Growth, Quantum Confinement and Transport Mechanisms of Ge Nanodot Arrays Formed on a SiO$_2$ Monolayer

Yasuo Nakayama*
Center for Frontier Science, Chiba University, 1-33 Yayoi-cho, Inage-ku, Chiba 263-8522, Japan

Iwao Matsuda
The Institute for Solid State Physics (ISSP), The University of Tokyo, 5-1-5 Kashiwanoha, Kashiwa City, Chiba 277-8581, Japan and Core Research for Evolutional Science and Technology (CREST), Japan Science and Technology Agency (JST), Saitama 332-0012, Japan

Shuji Hasegawa
Department of Physics, Graduate School of Science, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-0033, Japan and CREST, JST

Masakazu Ichikawa
Quantum-Phase Electronics Center, Department of Applied Physics, Graduate School of Engineering, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan and CREST, JST

(Received 31 July 2008; Accepted 7 August 2008; Published 23 August 2008)

In this review, recent findings on growth manners, quantum confinement phenomena, and carrier transport mechanisms of self-assembled Ge nanodots on an oxidized Si surface are summarized. A simple equation relating the dot size, which was estimated by STM images, with the Ge coverage was proposed. Quantum confinement was observed by photoemission spectroscopy (PES) and scanning tunneling spectroscopy (STS), and the actual height of the confining potential was determined from the dot-size vs. energy relationship through a three dimensional parabolic potential model. The transport mechanism of the nanodot arrays, which was estimated based on the measurements by a microscopic four-point-probe method, was distinct depending on the structure of the dot-substrate interface. All results suggest that the interface oxide layer and subnanometer-sized voids on it interconnecting the nanodots with the substrate not only regulate the quantized energy in the nanodots but also switch on/off carrier exchange between the nanodot and the substrate through variable interface potential barrier height.

[DOI: 10.1380/ejssnt.2008.191]

Keywords: Four-point probe conductivity measurement; Photoelectron spectroscopy; Electrical transport; Quantum effects; Germanium; Silicon; Nanodot; Interface barrier

I. INTRODUCTION

The current electronics devices are dominantly based on silicon. In contrast, optical semiconductor devices (e.g. lasers, infrared communication devices, and so on) are mostly made from III-V and II-VI compound semiconductors instead of Si. It is because Si is an exponent of indirect-gap semiconductors that gives in principle poor light-emission efficiency. There are fundamental difficulties on conjointing such optical compound semiconductors, especially the narrow-gap ones around the optical-communication wave-length. Therefore, quantum-size effect, which will expand the energy-band gap and change it into pseudo-direct-gap, has been expected to adjust these disadvantages to apply this material for optoelectronics devices. The most famous nanostructure of Ge/Si systems may be “hut clusters” that are spontaneously formed through Stranski-Krastanov (SK) growth mode. However, the size of the hut clusters is limited at smallest in the order of 10 nm whereas it must be scaled down below 10 nm in order to realize the quantum effect at room temperature (RT) [4–6]. Numerous efforts have been addressed to fabricate quantum-sized nanostructures of Ge through surface passivation of the Si substrates [7–20]. Among them, the method reported by Shklyaev and coworkers, the kernel of which is using the Si surface covered with a monolayer-thick SiO$_2$ layer as substrates, is particularly promising owing to sufficiently small size, size selectability, extremely high density, and photoluminescent capability at RT of its production of Ge nanodots [7, 8, 21–23].

In this review, recent results of the authors’ group including the related works from other groups are summarized concerning the growth mechanisms, quantum size phenomena and transport natures on the Ge nanodot arrays fabricated by the Shklyaev’s method. Electrical and optical output from the present nanodots are quite sen-
sitive to their physical properties such as the dot size, crystallization, the interface structure between the dots and the substrate, and so on. Hence we primarily show the growth mechanism of the nanodots on the oxidized Si surface (§ II). In this section, a simple function describing increase of the average dot-size depending on the Ge coverage is specified. On the next step, two types of approaches, photoemission spectroscopy (PES) and scanning tunneling spectroscopy (STS), individually succeeded in proving the quantum-size effect in the electronic states are introduced, which is a key factor to apply the Ge nanodots to optoelectronics (§ III). Analysis procedures and theoretical models are also briefly explained, through which one can evaluate actual values of the confining potential barrier heights depending on the interface conditions. In § IV, very recent understanding about the transport mechanisms on the present nanodot arrays is related to the aforementioned properties. We show that the transport nature is strongly dominated by electrical coupling between the nanodots and the substrate. This understanding was drawn by schematic studies of microscopic conductivity measurement, depending on temperature as well as the dot-size, and core-level PES. Finally, the above findings are summarized and the recent results concerning other nanodot systems of related semiconductor materials are briefly introduced in § V.

II. GROWTH MECHANISMS OF THE GE NANODOTS

A. Preparation of the SiO2 monolayer

The topical Ge nanodots can be fabricated on the Si substrates covered with the SiO2 monolayer. It has been reported that not only deposition condition of Ge but also condition of the SiO2 monolayer influence the structure of the nanodots [20]. Hence, we will specify the method of fabricating the substrate prior to describing the growth manner of the nanodots themselves.

