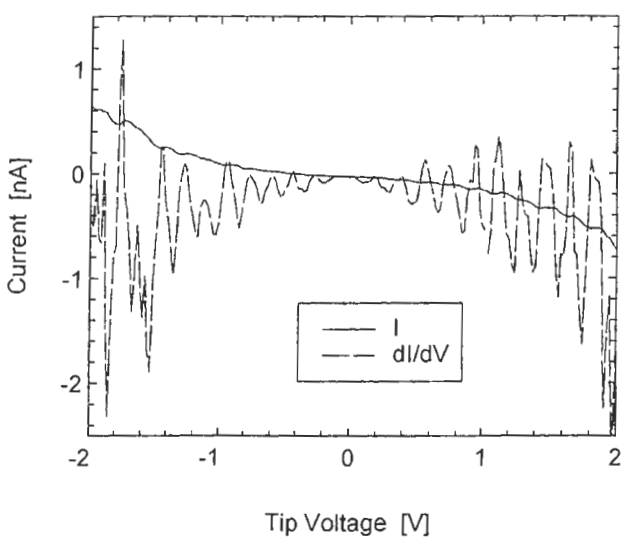

Fig.4 Current-voltage curve (shown by *I*) and its differentiated spectrum (*dI/dV*) obtained on an isolated gold nanodot on a Si(111)-(7×7) surface at room temperature, exhibiting equidistantly spaced steps of ≈ 200 mV.

a single-electron charge of the center island (quantum dot: QD) should be higher than the thermal energy k_BT [2,3], where C is a total capacitance (C_1+C_2) . As a first approximation the total capacitance C is considered to be of the same order as C_1 and C_2 and can be expressed classically as $C_1 \approx \varepsilon S/d$, where ε is the dielectric constant of a vacuum tunneling barrier, S is the junction area and d is the tunneling gap distance. Taking into account the typical values for d=1nm, $S=\pi \times 5 \times 5$ nm^2 and $\varepsilon = 8.855 \times 10^{-12}$ F/m, the capacitance is roughly estimated to be about 7×10^{-19} F. Thus the corresponding charging energy $E_C \approx 110$ meV is much larger than the thermal energy of nearly 26 meV at room temperature. Secondly the tunnel resistances R_1 and R_2 have to exceed the quantum resistance R_Q defined as h/e^2 (=25.8 kΩ) to overcome the quantum fluctuation. The resistance of the nanoscale depletion barrier R_2 can be roughly estimated by measuring the contact resistance of the point contact, which is about 100 kΩ in our case [21]. In the case of 1 Ωcm p-type Si(111), the reported resistance R_2 is about 1M Ω [16]. Because the vacuum tunneling resistance R_1 (≈1 GΩ) can be considered to be much larger than that of the nanoscale depletion barrier R_2, the double barrier tunnel junctions can be considered strongly asymmetric. In this case a sequence of equidistantly spaced steps with the voltage interval of $\Delta V=e/C_1$ will appear in the I-V spectrum. From the observed step width ΔV= 200 mV, the capacitance of the first junction can be estimated as $C_1 = e/\Delta V \approx 8 \times 10^{-19}$ F, that is consistent with the value estimated geometrically as above.

4. Conclusions

We have demonstrated that ultra small gold dots of nano-meter scale can be located at the specified positions on a Si(111)-(7×7) surface using tip-material transfer from the gold tip in ultrahigh vacuum. This new nanofabrication technique using the application of piezo z-pulse (z-pulse method) can form nanometer-scale gold mounds with the dimensions of about 5 nm across and about 1 nm high on the surface. Atomically resolved images of the reconstructed structure are still observable even after many cycles of point contact formation. The nanodot formation can be attributed to the spontaneous formation of nanometer-scale point contact of a gold tip apex to the surface. Thanks to its high deposition probability, fabrication of an almost continuous gold nanoline of 5 nm wide and 50 nm in length has been successfully performed. By measuring current-voltage characteristics with the STM tip located above a single gold nanodot, nearly equidistant steps with a spacing of about 200 mV were observed, which can be attributed to a manifestation of single electron tunneling effect (Coulomb staircase).

