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A novel room temperature oscillatory phenomenon in photoinduced scanning tunnelling microscope spectra of porous Si

V V Afonin†‡, V L Gurevich†‡, R Laiho†, A Pavlov† and Y Pavlova†

† Wihuri Physical Laboratory, University of Turku, FIN-20014 Turku, Finland
‡ Solid State Physics Division, A F Ioffe Institute, 194021 Saint Petersburg, Russia

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Abstract. A new phenomenon of periodic 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 tunnelling 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 $k_B T$. The oscillations are attributed to a Coulomb effect, i.e. to the periodic trapping of a multi-electron level in a quantum well within a Si nanocrystal under the combined influence of the Coulomb interaction among the carriers and the variation of the potential difference between the STM tip and the semiconductor surface.

1. Introduction

The purpose of the present paper is to report the observation of periodic oscillations in I–V characteristics of porous Si illuminated by visible light [1]. The experiment is performed at room temperature using a scanning tunnelling microscope (STM) in ambient atmosphere. The relative amplitude of the oscillating part in general depends on the position of the tip over the surface of porous Si. For certain positions it can be as big as 10% (whereas the Coulomb energy determined by the oscillation period is smaller than $k_B T$ by a factor of 0.25–0.1).

Electrochemically prepared porous silicon forms typically a sponge-like layer a few micrometres thick on a Si wafer [2]. Nanoporous Si shows strong room temperature photoluminescence attributed to quantum confinement of electron–hole pairs in nanosize details of the material [3]. Investigations by STM [4, 5] and atomic force microscopy (AFM) [6] have confirmed the existence of such structures on top of porous Si layers.

Electroluminescence experiments [7, 8] made with gold contacts evaporated on the surface of porous Si have shown that this material has relatively low electric conductivity. Several investigations into the photoconductivity of porous Si have been reported, but the photocurrent observed in different experiments varies over a large range [9–11]. This suggests that the surface properties of the material, including interface defects [12], have a strong influence on the measured current. Porous Si can capture injected carriers [13, 14], exhibits the surface photovoltage (SPV) effect with photoinduced trapping of charge [15] and shows persistent photoconductivity [16]. These phenomena are usually observed in structures with built-in potential barriers of various heights where the carriers can be optically induced in the close vicinity of these barriers.

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STM investigations of nanoporous Si are difficult because of the low electric conductivity of the material and its tendency to capture injected carriers. Using illumination with visible light, it is possible to raise the carrier density by several orders of magnitude [9]. Utilizing this property, high-quality STM images of porous Si can be obtained under illumination [16]. With the same method, the SPV effect may also be observed without interference of the interface defects induced by evaporated contacts, because the STM tip is separated from the surface by a tunnelling (vacuum) gap. With the aid of a SPV it is possible to obtain STM surface images even without an externally applied tunnelling voltage.

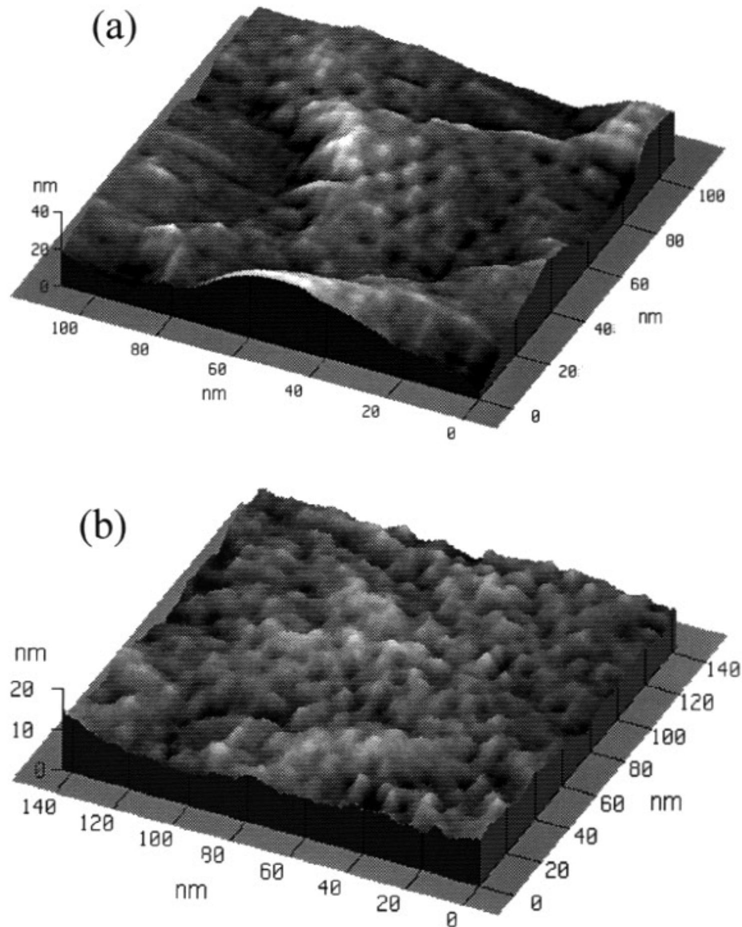

Figure 1. STM images of porous Si illuminated with laser light at $\lambda = 514$ nm and a fluence of 10 mW mm^{-2} (a) and with the Xe lamp (b).