The SiO2 monolayer can be formed on both Si(111) and (100) surfaces through an appropriate procedure as follows [7, 8]. Clean surfaces were prepared by a flash direct-current heating up to 1250°C after a degassing at 400°C ca. for one night in ultra-high-vacuum (UHV) condition. Oxygen exposure on the clean surfaces at a pressure of 2×10^{-4} Pa followed by gradual rising of the sample temperature from RT to 620°C for 10 minutes produces oxidized surfaces on the Si substrates. The thickness and the chemical composition of the oxide layer were characterized as a monatomic-thick (0.3 nm) film composed mainly by silicon dioxide (SiO2) by means of x-ray photoelectron spectroscopy [7]. The substrate covered with the SiO2 monolayer gives the (1×1) electron diffraction pattern which is ascribed to the buried Si lattice underneath the ultrathin oxide layer. STM images imply that the oxide layer itself is amorphous with many structural defects.

B. Epitaxial and Nonepitaxial Ge nanodots

It is well known that Ge overlayers grow in SK mode on clean Si surfaces because a lattice mismatch between Ge and Si is rather large whereas the surface energy of Ge is smaller than that of Si [4]. On the oxidized Si surfaces, however, formation of the wetting layer of Ge is hindered by a smaller surface energy of SiO2 compared to Ge. As a result, deposition of Ge onto the SiO2 monolayer produces spherical nanodots uniformly covering over whole the surface as shown in STM [24] and scanning transmission electron microscopy (STEM) [25] images [Figs. 1(a) and (b)].

A portion of deposited hot Ge atoms reacts with SiO2 as;

\[ \text{SiO}_2(s) + \text{Ge(ad)} \rightarrow \text{SiO} + \text{GeO}, \]

where both the products, silicon monooxide (SiO) and germanium monooxide (GeO), evaporate at relatively moderate temperature [7]. This reaction eats the SiO2 monolayer as well as the deposited Ge, which results in formation of sub-nanometer-sized voids penetrating into the oxide layer itself.
through the oxide layer. The rate of the void formation will compete against nucleation of the deposited Ge at the void sites to generate the nanodots. When the sample temperature is high enough and/or the deposition rate is moderate, void formation occurs primarily and the voids act as nucleation centers for the Ge nanodots. In this case, direct contact of the nanodots to the Si substrate through the voids makes the nanodots epitaxial to a lattice of the substrate, which provides a reflection high energy electron diffraction (RHEED) pattern with diffuse transmission spots [Fig. 1(c)]. On the contrary, fast deposition of Ge and/or insufficient sample temperature makes the nucleation process overcome the void formation. Since the nanodots produced everywhere on the substrate by this scheme are separated from the Si substrate by the SiO₂ layer, they are nonepitaxial to the substrate and provide another RHEED pattern with Debye rings [Fig. 1(d)]. Whether the nanodots are epitaxial or nonepitaxial is therefore distinctive each other by RHEED patterns. Postdeposition annealing after dot formation does not change the nonepitaxial nanodots into the epitaxial ones [7].

Direct observation of local structure of the epitaxial nanodots has been tried by transmission electron microscopy (TEM) techniques. High-resolution TEM results have also revealed that the crystal lattice of the epitaxial Ge nanodots is 3.5 % expanded (1.5 % compressed) compared to that of the Si substrate (bulk Ge) [26]. On the other hand, for the nonepitaxial case, Ge K-edge x-ray absorption near edge structure spectra show excellent correspondence with that of the bulk Ge [27], which implies that the structure of the nonepitaxial dots is identical to the bulk Ge. TEM images have proved that the nonepitaxial nanodots are entirely separated from the Si substrate [27].

C. Growth mechanisms

The dot size and number density were evaluated experimentally from STM images that were obtained in constant-current mode typically at $V_{\text{sample}} = 2.5$ V and $I_t = 0.25$ nA [Figs. 1(c) and (d)]. The average dot-radius $r$ was determined for each coverage of Ge deposition by conducting Gaussian fitting on size distributions generalized from counting data pixels belonging to individual nanodots [Fig. 2(a)].

