Coulomb Charging Effect in Self-Assembled Ge Quantum Dots Studied by Admittance Spectroscopy

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Quantum confined energy levels and the Coulomb charging effect of holes in self-assembled Ge dots embedded in Si barriers are studied using admittance spectroscopy at temperatures above 100 K. Ground state and first excited state occupancies of five to seven holes are identified by varying the Fermi-level position under different applied bias voltages in the admittance measurements. Hole-capture cross sections of the quantum levels are found to be extremely large and energy dependent. [S0031-9007(98)05719-6]

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In recent years, the investigation of semiconductor quantum dots has attracted a great deal of attention both from the viewpoint of fundamental physics and for technological applications. The quantum dot with a dimension smaller than 100 nm can be viewed as an artificial atom. Its electronic structure is composed of a series of discrete quantum levels. In addition, the self-capacitance of a small quantum dot is in the order of 10^{-17}–10^{-18} F. So the Coulomb charging energy of carriers filled in the dot cannot be ignored, which modifies the electronic energy level structures. The experimental techniques developed early to study the quantum levels and Coulomb charging effect [1–4] were basically performed on those very well defined nanostructures prepared by lithography. A powerful technique, the single-electron capacitance spectroscopy, developed by Ashoori *et al.* [5,6] has been employed to measure the energies of quantum levels of imbedding self-assembled InAs and InGaAs dots [7,8]. However, the work done up to now was performed at the temperature below 4 K. Anand *et al.* [9] studied the Coulomb charging effect in InP dots sandwiched in between two GaInP barrier layers using the deep level transient spectroscopy. The discrete energy levels were not obtained, since the Coulomb charging energy is smaller than kT at the measuring temperatures. In this work, we perform the measurement of the quantum levels and Coulomb charging of self-assembled Ge quantum dots imbedded in Si barriers by using the admittance spectroscopy that was originally developed to measure the defect levels of bulk materials [10] and the band offsets of heterojunctions [11]. The activation energies of ground hole state and first excited hole state are extracted, and the Coulomb charging effect is clearly observed at the measuring temperatures above 100 K. The advantages of this method are simple and straightforward. The requirement on the uniformity of the dot size distribution of the sample is quite tolerant. In addition, the hole capturing cross sections of the quantum levels and their energy dependence are obtained for the first time.

For a Si Schottky diode structure with Ge dots imbedded inside the Si depletion layer, the band discontinuity between Ge dot and Si barrier occurs basically at the valence band edge. Figure 1 shows the schematic diagram of the sample structure used in this study and its valence band structure. Three Ge dot layers sandwiched between Si spacers constitute three hole wells. The holes occupy the discrete quantum levels in the Ge dots (well regions). An ac voltage signal applied on the diode will create an ac admittance signal caused by the emission and capturing of holes from the dots to the Si barrier. In the following, we derive the analytical expressions for a sample with only one Ge dot layer. The formulas obtained are also applicable to the sample with three Ge dot layers.

According to the equivalent circuit model of admittance spectroscopy [11], the sample structure with a single layer of Ge dots can be looked at as a parallel circuit

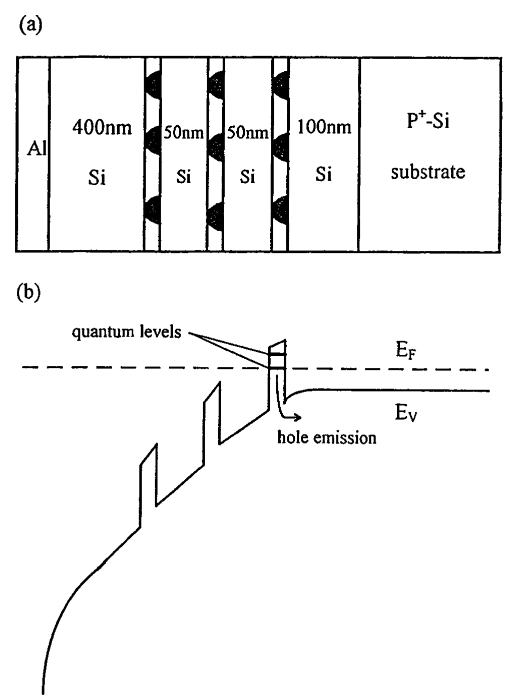

FIG. 1. Schematic diagram of the sample structure (a), and its valence band diagram under zero bias voltage (b).

