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Self-assembled germanium nano-structures by laser-assisted oxidation*

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The investigation on the oxidation behaviour of $Si_{1-x}Ge_x$ alloys (x=0.05, 0.15, and 0.25) is carried out. It is found for the first time that on the oxide film a germanium nano-cap with a thickness of 1.8–2.8nm and a few Ge nanoparticles with diameters ranging from 5.5 nm to 10 nm are formed by the low-temperature laser-assisted dry oxidation of $Si_{1-x}Ge_x$ substrate. A new scanning method on the decline cross-section of the multiple-layer sample is adopted to measure the layer thickness and the composition. Some new peaks in photoluminescence (PL) spectra are discovered, which could be related to the nano-cap and the nano-particles of germanium. A suitable model and several new calculating formulae with the unrestricted Hartree–Fock–Roothaan (UHFR) method and quantum confinement analysis are proposed to interpret the PL spectra and the nano-structure mechanism in the oxide.

Keywords: low-temperature oxidation, laser-assisted, nano-structure, PL spectra
PACC: 4255R, 4270Q, 7320D

1. Introduction

Recently, a few results of the research on oxidized epitaxial $Si_{1-x}Ge_x$ alloys ($x < 50$ %) have been reported to show that the SiO_2 layer forms on the epitaxial $Si_{1-x}Ge_x$, while Ge nano-particles accumulate at the oxide/$Si_{1-x}Ge_x$ interface,[1−5] and the oxidation of $Si_{1-x}Ge_x$ is faster than that of pure Si during wet oxidation.[6] Experimental observation has shown that a SiO_2 layer can be produced when Ge concentration is smaller than 50% in $Si_{1-x}Ge_x$ alloys, and Ge nano-particles pile up beneath the oxide layer.[7−12] In our experiments, for the first time, a germanium nano-cap in the SiO_2 layer is discovered after the laser-assisted dry oxidation of SiGe substrate at low-temperatures ($< 600^\circ$C). And the diameter distribution of the germanium nano-particles under the above low-temperature condition is broader than under the high-temperature condition[13−20] ($> 800^\circ$C). We focus on this novel method of the formation of the germanium nano-structures due to their potential application in optoelectronics, such as the integrated field effect device and the integrated CMOS device.

In detecting the x-ray energy spectrum, we adopt a new scanning method on the decline cross- section of the multiple-layer sample to measure the layer thicknesses and the compositions of the samples. Some new photoluminescence (PL) spectra related to Ge nano-cap and Ge particles are measured. Some modifications to the unrestricted Hartree–Fock–Roothaan (UHFR) method used in study of atoms and molecules are made to calculate the structures of the Ge nano-cap and the Ge nano-particles. A suitable model and several new calculating formulas are proposed with UHFR method and quantum confinement analysis to interpret the PL spectra and the nanostructure mechanism in the oxide.

2. Experiment

To reduce perturbation factors, we have made great efforts to carry out the dry oxidation of $Si_{1-x}Ge_x$ alloys. The samples used in the study were prepared as follows. The undoped strained $Si_{1-x}Ge_x$

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layers (2000-nm thick, 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 20 min, and then were rinsed in deionized water for 30 s followed by a 30 s dip in buffer hydrofluoric acid (HF) (NH4F: 49%HF, 10:1) to remove any native oxide.[13] After etching, the samples were dipped in deionized water for 30 s, and after being blown dry, they were immediately loaded into an oxidation furnace. Under the irradiation of a laser with a 519-nm wavelength and 10-mw power, the samples were oxidized in dry oxygen atmosphere at 500°C for different lengths of time.

The thicknesses of the oxide films and the germanium nano-caps were measured by a high precision ellipsometer (HPE). Optical measurements were performed by using the HPE at different incident angles. For optical characterization of the oxide films, the multiple-layer model and the effective medium approximation were used. The compositions and the thicknesses of oxidation samples were analysed by using Rutherford backscattering spectrometry (RBS) before and after the oxidation, and the spectra (channel and random spectra) were simulated using the Rump program from the Wisconsin University. High-resolution scanning transmission electron microscopy (HR-STEM) was used to observe microstructures of the Ge nano-cap and Ge nano-particles. The example of the TEM micrograph is shown in Fig.1.