Shklyaev et al. reported that the number density of the nanodots ($n$) is substantially independent to the growth temperature ($T_g$) and the deposition rate (i.e. Ge flux; $F$) [8]. Insensitiveness of $n$ to $F$ indicates the critical dot size for nucleation is zero, which can be ascribed to a nucleation reaction of individual Ge adatoms with SiO₂ [7]. The number density $n$ of the nanodots is determined as $n = (\tau_\gamma D)^{-1}$, where the lifetime of Ge adatoms $\tau_\gamma$ is expressed as $\tau_\gamma^{-1} = k^{(0)} \exp(-E_d/kT_g)$ ($k^{(0)}$ and $E_d$ are a pre-exponential factor and the activation energy of the nucleation reaction, respectively). Since the diffusion coefficient $D$ is expressed as $D = \nu a^2 \exp(-E_d/kT_g)$ where $\nu$, $a$ and $E_d$ are the frequency factor, the jump distance of the adatoms for surface diffusion, and the diffusion activation energy, respectively, $n$ is given by:

$$n = \frac{k^{(0)}}{\nu a^2} \exp\left(\frac{E_d - E_r}{kT_g}\right).$$  \hspace{1cm} (1)

Therefore independence of $n$ to $T_g$ suggests that $E_d \approx E_r$. Substitution of appropriate values for $k^{(0)}/\nu (= 10^{-2} \sim 10^{-3}$ nm) and $a (\approx 0.3$ nm on SiO₂) leads $n \sim 10^{12}$ cm⁻² which is of the same order of magnitude of the experimental values.

The above discussion indicates that $n$ is determined only by $k^{(0)}$, $\nu$ and $a$ and hence it is independent to the total amount of Ge [8]. In this case, $r$ will be proportional to a cube root of the nominal coverage of Ge ($\theta$) (i.e. deposition amount) because $\theta = n \cdot 4\pi r^3/3$ under a simplest assumption of sphere dots. When the dot-size becomes larger than inter-dot spacing, however, coalescence of neighboring dots is observed by in-situ TEM [26], which results in decrease of dot number (i.e. number density $n$).
After the whole surface area is covered with the nanodots, \( n \) will decrease linearly to the inverse cross-section of the dots \( (\pi r^2) \) because \( n \cdot \pi r^2 \) will be equal to the unit area. Thus \( r \) grows linearly with \( \theta \) when the nominal coverage is large enough, which was verified experimentally [28–30]. For the epitaxial case, consumption of deposited Ge atoms by the void-formation reaction should be taken into account besides. Above all, \( r \) can be written by a model function of \( \theta \) by:

\[
r = A\theta^\frac{1}{3} + B\theta[1 - \exp\left(-\frac{\theta}{C}\right)] - D\exp\left(-\frac{\theta}{E}\right).
\]  

(2)

A factor in the square brackets of the second term is a switch function, and the \( \theta^\frac{1}{3} \) dependence in the first term is overwhelmed by the second term after the switch is smoothly turned on beyond a certain coverage. The third term corresponding to the void-formation reaction makes dominant contribution on \( r \) for small \( \theta \) but will converge when \( \theta \) becomes large. The capital characters \( (A, B, C, D \text{ and } E) \) are determined by fitting of the experimental \( \theta-r \) dependence. Although this is only an approximated expression, this equation successfully reproduces the experimental \( \theta-r \) dependence as shown in Fig. 2(c) [31]. It is interesting to note that the fitting result for the epitaxial case predicts absence of dot-formation at small but finite coverage (e.g. 0.5 BL), which is consistent to the STM observation [7].

### III. QUANTUM CONFINEMENT INTO THE GE NANODOTS

#### A. Photoemission Spectroscopy

PES spectra of the SiO\(_2\) monolayer covering the Si(111) substrate [Fig. 3(a)] show a large peak at binding energy of \( \sim 7 \) eV ascribed to O-2\(p\) of Si-O-Si bonding [32, 33], from the peak onset of which the valence band maximum (VBM) of the SiO\(_2\) monolayer \( (E_{\text{VBM}}^{\text{SiO}_2}) \) is roughly determined as \( \sim 5 \) eV below the Fermi level \( (E_F) \). Taking into account that the mean free path of the present photoelectrons (a few nm) is much longer than the thickness of the oxide layer, PES signals existing within energy range between \( E_{\text{VBM}}^{\text{SiO}_2} \) and \( E_F \) is attributed to bulk states of the Si(111) substrate [28]. VBM of bulk Si \( (E_{\text{VBM}}^{\text{Si}}) \) is determined from the spectral onset as \( 0.87 \pm 0.02 \) eV below \( E_F \).

As shown in Fig. 3(a), formation of Ge nanodots does not generate a drastic change on PES spectra at a crude glance. Focusing on the vicinity of \( E_F \), however, helps one to notice a systematic change in the spectral edge as shown in Figs. 3(b) and (c). For the both types of the nanodots, the spectral onset monotonously shifts toward \( E_F \) as increasing the Ge coverage, which can be attributed to a sign of quantum size effect. Although size distribution of the nanodots makes it difficult to determine an absolute value of quantized energy levels in a nanodot of.
a certain size because PES gives us a size-averaged information, the amount of shift of spectral edge will provide information about a change in the highest-occupied quantized energy level [i.e. energy position of the ground state of the confined holes ($E_{\text{h-GS}}$)] resulting from change in dot size [34–38]. In order to prove the above attribution, the energy shift of the spectral edge should be quantitatively evaluated as a function of the dot size.

