Evidence for a negative interband photoconductivity in arrays of Ge/Si type-II quantum dots

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We find that conductivity of stacked arrays of Ge/*n*-Si quantum dots decreases under interband optical excitation. The negative photoeffect is explained by trapping the mobile electrons in the quantum wells created by the Hartree potential of holes photoexcited in the dots. A phenomenological theory of the effect is fitted to the data. The obtained electron trap energy, ~17 meV, is consistent with the results of self-consistent calculations.

Inter- and intraband optical transitions in self-assembled quantum dots (SAQD's) are believed to be of practical interest for the development of a new generation of infrared photodetectors and lasers which should operate from near- to far-infrared.[1] Apart from their possible technological applications, the SAQD's are an attractive subject from the viewpoint of fundamental physics. One prominent system, whose intriguing properties are still poorly understood, is the Ge/Si(001) heterostructure with Ge SAQD's. Ge/Si(001) quantum dots exhibit a type-II (staggered) band lineup. The large (~0.7 eV) valence-band offset characteristic of this heterojunction leads to an effective confinement of holes in the Ge regions. The holes create a Hartree potential resulting in a triangular quantum well for free electrons of Si at the Ge/Si interface (Fig. 1). Thus a fundamental feature of these SAQD's is expected to be that the trapping potential for electrons would be greatly enhanced with charging the dots with holes. In this paper, we predict and then demonstrate experimentally that this feature results in a negative interband photoconductivity (PC).

Consider an *n*-type Si layer with embedded undoped Ge nanoclusters as shown in Fig. 1. The dark conductivity of the system is determined by the mobile electrons thermally activated from the donor impurity states to the conduction band [Fig. 1(a)]. The effect of the interband radiation is to create holes in the valence band and electrons in the conduction band. Holes excited in Si will start to accumulate in Ge SAQD's, charging them positively. As a result, potential wells for electrons will arise at the Si/Ge interfaces in Si [Fig. 1(b)]. As the number of such electronic traps and/or the electron binding energy are increased upon illumination, the electrons (both equilibrium and nonequilibrium) become localized in the wells. The localization of electrons will decrease the concentration of mobile carriers and reduce the conductivity of the system.

Since the number of photoexcited electrons equals the number of photoexcited holes, a necessary condition for the negative photoeffect to occur is that a dot would be able to trap more electrons than there are holes, although these holes are entirely responsible for the most part of the trapping potential. To check whether this is the case, we calculate the electron binding energy for the Ge/Si quantum dots under investigation.

To obtain reasonable estimates, a realistic Ge nanocrystal geometry has to be used for model calculations. We consider a {105}-faceted Ge pyramid with a square base in the (001) plane and with base length of 15 nm and height of 1.5 nm. The nanocrystal rests on a 5 ML thick Ge wetting layer and is entirely surrounded by Si. First of all, the strain distribution inside and around QD was calculated using the valence force field model with the Keating potential.[2] Then the strain-induced modifications of the conduction and valence bands of Ge and Si were obtained by using the deformation potentials given in Ref. 3.

In order to obtain the electron energy, a set of three-dimensional self-consistent effective-mass Schrödinger equations was solved numerically for electrons and holes us-

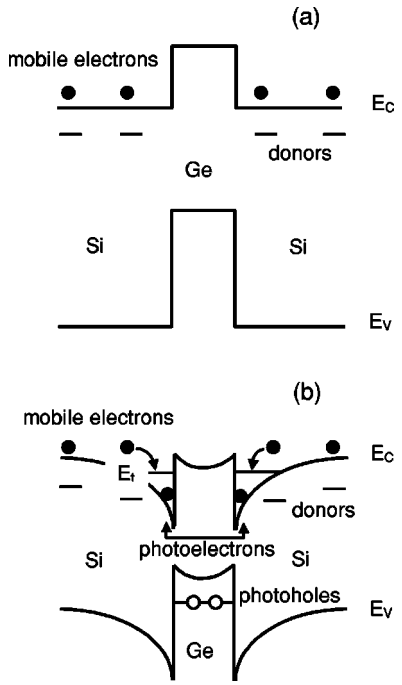

FIG. 1. Band structure of an *n*-type Ge/Si heterostructure with Ge SAQD's (a) in the absence of light and (b) under interband illumination. The figure illustrates the mechanism of negative interband photoconductivity. Potentials due to strain are not included.

