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Quantum confinement analysis of nanostructures in oxidation of SiGe alloys*

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We report the investigation on the oxidation behaviour of $Si_{1-x}Ge_x$ alloys (x=0.05, 0.15, and 0.25). It was found for the first time that a nanocap (thickness: 1.6–2.0nm) was formed on the oxide film after fast oxidation. Some new peaks in photoluminescence spectra were discovered, which could be related to the Ge nanocap, the Ge nanolayer (thickness: 0.8–1.2nm) and the Ge nanoparticles (with various diameters from 2.6nm to 7.4nm), respectively. A suitable model and several new calculating formulae combined with the Unrestricted Hartree–Fock–Roothaan (UHFR) method and quantum confinement analysis have been proposed to interpret the PL spectra and the nanostructure mechanism in the oxide and Ge segregation.

Keywords: quantum confinement, PL spectra, nanostructure, rapid oxidation
PACC: 7860F, 8116, 7280E

1. Introduction

Recently, some meaningful results on the oxidation of epitaxial SiGe alloys have been reported.[1–6] Experimental observation has shown that a SiO_2 layer can be produced when Ge concentration is smaller than 50% in SiGe alloys, and Ge nanoparticles pile up beneath the oxide layer.[7–12] In our experiment, a germanium nanocap in the top of the SiO_2 layer is for the first time discovered after rapid oxidation. And we can stably produce a Ge nanolayer between the oxide and SiGe substrate by oxidation. We focus on this novel method to form the germanium nanostructure due to its potential optoelectronic application. Some new photoluminescence (PL) spectra related to Ge nanocap, Ge nanolayer and Ge particles have been observed. We have made some revisions for the Unrestricted Hartree–Fock–Roothaan (UHFR) method used in treating atoms and molecules to calculate the Ge nanocap, the nanolayer and the Ge nanoparticles. A suitable model and a new calculating formula are proposed which combine the UHFR method and quantum confinement analysis to interpret the PL spectra and the nanostructure mechanism in the oxide and Ge segregation.

2. Experiment

To reduce the perturbing factors, we have made great efforts to carry out dry oxidation of SiGe alloys. The samples used in the study were prepared as follows. The undoped strained $Si_{1-x}Ge_x$ layers (2000nm, with x=0.05, 0.15 and 0.25) were first grown in a molecular beam epitaxy (MBE) system. Before oxidation, the samples were cleaned in a Summa cleaner (a mixture of choline and methanol) for 20min, and then rinsed in de-ionized water for 30s followed by a 30s dip in buffer hydrofluoric acid (HF) (NH_4F: 49%HF, 10:1) to remove any native oxide.[13] After etching, the samples were dipped in de-ionized water for 30s, blown dry, and immediately loaded into the oxidation furnace. The samples were oxidized using a conventional furnace in dry oxygen atmosphere at 800, 900 and 1000°C for various lengths of time.

The thickness of the oxide film, the germanium nanocap and the Ge-rich layer were measured by a high precision ellipsometer (HPE). Optical measurements were performed with various angles of incidence of the HPE. For optical characterization of the oxide films, the multiplayer models and the effective medium approximation were used. The composition

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and the thickness of oxidation samples were analysed using Rutherford backscattering spectrometry (RBS) before and after the oxidation, and the spectra (channel and random spectra) were simulated using the rump program of the Wisconsin University. High-resolution scanning transmission electron microscopy (HR-STEM) was used to observe microstructures of the Ge nanocap and Ge nanolayer.

The photoluminescence spectra under the 514nm excitation were measured using the Renishaw Raman Systems.

3. Results and discussion

We compared the RBS spectra of $Si_{1-x}Ge_x$ alloys (x=0.05, 0.15 and 0.25) after oxidation at different temperatures and for various lengths of time. It has been found that at a certain temperature and time length (for example, at 900°C for 30min), the Ge peak does not shift and only its intensity increases with increasing Ge content. The results indicate that the Ge segregation structure generally does not change with Ge content after oxidation of SiGe.

