Coulomb interaction controlled room temperature oscillation of tunnel current in porous Si

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A novel phenomenon of regular oscillations is observed in $I-V$ characteristics of porous silicon under illumination by visible light. The measurements are performed at room temperature using a scanning tunneling microscope. The heights of the oscillation peaks appear to be a linear function of the oscillation number. The experimental value of the Coulomb energy determined from the oscillation period is much smaller than k_BT. The oscillations are attributed to a Coulomb effect, i.e. to the periodic trapping of a multielectron level in a quantum well within a Si nanocrystal under the combined influence of the voltage variation at the STM tip and the Coulomb interaction among the carriers.

We have observed periodic oscillations in $I-V$ characteristics of porous Si illuminated by visible light. The experiment is performed at room temperature using a scanning tunneling microscope (STM). The relative amplitude of the oscillating part is about 10%. At the same time, the Coulomb energy determined from the distance between the adjacent oscillation peaks is smaller than the thermal energy k_BT at room temperature so that within the framework of the standard theory of Coulomb blockade the oscillation amplitude should be exponentially small.

Ours is a typical charge transport experiment in which a voltage difference is applied to a source (a metallic tip) and a drain (silicon, see Fig. 1) separated by an insulating gap. In the middle of the gap lies a third electrode (porous Si nanocrystal). Under illumination the electrons are excited into the conduction band whereas the holes are in the valence band. Part of the excited electrons annihilate with holes, another part is localized on traps while some electrons are left in the conduction band taking part in the charge transport. As the electron-phonon scattering is intensive the electrons will be in a partial thermodynamic equilibrium, i.e. they have an equilibrium distribution function. However, their chemical potential μ is determined by the illumination. Under the action of the voltage the electrons in the nanocrystal create a current from the conduction band into the semiconducting sink. The neutrality is maintained by the flow of electrons between the metal tip and the valence band of the nanocrystal.

Porous Si specimens were prepared by ordinary method using electro-chemical anodizing of p-Si(100) wafers of resistivity 5 Ω/cm for 5 minutes at the current 25 mA/cm^2. Before measurements the samples were stored for several days in the ambient to reach a quasistatic regime of natural oxidation [1]. As shown in Fig. 1, the tunnel junction for STM investigations was formed between the tip of the microscope and the porous Si layer grown on a wafer. To increase the number of free carriers, and the tunneling current I, the specimens were illuminated with light from a Xe lamp or a Kr/Ar laser working at $\lambda = 514$ or 647 nm (with power density up to $P_{max} \approx 10$ mW/mm^2). STM images of our samples show clusters (with size about 100 nm) of prolonged particles (columns) of 3 to 5 nm width and about 20 nm height on the top of the porous Si layer. The distance between the particles is 3–5 nm. The total thickness of the porous layer is about 3 μm. These structures are similar to the surface features of porous Si observed previously by AFM and STM [2].

Porous Si can capture injected carriers [3], exhibits both the surface photovoltaic effect with photoinduced trapping of charge in the oxide on the surface [4] and shows persistent photoconductivity [5]. These phenomena are usually observed in structures with built-in potential barriers where the excess carriers are injected optically into the vicinity of such a barrier. In the presence of the surface photovoltaic effect it is possible to get a tunneling current, I, sufficient to operate STM at values of the applied tunneling

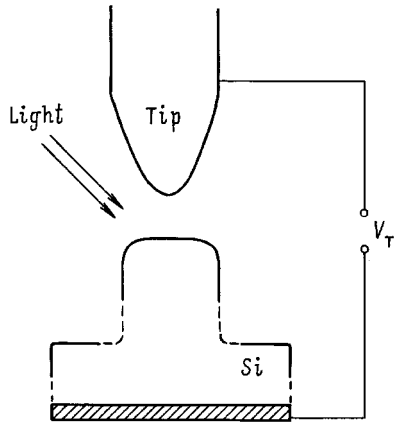

Figure 1. Schematic representation of a tungsten tip of a scanning tunneling microscope placed above an illuminated nanoparticle (column) of porous Si. The top of a nanoparticle, covered with an oxide layer, is separated from the bulk Si by a poorly conducting region of porous Si. Below the nanoparticle the bulk of the specimen with aluminized back side (shaded) is schematically depicted. V_T is the external voltage applied between the tip and the aluminized back side.