Fig.1. TEM micrograph of the $Si_{0.85}Ge_{0.15}$ film oxidized in dry oxygen atmosphere at 500°C for 6 hours, under the irradiation of a laser with a 519-nm wavelength and 10-mw power.

For accurate analysis of the compositions in different layers, we have taken a new scanning method on the decline cross-section of the multiple-layer of the sample. In detecting the x-ray energy spectrum, the decline angle θ between the decline cross-section of the sample and the horizon is small enough (~5°) to make it possible that the scanning spot of the electron beam can be fixed in a single nano-layer (~2 nm) (Fig.2).

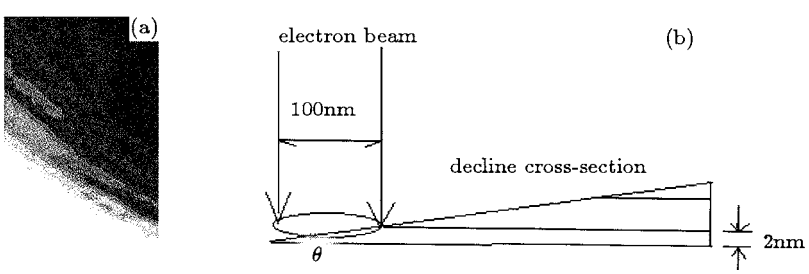


Fig.2. (a) TEM micrography of the decline cross-section of the multiple-layer sample in detecting the x-ray energy spectrum. (b) Description about the scanning method on the decline cross-section of the multiple-layer sample in detecting the x-ray energy spectrum (A 100-nm spot of the electron beam can be located in the 2-nm layer).

Figure 3 (a) shows the data of x-ray energy spectrum in STEM. Figure3 (b) shows the germanium distribution in the different layers of the sample after removing the accumulating effect over layers.

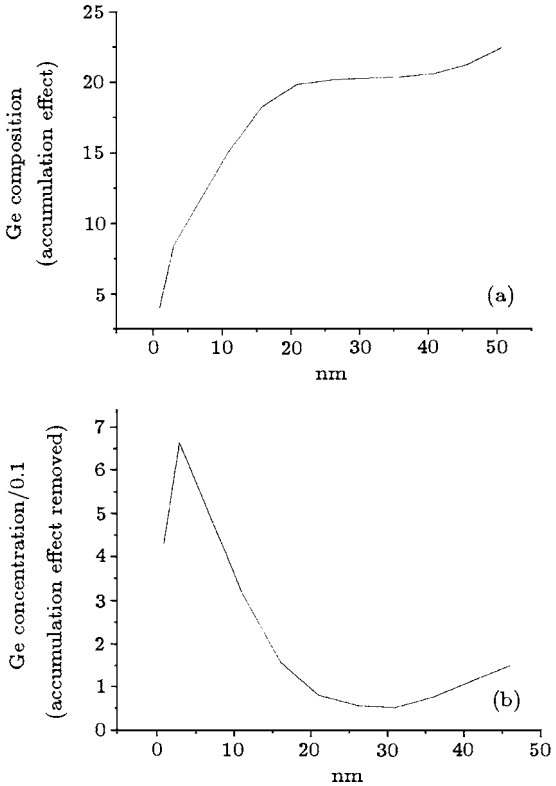


Fig.3. (a) Data distribution of the x-ray energy spectrum in STEM. (b) Germanium distribution in the different layers of the sample according to the data distribution of the x-ray energy spectrum after removing the accumulating effect over layers.

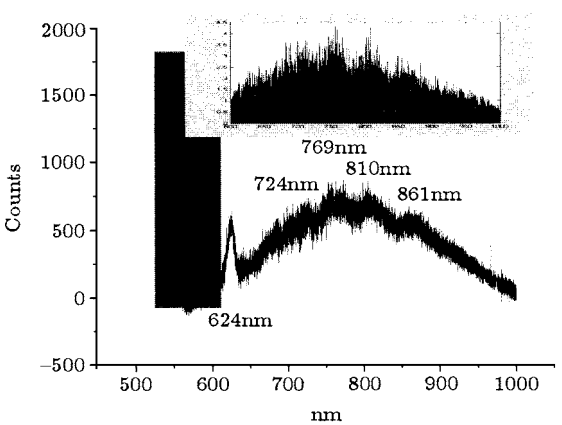


Fig.4. PL spectra of the $Si_{0.85}Ge_{0.15}$ film after oxidation at 500°C for 6 hours, under the irradiation of the laser.