Concerning PES results, a large dot will make stronger contribution to a spectrum than a smaller one because the former contains more Ge atoms compared to the latter. Hence dominant radii ($r_v$) in which the largest population of deposited Ge belongs were evaluated from histograms of appearance frequency of corresponding dot-radius multiplied by corresponding volume [Fig. 2(b)]. Also $\theta$-$r_v$ dependence [Fig. 2(d)] can be fitted by Eq. (2), which enables us to know what size of the nanodots principally dominates the PES spectra for each nominal coverage. On the other hand, energy positions of the spectral onset ($E_{\text{VBM}}^\text{cot}$) were quantitatively defined as shown in Figs. 3(b) and (c) by an intersection of two lines extrapolated from a spectral tail of the valence band of the Ge nanodots and background signals [34, 36, 37].

After the above estimations, the shift of the spectral onset $\Delta E_{\text{VBM}}$ ($\equiv E_{\text{VBM}}^\text{ot} - E_{\text{VBM}}^\text{Si}$) depending on $r_v$ can be drawn as shown in Fig. 4 [29, 30]. Occurrence of quantum size effect is clearly evinced in the systematic shift of the spectral edges (i.e. the highest-occupied quantized energies) away from $E_F$ as the dot size becomes smaller. It should also be pointed that the quantized energy level of the non-epitaxial nanodots is higher than that of the epitaxial ones even if $r_v$ is the same. The reason of the difference will be discussed in § III-C.

B. Scanning Tunneling Spectroscopy

Scanning tunneling spectroscopy (STS) is also a powerful tool to investigate quantum dots because it enables one to measure not only the occupied states but also the unoccupied states of individual dots [39–41]. Nakamura and coworkers evaluated “VBM” and “conduction band minima (CBM)” of individual epitaxial nanodots by STS at RT [42]. They reported that the “VBM” downshifted and the “CBM” shifted upwards as the dot size decreases, which should be attributed to a sign of the quantum size effect. In the present case, the observed “VBM” (“CBM”) reflects the ground state of confined holes (electrons) into the target nanodot. Since the energy standards of the quantized energy levels are band-edges of the bulk Ge whereas that of the STS measurement is $E_F$, the quantized energies of the hole ground state ($E_{\text{h-GS}}$) and the electron ground states ($E_{\text{e-GS}}$) were extracted from the onsets of STS spectra through subtracting the bulk VBM and CBM energies ($E_{\text{VBM}}^\text{bulk}$ and $E_{\text{CBM}}^\text{bulk}$) [Fig. 4(b)]. The amounts of the “VBM” and “CBM” shifted showed good agreement with the values predicted by a tight-binding (TB) calculation on the Ge nano crystals embedded in a SiO$_2$ matrix [43], which made it possible to determine $E_{\text{VBM}}^\text{bulk}$ and $E_{\text{CBM}}^\text{bulk}$ through fitting of the STS data with the TB curves. $E_{\text{h-GS}}$ estimated from the STS results are plotted as a function of size of the target nanodots in Fig. 4(a). The shift of $E_{\text{h-GS}}$ shows good consistency on the aforementioned PES results after shifting by an adequate energy reference [30]. A gradient of an $E_{\text{h-GS}}$ - $E_F$ plot was fitted as 1.02 $\pm$ 0.28 which is consistent to the expected value for intrinsic Ge nanodots ($\sim$ 1) [42].

C. Evaluation of confining potential barrier height

Numerous theoretical studies have been reported so far to quantify the electronic states of Ge nanodots, where the calculations have ranged from a simple analytical formula to numerical solutions of the first-principles theory [36, 43–46]. The simplest model is the infinite-depth well potential model of which the analytical solution is well-known that the GS quantization energy ($E_{\text{GS}}$) is proportional to inverse-square of the dot-size ($r^{-2}$). The parabolic potential model is another example which can be analytically solved. The GS energy level quantized by a three-dimensional (3D) spherical parabolic potential is given as:

$$E_{\text{GS}} = E_0 + \frac{2 \sqrt{V}}{r},$$  \hspace{1cm} (3)
FIG. 5: $\Delta E_{\text{VBM}}$ plotted as a function of (a) inverse and (b) inverse-square of $r_v$. Lines in (a) show the best fitted results of the parabolic potential model. Quantized energies of the infinite- and finite-depth well model are plotted in (b). Units of the left and bottom axes are the acceptor Rydberg [$R_A = m^*\hbar^2/\epsilon^2 = 13.6$ meV, where $m^*$ and $\epsilon$ are the conductivity effective mass and the dielectric constant of bulk Ge, and $R_A$ is the atomic Rydberg] and the acceptor Bohr radius [$a_B = \epsilon a_B/m^*\hbar = 3.35$ nm, where $a_B$ is the atomic Bohr radius], respectively [28].

where units of energy and length are the Rydberg and the Bohr radius, respectively, and $E_0$ is an energy reference [28]. In this case, $E_{\text{GS}}$ is expressed as a function of the potential-height $V$ as well as $r^{-1}$. Also numerical solutions have pointed that $E_{\text{GS}}$ shows positive dependences on $V$ and it is proportional to $r^{-\alpha}$ where $\alpha$ ranges between 1 and 2 [45].