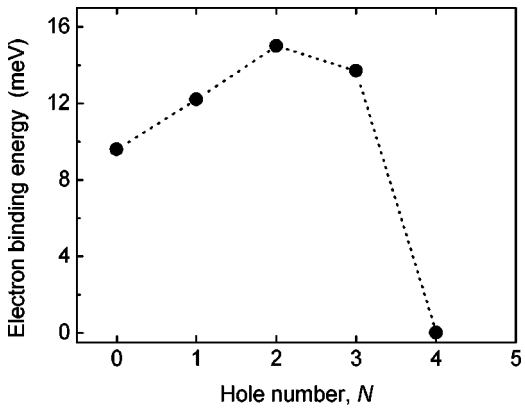

FIG. 2. Binding energy of extra $(N+1)$th electron in a dot containing N holes as a function of N.

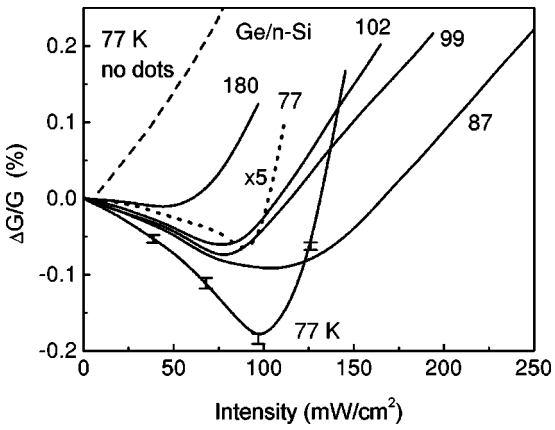

FIG. 3. Dependence of the relative photoconductivity on the interband illumination intensity in two n-type Si samples with Ge SAQD's (dot and solid lines) and in a sample without Ge nanoclusters (dashed line) at various temperatures. Solid lines correspond to antimony concentration $N_{epi}=2.5\times10^{16}$ cm^{-3}, the dotted line corresponds to $N_{epi}=8\times10^{16}$ cm^{-3}. Error bars indicate the typical uncertainty which applies to all curves.

ing the Hartree approximation. The interaction between charged particles was modeled by a statically screened Coulomb potential: $U_{ij}(\mathbf{r_i},\mathbf{r_j})=e^2/4\pi\epsilon\epsilon_0|\mathbf{r_i}-\mathbf{r_j}|$. In the conduction band, the band offset between Δ minima of unstrained Ge and Si is taken equal to 340 meV. In the valence band, the band offset without strain is 610 meV. The effective mass both in the conduction and valence bands is decoupled between the growth axis and the layer plane. The effective mass in the conduction band of Si is $m_z=0.92m_0$ and $m_{xy}=0.19m_0$. In the valence band of Ge, the effective mass is taken equal to $m_z=0.2m_0$ and $m_{xy}=0.39m_0$. Only the heavy-hole states are considered in the valence band, since the light-hole states lie close to the valence-band edge.

The binding energy of the $(N+1)$th (i.e., extra) electron in a dot charged with N holes as a function of N is depicted in Fig. 2. Our calculations clearly indicate that the dot can actually keep more electrons than there are holes. Note, a shallow bound electron state ($E_t\sim9$ meV) exists even when no holes are in the dots. This is due to nonuniform structural deformation of the silicon surrounding Ge islands, caused by the mismatch of the Ge and Si lattice constants. As the number of photoholes increases up to $N=2$, the energy level of an extra electron becomes deeper in the self-consistent potential well, which should result in more effective trapping of equilibrium electrons from the conduction band and in reduction of the conductivity. Once the number of holes exceeds 3, the electron binding energy tends to decrease rapidly. A deep insight into calculated structure of the electron wave functions reveals that two electrons occupy the ground state near the GE nanocluster apex, while the other two electrons are localized in their ground state below the Ge pyramid base. Thus the fifth electron should enter the excited state. But because of the larger extent of the excited state, the electron-hole interaction gets smaller and the binding energy is greatly reduced. Self-consistent calculations depicted in Fig. 2 imply that at $N=2$ the conductivity should have a minimum value.

