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2014

Yoo, W. S., Kang, K., Ueda, T., Ishigaki, T., Nishigaki, H., Hasuike, N., et al. (2014).
Characterization of hetero-epitaxial Ge films on Si using multiwavelength micro-raman
spectroscopy. ECS journal of solid state science and technology, 4(2), Pg 9-15.

<https://hdl.handle.net/10356/106992>

<https://doi.org/10.1149/2.0041502jss>

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Characterization of Hetero-Epitaxial Ge Films on Si Using Multiwavelength Micro-Raman Spectroscopy

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To meet various physical property requirements of materials for advanced applications for specific devices, combinations of Si/Ge, Ge/Si, Si_{1-x}Ge_x/Si, are frequently introduced in the device fabrication process. Epitaxy, condensation and annealing processes are commonly used. Since a small variation in composition, strain and crystallinity can result in reduced device performance or failure, the composition, strain and crystallinity must be carefully monitored and controlled throughout the manufacturing process. We have studied the dependence of Ge and Si intermixing on annealing temperature and Raman excitation wavelength. Using multiwavelength Raman spectroscopy, we found Ge and Si intermixing in epitaxially grown Ge(100)/Si(100) after successive thermal anneals. Very strong dependence of signal-to-noise (S/N) ratio measurements on excitation wavelength and film structure was observed. Suitable excitation wavelengths must be chosen to properly characterize Si and Ge-based heteroepitaxial layers based on the thickness, stacking order and composition of epitaxial films having different optical properties at different wavelengths.

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Manuscript submitted September 30, 2014; revised manuscript received October 20, 2014. Published November 11, 2014. This was Paper 1766 presented at the Cancun, Mexico, Meeting of the Society, October 5–9, 2014.

As a natural way to extend the lifespan of Si in fast and highly functional devices, integration of hetero-components such as Ge, or alloys of Ge with Si, has been widely pursued. Ge has very promising electronic properties: 2.75 times higher electron mobility (3900 cm²/V·sec), 4.0 times higher hole mobility (1900 cm²/V·sec) and one half the bandgap energy (0.67 eV) at room temperature as compared to Si.^{1,2} Ge has a lattice constant 4.2% larger than that of Si while they have the same crystalline structure (face centered cubic (fcc), diamond structure). The smaller bandgap of Ge, compared with Si, has enabled the bandgap engineering of heterostructures for very fast and high frequency operating devices. The 4.2% lattice mismatch between Ge and Si makes continuous high quality and smooth film growth difficult. Ge island formation takes place beyond the critical thickness of a few atomic layers. Relatively high surface roughness makes process integration difficult.^{3–6} For planarization of Ge heteroepitaxial layers, chemical mechanical polishing (CMP) was also studied.^{7,8} For optoelectronic device applications, Ge-on-insulator (GeOI) wafer fabrication techniques have been studied.^{6,9,10} To solve lattice mismatch originated heteroepitaxial problems, various techniques such as the growth of graded buffer layers, and/or surfactant mediated epitaxy, have been successfully implemented.^{11–15}

To meet various physical property requirements of materials for advanced application, specific devices, combinations of Si/Ge, Ge/Si, Si_{1-x}Ge_x/Si are frequently introduced. Potential applications of hetero-epitaxial Ge technology are Ge complementary metal-oxide-semiconductor (CMOS) for high performance devices, short wave infrared (SWIR) Ge photodetector for Si-based optoelectronic devices, and integrated Ge/Si (Ge p-MOS and Si n-MOS) devices.^{16–18} Epitaxy, condensation and annealing processes are commonly used for fabricating these heterostructures.^{11–20} Because a small variation in composition, strain, profile and crystallinity can result in reduced device performance or failure, the composition, strain and crystallinity must be carefully monitored and controlled throughout the manufacturing process.

In this paper, we have characterized as-grown heteroepitaxial Ge/Si wafers and annealed heteroepitaxial Ge/Si wafers using multiwavelength Raman spectroscopy for noncontact, composition depth profiling and analyzing strain in heteroepitaxial Ge films.