Concerning the topical Ge nanodots, carriers are confined into the nanodots by a potential barrier caused by the SiO$_2$ monolayer intercalating between the nanodots and the substrate. The epitaxial and nonepitaxial nanodots should therefore give individual confining barrier heights resulting from the different interface conditions (as mentioned in § II-B). Hence disagreement of the quantized energy of the same-sized epitaxial and nonepitaxial nanodots, shown in Fig. 4, can be ascribed to difference in $V$. It also suggests that one can evaluate the substantial values of $V$ from $r$-dependent variation of $E_{\text{GS}}$.

Figure 5(a) displays $\Delta E_{\text{VBM}}$ that corresponds to shift of the quantized energy of confined holes ($\Delta E_{h-\text{GS}}$) as mentioned above — as a function of $1/r_v$, where the slopes of these plots correspond to $V$ under the 3D parabolic potential model. The confining potential height is evaluated as $6.7(\pm 0.9)$ eV for the nonepitaxial Ge nanodots and $2.1(\pm 0.4)$ eV for the epitaxial ones [29, 30]. The latter value is larger than the energy offset of the VBM between bulk Ge (0.33 eV below $E_F$) and SiO$_2$ (5 eV) that is expected to form the substance of the potential barrier [Fig. 6]. Such enlargement of the actual barrier height of the nonepitaxial dots can be ascribed to the fact that each dot touches the oxidized Si surface at only a small area whereas the major part of the surface area of the nanodot is surrounded by vacuum. On the other hand, the reduction of the confining barrier height of the epitaxial dots compared to that of the nonepitaxial ones should be attributed to the voids penetrating though the SiO$_2$ monolayer.

So far, the shape of such potential barrier caused by a band discontinuity have generally been approximated by a well [47, 48]. Quantized energy $E_{\text{GS}}$ of a 3D spherical well of a finite depth is related with the well radius $r$ and depth $V$ as follows [49]:

$$\alpha \cot \alpha r = -\beta,$$

where

$$\alpha = \sqrt{\frac{2m^* (V - E_{\text{GS}})}{\hbar^2}}$$

and

$$\beta = \sqrt{\frac{2m^* E_{\text{GS}}}{\hbar^2}}.$$
IV. TRANSPORT MECHANISMS

A. Conduction paths

On the present Ge nanodot arrays, one can deconvolute, even though hypothetically, the electric conductance into three types of conduction paths as sketched in Fig. 7; a path ascribed to lateral conduction across the nanodot arrays (σ1), a path induced by the voids on the SiO2 monolayer (σ2), and a path though the substrate (σ0) [31]. If the nanodot array itself does not transmit the carriers, σ1 can be regarded as zero. Similarly, if the voids do not act as an effective path for the carriers, in other words the epitaxial nanodot arrays show equal electrical conductance to the nonepitaxial ones, it means σ2 = 0. Since the SiO2 monolayer is unlikely to carry the carriers, σ0 should be held by the space charge (SC) region (σSC) and bulk (σbulk) of the Si substrate. Among the components given above, only σbulk cannot be influenced by Ge dot formation whereas the others may vary depending on the dot-size r. The total conductance obtained from I-V characteristics is therefore expressed as:

\[
\sigma^\text{NE}(r) = \sigma^\text{NE}_0(0) + \sigma_1(r),
\]
\[
\sigma^\text{Epi}(r) = \sigma^\text{Epi}_0(r) + \sigma_1(r) + \sigma_2(r),
\]
\[
\sigma_0(r) = \sigma_0(0) + \Delta \sigma_0(r) = \sigma_{\text{bulk}} + \sigma_{\text{SC}}(0) + \Delta \sigma_{\text{SC}}(r),
\]

where the superscripts “Epi” and “NE” indicate the epitaxial and nonepitaxial nanodot arrays, respectively, and σ1(r) is assumed to be common for the two types of nanodots because the surface morphology looks equivalent for the epitaxial and nonepitaxial dots when r is the same.

Such treatment might be intelligible as an analogy of the conductivity of adsorbate-induced superstructures on Si, where the conductivity can be divided as \( \sigma = \sigma_{\text{SS}} + \sigma_{\text{SC}} + \sigma_{\text{bulk}} \) and changes of it after adsorption can be attributed to that of the surface state (SS) and SC (\( \Delta \sigma(\theta) = \sigma_{\text{SS}}(\theta) + \Delta \sigma_{\text{SC}}(\theta) \)) [50–52]. The surface state corresponds to the nanodot arrays for the present case. In order to extract \( \sigma_{\text{SS}}(\theta) \) from the measured conductivity change, \( \Delta \sigma_{\text{SC}}(\theta) \) is usually estimated primarily by using core-level PES results to know the band bending below the surface. After this fashion, we will also start with an evaluation of \( \Delta \sigma_{\text{SC}} \) (§ IV-B) followed by discussion concerning “\( \sigma_{\text{SS}} \)” that is constituted by \( \sigma_1 \) and \( \sigma_2 \) (§ IV-C).