In this paper we describe regular (periodic) oscillation of the tunnelling current observed between the STM tip and an illuminated porous Si surface at room temperature. The phenomenon is attributed to a Coulomb effect due to periodic trapping of a multi-electron level in a quantum well within a Si nanocrystal. The trapping takes place under the combined influence of the voltage variation of the STM tip and the Coulomb interaction

among the carriers. Correlation of electron tunnelling with charging effects has been extensively investigated in recent years (see, for instance, reference [17]) and was clearly demonstrated in multi-junction normal-conduction devices [18] at rather low temperatures T. Quite recently, however, it was observed at room temperatures [19]. The high-temperature experiments were carried out on very small samples. In the present paper we propose and investigate a different way to reach the high-temperature limit for the charging effects in nanostructures.

2. Experimental results

Porous Si specimens were prepared by the ordinary method, using electrochemical anodizing of p-Si(100) wafers of resistivity 5 Ω cm^{-1} for five minutes at the current 25 mA cm^{-2}. In the course of the experiments, several samples were prepared from the same starting material. The total thickness of the porous layer was about 3 μm. Before the measurements the samples were stored for several days in the ambient atmosphere to reach a quasistatic regime of natural oxidation [20]. The tunnel junction for STM investigations was formed between the tungsten tip of the microscope and the porous Si layer grown on a wafer. To increase the number of free carriers, and the tunnelling 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 the power density up to $P_{\mathrm{max}} \approx 10$ mW mm^{-2}).

In figure 1 we show STM images obtained on our samples under illumination with the laser (a) or with the (unfiltered) Xe lamp (b). The image (a) consists of a mixture of relatively flat parts and clusters (with size about 100 nm) of partially resolved particles (columns) of $\sim$5 nm width and of several tens of nm height on the top of the porous Si layer. The distance between the particles was 3–5 nm. The surface shown in (b) is almost fully composed of particles and pores having the same size as in (a). The observed structures are similar to the surface features of porous Si observed previously by AFM and STM [4–6, 16].

In the presence of a SPV it is possible to measure a tunnelling current, I, sufficient to operate the STM at values of the applied tunnelling voltage around zero. The I–V curves obtained in this way [16] 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 by several orders of magnitude [9] although the actual current value varies strongly between different experiments [10, 9]. Furthermore, metal electrodes evaporated on Si usually introduce interface states [12] which may seriously influence the transfer of charge. Such defects are not present in transport experiments on vacuum tunnelling like ours.

At small V_T (up to a few tens of mV), a regular modulation of the I–V curve as shown in figures 2(a) and 3 (corresponding to different samples) is observed when V_T is swept slowly (for 20 s) from -30 mV to $+30$ mV. The oscillations are observed at randomly selected points of the tip above the sample surface, irrespective of the light source and the wavelength of the Kr/Ar laser. As is evident from the inset of figure 2(a), the oscillations are periodic in V_T with average periods $\Delta V_T = 6.7$ mV (figure 2(a)) and $\Delta V_T = 2.5$ mV (figure 3). The current steps shown in figure 2(b) vary approximately from 0.3 nA to 0.8 nA and those in figure 3 vary from 0.1 nA to 0.5 nA. When V_T is swept from the negative values towards positive values, the size of ΔI increases at first steeply from the first point on the left and then slowly decreases in a linear way after the kink in the ΔI versus V_T plot. In the experiment the dynamic resistance of the junction as calculated from the I–V_T curves varies within the range $R = 8$–17 MΩ. These values are of the same order as is usually

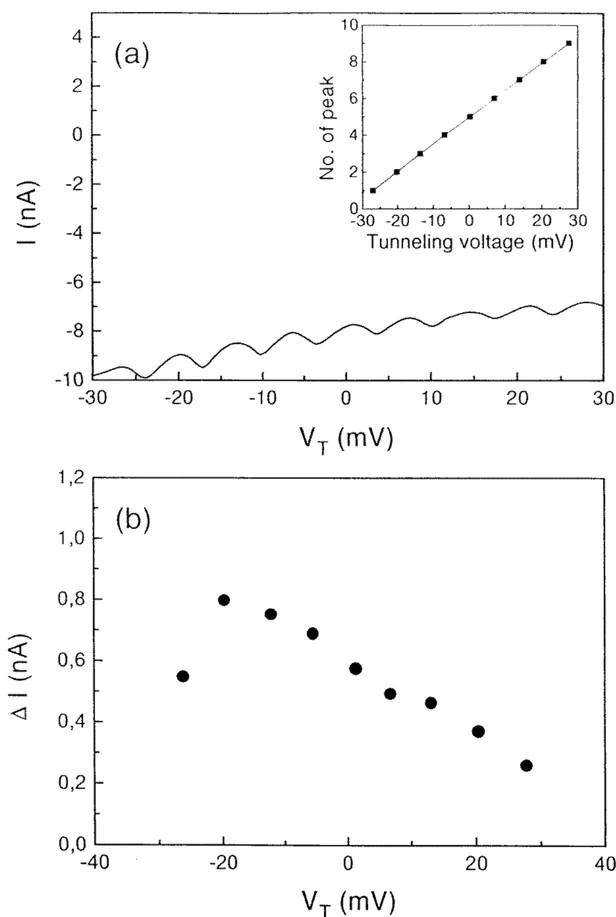

Figure 2. (a) The oscillation of the tunnelling current I between the STM tip and the porous Si surface illuminated at $\lambda = 647$ nm by the Kr/Ar laser, when the value of V_T is changed. (b) The dependence of the amplitude ΔI of the current modulation on the voltage V_T.

observed in normal STM experiments. The current modulations far exceed the measured instability (<0.5%) of the laser output.