To verify experimentally our prediction, we investigated the PC in two Ge/Si n-type epitaxial structures grown on a Si(001) substrate with the phosphorus concentration $N_s=10^{15}$ cm^{-3}. The substrate thickness is $L_s=300$ μm. Each sample consists of ten layers of Ge islands separated by 30-nm Si spacers. The total thickness of the epitaxial layer is $L_{epi}\approx0.3$ μm. The Sb-doping level of the Si spacers is $N_{epi}=2.5\times10^{16}$ cm^{-3} in the first sample and $N_{epi}=8\times10^{16}$ cm^{-3} in the second one. Structural characterizations of the Ge dots were performed by scanning tunneling microscopy[4] (STM) and also by cross-sectional transmission electron microscopy.[5] For the STM measurements, a reference sample with only one Ge dot layer without a Si cap was grown under the same growth condition. The SAQD's are found to be pyramidal with base orientation along [100] and [010] directions. The average size of the dot base length is around 15 nm, the height is ≈1.5 nm, and the dot uniformity is about $\pm20\%$. The areal density of the dots is $n_{QD}=3\times10^{11}$ cm^{-2}. Al source and drain electrodes were deposited on top of the structure and heated at 450 °C in a N_2 atmosphere to form reproducible Ohmic contacts. The distance between electrodes is 0.3 cm. A GaAs light-emitting diode (LED) with an emission maximum at a wavelength of 0.9 μm was used as a light source. The typical photon energy, ≈1.3 eV, is larger than the Si and Ge band gaps, therefore the LED radiation would excite the interband transitions. The emission intensity of the LED was modulated with a frequency of 2 kHz. The photocurrent was measured at the modulation frequency using a current amplifier together with the lock-in technique. The source-drain voltage was fixed at 20 mV which ensures Ohmic conduction in the temperature range from 300 to 77 K.

The fractional change in the conductivity of the sample with $N_{epi}=2.5\times10^{16}$ cm^{-3} as a function of the illumination power density P is depicted in Fig. 3. Also shown is the PC of the sample in which the epitaxial layer with Ge SAQD's has been removed by a controlled chemical etching (dash line). HF:HNO_3 (1:200) solution was used. The conductivity of the sample containing no dots is positive and almost linearly increases with increasing P due to generation of excess carriers. The SAQD sample exhibits negative PC in the range of illumination intensities $P=0-100$ mW/cm^2. The second n-type SADQ sample also shows the negative PC except that a smaller magnitude of the effect is observed [dot line in Fig. 3].

At $P>100$ mW/cm^2, a transition from negative to posi-

tive PC is observed. We associate the change of the PC sign with reduction of the trap energy E_t. Self-consistent calculations shown in Fig. 2 demonstrate that the maximum value of E_t is reached when each dot contains two holes. Let us estimate the number of photoholes in the dots at $P \sim 100$ mW/cm^2. When the sample is illuminated, electrons and holes are photogenerated through the light penetration length (≈ 10 μm for the 0.9-μm wavelength). The excess carriers diffuse from the Si bulk towards the Ge SAQD's and are accumulated in the dots. Since the carrier diffusion length in Si [10^2–10^3 μm (Ref. 6)] is much larger than the light penetration length, all the photogenerated carriers in Si can be trapped in the bound states in the region of SAQD's. In this case, the average injected number of holes (and electrons) in each dot is given by $N = P\tau/h\nu n_{\mathrm{QD}} N_{\mathrm{QD}}$, where τ is the interband recombination lifetime, $h\nu$ is the photon energy, n_{QD} is the SAQD density, N_{QD} is the number of SAQD layers. For $P = 100$ mW/cm^2, $\tau \sim 15$ μs,[7] $h\nu = 1.3$ eV, $n_{\mathrm{QD}} = 3 \times 10^{11}$ cm^{-2} and $N_{\mathrm{QD}} = 10$, the number of photoexcited holes trapped in each dot is actually determined to be $N \approx 2$, in excellent agreement with the theoretical results of Fig. 2.

A full theoretical treatment of the photoconductivity would be a formidable task. Assuming that each dot can trap only one extra electron, we describe below a simplified model which produces reasonable results for the conductivity minimum. In the model that follows, we also neglect the presence of shallow electron traps in the dark.