B. Core-level photoemission

Adsorption of foreign materials generally causes charge transfer between the adsorbates and the substrate owing to difference in their chemical potential. Also in the topological systems, charge transfer between the Ge nanodots and the Si substrate may not be forbidden by the SiO2 monolayer because it is extremely thin. On Si (or other semiconductors given a limited carrier concentration), such charge transfer results in formation of the SC layer in which the electric potential gradually varies from the surface due to the excess charges distributing in a region of some thickness. The valence and conduction bands are bent by the SC, which changes the electric conductivity parallel to the interface. Change in the conductivity in the SC region can be calculated as a function of magnitude of the band-bending (i.e. \( E_F \) position with respect to the VBM of Si) by solving the Poisson’s equation [52]. On the other hand, the SC not only bends the valence and conduction bands but also makes core-levels shift parallel, which allow one to track the change of the band bending from the core-level shift of such as Si-2p [53].

Figure 8(a) shows Si-2p PES spectra of the epitaxial and non-epitaxial Ge nanodots with that of the SiO2 monolayer presented for comparison [54]. Since the spectra were obtained at the photon energy of 140 eV; consequently kinetic energies of photoelectrons from the Si-2p levels (binding energies of 100 eV) are around 35 eV, the spectra bring ones surface sensitive information owing to a limited electron mean free path (< 1 nm). The SiO2 monolayer reveals slight shift of Si-2p peak position from the 7 × 7 surface, whereas Ge deposition on the oxide layer makes the peaks move to lower binding energy. By using the reported value (0.63 eV [53]) for the \( E_F \) position with respect to the VBM of Si 7 × 7, the \( E_F \) position after formation of the Ge nanodots is evaluated as shown in Fig. 8(b). Shift of the \( E_F \) position can be fitted with an exponential function of the nominal Ge coverage. Corresponding amount of \( \Delta \sigma_{\text{SC}} \) with respect to the that of the substrate covered by the SiO2 monolayer only is over-
of the Ge coverage (bottom axis), and calculated values of nonepitaxial (blue ones) nanodot arrays plotted as a function from the Si-2p axis. Colored lines are fitting lines. (c) The calculated $\Delta \sigma$ (deducting rays themselves to the conductance can be evaluated by the relationship described in §IV-E) from the slope of the $E_a$ plotted as a function of the coverage. (b) ‘Partial conductances’ of the path $\sigma_1$ and $\sigma_2$ plotted as a function of the dot radius $r$.

Laid on the same plots as a function of the $E_a$ position. The calculated values of $\Delta \sigma_{SC}$ clearly evince that, in the present case, the band-bending change will make negative contribution on the electric conductivity, as shown in Fig. 8(c), throughout the whole range of the Ge coverage. Therefore, the increase of conductivity by Ge dot formation, which is shown in the next section, is not attributed to the $\sigma_0(r)$ of the substrate, but to $\sigma_1(r)$ and $\sigma_2(r)$.

C. Dot-size dependence

All the data of electric conductance shown below were measured by a monolithic four-point-probe [55] with a probe spacing of 20 μm, softly contacting onto the surface. This method, called as “micro-four-point probe (μFP4P)”, enables one to estimate the surface conductance excluding the contact resistance without any perceptible damage on the surface [56]. The conductance was evaluated from the slope of the $I-V$ curves around the zero current.

Figure 9(a) presents variation of the conductance of the epitaxial and nonepitaxial Ge nanodot arrays at 320 K as a function of Ge coverage ($\theta$). The values at $\theta = 0$, the conductance of the SiO$_2$ monolayer, correspond to $\sigma_0(0) = \sigma_{\text{walk}} + \sigma_{\text{SC}}(0))$. Contribution of the nanodot arrays themselves to the conductance can be evaluated by deducting $\sigma_0(0)$ and $\Delta \sigma_{\text{SC}}$ (calculated in §IV-B) from the measured total conductance, $\sigma_1$ extracted from $\sigma_{\text{NE}}$ is plotted as a function of $r$ in Fig. 9(b), where the Ge coverage $\theta$ is converted to the dot radius $r$ using the relationship described in §II-C. It manifests a discontinuous increase around $r = 3$ nm, which might be ascribed to the formation of a percolation network of tunneling transport across the nanodots’ edges [57]. On the other hand, by using $\sigma_1(r)$ revealed above, $\sigma_2(r)$ can be drawn from the conductance of the epitaxial nanodot arrays through

D. Temperature dependence

For the epitaxial case, a logarithm of the conductance ($ln(\sigma)$) varies roughly proportional to the inverse-temperature ($1/T$) as shown in Fig. 10(a). It suggests that the conduction nature of the epitaxial nanodot arrays is dominated by the thermal activation process, where the conductivity can be approximated as [3];

$$\sigma(T) = \sigma_0 \exp(-\frac{E_a}{2k_B T}).$$

(8)