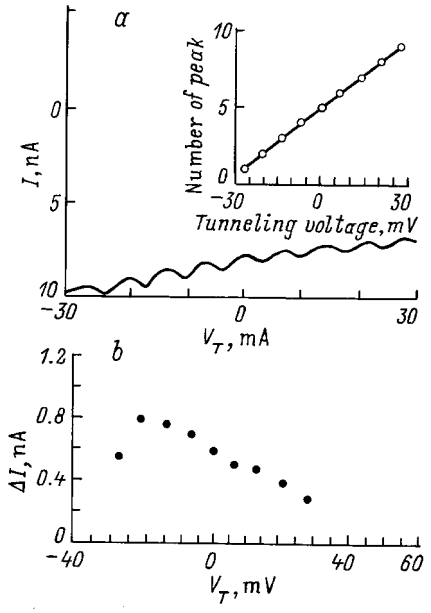

Figure 2. *a*) Oscillation of the tunneling current I between the STM tip and porous Si surface illuminated at $\lambda = 647$ nm from the Kr/Ar laser, when the value of V_T is changed. *b*) Dependence of the amplitude ΔI of the current modulation on the voltage V_T.

voltage $V_T = 0$. The $I-V$ curves obtained in this way have shapes similar to those observed under illumination (i. e. photoconductivity) using a thin metal film electrode on porous Si [6]. The enhancement of the carrier density by light may be 2–3 orders of magnitude [7] although the actual current value varies strongly in different experiments [6,7]. Furthermore, metal electrodes evaporated on Si usually introduce interface states [8] which may seriously influence the transfer of charge. Such defects are not present in transport experiments by vacuum tunneling like ours.

At small V_T (up to few tens of mV) a regular modulation of the $I-V$ curve as shown in Fig. 2, *a* is observed when V_T is swept slowly (within 20 s) from -30 to $+30$ mV at a randomly selected point of the tip above the sample surface, irrespective of the light source or the wavelength of the Kr/Ar laser. As is evident from the inset of the figure, the oscillations are periodic in V_T with an average period $\Delta V_T = 6.7$ mV. The current steps shown in Fig. 2, *b* vary from 0.3 to 0.8 nA. When V_T is swept from the negative towards positive values the size of ΔI increases at first steeply and then slowly decreases in a linear way after a kink in the ΔI versus V_T plot.

The shape of the $I-V$ curves and the current oscillations observed on different places of the sample surface are generally similar to the pattern shown in Fig. 2. However, the number of such clearly discernible oscillations of I may vary from point to point and values of ΔV_T between $2.5-6.7$ mV have been observed in different experiments and different samples. It means variation of $\Delta V_T/k_B T$ between $0.1-0.25$. Points of the sample surface showing small modulation of the $I-V_T$ curve could be found relatively easy. But only a small fraction of them (10–15%) had amplitude comparable with the plot in Fig. 2, *a*. We attribute these oscillations to a Coulomb effect that will be described below.

Electron tunneling in correlation with charging effects was extensively investigated during recent years (see, for instance, Ref. [9]) and were clearly demonstrated in multi-junction normal-conducting devices [10] at rather low temperatures T. Quite recently, however, they were observed at room temperatures [11,12]. The high temperature experiments were made on very small samples. In the present paper we propose and investigate a different way to reach the high temperature limit in charging effects.