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of the conductance G_{dot} and the capacitance C_{dot} of the dots in the series with a capacitance C_{S} of the Schottky barrier. At a measurement frequency ω, when the temperature scans through a certain value T_m which meets the following relation:

$$G_{\mathrm{dot}}(T_m) = (C_{\mathrm{S}} + C_{\mathrm{dot}})\omega\,, \qquad (1)$$

the conductance of the sample reaches a maximum $G(T_m)$.

To bring the admittance measurement applicable to the quantum dot samples, one must first derive the theoretical expression of G_{dot} as a function of its quantum level energy. Suppose g_i is the degeneracy of a quantum level E_i $(i = 1, 2, \ldots)$, the probability of a hole occupying E_i is given by the Fermi distribution function

$$f_i = \frac{1}{1 + (1/g_i)\exp[(E_f - E_i)/kT]}\,, \qquad (2)$$

where E_f is the Fermi level, k is the Boltzmann constant, and T is the temperature.

If the thermal emission rate and the capture cross section of holes on the level E_i are e_i and σ_i, respectively, the average thermal velocity is ν, and the hole concentration in the silicon barrier is p_0; the thermal equilibrium condition of hole emission and capturing from E_i is

$$e_i f_i = \sigma_i \nu p_0 (1 - f_i)\,. \qquad (3)$$

Substituting f_i by Eq. (2), using $p_0 = N_V \exp[-(E_f - E_V)/kT]$, and considering an external electric field F applied across the quantum dot, the emission rate of holes is extracted to be

$$e_i(F) = \frac{\sigma_i \nu N_V}{g_i} \exp\left(-\frac{E_i - E_V}{kT}\right) \exp\left(\frac{qFd}{2kT}\right), \qquad (4)$$

where N_V is the effective density of hole states in silicon, E_V is the valence band edge of silicon, q is the electron charge, and d is the height of the dot. Suppose that the areal density of quantum dots is N_{dot}, the number of the discrete energy level in the dot is L, and the number of carriers on the level E_i is g_i'; then the current density J caused by the emission of holes can be expressed as

$$\begin{aligned} J(F) &= \sum_{i=0}^{L} N_{\mathrm{dot}} g_i' q [e_i(F) - e_i(0)] \\ &= \sum_{i=0}^{L} N_{\mathrm{dot}} \nu q N_V \frac{g_i'}{g_i} \sigma_t \exp\left(-\frac{E_i - E_V}{kT}\right) \\ &\quad \times \left[\exp\left(\frac{Fdq}{2kT}\right) - 1\right]. \end{aligned} \qquad (5)$$

Under a weak electric field, the conductance of quantum dots can be obtained from the first order approximation of Eq. (5) as

$$G_{\mathrm{dot}} = \alpha T \sum_{i=0}^{L} \frac{g_i'}{g_i} \sigma_t \exp\left(-\frac{E_i - E_v}{kT}\right), \qquad (6)$$

where α is a temperature-independent constant:

$$\alpha = \frac{8}{h^3} \pi S q^2 N_{\mathrm{dot}} m^* k\,. \qquad (7)$$

S is the area of the electrode. In the derivation, the relations $N_V = 2(2\pi m^* kT/h^2)^{3/2}$ and $\nu = (8kT/\pi m^*)^{1/2}$ (where m^* is the effective mass of hole in the silicon valence band) have been used.