The activation energy of the carriers ($E_a$) can be evaluated from the gradient of the ($1/T$)-$ln(\sigma)$. As shown in Fig. 10(c), $E_a$ of the epitaxial dots shows systematical decrease as the dot-size grows, which implies an association with the quantum size effect. Also for the nonepitaxial case, even though the data points of ($1/T$)-$ln(\sigma)$ relation are limited in a narrow range of temperature, the apparent $E_a$ was drawn by the same manner as a function of $r$ [Fig. 10(c)]. Contrary to the epitaxial case, the estimated $E_a$ of the nonepitaxial dots does not show a straightforward dependence on $r$. These results suggest that the conduction nature of the nonepitaxial nanodot arrays is dominated by a mechanism different from that of the epitaxial ones. It should also be noted that the poorer conduction of the nonepitaxial nanodots than the epitaxial ones despite the smaller $E_a$ should be ascribed to smaller value of $\sigma_{\text{pre}}$ probably because of lower effective mobility of the carriers.

E. Summary of the transport mechanisms

Since the thermal activation scheme on electric conduction is held by thermally excited carriers, $E_a$ should correspond to an energy difference between certain occupied and unoccupied states. As mentioned above, the
highest occupied states (HOS) and the lowest unoccupied states (LUS) of both the Ge nanodots and the Si substrate vary depending on the Ge dot size (Ge coverage). The HOS of Ge dots and the VBM of the Si substrate were already estimated from the PES results in § III-A [Fig. 4] and § IV-B [Fig. 8(b)], respectively. The LUS of the Ge dots moves symmetry to the HOS with respect to $E_F$, which had been revealed by STS results as mentioned in § III-B, whereas the CBM of Si must shift parallel to the VBM with preserving the gap-width (1.12 eV). Respectively energy positions are plotted in Fig. 11(a) and (b) as a function of $r$ for the epitaxial and nonepitaxial nanodots, respectively.

On the other hand, the nanodot layer itself hardly contributes to electric conduction, especially when $r < 3$ nm, as pointed out in § IV-C. It means that the carriers must go into the Si substrate to play a part on electric conductivity. Although the minimum excitation energy corresponds to the gap between HOS and LUS of the nanodots, the holes at Ge-HOS from conducting in the sub-dot - Si interface will prevent the electrons at Ge-LUS to go into the Si substrate to play a part on electric conductivity. Hence enhancement of electric conductivity after Ge dot formation should be attributed to the overexcited carriers in the Ge nanodots exceeding those energy offsets.

As shown in Fig. 11(c), for the epitaxial case, calculated overexcitation energies of electrons (which corresponds to energy difference between Ge-HOS and Si-CBM) and holes (Ge-LUS and Si-VBM) agree excellently with $E_a$ drawn from the experimental $1/(T-T_0)\ln \sigma$ plots. The carrier provision nature is depicted in Fig. 11(e). Although, even for the overexcited carriers, there is the other potential barrier caused by energy offsets between Si and SiO$_2$, the carriers may pass through the barrier by tunneling because the barrier layer is thin enough.

For the nonepitaxial case, the apparent $E_a$ looks irrelevant to those overexcitation energies [Fig. 11(d)], which strongly suggests that such thermally excited carriers play a trivial role on the electric conductivity. Figure 11(b) indicates that the expected overexcitation energies are equivalent to those of the epitaxial ones, thus a comparable number of the carriers should be generated even in the nonepitaxial nanodots. Taking into consideration that the confining potential barrier is significantly higher for the nonepitaxial nanodots than the epitaxial ones as mentioned in § III-C, it is not strange if the carriers in the nanodots are hindered by the barrier from passing into the Si substrate [Fig. 11(f)]. Actually Nakamura and coworkers reported much longer escape time of the carriers in the nonepitaxial Ge nanodots compared to that of the epitaxial ones, which was evaluated by time-dependent tunneling current measured by STM [39]. On the other hand, effective provision of the overexcited carriers in the epitaxial nanodots to the Si substrate is likely to result from the reduction of the interface barrier due to the voids at the SiO$_2$ monolayer. The substance of $\sigma_2$, a conduction path induced by the voids, should be carrier provision from the nanodots to the substrate by tunneling through the reduced potential barrier at the interface.

After all, the transport scheme of the topical nanodot arrays can be summarized as follows. The nanodot arrays themselves consisting of small ($r < 3$ nm) Ge dots should be considered as segmented conductors that hardly contribute to the electric conductivity themselves, whereas they cause slight increase of the conductivity as the dot size grows probably due to percolation. The nonepitaxial nanodot arrays are substantially insulated from the Si substrate by the SiO$_2$ monolayer. In case of the epitaxial nanodots, however, electrical connection is realized by the voids reducing the potential barrier of the SiO$_2$ layer. Effectual carrier exchange between the nanodots and the substrate is therefore attained, which enhances the conductivity significantly.