Experimental

Approximately 1 μm thick Ge films were epitaxially grown on p-Si (100) wafers with resistivity ranging from 4 ~ 10 Ω·cm in a commercially available low pressure chemical vapor deposition (LPCVD) reactor operating in the temperature range of 550 ~ 700°C. Most Ge(100) films were heteroepitaxially grown on Si(100) wafers using three steps: low temperature (LT) Ge seed growth at 400°C, slow temperature ramp up at a ramp rate of ~6.5°C/min from 400°C to 600°C, and high temperature (HT) Ge film growth at 600°C. Details of Ge epitaxial growth on Si are published elsewhere.⁵ Characterization results using optical microscopy, cross-sectional scanning electron microscopy (X-SEM), cross-sectional transmission electron microscopy (X-TEM), atomic force microscopy (AFM) and secondary ion mass spectroscopy (SIMS) were reported. Primitive X-ray diffraction (XRD) and Raman characterization results can be found in the paper. Due to the large (4.2%) lattice mismatch between Ge and Si, the epitaxial Ge films typically have high density threading dislocations (TD) at the Ge/Si interface. For 1 μm thick epitaxial Ge film on Si, the threading dislocation density (TDD) is as high as 10⁸ cm⁻².²¹ The TDD tends to decrease as the epitaxial Ge film grows and it becomes an order of magnitude smaller in 2 μm thick epitaxial Ge on Si. The TDD also decreases after a few minutes of thermal annealing (or cycling) above the epitaxial growth temperature.^{21–24}

Selected epitaxial Ge/Si wafers were annealed in the temperature range of 800 ~ 875°C for 3 min to investigate the effects of thermal annealing (cycling) on possible changes in composition (intermixing of Ge and Si) during typical TDD reduction annealing conditions.

On the selected as-grown heteroepitaxial Ge(100)/Si(100) wafers, most of the (0.8 μm) epitaxial Ge films were removed by CMP to investigate the composition and the possibility of Ge-Si intermixing near the Ge/Si interface. The final epitaxial Ge layer thickness was reduced to ~0.2 μm after CMP.

All heteroepitaxial Ge/Si wafers were examined by multiwavelength Raman spectroscopy in the wavenumber range of 250 ~ 600 cm⁻¹ before and after annealing and/or CMP. Four different wavelengths of 457.9, 488.0, 514.5 and 785 nm laser lines with different probing depths were used as the Raman excitation source. Raman measurement was performed in a 180° backscattering mode. The excitation laser beam was irradiated from the epitaxial Ge film side through a microscope objective lens. The diameter of the excitation laser beam on the wafer surface was approximately 1 μm. Effective

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Raman excitation wavelengths for various Ge/Si and possible alloy structures of Ge with Si were investigated.

Since the heating associated with the excitation laser beam has a significant impact on the peak positions, the excitation laser power was adjusted below the threshold power density at the sample surface in all Raman measurements. The laser power was either adjusted at the laser source or using an attenuation filter. Sample heating by the excitation laser beam was kept to a minimum and did not impact Raman peak positions.

For strain analysis of epitaxial Ge(100) films and comparison with multi wavelength Raman characterization results, θ -2 θ XRD scans were done on a bulk Ge(100) wafer and heteroepitaxially grown Ge(100) film on Si(100) wafers.

Results and Discussion

X-ray diffraction.— Linear scale and log scale XRD θ -2 θ scan results on 1.0 μm thick epitaxial Ge(100)/Si(100) wafer and reference Ge(100) wafers are plotted in Fig. 1. The Cu $K\alpha_1$ line ($\lambda = 0.154056\text{ nm}$) was used as an excitation source. A Si(004) peak was measured at 69.13° and a Ge(004) peak from the reference Ge(100) wafer was measured at 65.99° . They correspond to the lattice mismatch of $\sim 4.2\%$ between Si(100) and Ge(100).

The Ge(004) peak from heteroepitaxial Ge(100) film on Si(100) was measured at 66.11° , 0.12° greater than that of the Ge(004) peak from the reference Ge(100) wafer. The average tensile strain of heteroepitaxial Ge(100) film throughout the thickness in the [001] direction (perpendicular to the wafer surface) is estimated to be $\sim 0.16\%$. The origin of tensile strain in Ge(100) film is speculated to be the difference between coefficients of thermal expansion (CTE) of Ge and Si. The tensile strain in Ge film may have been thermally induced during a cool down step from the relaxed state during growth at the high temperature.⁵

The linear scale XRD patterns (Fig. 1(a)) show sharp peaks of Ge and Si. They are useful to determine probable crystalline structure based on diffraction angles, but they are too rough to be used for determining crystallographic homogeneity in heteroepitaxial films and substrates. The log scale XRD patterns can reveal more details (Fig. 1(b)). As seen in the log scale the XRD pattern from heteroepitaxial Ge(100) on Si(100) wafer, both Ge(004) peak and Si(004) peak were significantly asymmetric. However, the Ge(004) peak was severely distorted suggesting the heteroepitaxial Ge(100) layer is not