To begin with discussion of the origin of this oscillation we will start with the simplest possible example comprising, however, all the relevant features of the phenomenon (as we understand it). We will consider electrostatic interaction of a gate electrode (the STM tip in our case) with a nanocrystal of a good conductor.

We start with equation for the electrostatic energy $\mathcal{U}$ of the relevant part of the system (gate electrode + nanocrystal). Assume that the gate electrode is at a constant potential ϕ while the nanocrystal is characterized by the charge variable q. We will subtract from the total electrostatic energy the work of the source maintaining the potential constant (cf with Landau and Lifshitz [13], §5). Then

$$\mathcal{U} = (q - C_{12}\phi)^2 / 2C_{11} - C_{22}\phi^2/2. \qquad (1)$$

Here C_{ik} is the capacitance matrix (where we ascribe index 1 to the conductor while index 2 is ascribed to the gate electrode). One can rewrite the first term as $(1/2)C_{11}\Phi^2(q, \phi)$, Φ being the potential of the nanocrystal which can be considered as a function of two variables, q and ϕ. This is an electrostatic energy of the nanocrystal in the field of the gate electrode. The equations are valid provided that all the charges are situated at the sample's surface. Here we imply that, in addition to the electrostatic forces, there are also sufficiently large forces of a different origin ensuring the overall stability of the Coulomb system. For the energy stabilizing the system we introduce notation W. In the example we consider now this is a work function of an electron at the metal's surface.

Let us discuss the first term on the right-hand side of Eq. (1). Term $q^2/2C_{11}$ describes the mutual repulsion of the excess charges. Term $C_{12}^2\phi^2/2C_{11}$ represents the repulsion of the polarization charges induced by the gate voltage. Finally, term $-C_{12}q\phi/C_{11}$ describes the interaction between these two types of charges.

Now we will turn to a more realistic situation in regard to our experiment. Consider a conductor with a small number of carriers (electrons and holes), so that they cannot screen out the gate field in the whole nanocrystal. Let us assume presence of a potential well inside the conductor, so that the conductor is nonhomogeneous. Were the well sufficiently deep and wide, all the electrons would be trapped in the well, so that the system could be looked upon as a small piece of metal in a dielectric matrix. For the mechanic energy of such a metal droplet one can also use Eq. (1). Let us now assume that the potential well is shallow. In this

situation one can expect that W will be sufficiently small (see below). If W is smaller than $(1/2)C_{11}\phi_1^2$ the electrons could not be trapped in the well. For $W = 0$ only a state of indifferent equilibrium where $q_1 = C_{12}\phi_2$ can exist. This is a manifestation of the Earnshaw theorem (according to which a classical system where there is only electrostatic interaction cannot be stable).

Further in the present paper we will be interested in the case where $W < E_C$ (here $E_C = e_0^2/2C_{11}$, e_0 being the electron charge). Such states can be stable only if the energy of repulsion of the excess charge as well as of the polarization charge is almost compensated by the energy of their interaction. The limits of stability of such a state are very narrow, i.e. the states with the charge that differs from $C_{12}\phi_2$ by $\pm e_0$, i.e. by a single elementary charge, would be unstable [see below — Eq. (2)]. It means that the multielectron state consisting of the excess charge and polarization cloud will be distributed as a whole over the whole volume of the nanocrystal. These considerations permit one to define W in our case. It will be equal to the distance between the uppermost level within the well and the bottom of the conduction band.

Thus we postulate existence of a multielectron state characterized by a multielectron charge q and existing for those values of the gate voltage where $C_{12}\phi/e_0$ is very close to an integer. Such a state cannot take part in the current transport (the electrons bound within the well cannot move along the potential drop). Due to the same condition $W < E_C$ this state is unstable for such values of the gate potential where $C_{12}\phi/e_0$ sufficiently deviates from an integer. This physical picture is selfconsistent as the state of indifferent equilibrium is stabilized by a small potential of nonelectrostatic origin. Formally we could just state that the electrostatic energy $\mathcal{U}$ is diagonalized by introduction of a variable $q' = q_1 - C_{12}\phi$.

