Quantum regulation of Ge nanodot state by controlling barrier of the interface layer

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Quantized energy in Ge nanodots aligned over oxidized Si surfaces could be regulated by modifying an interface atomic layer. The confining potential was evaluated from dot-size dependent energy shift of the ground state of confined holes, which revealed that epitaxial nanodots showed a lower confining potential barrier than nonepitaxial ones. The present results provide a new way to tune quantized energy levels of Ge nanodots not only by their size but also by interface condition.

Quantum-size Ge nanostructures have been considered to be a promising material for Si-based optoelectronics devices. The quantum confinement phenomena are induced at room temperature if the structure size is smaller than 10 nm. However, well-used conventional process of self-organization has only enabled us to fabricate Ge clusters down to 30 nm in diameter. In this context, Ge nanodots formed on an oxidized Si surface would be particularly promising owing to their sufficiently small size (smaller than 10 nm in diameter), size tunability, extremely high density (larger than $10^{12}$ cm$^{-2}$), as well as photoluminescence capability at RT. A reflection-high-energy electron diffraction (RHEED) pattern of the Ge nanodots produced by this method at growth temperature of 350 °C shows Debye rings which are caused by the random orientation of Ge dots with respect to the Si substrate [Fig. 1(a)]. It means that the nanodots are separated from the Si substrate by the SiO$_2$ thin layer as sketched in Fig. 1(c). On the other hand, the Ge nanodots grown at 550 °C provide another RHEED pattern with diffuse spots, as shown in Fig. 1(b), indicating that the nanodots grow epitaxially to the Si(111) substrate. This is due to voids created in the SiO$_2$ layer, and the Ge nanodots can therefore align and grow epitaxially to the Si(111) through the voids [Fig. 1(d)]. Transmission electron microscopy (TEM) images also support the existence of voids through the SiO$_2$ film beneath the dot.

We recently reported quantum confinement effect into the epitaxial Ge nanodots by means of photoemission spectroscopy (PES) and scanning tunneling microscopy (STM). The obtained confinement potential barrier was significantly smaller than the value expected from the energy position of valence band maxima (VBM) of SiO$_2$ and bulk Ge. These facts imply that the potential barrier at the Ge/SiO$_2$–Si interface is expected to be tunable by changing the growth temperature. The potential barrier height is thought to be an essential value correlating with the energy position of the quantized states and also with electroluminescence efficiency via accessibility of the carriers into the nanodots. In the present study, we have conducted PES and STM studies on the Ge nanodots formed under different growth conditions, which clearly indicates that the confining potential barrier height is regulated by the interface condition.

Ge nanodots on the ultrathin SiO$_2$ layer was prepared by the same procedure as reported before. The Si substrates were cut from a mirror-polished $n$-type Si(111) wafer (1–10 Ω cm). A clean Si(111) 7×7 surface was primarily prepared by repeating cycles of resistive heating up to

FIG. 1. [(a) and (b)] Typical RHEED patterns, [(c) and (d)] schematic drawings of the structures, and [(e) and (f)] the expected energy diagrams in valence band region of nonepitaxial [(a), (c), and (e)] and epitaxial Ge nanodots [(b), (d), and (f)], respectively. The Ge nanodots (black) are formed on a Si(111) substrate (dark gray) covered with an ultrathin SiO$_2$ (light gray).
1200 °C in ultrahigh vacuum (UHV). Oxygen exposure (2 × 10⁻⁴ Pa) onto the surface in increasing the sample temperature up to 630 °C generates a 0.3-nm-thick SiO₂ layer over the Si(111). Ge was deposited onto the ultrathin SiO₂ layer from an alumina-coated tungsten basket. The evaporation rate of Ge was separately determined from a completion of 5×5 RHEED pattern on the clean Si(111) 7×7 kept at 610 °C [which was defined as 3 BL (bilayer)]. 1 BL corresponds to 1.57×10¹⁵ cm⁻², atom density in a double layer of Si(111) truncated surface. PES measurements were carried out with He Iα radiation (21.22 eV) and a commercial electron spectrometer (VG, ADES 400). The E_F was determined from a tantalum clamp plate which was in good electrical contact with the sample. All spectra were taken at normal-emission angle. STM observation was performed at room temperature by a commercial STM apparatus with normal-emission angle. STM observation was performed at room temperature up to 630 °C generates a 0.3-nm-thick SiO₂ layer over the Si substrate. From the magnified spectra near E_F from the surface without Ge dots [dotted line in Fig. 3(b)], the threshold of the spectra around E_R=0.9 eV should be assigned to the VBM of the Si(111) substrate (E_VBM). By adding Ge nanodots, the spectral onset shifts closer to E_F than E_VBM. The origin of such components can be ascribed to the electronic state in the Ge nanodots. This spectral onset corresponds to the highest occupied state (VBM of Ge nanodots), which is, in other words, the ground state of holes (h-GS) generated in the Ge nanodots by quantum confinement effect. By following a method in Ref. 14, we estimate the energy position of VBM of the Ge dots as an intersection of two lines extrapolated from a spectral tail of the valence band of the Ge nanodots and background signals. Although such analysis cannot provide the absolute value of the binding energy of h-GS (E_h-GS), it will allow us to trace the shift of E_h-GS [see Figs. 1(e) and 1(f) for the definitions of energy levels].