At a certain temperature, the Ge peak shifts to lower energy with higher intensity as oxidation time increases. The results indicate that SiO_2 forms in the top layer and Ge piles up at the oxide/SiGe interface, which leads to the generation of a Ge-rich layer. With increasing oxidation time, the Ge clusters are expelled into deeper layers of the sample, and the top layer of pure SiO_2 is produced. The longer the oxidation time (>one hour at 1000°C, say), the broader the Ge peak of the sample, which demonstrates that considerable inter-diffusion of Si and Ge has taken place in the SiGe alloys. It is obvious that, for a certain oxidation time, the oxidation at 1000°C produces a thicker and purer SiO_2 layer than at 800°C. The broader Ge peak at 1000°C also indicates that the inter-diffusion of Ge appears in the SiGe alloys.

Table 1 shows the parameters of the nanostructure in $Si_{0.85}Ge_{0.15}$ film after oxidation for 5min at 900°C, which was measured by using HPE. These results are in good agreement with that of the RBS and the HR-STEM.[14]

Table 1. Parameters of the nanostructure in $Si_{0.85}Ge_{0.15}$ film after oxidation for 10min at 900°C.

Layers	Thickness/nm	Composition
Nanocap	1.6–2.0	Ge
Oxide	26.4	SiO_2
Rich-Ge	0.8–1.2	Ge
SiGe film	2000	Si: 85%, Ge: 15%

We use Deal's model[15–19] for interpreting the oxidation kinetics of the oxidation of SiGe in dry atmosphere, which assumes that the thermal oxidation in Si proceeds via diffusion of oxidant through the oxide to the SiO_2/Si interface at which the oxide reacts with Si to form SiO_2. On the other hand, in dry oxygen atmosphere at 1000°K oxidation of Si and Ge can form SiO_2 and GeO_2 according to the following reactions:

$$Si + O_2 \longrightarrow SiO_2 \quad \text{for} \quad dG = -732\text{kJ/mol } O_2,$$

$$Ge + O_2 \longrightarrow GeO_2 \quad \text{for} \quad dG = -376\text{kJ/mol } O_2.$$

In the above reactions, dG is the change of the free-energy. Therefore, if GeO_2 contacts $Si_{1-x}Ge_x$, then GeO_2 will be changed according to the reduction reaction

$$Si + GeO_2 \longrightarrow SiO_2 + Ge. \qquad (1)$$

The oxidation reaction can be divided into two steps. First, the simultaneous oxidation of Si and Ge produces a mixture surface of either (Si, Ge) SiO_2 or SiO_2-Ge. In this step, the most important thing is that after the fast oxidation (the $Si_{0.85}Ge_{0.15}$ alloy at 900°C for 5min–10min), a nanocap (1.6–2.0nm thickness) forms on the oxide layer with segregating Ge atoms from SiO_2. Second, Ge is essentially rejected from the SiO_2 layer and a Ge-rich film (0.8–1.2nm) is generated between the oxide and the SiGe substrate.

4. Quantum confinement analysis

We consider the system of single-electron and few-electron in a nanolayer and a nanoparticle of germanium. The effective mass Hamiltonian of the system is (in Rydberg units)

$$H = \sum_i \{-[\nabla_i^2 + V(R_i)]\} + \sum_i \sum_j (1/R_{ij}), \qquad (2)$$

where R_i is the position vector of the ith electron, R_{ij} is the electron–electron distance.

In Ge nanocap and Ge nanolayer, the quantum confinement potential $V(R_i)$ is taken as

$V(R_i) = V_1$, (above the layer top); $V(R_i) = V_2$, (below the layer bottom); $V(R_i)$=0, (in the layer).

In Ge nanoparticle, the quantum confinement potential $V(R_i)$ is given by

$V(R_i) = V_0$, (for $R_i > R_0$, the radius of nanoparticle); $V(R_i)$=0 (inside of nanoparticle).

We neglect the change of effective mass and dielectric constant at the well/barrier interface in the

calculation. The Schrödinger equation for the one-electron and N-electron system has been solved by combining the UHFR method and the quantum confinement method.