Now we can calculate the probability of realization of the n-electron state for finite temperatures T. Besides electrons in an ordinary conduction band, an n-electron state discussed above can also be excited provided that

$$E_n = E_C(n - N)^2 < W. \tag{2}$$

Here $N = C_{12}\phi/e$. This state may be not excited at all, then $n = 0$. If it is excited then $n = [N]$ where by $[N]$ we denote the integer part of N. Thus the existence and spectrum of the bound electron state depends on the voltage at the gate electrode.

Let the number of one-electron levels in the well be g. The number of ways for n electrons to occupy g levels is C_g^n (cf with Ref. [14]). For simplicity, we assume that the distance between energy levels in the well is the smallest energy scale. Then the additional part of the thermodynamic potential due to multielectron excitation is

$$\Omega_n = -k_B T \ln\left(1 + C_g^n \exp\frac{\mu n - E_n}{k_B T}\right). \tag{3}$$

Thus the average number of electrons bound within a well is

$$\bar{n} = -k_B T \frac{\partial \Omega}{\partial \mu} = \frac{n C_g^n \exp\left[(\mu n - E_n)/k_B T\right]}{1 + C_g^n \exp\left[(\mu n - E_n)/k_B T\right]}. \tag{4}$$

We are interested in the case where

$$E_n \approx W < E_C \ll k_B T. \tag{5}$$

One can see that the oscillation amplitude is not exponentially small provided that

$$C_g^n \exp(\mu n/k_B T) \gg 1. \tag{6}$$

In our case of illuminated nanocrystal the number of electrons, N_P rather than the chemical potential is fixed. The chemical potential should be calculated from equation $N_P = N_b \exp(\mu/k_B T) + n$ where

$$N_b = \mathcal{V} \int d\epsilon \nu(\epsilon) \exp(-\epsilon/k_B T). \tag{7}$$

Here $\mathcal{V}$ is the volume of the nanocrystal while $\nu(\epsilon)$ is the density of electron states. Here we assume that the electrons in the conduction band are nondegenerate. One can see that this is the case if $(N_P - n)/N_b \ll 1$.

For $n \ll g$ one can use the following approximate equation $g! = (g - n)! g^n$. Then Eq. (6) can be rewritten as

$$\frac{1}{n! N_b^n} g^n (N_P - n)^n \gg 1. \tag{8}$$

This is a product of big and small parameters. When the product is small the oscillation amplitude goes down. In the case we are interested in where Eq. (6) is valid there are n electrons in the well in spite of the fact that the chemical potential is negative and its absolute value is bigger than $k_B T$. This is due to a large statistical weight of the states in the well. As a result, we have for the current $I = GV(1 - n/N_P)$ where V is the voltage applied across the nanocrystal, including the potential barriers at its surfaces, G is the conductance of the nanocrystal for $V \to 0$. Here we made use of the fact that for the Boltzmann statistics the electron distribution function has a factor $\exp(\mu/k_B T)$. The ratio of the oscillatory part of the current, ΔI, to the non-oscillating part for $[N] < n_0$ is given by $|\Delta I|/I = n/N_P$.

When inequality Eq. (6) is reversed the oscillation amplitude goes to zero as this small parameter, i.e. exponentially. The case $g - n \ll g$ can be treated in the same manner as above with replacement $n \to g - n$. When $g - n$ goes down so that inequality (6) is reversed the oscillation amplitude is again exponentially small.

In some sense the phenomenon discussed and Coulomb blockade have opposite physcal meaning. In our situation the state where n electrons have the lowest energy is pinned to the potential well under the combined influence of the Coulomb interaction among the carriers and the gate voltage variation. As a result, the electrons are excluded from the conduction process provided that $W < E_C$. This means that for a particular value of ϕ only one multielectron state with corresponding number n can be bounded. To the contrary, the manifestation of the Coulomb blockade is that for $k_B T < E_C$ only such a state conducts the current.