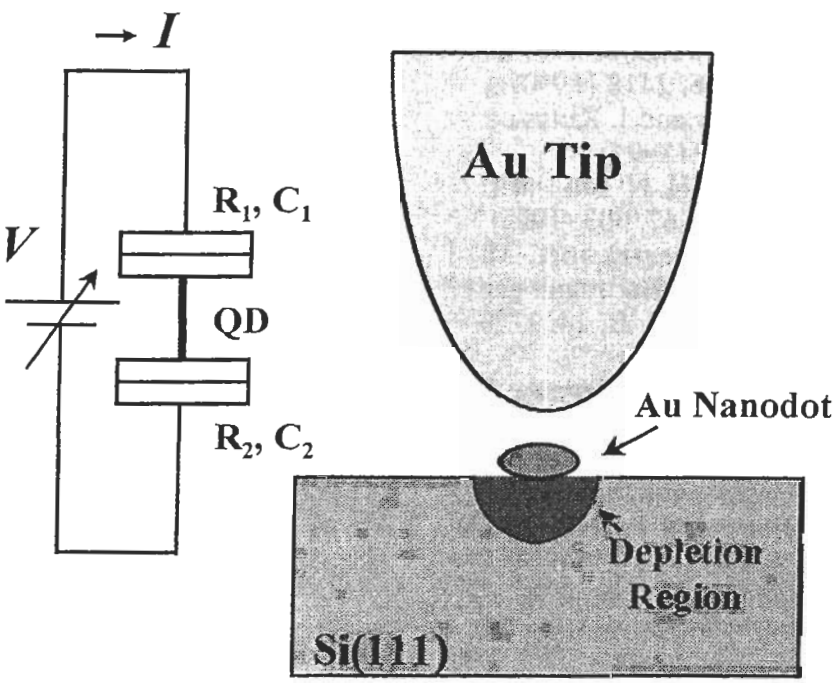

Fig.5 Schematic representation of a possible double-barrier-tunnel-junction model for the experimental arrangement of the I-V measurement on a single gold quantum dot (QD). The resistances and capacitances for the vacuum gap and the depletion region are (R_1, C_1) and (R_2, C_2), respectively.

References

1. S. Datta: *Electronic Transport in Mesoscopic Systems,* (Cambridge Univ. Press, Cambridge, 1995) pp. 246
2. L. J. Geerligs, *Physics of Nanostructures,* ed. by J. H. Davies and A. R. Long, (SUSSP Publications, Edinburgh, 1992) pp. 171
3. D. V. Averin and K. K. Likharev, *Single Charge Tunneling, ed.* by H. Grabert and M. H. Devoret, (Plenum Press, New York, 1992) pp. 311
4. G. Binnig, H. Rohrer, Ch. Gerber and E. Weibel, Phys. Rev. Lett., **49**, 52 (1982)
5. G. Binnig, C.F. Quate and Ch. Gerber, Phys. Rev. Lett., **56**, 930 (1986)
6. R. Wiesendanger, *Scanning Probe Microscopy and Spectroscopy,* (Cambridge Univ. Press, Cambridge, 1994) pp. 542
7. M. F. Crommie, C. P. Lutz and D. M. Eigler, Science **262**, 218 (1993)
8. L. Bartels, G. Meyer and K.-H. Rieder, Appl. Phys. Lett. **71**, 213 (1997)
9. M. A. McCord and D. D. Awschalom, Appl. Phys. Lett. **57**, 2153 (1990)
10. D. Sawara, J. R. Williamson, C. K. Shih and S. K. Banerjee, J. Vac. Sci. Technol. B, **14**, 1344 (1997)
11. T.-C. Schen, C. Wang, J. W. Lyding and J. R. Tucker, Appl. Phys. Lett. **66**, 976 (1995)
12. C. Van Haesendonck, L. Stockman, G. Neuttiens, C. Strunk and Y. Bruynseraede, J. Vac. Sci. Technol. B, **13**, 1290 (1995)
13. H. J. Mamin, P. H. Guethner and D. Ruger, Phys. Rev. Lett. **65**, 2418 (1990)
14. G. S. Hsiao, R. M. Penner and J. Kingsley, Appl. Phys. Lett. **64**, 1350 (1994)
15. T. C. Chang, C. S. Chang, H. N. Lin and T. T. Tsong, Appl. Phys. Lett. **67**, 903 (1995)
16. P. Radojkovic, M. Schwartzkopff, M. Enachescu, E. Stefanov, E. Hartmann and F. Koch, J. Vac. Sci. Technol. B, 14, 1229 (1996)
17. K. Matsumoto, M. Ishii and K. Segawa, J. Vac. Sci. Technol. B, **14**, 1331 (1996)
18. W. Xie, X. Dai, L. S. Xu, D. A. Allee and J. Spector, Nanotechnology, **8**, 88 (1997)
19. D. Fujita, Q.-D. Jiang and H. Nejoh, J. Vac. Sci. Technol. B **14**, 3413 (1996)
20. D. Fujita, Q.-D. Jiang, Z.-C. Dong, H.-Y. Sheng and H. Nejoh, Nanotechnology, **8**, A10 (1997)
21. D. Fujita, Z.-C. Dong, H.-Y. Sheng and H. Nejoh, Appl. Phys. A, (1998) in press.
22. T. T. Tsong, Phys. Rev. B., **44**, 13703 (1991)
23. K. Takayanagi, Y. Tanishiro, S. Takahashi, and M. Takahashi, Surf. Sci., 164, 367 (1985)
24. H. Luth, *Surfaces and Interfaces of Solids,* (Springer, Berlin, 1993) pp. 372