V. CONCLUSIONS AND PERSPECTIVES

In this review paper, we summarized the growth mechanisms, quantum size effect, and carrier transport nature of the Ge nanodots on the SiO$_2$ monolayer. The growth of the dot size can be approximated by a simple equation as a function of the nominal Ge coverage, in which both inter-dot coalescence and occurrence of the chemical reaction between Ge and SiO$_2$ are taken into account. Quantum confinement of the carriers into the topical nanodots...
FIG. 11: [(a), (b)] Expected energy positions of the related band edges of the (a) epitaxial and (b) nonepitaxial nanodots and the Si substrates beneath those plotted as a function of \( r \). [(c), (d)] \( E_a \) evaluated from the above \((1/T) \ln \sigma\) relationship (filled diamonds with error bars) plotted as a function of \( r \). Expected activation energies corresponding to overexcited electrons and holes are also shown as open squares and circles, respectively. [(e),(f)] Schematics of the carrier exchanging processes at the Ge-SiO\(_2\)-Si interfaces for the (e) epitaxial and (f) non-epitaxial nanodots.

abides by the 3D spherical parabolic, instead of the well, potential model where the quantized energy depends on the interface barrier height. It implies that one can regulate the energy gap width of the nanodot by controlling the interface condition without changing the dot size (i.e. number density). On the other hand, carrier transport nature does also depend strongly on the interface barrier height. The higher barrier substantially isolates the nonepitaxial nanodot arrays from the substrate, whereas the reduced barrier allows the epitaxial ones to exchange the carriers to the substrate effectively. This fact points out that controlling the potential barrier height of the interface layer is indispensable for achieving sufficient electrical coupling between the nanodots and the substrate. Nakamura and coworkers proposed another way to reduce interface barrier by using Si\(_x\)Ge\(_{1-x}\) oxide layer, which can be fabricated by oxidation of a Si substrate predeposited by 1 BL Ge, instead of the SiO\(_2\) [58]. It is interesting to note that, concerning the Ge nanodots on the Si\(_x\)Ge\(_{1-x}\)O\(_y\) layer, one can manipulate the individual nanodots as one likes by means of an STM tip [59]. On the other hand, nanodot arrays of direct-gap semiconductors (such as \( \beta\)-FeSi\(_2\) and Ge\(_{1-x}\)Sn\(_x\)) have been successfully obtained on the SiO\(_2\) monolayer in high densities [60, 61], on which occurrence of the quantum size effect has been verified by means of STS and PES [62–64]. Close insight for the interface barriers and the transport mechanism which is available by the schemes described above is anticipated also for such new nanomaterials. The authors believe that such various quantum-sized semiconductor nanodots will open up future development of optoelectronics applications compatible to the current Si-based electronics devices.

Acknowledgments

The authors would like to thank Dr. Y. Nakamura of The University of Tokyo and Dr. S.-P. Cho of Nagoya University for fruitful discussion. Collaboration with Dr. H. Okino and Dr. T. Hirahara of The University of Tokyo and help of Professor A. Kakizaki and Ms. A. Harasawa of ISSP and Professor K. Uno of High Energy Accelerator Research Organization (KEK) for PES measurements are gratefully acknowledged. Conductivity measurement was performed with support by Dr. S. Yamazaki of ISSP. A part of the present PES results were obtained by Dr. A. Konchenko of CREST, JST. \( \Delta \sigma_{SC} \) was calculated by using a program made by Dr. S. Yoshimoto of The University of Tokyo. The core-level PES experiments were conducted at BL-1C and BL-18A in the Photon Factory (PF) of KEK under the approval of the PF Program Advisory Committee (Proposal No. 2005G089). This work was financially supported by CREST, JST, and partially by Japan Society for the Promotion of Science (JSPS).

[1] H. Presting, H. Kibbel, M. Jaros, R. M. Turton, U. Mencziger, G. Abstreiter, and H. G. Grimmmeiss, Semicond. Sci. Technol. 7, 1127 (1992).
[2] D. J. Paul, Semicond. Sci. Technol. 19, R75 (2004).
[3] S. M. Sze, in Physics of Semiconductor Devices, 2nd ed. (Wiley, New York, 1986).
[4] Y.-W. Mo, D. E. Savage, B. S. Swartzentruber, and M. G. Lagally, Phys. Rev. Lett. 65, 1020 (1990).
[5] A. A. Shklyaev, M. Shibata, and M. Ichikawa, Phys. Rev. B 58, 15647 (1998).
[6] M. Küstner and B. Voigtländer, Phys. Rev. Lett. 82, 2745 (1999).
[7] A. A. Shklyaev, M. Shibata, and M. Ichikawa, Phys. Rev. B 62, 1540 (2000).
[8] A. A. Shklyaev and M. Ichikawa, Surf. Sci. 514, 19 (2002).
[9] A. Barski, M. Devivaz, J. L. Rouvière, and D. Buttard,

200 http://www.sssj.org/ejssnt (J-Stage: http://www.jstage.jst.go.jp/browse/ejssnt/)