The simulation results with the MC method related to more stable structures of the germanium clusters with diameters of 7.1 nm, 7.7 nm, 8.3 nm and 9.1 nm are shown in the inset.

The photoluminescence spectra under the excitation at 514 nm were measured by using the RENISHAW Raman System. In Fig.4, we have obtained a PL peak at a wavelength of 624 nm when the light beam spot was fixed in the Ge nano-cap by the above new scanning method on the decline cross-section of the sample, which was oxidized in dry oxygen atmosphere at 500°C for 6 hours under the irradiation of a laser with a 519-nm wavelength and 10-mw power.

3. Results and discussion

We use Deal's model[15–20] for interpreting the oxidation kinetics of the oxidation of $Si_{1-x}Ge_x$ in dry atmosphere, in which the basic understanding of the kinetics of thermal oxidation in Si comes from the fact that the growth occurs by diffusion of oxidant through the oxide to the SiO_2/Si interface where the oxide reacts with Si to form SiO_2. On the other hand, in dry oxygen atmosphere the oxidations of Si and Ge can form SiO_2 and GeO_2, respectively, according to the following reactions:

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

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

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

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

The experimental results show that in the oxidation of $Si_{1-x}Ge_x$, the laser irradiation on the sample can produce the process of the silicon oxidation and the germanium segregation at low-temperatures (< 600°C) as well as at high-temperatures[14,20] (> 800°C) because of the energy transmission from the laser beam to the germanium atoms. And it is highly important that the photons of laser can bring many germanium atoms to the top of the oxide and make them pile up a nano-cap after the segregation of the Ge atoms. It is very interesting that the segregated germanium atoms have a strong potential of the diffusion to the photon field.

The oxidation reaction can be divided into three steps. First, the simultaneous oxidations of Si and Ge produce a mixture surface of either (Si, Ge) SiO_2 and GeO_2 or SiO_2–Ge, and many oxygen atoms diffuse to a deeper region and catch more Si atoms and Ge atoms. Second, the germanium atoms gradually segregate from the oxide and condense to build some clusters in the SiO_2 film. Under the high-temperature condition or under the laser irradiation condition, the Ge clusters are rejected out of oxidation layer. Third, the laser beam makes the germanium clusters bigger

and brings them piling up to form a Ge nano-cap (1.8 nm–2.8 nm in thickness) of the oxide layer, and the passive surface (SiO_2-Ge) is also formed.

Quantum confinement analysis

We consider a single-electron system or a few-electron system in the nano-cap and the nano-particle. The effective mass Hamiltonian of the system is (in units of Rydberg)[20,21]

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

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

In the germanium nano-cap, the quantum confinement potential $V(R_i)$ is taken as follows:

$$V(R_i) = V_0, \quad \text{(up the passive layer)},$$
$$V(R_i) = \infty, \quad \text{(down the oxide layer)},$$
$$V(R_i) = 0, \quad \text{(in the nano} - \text{cap)}.$$

To the Ge nano-particle the quantum confinement potential $V(R_i)$ is given as follows:

$$V(R_i) = \infty, (R_i > R_0 \quad \text{radius of nano} - \text{particle}),$$
$$V(R_i) = 0, \quad \text{(Inside nano} - \text{particle)}.$$

Under the boundary condition of the above well / barrier interface, the Schrödinger equation for the single-electron or N-electron system has been solved with the UHFR method.

In the emission spectra shown in Fig.4, it can be clearly found that there is a sharp emission peak at a wavelength of 624 nm, which has not yet been reported before. Since the energy (1.98 eV) of the emission photon at 624 nm is much higher than the bulk energy gaps of Si (1.12 eV) and Ge (0.67 eV) and the peak is very narrow (the width Δ is ~60m eV), it is highly likely that this emission peak originates from the quantum-confinement effect of the Ge nano-cap in the oxidation sample.