Under the 514nm excitation, the cross-sectional PL spectrum of the $Si_{0.85}Ge_{0.15}$ film after oxidation at 900°C for 10min is shown in Fig.1. The measuring temperature of the PL spectra is 300°K. In the emission spectra, it can clearly be found that there is a sharp peak at 541nm and an emission band from 550nm to 720nm. The 541nm emission peak has never been reported before. Since the energy of the 541nm emission photon (2.29eV) is much larger than the bulk energy gaps of Si (1.12eV) and Ge (0.67eV), and the emission spectrum distribution is very narrow and sharp, it is most likely that this emission peak originates from the quantum-confinement effect of Ge nanocap and Ge nanolayer in the oxidation sample.

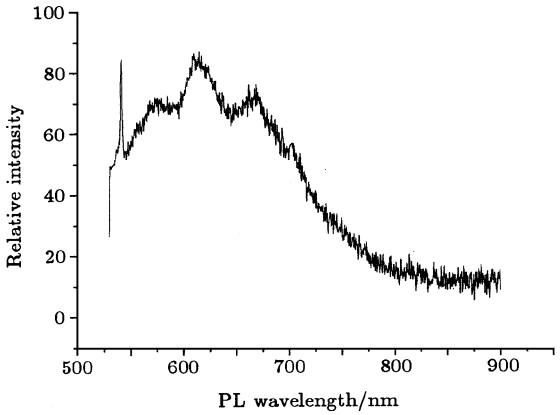


Fig.1. Cross-sectional PL spectrum of the $Si_{0.85}Ge_{0.15}$ film after oxidation at 900°C for 10min.

Through solving the Schrödinger equation by combining the UHFR method and quantum confinement analysis, we can deduce several new calculating formulae to interpret the PL spectra related to the quantum-confined Stark effect. The confined energy gap of the Ge nanocap (layer quantum well with thickness L and $V_1 = \infty$, $V_2 = \infty$) can be described by (in SI units)

$$E_{\text{confined gap}} = E_{\text{bulk gap}} + 3h^2/8(1/L^2), \qquad (3)$$

where $E_{\text{bulk gap}}$ is the bulk energy gap of germanium and $E_{\text{confined gap}}$ is the Ge energy gap taking account of the quantum-confined Stark effect.

It is reasonable that we assume both an infinite potential barrier (V_1 reaches infinity) by the SiO_2 side and a finite potential barrier V_2 by the SiGe film forming a nanolayer well (width L). With the effective-mass approximation, the confined energy gap of the Ge nanolayer is given by

$$\begin{aligned} &E_{\text{confined gap}} \\ &= E_{\text{bulk gap}} + 3h^2/8\{1/L^2 - h/[(2mV_2)^{1/2}L^3]\} \\ &\quad \times (2/(m_c + m_v)), \end{aligned} \qquad (4)$$

where the first term $E_{\text{bulk gap}}$ is 0.67eV, and the value of the second term (quantum confinement effect) is 1.62eV. m_c and m_v are the conduction and valence-band effective mass respectively (m_c=0.22m_e, m_v=0.32m_e, m_e: rest mass of electron), $m = (m_c + m_v)/2$=0.27m_e, and V_2=0.40eV. In fact, the emission region of the 541nm peak can certainly be located at the Ge nanocap and Ge layer by scanning of the laser beam (excitation source) in Raman systems of Renishaw. As shown in Fig.2, there are three small tips on the peak at the 541nm wavelength, which comes from the affection of Ge phonon branches (LO, TO (30meV–40meV) and LA (20meV–30meV)). The luminescence effect is very useful in optoelectronic integration on SiGe wafers. We can also change the emission wavelength of the sample by modifying the confinement potential well structure of the Ge layer (adjusting a value of V_2) by changing the composition of SiGe alloy.