Figure 1. Linear and log scale θ -2 θ XRD patterns from 1.0 μm thick epitaxial Ge(100)/Si(100) wafer and reference Ge(100) wafer.

crystallographically homogeneous in the growth (vertical) direction. The presence of variations in Ge lattice spacing in the growth direction is obvious. However, the distribution of Ge lattice spacing variations, and its origin, cannot be simply determined. The lattice spacing can be varied by lattice stress/strain with or without compositional change such as intermixing of Ge and Si ($\text{Si}_{1-x}\text{Ge}_x$ formation) at the growth interface.⁵ The presence of Ge and Si intermixing must be verified by different techniques such as SIMS and Raman spectroscopy.

514.5 nm excitation Raman spectra.— A 514.5 nm Ar^+ ion laser line is frequently used for Raman characterization of semiconductor materials due to its availability, intensity and stability as an excitation source.^{9,25-28} Figure 2 shows 514.5 nm excited linear and log scale Raman spectra from reference Si, reference Ge, reference thin (0.2 μm thick) epitaxial Ge(100)/Si(100) and epitaxially grown 1.0 μm thick Ge/Si wafers after thermal annealing in the temperature range of $800 \sim 875^\circ\text{C}$. The annealing time was fixed at 3 min for all epitaxial Ge/Si wafers.

Ge and Si show very sharp Raman peaks at 300 cm^{-1} and 520.3 cm^{-1} , respectively. The peak position shifts under the presence of strain/stress and isotopic variations.^{4,5,9,27-31} Alloys of Si and Ge ($\text{Si}_{1-x}\text{Ge}_x$) typically show three Raman peaks of Ge-Ge ($\sim 300\text{ cm}^{-1}$), Si-Ge ($\sim 400\text{ cm}^{-1}$) and Si-Si ($\sim 500\text{ cm}^{-1}$). The position and intensity of the three peaks depends on the composition of the alloys. According to experimental results and theoretical calculations, the Ge-Ge peak linearly shifts from 300 cm^{-1} (the pure Ge peak) to $\sim 280\text{ cm}^{-1}$ as the Ge content (x) is decreased from 1 to 0. The Si-Ge peak shows an inverted U shape in the wavenumber range of $392 \sim 408\text{ cm}^{-1}$ and the maximum shift of $\sim 408\text{ cm}^{-1}$ appears at $\text{Si}_{0.5}\text{Ge}_{0.5}$ ($x=0.5$). The Si-Si peak linearly shifts from 520 cm^{-1} (the pure Si peak) to 460 cm^{-1} as the Ge content (x) is increased from 0 to 1. The Ge-Ge peak and Si-Si peak of $\text{Si}_{1-x}\text{Ge}_x$ moves in the opposite direction with Ge content increase. The alloy composition can be estimated from Raman spectra (position and intensity ratios of the

Figure 2. Linear and log scale Raman spectra from 1.0 μm thick epitaxial Ge(100)/Si(100) wafers after thermal annealing in the range of $800 \sim 875^\circ\text{C}$. Raman spectra from Si, thin (0.2 μm thick) epitaxial Ge(100)/Si(100) and Ge wafers were also shown as references. (Excitation wavelength: 514.5 nm).

three peaks).^{32–35} The presence of Ge and Si intermixing can easily be determined by searching for the Si-Ge peak at $\sim 400\text{ cm}^{-1}$.