Two assumptions are made. First, suppose that the energy separations between neighboring levels are large enough that when the Fermi level is located near a level E_I, the higher hole excited states $(i > I)$ are empty while the lower levels $(i < I)$ are fully occupied. Second, the ratio of cross sections of two neighboring levels is small enough, i.e., $\ln(\sigma_{i-I}/\sigma_i) < (E_{i-I} - E_i)/kT - I$. It can be easily verified that Eq. (6) can be approximately written as

$$G_{\mathrm{dot}} = \alpha T \left(\frac{g_I'}{g_I}\right) \sigma_I \exp\left(-\frac{E_I - E_V}{kT}\right). \qquad (8)$$

Substituting Eq. (8) into Eq. (1), the condition for the sample conductance reaching a maximum is

$$\omega/T_m = \alpha_I \sigma_I \exp\left(\frac{E_I - E_V}{kT_m}\right), \qquad (9)$$

where $\alpha_I = \alpha/(C_{\mathrm{s}} + C_{\mathrm{dot}})(g_I'/g_I)$. The Arrhenius relation of the above formula is

$$\ln(\omega/T_m) = \ln(\alpha_I \sigma_I) - Ea_I/kT_m\,, \qquad (10)$$

where $Ea_I = E_I - E_V$ is the activation energy of the Ith level. By measuring the peak temperatures T_m of G-T spectra at different frequencies and drawing an experimental Arrhenius plot, the activation energy thus could be determined by the slop of the plot according to Eq. (10). Because of the small physical dimensions of the dots, the Coulomb charging effect cannot be ignored. The Coulomb charging energy required to charge N holes into a disklike dot is given by [7]

$$E_N = (N - 1/2)e^2/4\varepsilon\varepsilon_0 D\,, \qquad (11)$$

where D is the typical diameter of dots. On account of the Coulomb charging energy, the activation energy of carriers should be expressed as

$$Ea_I = E_I - E_V - E_N\,. \qquad (12)$$

The activation energy $E\alpha_I$ and the cross section σ_I can be obtained from the slope and intersect of the Arrhenius plot $\ln(\omega/T_m) \sim 1/kT_m$.

The sample used in this study was grown by the molecular beam epitaxy. Three periods of alternatively stacked 1.3 nm Ge dot layer and 50 nm Si spacer layer were deposited on a 100 nm thick Si buffer layer at the temperature of 500 °C and capped with a 400 nm thick Si layer on the top. All the Si layers were doped with boron to a concentration of about 1×10^{16} cm^{-3}. Figure 1 shows the schematic diagram of the sample structure and its valence band diagram under zero bias. The cross-sectional transmission electron microscopic (TEM) observation verified the formation of Ge islands with their dimensions of typically 3 nm in height and 13 nm in diameter. The nonuniformity of the dot size is estimated to be ±10%. The areal density of the dots is about 2×10^8 cm^{-2} as determined by the atomic force microscopic observation on a sample with only one Ge dot layer without a Si cap prepared under the same growth condition.

The sample was fabricated into a Schottky diode structure with an Al electrode at the top side and an Ohmic contact at the back side. The diameter of the Al electrode is about 0.9 mm. The admittance spectra were measured under different reverse bias voltages by using a Hewlett Packard 4275A LCR meter at the frequencies of 1 MHz, 500 KHz, 300 KHz, 100 KHz, and 50 KHz within the temperature range of ~100–250 K.

Figure 2(a) shows the conductance spectra at the frequency of 1 MHz under different bias voltages in the range of +0.2 to −1.4 V. The Arrhenius plots $\ln(\omega/T_m) \sim 1/kT_m$ obtained from the conductance spectra under different bias voltages are shown in Fig. 2(b). The linear correlation coefficients of all the lines are larger than 0.9998. From the slopes of these lines, the activation energies are obtained according to Eq. (10). The results are shown in Fig. 3(a), where five discrete values are indicated at the energies of 417(Ea_1), 388(Ea_2), 263(Ea_3), 233(Ea_4), and 202(Ea_5) meV, respectively. The conductance peak at −1.2 V is too weak, so the value of activation energy at −1.2 V was derived by another method, i.e., the capacitance differential method [12].