It is reasonable to assume an infinite potential barrier by the SiO_2 side and a finite potential barrier V_0 by the passive layer of surface, and the two barriers form a quantum well (L width). With the effective-mass approximation, the confined energy gap of the Ge nano-cap is given by (in the SI system of units)[20,21]

$$E_{\text{confined gap}} = E_{\text{bulk gap}} + 3h^2/8(1/L^2 - h/((2mV_0)^{1/2}L^3)) \times (2/(m_c + m_v)). \quad (3)$$

On the right-hand side in the above expression, the first term $E_{\text{bulk gap}}$ is 0.67 eV, and the value of the second term (quantum confinement effect) is 1.31 eV. Here, m_c is the effective mass beneath the valley of conduction-band and m_v is the effective mass on the top of the valence-band (m_c= 0.22 m_e, m_v= 0.32 m_e, where m_e is the static mass of electron), $m = (m_c + m_v)/2 = 0.27\ m_e$, and V_0=2.0 eV–2.4 eV. The peak width Δ (~60m eV) probably comes from the width distribution of the quantum well (L) and the effect of the germanium phonon branches (LO, TO (30m eV–40m eV) and LA (20m eV–30m eV), where LO stands for longitudinal optical phonon, TO for transversal optical phonon, LA for longitudinal audio phonon). The luminescence effect may be very useful in optoelectronic integration on $Si_{1-x}Ge_x$ wafers.

In the PL spectra of Fig.4, an emission band from 650 nm to 900 nm could originate from the diameter distribution of germanium nano-particles (Ge cluster diameters are in a range of 5.5 nm–10 nm). It is clear that there are four peaks at 722 nm, 762 nm, 802 nm and 856 nm along the emission band, which are correlated with the quantum confinement effect of the germanium clusters with diameters of 7.1 nm, 7.7 nm, 8.3 nm and 9.1 nm respectively. It is demonstrated that the germanium clusters with diameters of 7.1 nm, 7.7 nm, 8.3 nm and 9.1 nm are more stable under the above conditions (the inset in Fig.4 shows the simulation result with the MC method).

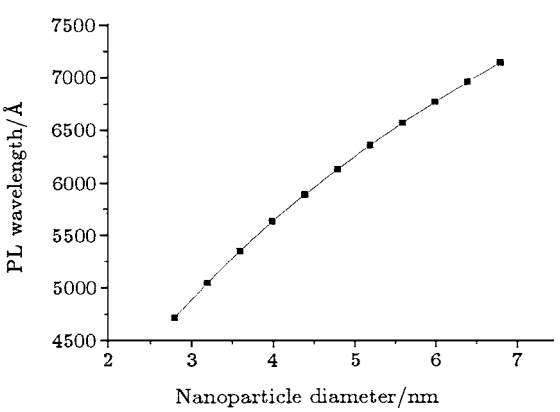


Fig.5. Relation between the wavelength (in Å) of PL peak and the diameter(in nm) of germanium nanoparticles.

Figure 5 shows our calculations from the quantum confinement analysis, which are in good agreement with the measurements. The quantum confinement gap can be calculated by

$$E_{\text{confined gap}} = E_{\text{bulk gap}} + C(1/d^2). \quad (4).$$

In this formula, d is the diameter of a germanium nanoparticle and C is the modification parameter of a Ge cluster.

4. Conclusion

We have found that a germanium nano-cap (1.8 nm–2.8 nm in thickness) on the top of the SiO_2 layer can be formed by the irradiation of a laser with a 519-nm wavelength and 10-mw power, as $Si_{1-x}Ge_x$ alloys are oxidized in dry oxygen atmosphere at 500°C for 6 hours, which may be very useful in integrated optoelectronic devices. A new scanning method on the decline cross-section of the multiple-layer sample is taken in the measurement of the nano-cap thickness and the composition. We have analysed the PL spectra related to the germanium nano-structures in the oxidation sample. Some new PL spectra are discovered, such as, a sharp and intensive PL peak at 624 nm originating from the germanium nano-cap, and the emission bands ranging from 650 nm to 900 nm coming from the germanium nano-particles with diameters of 5.5 nm–10 nm. A quantum confinement model and several new calculating formulas are proposed with the UHFR method and the quantum confinement analysis to explain the PL spectra. The photoluminescence effect of the germanium nano-cap and the germanium nano-particles has a valuable application in the optoelectronics integration on $Si_{1-x}Ge_x$ wafers probably.

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