The linear plot of the Raman spectra (Fig. 2(a)) only showed a Ge peak $\sim 300\text{ cm}^{-1}$ and Si peak around $\sim 520\text{ cm}^{-1}$. No Si-Ge peak near $\sim 400\text{ cm}^{-1}$ from $\text{Si}_{1-x}\text{Ge}_x$ alloy was recognized. The Ge reference wafer and $1.0\text{ }\mu\text{m}$ thick epitaxial Ge/Si wafers annealed below 850°C showed a single Ge peak at $\sim 300\text{ cm}^{-1}$ implying the wafer surface is pure Ge within the probing depth of 514.5 nm excitation wavelength. The thin ($0.2\text{ }\mu\text{m}$ thick) Ge/Si reference wafer showed two peaks (one strong Ge peak at $\sim 300\text{ cm}^{-1}$ and one weak Si peak at $\sim 520\text{ cm}^{-1}$). There is no Si-Ge peak near $\sim 400\text{ cm}^{-1}$ from a $\text{Si}_{1-x}\text{Ge}_x$ alloy from the thin ($0.2\text{ }\mu\text{m}$ thick) Ge/Si reference wafer. The $1.0\text{ }\mu\text{m}$ thick epitaxial Ge/Si wafers annealed at 850°C showed one very weak Ge peak at $\sim 300\text{ cm}^{-1}$ and a strong Si peak at $\sim 520\text{ cm}^{-1}$. The Si reference wafer and $1.0\text{ }\mu\text{m}$ thick epitaxial Ge/Si wafers annealed at 875°C showed one strong Si peak at $\sim 520\text{ cm}^{-1}$. The Ge peak at $\sim 300\text{ cm}^{-1}$ completely disappeared from the $1.0\text{ }\mu\text{m}$ thick epitaxial Ge/Si wafers annealed at 875°C . No sign of $\text{Si}_{1-x}\text{Ge}_x$ alloy formation was observed from the linear plot Raman spectra. To investigate the disappearance of the Ge peak and possible change of the epitaxial layer composition after high temperature thermal annealing, the Raman spectra were re-plotted in log scale (Fig. 2(b)).

The log plot of Raman spectra (Fig. 2(b)) showed little detail of the very weak Raman peaks. Ge peak $\sim 300\text{ cm}^{-1}$, Si-Ge peak $\sim 400\text{ cm}^{-1}$, Si peak around $\sim 520\text{ cm}^{-1}$ and broad background corresponding to phonon density of states (DOS) of Si in the wavenumber range of $250 \sim 450\text{ cm}^{-1}$ were found. Similar to the linear plot of Raman spectra, the Ge reference wafer and $1.0\text{ }\mu\text{m}$ thick epitaxial Ge/Si wafers annealed at 850°C only showed a single Ge peak at $\sim 300\text{ cm}^{-1}$ implying the wafer surface is pure Ge. However, the $1.0\text{ }\mu\text{m}$ thick epitaxial Ge/Si wafer annealed below 850°C showed a Ge peak at $\sim 300\text{ cm}^{-1}$, a Si peak at $\sim 520\text{ cm}^{-1}$ and a distinct peak $\sim 410\text{ cm}^{-1}$ corresponding to Si-Ge alloy. It indicates Si-Ge alloy formation during annealing at 850°C . Both the Ge peak at $\sim 300\text{ cm}^{-1}$ and Si peak at $\sim 520\text{ cm}^{-1}$ were slightly shifted downwards from pure Ge and pure Si peaks due to the Si-Ge alloy formation. The $1.0\text{ }\mu\text{m}$ thick epitaxial Ge(100)/Si(100) wafer annealed at 875°C showed almost identical Raman spectra with broad background peaks related to the phonon DOS from the reference Si wafer. The Ge atoms may have diffused into the Si wafer and average Ge concentration may have become very low after 875°C annealing so that no Si-Ge and Ge related Raman peaks were observed, even from the Raman spectra plotted in the log scale. When either Ge or Si content is less than 5 atomic percent (at. %) in thin heteroepitaxial films on foreign wafers (such $\text{Si}_{>0.95}\text{Ge}_{<0.05}/\text{Si}$ or $\text{Si}_{<0.05}\text{Ge}_{>0.95}/\text{Ge}$), it is difficult to distinguish the Raman peak from the Si-Ge alloy films from the Raman peak from the wafer. This is because the Raman peak from the Si-Ge alloy becomes very weak and overlaps with the Raman peak from the wafer. A log scale plot of Raman spectra can be more effective in detecting Si-Ge alloy formation when the Si-Ge related Raman peak $\sim 400\text{ cm}^{-1}$ is very weak or unrecognizable.

Multiwavelength excitation Raman spectra.— It is well known that the probing depth of Raman measurements depends on excitation wavelength and optical properties of the specimen. The optical properties of a specimen can vary over a wide range depending on materials, thickness, number of layers, stacking order, presence of patterns etc. The excitation wavelength of Raman measurements must be carefully chosen after considering various factors listed above. To investigate the effect of Raman excitation wavelengths on the detection capability of Si and Ge intermixing (or alloy formation), Raman spectra from the same set of reference wafers and Ge(100)/Si(100) wafers were measured under three excitation wavelengths of 457.9 , 488.0 and 514.5 nm . For rough compositional characterization and sensitive detection of Si-Ge alloy formation, all Raman spectra were plotted in both linear and log scales (Fig. 3).