The shape of the I–V curves and the current oscillations observed at different places on the sample surface are generally similar to the patterns shown in figures 2 and 3. However, the number of such clearly discernible oscillations of I may vary from point to point and values of ΔV_T between 3 and 8 mV have been observed in different experiments, independently of the samples. This means variation of $\Delta V_T/k_B T$ between 0.1 and 0.25. Points of the sample surface showing small modulation of the I–V_T curve could be found relatively easily. But only a small fraction of them (10–15%) had amplitudes comparable with those of the plots in figures 2(a) and 3.

In figure 4 two I–V curves, measured one after another, at the same point of the sample under illumination with the Xe lamp are depicted. The much higher noise of the data when compared with figures 2 and 3 is presumably due to the lamp having a lower stability than the laser. Despite the noise, we can conclude that the period of the oscillations (~0.8 mV) is the same in these two scans. It is likely that their amplitudes are also preserved. The

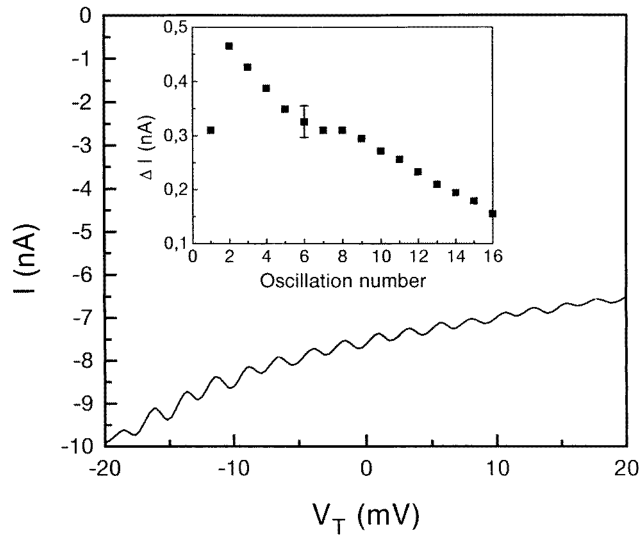

Figure 3. The oscillation of the tunnelling current I between the STM tip at the porous Si surface illuminated at $\lambda = 647$ nm by the Kr/Ar laser, when the value of V_T is changed. The inset shows the dependence of the amplitude ΔI of the current modulation expressed by the number of the oscillations starting from $V_T = -20$ mV.

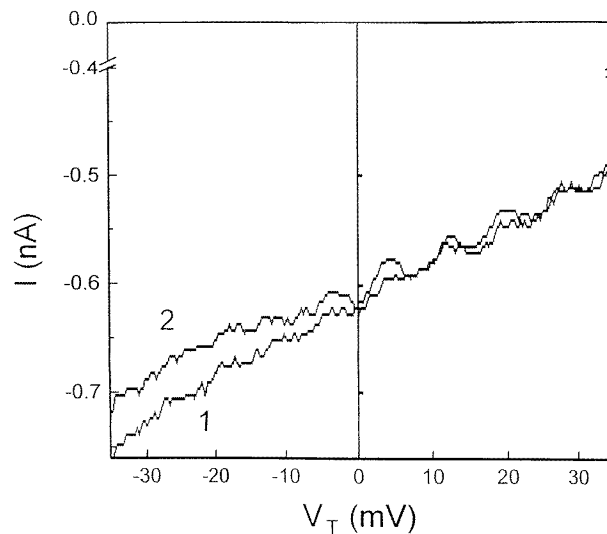

Figure 4. The time stability and repeatability of the I–V curves measured at the same point of the sample under illumination with the Xe lamp. The numbers 1 and 2 indicate the order of the sweeps of V_T.

difference between the curves 1 and 2 for the negative tip voltages can be attributed to slow dynamics of the trapping of the photogenerated carriers on the surface of the sample. It may be noted that the energies of the tunnelling electrons in our experiments are far below the threshold values (2 nA, ∼7 V) above which a stable nanostructuring of porous Si films by STM has been observed [21].

The oscillatory pattern that we have observed shows a negative differential resistance. One should, however, be cautious when considering its possible manifestations. The point is that the total voltage is a sum of the applied voltage and the photovoltage due to the illumination. On the one hand, one cannot separate these sources of voltage because one can remove the photovoltage only by removing the illumination which is an indispensable condition for the observation of the negative differential resistance itself. On the other hand, the reactions of the photovoltage to external perturbations are, as a rule, very slow [16] which should influence the non-stationary phenomena, where the negative differential resistance can be involved.