To identify the hole emission processes related with these five energy levels, we did the C-V measurement from which the shift of the Fermi level with respect to the quantum levels in the dots could be deduced. According to C-V measurement, it is found that the three dot layers (the topmost, middle, and deepest ones) are unoccupied by holes at the bias voltages below +1.0, +0.2, and −1.2 V, respectively. At the bias voltage of −1.4 V, the depletion region of the Schottky contact has extended over the Ge dot region. All the hole states in the quantum dots are empty. Thus, no conductance peak is expected in the admittance spectrum. In the bias region of −1.2 to +0.2 V, the boundary of the depletion region is basically pinned near the place of the deepest dot layer. The variation of bias voltage moves the Fermi level with respect to the quantum levels in this dot layer. The hole population in the dot increases as the reverse bias decreases. For another two dot layers, the Fermi level is located well above the quantum levels so there is no hole emissions contributed by these two layers. At the reverse bias voltage larger than 0.8 V, the holes occupy the lowest (ground) hole state in the deepest dot layer. According to Eq. (11), the Coulomb charging energy per added hole in a disklike dot with a diameter of 13 nm is estimated to be 30 meV, which is quite close to the energy differences between Ea_1 and Ea_2. Accordingly, it could be deduced that the activation energies Ea_1 and Ea_2 correspond to the hole emissions from the single charged and double charged hole ground states of the dot. The s-like ground state can accommodate only two holes. With the decrease of reverse bias, the additional holes will occupy the p-like first excited state. Therefore, the activation energy changes to 263 meV with the third hole occupying the excited state and to 233 and 202 meV with additional Coulomb charging energies of the fourth and fifth holes. The charging of the sixth holes to the excited state is expected to occur at a larger forward bias voltage (>0.4 V). In that case it is difficult to measure the admittance spectra since the signal will be smeared out by the large forward current. By using Eq. (12), the energy levels of ground state and the first excited state of the dots with respect to the Si valence band edge are derived to be 432 and 338 meV, respectively.

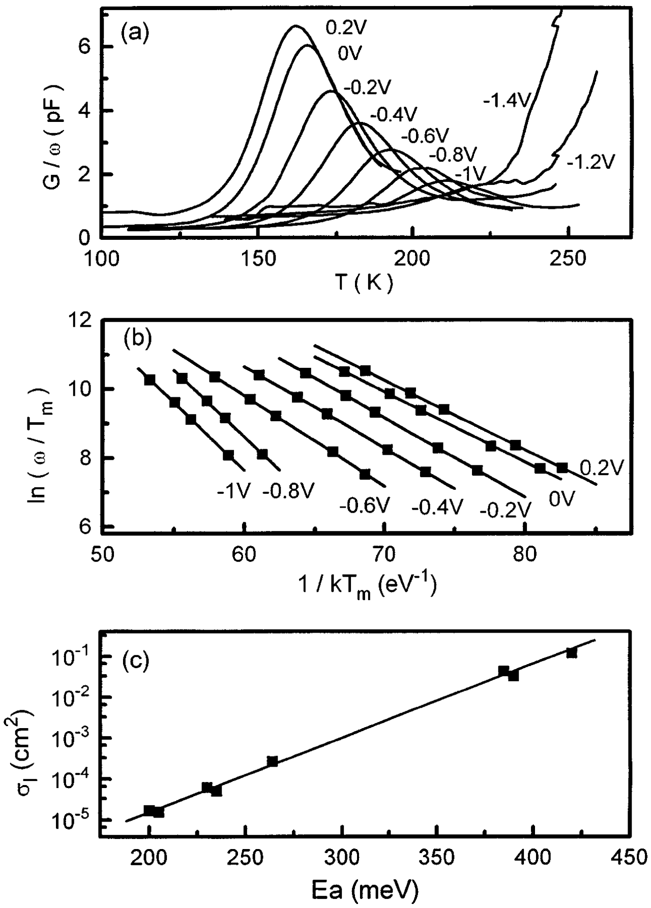

FIG. 2. (a) The conductance spectra at the frequency of 1 MHz under different bias voltages; (b) the Arrhenius plots of $\ln(\omega/T_m) \sim 1/kT_m$ obtained from the conductance spectra under different bias voltages; and (c) the carrier capture cross section as a function of activation energy.