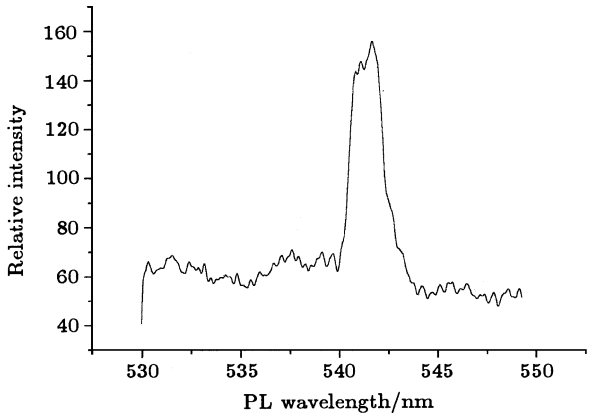


Fig.2. 541nm PL peak in the cross-sectional PL spectrum of the $Si_{0.85}Ge_{0.15}$ film after oxidation at 900°C for 10min. Three small tips on the peak at the 541nm wavelength properly come from the effect of Ge phonon branches (LO, TO and LA).

An emission band from 550nm to 720nm in the PL spectra would originate from size distribution of Ge nanoparticles (Ge clusters diameter: 2.6nm–7.4nm). In Fig.1, it is clear that there are three peaks at 572nm, 620nm and 671nm along the emission band, which are correlated to 3.9nm, 4.9nm and 6.0nm diameter clusters, respectively. It is clear that the Ge clusters have more stable structures with 3.9nm, 4.9nm and 6.0nm diameter.

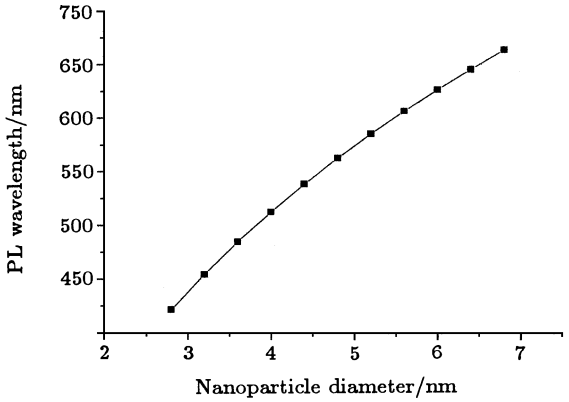


Fig.3. PL peak wavelength as a function of the diameter of Ge nanoparticles.

Figure 3 shows the result of our sophisticated calculations with the quantum confinement analysis, which is in good agreement with the experimental results. As shown in Fig.1, the outline of the emission band in the PL spectra from 550nm to 720nm looks like a normal distribution approximately, but, in fact, the appearance of the three little peaks at 572nm, 620nm and 671nm wavelengths indicates a special distribution in the PL spectra. This is a new effect of the Ge distribution in nanoscale. The quantum confinement gap can be calculated by

$$E_{\text{confined gap}} = E_{\text{bulk gap}} + C(1/d), \qquad (5)$$

in which d is the diameter of Ge nanoparticles and C is a cluster parameter.

5. Conclusion

We have investigated the oxidation behaviour of $Si_{1-x}Ge_x$ alloys (x=0.05, 0.15, and 0.25). A nanocap (1.6–2.0nm in thickness) on the oxide layer was found to have formed after the fast oxidation of $Si_{0.85}Ge_{0.15}$ alloy, which may be very useful in optoelectronic devices. A Ge nanolayer between SiO_2 film and SiGe substrate was produced, which may result in special optical and electrical properties. We have analysed the PL spectra related to the Ge nanostructure in the oxidation of $Si_{1-x}Ge_x$ alloys. Some new features of the PL spectra have been discovered in the oxidation samples, such as a sharp and intensive 541nm PL peak originating from the Ge nanocap and Ge nanolayer, and the emission band from 550nm to 720nm coming from Ge nanoparticles with diameters of 2.6nm–7.4nm. A quantum confinement model has been proposed, and some calculation combined with the UHFR method and the quantum confinement analysis has been provided to explain the PL spectra. We have given several new calculation formulae to solve the Ge nanostructure problems. The photoluminescence emission of the Ge nanocap and Ge nanolayer is very useful in optoelectronic integration on SiGe wafers. We can also change the emission wavelength of the sample by modifying the confinement potential well structure of the Ge layer (adjusting the value of V_2) by changing the composition of SiGe alloy.

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