The layer conductivity in the dark is given by

$$G = e\mu_s n_s L_s + e\mu_{epi} n_{epi} L_{epi}, \tag{1}$$

where μ_s is the electron mobility in the Si substrate, n_s is the free-electron concentration in the substrate, μ_{epi} is the electron mobility in the epitaxial Si layer with neutral dots, n_{epi} is the free-electron concentration in the epitaxial Si layer. When the sample is illuminated, the conductivity may be expressed as

$$G_{ph} = e\mu_s n_s L_s + e\mu_{\mathrm{QD}} n_0 L_{epi}, \tag{2}$$

where μ_{QD} is the electron mobility in the epitaxial Si layer with the charged SAQD's, n_0 is the free-electron concentration in the epitaxial Si layer containing the photoinduced electron traps. Here we assume that photoholes are localized deep on the dot states and not participate in conduction [the energy of the hole ground state is ~ 400 meV (Ref. 4)]. Both values n_s and n_{epi} can be deduced from the following well-known set of equations:[8]

$$n_{epi} + n'_{epi} = N_{epi}, \tag{3a}$$

$$n_{epi} = N_c \exp[-(E_c - E_F)/kT], \tag{3b}$$

$$n'_{epi} = N_{epi}\left[1 + \frac{1}{2}\exp[(E_c - E_{epi} - E_F)/kT]\right]^{-1} \tag{3c}$$

for n_{epi}. Here n'_{epi} is the concentration of the occupied donors, $N_c = 2(2\pi m^* kT/h^2)^{3/2}$ is the effective density of states in the conduction band of Si, E_F is the Fermi energy, E_c is the conduction band edge, and E_{epi} is the ionization energy of the donor level. Equation (3a) comes from the electroneutrality of the system, Eqs. (3b) and (3c) are result of the Fermi statistics. The solution of Eqs. (3a), (3b), and (3c) has the form

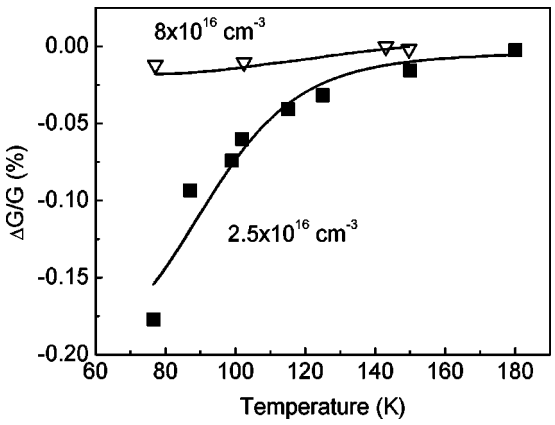

FIG. 4. Temperature dependence of the photoconductivity minimum for two SAQD's samples with different antimony concentrations N_{epi}. The solid lines refer to theory, as explained in text.

$$n_{epi} = \frac{2N_{epi}}{\sqrt{1 + 8N_c^{-1}N_{epi}\exp(E_{epi}/kT)} + 1}. \tag{4}$$

A similar expression is valid also for n_s, except that the parameters N_s and E_s would be used instead of N_{epi} and E_{epi}.

If the epitaxial layer contains the electron traps with concentration N_t, the concentration of electrons in the conduction band can be calculated from the following expressions:

$$n_0 + n'_{epi} + n_t = N_{epi}, \tag{5a}$$

$$n_0 = N_c \exp[-(E_c - E_F)/kT], \tag{5b}$$

$$n_t = N_t\left[1 + \frac{1}{2}\exp[(E_c - E_t - E_F)/kT]\right]^{-1}, \tag{5c}$$

where n_t is the concentration of traps filled with electrons, and n'_{epi} is still determined by Eq. (3c). From Eqs. (3c), (5a), (5b), and (5c) one obtains that n_0 satisfies a cubic equation

$$\begin{aligned} 0 = {} & n_0^3 + n_0^2\left[\frac{1}{2}N_c\left[\exp\left(-\frac{E_t}{kT}\right) + \exp\left(-\frac{E_{epi}}{kT}\right)\right] + N_t\right] \\ & + \frac{1}{2}n_0\left[\frac{1}{2}N_c^2\exp\left(-\frac{E_{epi} + E_t}{kT}\right) + N_c(N_t - N_{epi})\right. \\ & \left.\times\exp\left(-\frac{E_{epi}}{kT}\right)\right] - \frac{1}{4}N_{epi}N_c^2\exp\left(-\frac{E_{epi} + E_t}{kT}\right). \end{aligned} \tag{6}$$