3. Theoretical considerations

To begin with, let us discuss a well-known situation (see, for instance, reference [22]) where one has a nanocrystal of a good conductor interacting with a gate electrode. It is natural (see below) to assume that the nanocrystal is characterized by an excess charge $q_1 = ne_0$ (where e_0 is the electron charge) while the gate is maintained at a constant potential ϕ_2. We will calculate the *mechanical energy* $\mathcal{U}$ of such a system (see [23], section 5). One should keep in mind that it differs from the usual electrostatic energy of a conductor:

$$\mathcal{E} = (1/2)(q_1\phi_1 + q_2\phi_2). \tag{1}$$

(we ascribe index 1 to the conductor while index 2 is ascribed to the gate electrode). Indeed, to maintain a constant gate potential under variation of the nanocrystal charge q_1 one should use a battery which performs work. The latter is equal to $q_2\phi_2$. In order to obtain the mechanical energy, one should subtract this quantity from $\mathcal{E}$:

$$\mathcal{U} = \mathcal{E} - q_2\phi_2 = (1/2)(q_1\phi_1 - q_2\phi_2). \tag{2}$$

Using the linear relations between the charges and potentials

$$q_i = \sum_k C_{ik}\phi_k \tag{3}$$

where C_{ik} is the capacitance matrix, one gets

$$\mathcal{U} = (q_1 - C_{12}\phi_2)^2/2C_{11} - C_{22}\phi_2^2/2. \tag{4}$$

One can rewrite the first term as $(1/2)C_{11}\phi_1^2(q_1, \phi_2)$, where ϕ_1 is a function of two variables, q_1 and ϕ_2. This is an electrostatic energy of the excess charge in the field of the gate electrode. These equations are valid provided that all of the charges are situated at the sample's surfaces. 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 the notation W. In the example that we consider now, this is a work function of an electron at the metal's surface.

The first term on the right-hand side of equation (4) is a sum of three terms. The term $q_1^2/2C_{11}$ describes the mutual repulsion of the excess charges. The term $C_{12}^2\phi_2^2/2C_{11}$ represents the repulsion of the polarization charges induced by the gate voltage. Finally, the term $-C_{12}q_1\phi_2/C_{11}$ describes the interaction between these two types of charge.

Now we will turn to a more realistic situation as regards our experiment. Consider a semiconductor with a number of carriers (electrons and holes) sufficiently small that they cannot screen out the gate field throughout the whole nanocrystal. Let us assume the presence of a potential well inside the conductor, so that the conductor is non-homogeneous. Were the well sufficiently deep and wide, all of the electrons would be trapped in the well,

so the system could be looked upon as a small piece of metal in a dielectric matrix. For the mechanical energy of such a metal droplet, one can also use equation (4).

Let us now assume that, in addition to the deep potential wells visible in the optical properties of the porous Si (and maybe even within these deep wells), comparatively shallow wells can also be present near the surface. They can be due to the internal strains, fluctuations of impurity concentrations or surface properties etc [24, 25]. Such wells cannot manifest themselves in the optical properties in the same simple way as the deep wells do. For the shallow wells, W will be sufficiently small (see below). If W was 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 on, we will be interested in the case where $W < E_C$ (here $E_C = e_0^2/2C_{11}$). Such states can be stable only if the energy of repulsion of the excess charge as well as that 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 electron charge, would be unstable. This means that the multi-electron state consisting of the excess charge and polarization cloud will be distributed as a whole over the volume of the nanocrystal. These considerations permit one to define W. It will be equal to the distance between the uppermost level within the well and the bottom of the conduction band.

Thus we postulate the existence of a multi-electron state characterized by a multi-electron 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, $W \ll E_C$, this state is unstable for those values of the gate potential for which $C_{12}\phi/e_0$ sufficiently deviates from an integer. As indicated above, this physical picture is self-consistent, as the state of indifferent equilibrium is stabilized by a small potential of non-electrostatic origin.

We could have introduced such a multi-electron state without relying on the analogy with a good conductor. It is sufficient to note that the electrostatic energy $\mathcal{U}$ is diagonalized by the introduction of a variable $q' = q_1 - C_{12}\phi_2$. However, in this case too it is necessary to remember the condition imposed by the Earnshaw theorem. Here the stability is ensured provided that $W < E_C$. Formally one can describe this phenomenon by introducing into the equation for the new state a potential well of the depth W. Such a state would exist only if the carriers were localized within the well. Otherwise the electrons as well as the polarization cloud would be spread over the whole volume of the nanocrystal. Further on, we will be interested in rather high temperatures ($k_B T \gg E_C$). This permits one not to consider the Coulomb interaction between the carriers outside the potential well. Indeed, the orthodox theory of the Coulomb blockade gives for this case effects that are as small as $\exp(-\pi^2 k_B T/E_C)$. The problem of applicability of such a Hamiltonian is crucial. We will discuss it using a simple microscopical model in appendix A.

Now we should calculate the probability for such a state to be occupied for finite temperatures T. One should take into account the fact that, besides the electrons in an ordinary conduction band, an n-electron state discussed above can exist provided that

$$E_n = E_C(n - N)^2 < W. \quad (5)$$

Here $N = C_{12}\phi_2/e_0$. This state may not exist at all; then $n = 0$. If it exists, then $n = [N]$, where by $[N]$ we denote the integer part of N. Thus the existence and spectrum of the bound electron state depend on the voltage at the gate electrode. This is a rather unusual

situation—the number of electrons in the well can be either 0 or $[N]$. (For the usual Fermi–Dirac distribution the occupation number for a level can be either 0 or 1.) To calculate the probability of an occupancy one should start with the Gibbs distribution.