Let us discuss possible origin of the well in our experiment. In principle any relatively shallow potential well with

a small interlevel distance can bring about the oscillatory behavior. We feel, however, that in the systems like porous Si there is a special reason for existence of such wells. We mean that the inhomogeneity of the nanocrystal surface and its oxidations can be responsible for the well formation. Due to the oxidation of the surface (and maybe also illumination) the bands are bent upward near the surface. One may expect that due to a poor screening the scale of the bands' bending may be even comparable to the size of the nanocrystal itself. The bending is in general different in different points of the nanocrystal surface. The band bendings should result in formation of potential wells for the conduction electrons or holes. Some of these wells would not let the carriers reach the regions from which they can tunnel out of the nanocrystal. Thus the band bendings can be centres of multielectron state pinning.

Comparing the data in Fig. 2 with Eq. (1) we come to the conclusion that the holes (rather than electrons) are localized in the well ($C_{12} < 0$). If one linearly extrapolates the current-voltage characteristic in Fig. 2 it crosses the abscissa axis at $V = -60$ mV. This is a typical value of the surface photovoltage for Si [15].

The oscillation pattern is sinusoidal rather than a system of sharp peaks. This may be due to the fact that W is of the order of E_C [see Eq. (2)], so that the effect is due to the levels within a stripe of the width E_C in a rather deep well.

The oscillation we discuss has a period of several mV. Oscillation of dI/dV (at a constant tunnel current I) with the period of several V have been observed on some metals — see [16] and the references therein. The oscillation is ascribed to the resonances between the de Broglie wavelength of electron and the distance between the tip and the metal's surface. Such interpretation cannot be valid in our case as it would demand enhancement of the distance between the metal tip and the porous Si surface to ~ 1000 Å.

It is possible to pick out the amplitude of the oscillating current from the total current (see Fig. 2, *b*). The accuracy of the amplitude measurement is about 15% of the amplitude. The oscillation pattern ceases not abruptly but in a gradual way (see the left points in Fig. 2, *b*). The states with large values of n can be achieved only if the highest levels in the well are filled. If the electron life time on the highest levels is finite (as the uppermost levels can be hybridized between the well and conduction band) it may provide an explanation for the behaviour of this sort.

The following estimates are given for the least favourable case where the degeneracy parameter is of the order of 1, i. e. $N_b \sim N_P$. For a $5 \times 10 \times 30$ nm nanocrystal we have $N_P \approx 150$. As one can see in Fig. 2, *a*, $|\Delta I|/I \approx 0.1$. Thus it is sufficient to have 5–10 levels in the well to explain the observed phenomenon. Such numbers demand rather high concentrations of electrons within the nanocrystal. We believe that such concentrations can be achieved because the probability for an electron to tunnel out of the nanocrystal is very low. We remind that we assume existence of continuous conduction and valence bands in the nanocrystal but not in the sample as a whole. Thus one can expect accumulation of the carriers in the nanocrystal.

Let us estimate the numbers of electrons involved so that the oscillation could be observable. Eq. (6) gives

$$\left(\frac{egN_P}{nN_b}\right)^n \gg 1 \qquad (9)$$

(where $e = 2.72$) for $N_P \gg n \gg 1$. This inequality is fulfilled due to the high power n in Eq. (9).

In summary, we have observed for the first time room temperature periodic oscillations in the $I-V$ characteristics of STM current tunneling into porous Si which is illuminated by a visible light. The heights of the oscillation peaks appear to be a linear function of the oscillation number. The oscillations are attributed to the periodic trapping of a multielectron level in a quantum well (situated in a Si nanocrystal) under the combined influence of the gate voltage variation and the Coulomb interaction among the carriers. We believe that in future regular nanostructures possessing the properties necessary for observation of this effect can be tailored.

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