We solve Eq. (6) numerically. Experimentally determined values of the minimum of the relative photoconductivity of two samples with different Sb concentrations (symbols) as a function of temperature are given in Fig. 4, together with theoretical curves calculated by Eqs. (6), (1), (2), and (4) (solid lines). To obtain the best fits, we vary the values of the electron binding energy E_t and the ratio of the electron mobilities after and before charging of the dots $\mu_{\mathrm{QD}}/\mu_{epi}$. All other parameters are known. We use $E_s \equiv E_{\mathrm{P}} = 45$ meV,

$E_{epi} \equiv E_{Sb} = 39$ meV (Ref. 9), and $N_t L_{epi} \equiv N_{QD} n_{QD} = 3 \times 10^{12}$ cm^{-2}. We fix also $\mu_s / \mu_{epi} = 6$ (determined by separate Hall measurements at $T = 300$ K), and assume that this ratio is independent of temperature.

From the fits, we determine an energy of the photoinduced traps of 17 ± 4 meV and a ratio of mobilities μ_{QD} / μ_{epi} of 1.02 ± 0.04 for both samples. The value of E_t seems to be in reasonable agreement with the results of self-consistent calculations for this system at $N = 2$. To obtain data that are more accurate, the temperature dependence of the mobilities, finite compensation in silicon layers, and thermal emission of the photoelectrons to the conduction band must be correctly taken into account. We hope that our result will stimulate complete and consistent theory of the negative photoconductivity in type-II quantum dots.

As $\mu_{QD} / \mu_{epi} \approx 1$, the mobility in the epilayer with SAQD's is not reduced by the presence of electrostatic scattering potential of the charged dots. Hall measurements in a set of structures with Ge/Si SAQD's showed that carrier mobility is independent of the impurity concentration at $N_{epi} < 10^{17}$ cm^{-3} and is equal to ≈ 200 cm^2 V^{-1} s^{-1} at 300 K. The probable reason is that the mobility in SAQD's samples is determined by scattering of carriers by Ge/Si interfaces or structural defects.

To demonstrate that the observed negative photoeffect does come mainly from a smaller population of mobile electrons under illumination and not from a reduction of the mobility, we measure photoconductivity of a *p*-type Ge/Si heterostructure (Fig. 5). The sample was grown under conditions similar to those of the *n*-type structures, except that both the substrate and the epitaxial layer were doped with boron ($\approx 10^{15}$ cm^{-3} in the substrate and $\approx 2 \times 10^{16}$ cm^{-3} in the epilayer). It is clear that the region with negative PC is absent in the *p*-type structure. Instead, an extended region with small positive PC due to trapping nonequilibrium carriers of both types is observed. Under an intensive illumination, the electron binding energy is reduced resulting in increasing the number of electrons in the conduction band and in the appearance of the positive PC. This result may be considered as additional proof of our explanation of the negative photoconductivity in the *n*-type Ge/Si quantum dots.

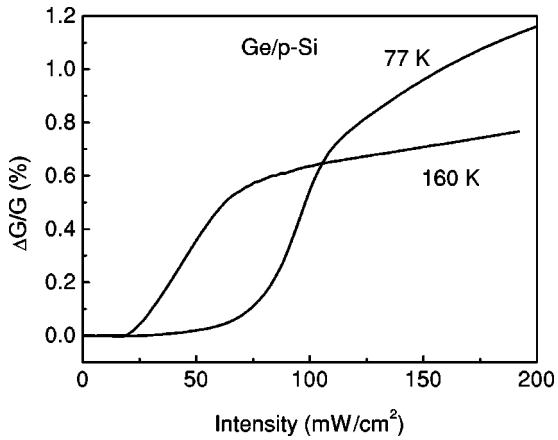

FIG. 5. Dependence of the relative photoconductivity on the interband illumination intensity in *p*-type Si with Ge quantum dots.

In summary, we would like to emphasize that the observed negative photoeffect is an inherent feature of the type-II quantum dots, because in type-I systems both electrons and holes are confined in the potential wells created by the conduction and valence-band discontinuities independently of the charge state of SAQD's.

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