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. reference [26]). For simplicity, we assume that the distance between the energy levels in the well is the smallest energy scale. Then the additional part of the thermodynamic potential due to multi-electron excitation is

$$\Omega_n = -k_B T \ln\left(1 + C_g^n \exp\frac{\mu n - E_n}{k_B T}\right). \tag{6}$$

Thus the average number of electrons bound within a well is

$$\overline{n} = -k_B T \frac{\partial \Omega_n}{\partial \mu} = \frac{n C_g^n \exp[(\mu n - E_n)/k_B T]}{1 + C_g^n \exp[(\mu n - E_n)/k_B T]}. \tag{7}$$

We are interested in the case where

$$W \approx E_C \ll k_B T. \tag{8}$$

One can see that $\overline{n}$ is not exponentially small provided that

$$C_g^n \exp(\mu n/k_B T) \gg 1. \tag{9}$$

Then $\overline{n} = n$. In our case of an illuminated nanocrystal, the number of electrons, N_P, rather than the chemical potential is fixed. This is a state of a partial thermodynamic equilibrium where the chemical potential should be calculated from the equation

$$N_P = N_b \exp(\mu/k_B T) + n$$

with

$$N_b = \mathcal{V} \int d\epsilon \;\nu(\epsilon) \exp(-\epsilon/k_B T). \tag{10}$$

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 non-degenerate. 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 equation (9) can be rewritten as

$$\frac{1}{n! N_b^n} g^n (N_P - n)^n \gg 1. \tag{11}$$

This is a product of large and small parameters. When the product is small the oscillation amplitude goes down. For the case that we are interested in where equation (9) 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

$$I = GV(1 - n/N_P).$$

Here V is the voltage across the nanocrystal, including the potential barriers at its surfaces, and G is the conductance of the nanocrystal for $V \to 0$ which is proportional to the number of free carriers within the nanocrystal, N_P. 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 $[N] < g$ is given by

$$|\Delta I|/I = n/N_P. \tag{12}$$

When inequality (9) is reversed, the oscillation amplitude goes to zero as this small parameter, i.e. exponentially. The case where $g - n \ll g$ can be treated in the same manner as above, with the replacement $n \to g - n$. When $g - n$ reduces, with the result that inequality (9) is reversed, the oscillation amplitude is again exponentially small.

In some sense the phenomenon discussed and the Coulomb blockade have opposite physical meanings. 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_2 only one multi-electron state with corresponding number n can be bounded. In contrast, the manifestation of the Coulomb blockade is that for $k_B T < E_C$ only such a state conducts the current.

4. Comparison with experiment

As we indicated above, in principle any relatively shallow potential well with a small interlevel distance can bring about the oscillatory behaviour. Comparing the data in figures 2 and 3 with equation (4), 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 figure 2, it crosses the abscissa axis at $V = -60$ mV. This is a typical value of the surface photovoltage for Si [27].

Figures 2 and 3 differ in oscillation period. $\Delta V/k_B T$ is 0.25 for the curve in figure 2 and is 0.1 for the curve in figure 3. The oscillation curves were obtained for two different samples in two experiments.

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 equation (5)), so the effect is due to the levels within a stripe of the width E_C in a rather deep well.

The oscillation that we discuss has a period of several mV. Oscillations of dI/dV (at a constant tunnel current I) with periods of several V have been observed for some metals—see [28] and the references therein. The oscillation is ascribed to the resonances between the de Broglie wavelength of the electron and the distance between the tip and the metal's surface. Such an 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 ~100 nm.

It is possible to single out the amplitude of the oscillating current from the total current (see figures 2(b) and 3). The accuracy of the amplitude measurement is about 15% of the oscillation amplitude. The oscillations die off not abruptly but in a somewhat gradual way (see the left-hand-side points in figures 2(b) and 3). The states with large values of n can be achieved only if the highest levels in the well are filled. If the electron lifetime in the highest levels is finite (as the uppermost levels can be hybridized between the well and conduction band), it may provide an explanation for behaviour of this sort.

The following estimates are given for the 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 figures 2(a) and 3, $|\Delta I|/I \approx 0.1$. Thus it is sufficient to have about ten levels in the well to explain the observed phenomenon.

To make estimates of N_b we have used a quasiclassical approach which gives

$$N_b = \frac{2\sqrt{2}}{3\pi^2}\left(\frac{mk_B T}{\hbar^2}\right)^{3/2}\mathcal{V}. \tag{13}$$

Such an approach is applicable for $N_b \gg 1$. If we apply the same equation for a well with

$W \sim E_c \sim 0.25k_\mathrm{B}T$ and a volume of the order of $0.1\mathcal{V}$, we get that it can have several levels. Of course, the quasiclassical approach is inapplicable in this case. The exact number of levels depends on the shape of the well.

In such a case one can expect there to be an adequate number of levels in such a well. Besides, the well required for our purpose should not necessarily be shallow. The well can be deep, having a number of closely spaced upper levels within a layer of the width E_c. Then it is these levels that will be responsible for the oscillation of the current.

Thus one can see that one needs a rather high concentration 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 recall that we assume the existence of continuous conduction and valence bands in the nanocrystal but not in the sample as a whole. We also emphasize that good STM images under the application of a voltage of several tens of mV could be observed under just illumination. This inevitably means a significant variation of the carrier concentration at least in some nanocrystals at the porous Si surface. Moreover, as has already been pointed out [16], these images may exaggerate the regions that have higher photoconductivity than the surroundings. Thus one can expect accumulation of the carriers in the nanocrystal.