Figure 4 shows the energy shift of E_h-GS with respect to the VBM of Si substrate (E_VBM), ∆E [see Fig. 1(e) for definition], plotted as a function of the dominant radius (r) of the Ge nanodots. E_h-GS shifts away from E_VBM as the nanodots grow. It should be also noted that the energy positions of...
$E_{h,GS}$ are different depending on the growth temperature even at the same sizes of dots.

Energy level $E_{h,GS}$ in a spherical quantum dots is analytically solvable by assuming a harmonic confining potential,\textsuperscript{14,16,17}

$$E_{h,GS} = - V + 2\alpha_B \sqrt{\frac{R_y}{m^*_h}} \sqrt{\frac{V}{r}} = E_0 - \Delta E,$$

(1)

where $R_y$ is the atomic Rydberg and $\alpha_B$ is the atomic Bohr radius. We adopt the effective mass of holes as $m^*_h$. $E_0$ is an energy reference and it is unnecessary to be determined in the present procedure, while a common value is adopted for $E_0$ for both the epitaxial and nonepitaxial nanodots. Equation (1) means that the energy levels in the dots are governed by two physical properties, the confining potential barrier height $V$ and the dot radius $r$.

We have demonstrated a least-squares fit of the experimental $\Delta E$ with Eq. (1) for each growth temperature, as shown in Fig. 4. It gives the confining potential barrier height of 6.7 ($\pm$ 0.9) eV for the growth temperature of 350 °C and 2.1 ($\pm$ 0.4) eV for 550 °C. In the case of the nonepitaxial nanodots (grown at 350 °C), the obtained confining potential height is substantially larger than the potential barrier expected from the energy difference between the valence band maximum of bulk Ge (0.33 eV below $E_F$)\textsuperscript{22} and $E_{SIO_2}$ of the underlying ultrathin SiO$_2$ film [ca. 5 eV below $E_F$, see Fig. 3(a)]. We speculate that such an enlargement of the effective potential barrier is due to the fact that the major part of the surface area of the spherical nanodots is surrounded by vacuum and only a small area of the dot surface touches the oxidized Si surface. On the other hand, the confining potential for the epitaxial nanodots (grown at 550 °C) is significantly reduced compared to that of the non-epitaxial ones. This potential reduction should be attributed to the voids penetrating through the SiO$_2$ film. Thus the growth condition and resulting interface structure sensitively affect the quantum confinement in the nanodots.

The different barrier heights of confining potential cause the energy shifts of quantized states in the dots. Since the origin of the PL from Ge dots–SiO$_2$ systems has been assumed as the recombination between the confined holes in the Ge dots and electrons trapped at the defects on the adjoining SiO$_2$,\textsuperscript{3,10,14} our present results suggest a possibility for regulating the quantum-dot state through controlling the potential barrier height between the dots and substrate even if the dot size is unchanged.

In conclusion, we have carried out PES and STM studies on Ge nanodots formed at different growth temperatures and evaluated the confining potential barrier height for each temperature from the dot-size dependent shift of the energy position of the highest occupied quantum state. The confining potential is effectively reduced by the voids created at the ultrathin SiO$_2$ film between the dots and the substrate. The present results will provide an additional way for tuning the optoelectronic properties of the Ge nanodots.

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