The upper two Ge dot layers do not participate in the hole emission process in our measurements. The role played by these two layers is to block the extension of the Schottky barrier region over the third dot layer under zero bias.

To confirm the rationality of the above work, we did the admittance spectroscopic measurements on another sample with similar structure but larger dot diameters. The steplike behavior of the activation energy could

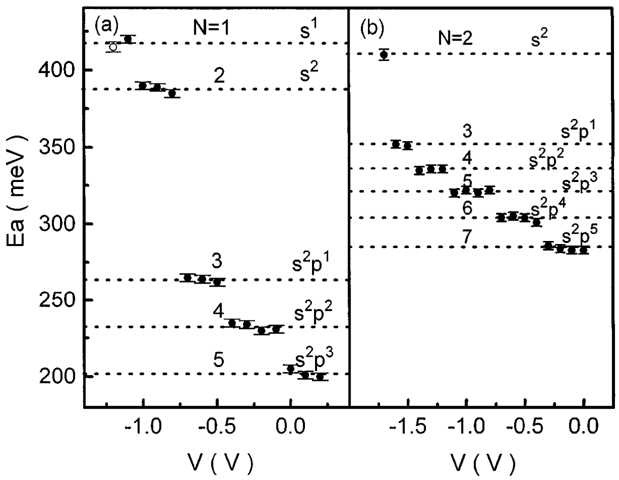

FIG. 3. The activation energies under different bias voltages of samples with typical Ge dot sizes of (a) 13 nm and (b) 25 nm.

also be seen as shown in Fig. 3(b), where the highest activation energy 410 meV corresponds to the double-charged ground hole state, while the other five levels are related with the first excited state charged with one to five holes. The Coulomb charging energy is about 17 meV corresponding to a typical dot diameter of 23 nm, which is quite close to the size of about 25 nm determined by TEM. The ground state charged with one electron would be detected at the bias voltage of -1.8 V, where the leakage current of the sample is too large, so that the activation energy determined experimentally is not very correct; the data are not included here.

Since the conductance peaks are broad bands, the size nonuniformity of the dots does not affect the determination of the peak temperatures in the spectra. We have done a simulation of the conductance spectrum of the first sample. With a size fluctuation of $\pm 10\%$, the width of the conductance peak will change from 16 to about 25 K, while the peak temperature changes only about 0.5 K. Since the shifts of T_m are all positive at different frequencies, so the slope of the Arrehenius plot and the activation energy determined are about the same as those without considering the size distribution. This is one of the advantages of the admittance spectroscopy especially for using it in the self-assembled quantum dot samples.

According to Eq. (10), the cross sections σ_I can be obtained from the intersections of the lines in Fig. 2(b). The results are shown in Fig. 2(c). σ_I varies exponentially with the activation energy. The values of σ_I are in the order of $\sim 10^{-2}$–10^{-5} cm^2 which are at least 10 orders of magnitude larger than that of defects in semiconductors. The great capability of capturing carriers by the quantum dots implies that the quantum confinement effect plays an important role in strengthening the carrier emission and capturing processes. The cross section data might be useful in connection with the carrier relaxation process in the quantum dot.

In summary, the admittance spectroscopy has been successfully used to study the discrete quantum energy levels of Ge quantum dots embedded in Si barriers. By varying the bias voltage, the population of carriers in the dot changes and the Coulomb charging effect could be clearly seen from the steplike change of the activation energy of the hole emission. Up to five (or seven) holes charged in a Ge dot with the lateral dimension of 13 nm (or 25 nm) is observed. The energy levels of ground state and first excited state are determined. The advantages of this method are the relatively high measuring temperature, large signal-to-noise ratio, simple and straightforward as well as the possibility of measuring the carrier capturing cross section.

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