Below, we estimate the number of electrons that must be involved for the oscillation to be observable. Equation (11) gives

$$\left(\frac{egN_P}{nN_b}\right)^n \gg 1 \tag{14}$$

(where $e = 2.72$) for $N_P \gg n \gg 1$. This inequality is fulfilled due to the high power n in equation (14). If the gate voltage becomes so high that g becomes almost equal to n, the oscillations will die off (see section 3).

5. Summary

We have observed for the first time room temperature periodic oscillations in the I–V characteristics of STM current tunnelling into porous Si which is illuminated by visible light. The analysis of the experimental data gives the following facts.

(i) Although the ratio $E_c/k_\mathrm{B}T$ varies between the limits 0.1 and 0.25, the relative amplitude of the oscillations may be rather big, i.e. about 10%.

(ii) The heights of the oscillation peaks appear to be a linear function of the oscillation number.

(iii) The oscillations sharply cease when the voltage reaches a certain threshold value.

This set of facts cannot find even a qualitative explanation within an orthodox theory of Coulomb blockades.

According to our interpretation, the oscillations are attributable to the periodic trapping of a multi-electron 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 wish to emphasize that for the theoretical interpretation of the experiment only two features are essential.

(A) The existence within the excitation spectrum of a multi-electron excitation that cannot carry current. It must have a small coupling energy so that the states which differ by $\pm e_0$ are unstable.

(B) A large statistical weight of this state.

Items 1–3 have found a natural explanation within the framework of the proposed theory. We believe that in future, it will be possible to tailor regular nanostructures possessing the properties necessary for observation of this effect.

Acknowledgments

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Appendix A. An example of a system described by Hamiltonian (4)

Here we wish to discuss a possible example of an arrangement of conductors and charges described by the Hamiltonian (4) (section 3) which was introduced there phenomenologically. We do not propose to give here a first-principles general derivation of the Hamiltonian. We only wish to indicate a possible relatively simple arrangement of the charges and discuss a condition of compensation between the Coulomb repulsion of electrons on the one hand and the attraction between the excess charge and the polarization cloud on the other hand.

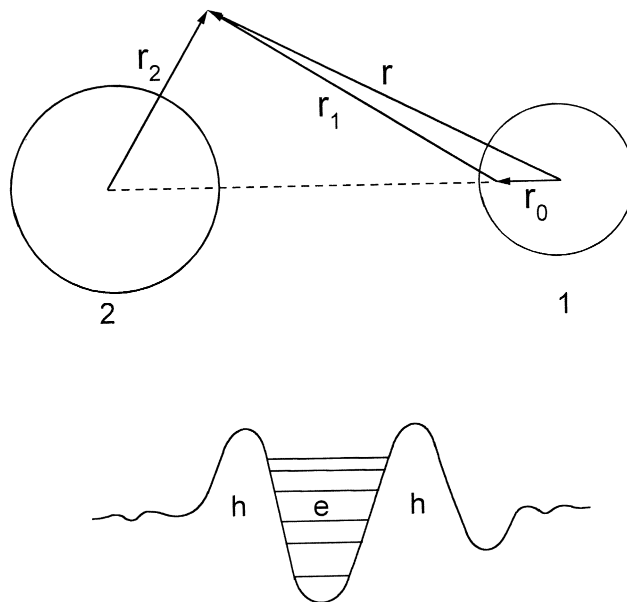

Figure A1. A schematic representation of the interaction of the charges distributed over the surfaces of two spheres. Potential wells for electrons and holes.

First of all, we have to elucidate the physical reason for the diagonalization of Hamiltonian (4) by introduction of the charge $q' = q_1 - C_{12}\phi_2$. To begin with, we will consider the case of metal spheres (cf. the beginning of section 3). For simplicity, we assume that the spheres are far apart, i.e. the distance between the centres of the spheres L is much bigger than their radii (see figure A1). Then, to obtain the equation for the total

potential $\Phi(\boldsymbol{r})$ as a function of the coordinates, one can neglect the influence of the small sphere (representing the nanocrystal) on the large sphere (representing the gate electrode) and assume that the charge of the latter, q_2, is fixed, i.e. isolated.

The solution of this problem is well known. When the small sphere is grounded, the potential outside the spheres is a sum of the potentials of the large sphere and of the image charge, $q = -q_2 R_1/L$ (R_1 and R_2 are the radii of the small and large spheres, respectively). The distance between the point image charge and the centre of the small sphere is $r_0 = R_1^2/L$. One can see (see [23], section 3) that the charge induced on the surface of the small sphere is equal to the image charge q. Then, making use of equation (3), one gets that $q = C_{12}\phi_2$ (we assume that $\phi_1 = 0$ in this case). The same result can be obtained by using the expression for the coefficient $C_{12} = -R_1 R_2/L$ (see [23], section 2).

The value and position of the image charge are determined by the condition $\phi_1 = 0$ at the surface of the small sphere. If the small sphere is not grounded but has an excess charge q_1, it is necessary to add to its surface charge $q' = q_1 - C_{12}\phi_2$ and spread it uniformly. As a result,

$$\Phi(\boldsymbol{r}) = \frac{q_2}{r_2} + \frac{C_{12}\phi_2}{r_1} + \frac{q_1 - C_{12}\phi_2}{r}. \qquad \text{(A1)}$$

r, r_1, r_2 are defined in figure A1.

Thus we have two independent charges, namely:

(i) charge $C_{12}\phi_2$; this makes the potential at the surface of the small sphere vanish; its value and the distribution over the surface do not depend on the excess charge;

(ii) charge q'; this determines the excess charge; it is distributed over the surface such that the surface is equipotential.

Now we will consider the variation of the charge arrangement in the spherical nanocrystal where the number of free carriers is insufficient for a full electric field screening inside the nanocrystal. The electrostatic potential within the nanocrystal satisfies the Poisson equation. First we discuss a situation where the nanocrystal's surface is maintained at a constant potential $\phi_1 = 0$. The form of the potential and of the charge distribution outside the nanocrystal and on its surface are determined by the same considerations as above for the value and the position of the image charge. According to these considerations, the electrons repelling each other and concentrating near the surface at the same time tend to screen out the external field as much as possible. Their centre of mass is displaced towards the gate electrode. The full induced charge is about $C_{12}\phi_2$.

Now we turn to discussion of a situation in which the nanocrystal has an excess charge q_1. Assume that the Poisson equation can be linearized in the variation of the external field. This assumption is natural as we consider a relatively weak screening.

Consider the nanocrystal as a part of a circuit where variation of the excess charge q_1 is possible. Let the electrons ($q_1 < 0$) be responsible for the charge conduction while the holes cannot tunnel out of the nanocrystal. To be definite, let us assume that the voltage at the gate electrode is positive. The electrons will again screen the external field as much as possible and repel each other. As a result, they concentrate near the surface. As above, the centre of their charge will be displaced from the centre of the sphere towards the gate electrode. The hole part of the charge, $-C_{12}\phi_2$, will have a maximum within the nanocrystal. Thus we have two independent charges corresponding to the two solutions of the electrostatic problem discussed above.

Now, assume that within the nanocrystal in the hole region there is a potential well (see figure A1). One can recall that the concept of a potential of such a form is supported by the first few points on the left in figures 2 and 3.

To begin with, assume $C_{12}\phi_2/e_0 = N$ to be an integer. Can we obtain a bound multi-electron state for the case where the depth of the potential well is smaller than (but of the order of) the characteristic Coulomb energy E_C? We will try to localize the electron and hole parts of charge q' in the wells as depicted in figure A1. We assume that the characteristic energies of electron–electron and electron–hole interactions are of the same order. At the same time, the screening electron charge $C_{12}\phi_2$ is nearer to the surface and it is possible, in a sense, to neglect the interaction with it. Then each electron interacts with $N-1$ other electrons and with N holes. In other words, its Coulomb energy is $-E_C$. For the holes one can write the same estimate. This means that one can hope to compensate the Coulomb electron energy by the interaction with the polarization cloud.

This estimate is of course very rough. Calculations related to the electron–hole liquid in Si [29] (with regard to the real band structure of Si) show cancellation of various contributions to the Coulomb energy. Obviously, the situation in real nanocrystals of porous Si is even more complicated. This is why we have introduced a phenomenological Hamiltonian for interpretation of the experiment.

Under the circumstances, one can ask the following question. Is it possible to localize within the well only a part of the excess charge, having compensated the electron–electron repulsion by the attraction to the same number of holes? The rest part of the excess electron charge and holes will have the same spatial distribution as in the homogeneous case. The electrons will be nearer to the surface while the holes will be predominantly near the potential well. This should enhance the Coulomb energy of the holes. As a result, the multi-electron excitation will be unstable.

Now let N be a non-integer, because of polarization of the Si atoms within the well. Can one obtain a multi-electron bound state compensating the Coulomb energy of the holes by an integer number of electrons, $[N]$? This is possible provided that

$$\frac{e_0^2}{r_c}(N-[N])^2$$

is smaller than E_C. Here r_c is a characteristic dimension of the well. This is what equation (5) gives. This reasoning has used the fact that the second charge is small. The multi-electron state is, in fact, neutral. Therefore it can be localized within a shallow well.

Appendix B. Transition probability

So far, we have discussed the influence of the multi-electron state in a well on the average current I. However, such a state has a finite lifetime τ and the average current can be observed directly only if the lifetime is sufficiently short. In the present section we wish to estimate this characteristic time (which incidentally is also the time of the current fluctuations).

At the high temperatures that we are interested in, the lifetime is determined by the electron–phonon processes. According to section 3, removal of one electron from the potential well should destroy the excitation. Therefore we should calculate the probability of an electron–phonon collision where the initial state of the electron is within the well while the final state is in the conduction band outside the region occupied by the multi-electron excitation.

We assume that during the characteristic time of the transition, $1/\omega_{\boldsymbol{k}}$ (where $\omega_{\boldsymbol{k}}$ is the phonon frequency) is smaller than the characteristic time of reaction of the circuit, $\mathcal{R}C$, where $\mathcal{R}$ is the resistance while C is the capacitance of the circuit. Then the source of the voltage cannot change the electron energy during such a short time. Under these

circumstances one can assume an abrupt variation of the Hamiltonian and the wave functions of the rest of the electrons trapped in the well would not change. However, they would no longer be stationary wave functions, but would rather be wave packets whose evolution will be determined by the Schrödinger equation. These electron states will thermalize during the characteristic electron–phonon collision time. The latter is the relaxation time of an electron in the conduction band (or a hole in the valence band). It should not be confused with the time τ that we are going to calculate.

It is sufficient for our purpose to consider a one-electron transition where both the initial and final states are free (i.e. non-interacting with other electrons). The initial state is free because if $n = N$ the interaction is compensated by the polarization cloud. The final state is just a band state.

We will consider as the initial state

$$|i\rangle = \frac{1}{\sqrt{v}} \cos(\boldsymbol{q} \cdot \boldsymbol{r}/\hbar) \tag{B1}$$

where v is the volume of the well. For simplicity, we assume that the well is rectangular. This assumption does not significantly influence the estimates below. The final electron state is

$$|f\rangle = \frac{1}{\sqrt{\mathcal{V}}} \exp(\mathrm{i}\boldsymbol{p} \cdot \boldsymbol{r}/\hbar) \tag{B2}$$

where $\mathcal{V}$ is the volume of the nanocrystal.

To make an order-of-magnitude estimate and to show how the probability can be calculated, we treat the simplest model. That is, we assume the electron and phonon spectra and the electron–phonon interaction to be isotropic. Then the electrons interact only with the longitudinal phonons. The interaction Hamiltonian is

$$H = \Lambda\, \boldsymbol{\nabla} \cdot \boldsymbol{u} \tag{B3}$$

where Λ is the deformation potential constant while $\boldsymbol{u}$ is the operator of elastic displacement, so

$$\boldsymbol{\nabla} \cdot \boldsymbol{u} = \sqrt{\frac{\hbar}{2\rho\mathcal{V}}} \sum_{\boldsymbol{k}} \frac{k}{\sqrt{\omega_{\boldsymbol{k}}}} \exp(\mathrm{i}\boldsymbol{k} \cdot \boldsymbol{r})(c_{\boldsymbol{k}} + c^{\dagger}_{-\boldsymbol{k}}). \tag{B4}$$

Here ρ is the mass density of the nanocrystal, $\omega_{\boldsymbol{k}} = sk$ is the phonon frequency, s is the velocity of sound, $c_{\boldsymbol{k}}$ and $c^{\dagger}_{-\boldsymbol{k}}$ are the phonon creation and annihilation operators.

We assume that the initial state of the electron making a transition due to the electron–phonon interaction occupies a sufficiently high level within the well. Then the quasimomentum of colliding quasiparticles is conserved. We have for the transition probability $1/\tau$ the expression

$$\frac{1}{\tau} = \frac{\Lambda^2 k_{\mathrm{B}} T}{8\pi^2 \rho s^2 \hbar} \int \mathrm{d}^3k \,\left[\delta(\epsilon_{\hbar\boldsymbol{k}-\boldsymbol{q}} - \hbar\omega_{\boldsymbol{k}} + W) + \delta(\epsilon_{\hbar\boldsymbol{k}+\boldsymbol{q}} - \hbar\omega_{\boldsymbol{k}} + W)\right]. \tag{B5}$$

Let us investigate the first δ-function on the right-hand side of equation (B5). It amounts to the following quadratic equation in the variable k:

$$(\hbar k)^2 + q^2 - 2\hbar kq\cos\theta - 2ms\hbar k + 2mW = 0 \tag{B6}$$

where θ is the angle between $\boldsymbol{q}$ and $\boldsymbol{k}$. As we will see below, $W \ll q^2/2m$. Therefore we will discard W in equation (B6). Analysis of equation (B6) shows that the process is allowed only for the k-values within the interval

$$k_1 < k < k_2. \tag{B7}$$

Here

$$k_{1,2} = \frac{q}{\hbar}\left(1 \mp \sqrt{\frac{2ms}{q} - \theta^2}\right)$$

where

$$|\theta| < \sqrt{2ms/q}.$$

The second δ-function on the right-hand side of equation (B5) gives the same contribution to $1/\tau$. As a result, we get

$$\frac{1}{\tau} = \frac{\Lambda^2 k_B T q^{1/2} m^{3/2}}{4\sqrt{2}\pi\rho s^{3/2}\hbar^4}. \tag{B8}$$

For the estimate, we will assume the following values of the parameters in equation (B8): $\Lambda = 7$ eV; $T = 300$ K; $q = 6 \times 10^{-21}$ g cm s^{-1} (so the corresponding electron energy is equal to $q^2/2m = 25$ meV); $s = 5 \times 10^5$ cm s^{-1}; $\rho = 2$ g cm^{-3}; $m = 0.5m_0$ (where m_0 is the free-electron mass); $W/k_B = 25$–70 K. The last quantity does not enter equation (B8), but we need it to be sure that the inequality $W \ll q^2/2m$ is fulfilled. As a result, we get

$$1/\tau \sim 3 \times 10^{11}\ \text{s}^{-1}. \tag{B9}$$

This time is longer than the time of electron–phonon collisions for the carriers in the conduction (or valence) band—mainly because only a small phase volume determined by inequalities (B7) contributes to $1/\tau$.

We have calculated the time of one-electron transition. Any of n electrons within the well can make such a transition. To estimate the full probability of destruction of the multi-electron trapped state one should multiply equation (B8) by n. The characteristic transition time (not to be confused with the lifetime $1/\tau$ calculated above!) which is of the order of

$$1/\omega = \hbar/sq \sim 3 \times 10^{-13}\ \text{s}$$

appears to be much shorter than $\mathcal{R}C \sim 10^{-10}$ s, as we assumed above.

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