The Raman spectra from the same set of reference and epitaxial Ge/Si wafers under three different excitation wavelengths look very

similar. The 488.0 nm excited Raman spectra generally showed noisier results (low signal-to-noise (S/N) ratio) even though the overall intensity of Raman peaks of Ge and Si are stronger than those measured under 457.9 and 514.5 nm excitation. The poor S/N ratio under 488.0 nm excitation Raman spectra is believed to be due to increased stray light in the Raman spectrometer near the particular diffraction grating angle. The S/N ratio can be improved if a different diffraction grating with different groove density is used. As the excitation wavelength is shorter, the Ge-Ge peak near $\sim 300\text{ cm}^{-1}$, Si-Ge peak near $\sim 400\text{ cm}^{-1}$ and Si-Si peak near $\sim 500\text{ cm}^{-1}$ from the $\text{Si}_{1-x}\text{Ge}_x$ (Si-Ge alloy) layer of $1.0\text{ }\mu\text{m}$ thick epitaxial Ge(100)/Si(100) wafer, annealed at 850°C , became clearer. Based on the Si-Si peak position at $\sim 490\text{ cm}^{-1}$ in Fig. 3(a), the Ge content in $\text{Si}_{1-x}\text{Ge}_x$ (Si-Ge alloy) layer is estimated to be $\sim 30\text{ at. } \%$ ($x \approx 0.30$).

Under the same spectrometer configuration, Raman spectral resolution is higher at longer excitation wavelengths due to the higher dispersion at longer wavelengths. Detailed Raman spectra are generally expected from the longer wavelength excited Raman measurements from the specimen with a Si-Ge alloy with uniform Ge composition in the depth direction. Raman spectra from the $1.0\text{ }\mu\text{m}$ thick epitaxial Ge(100)/Si(100) wafer, annealed at 850°C , showed completely opposite trends. This suggests that the Ge content (x value) in the $\text{Si}_{1-x}\text{Ge}_x$ layer formed by thermal annealing at 850°C is either not uniform throughout the Si-Ge alloy layer (in the depth direction) or not homogeneous in composition in the heteroepitaxial Ge layer (in plane). Formation of small $\text{Si}_{1-x}\text{Ge}_x$ islands on the heteroepitaxial Ge layers can also result from the opposite trends. Considering the probing depth ($\sim 8\text{ nm}$) in Ge under $457.9 \sim 514.5\text{ nm}$ excitation and spatial resolution (or diameter of the laser beam: $1\text{ }\mu\text{m}$), inhomogeneous composition of heteroepitaxial Ge layer after 850°C anneal due to Si diffusion is a very likely occurrence. Since the Si-Ge alloy layer is formed by thermal diffusion of Si and Ge atoms, a Ge content gradient in the Si-Ge alloy layer is easily expected. The detection of Si-Ge alloy formation (Ge/Si intermixing) within the probing depth of Raman excitation wavelength can be done at any excitation wavelength. However, multiwavelength excited Raman measurements are essential to detect the Ge content gradient in the Si-Ge alloy layer.

Probing depth vs. Raman excitation wavelength.— It is important to understand the probing depth of Raman excitation wavelengths in Si, Ge and Si-Ge alloys. Optical properties of Si and Ge must be considered to properly select optimal Raman excitation wavelengths. Figure 4 shows (a) absorption coefficient, (b) transmittance and (c) room temperature photoluminescence (PL) spectra of Si and Ge in the wavelength range of $0.2\text{ }\mu\text{m}$ and $3.0\text{ }\mu\text{m}$.

The bandgap (E_g) values of Si and Ge are 1.12 and 0.67 eV , respectively. The light absorption edges (absorption coefficient (α) of 10^2 cm^{-1}) of Si and Ge are located at ~ 1.0 and $\sim 1.6\text{ }\mu\text{m}$. Si is $\sim 56\%$ transparent at wavelengths longer than $1.05\text{ }\mu\text{m}$ and Ge is $\sim 44\%$ transparent at wavelengths longer than $1.75\text{ }\mu\text{m}$. The bandgap and optical properties of Si-Ge alloys ($\text{Si}_{1-x}\text{Ge}_x$) lie between those of Si and Ge. As the Ge content (x) increases, the bandgap and optical properties of $\text{Si}_{1-x}\text{Ge}_x$ depart from the Si properties and approach the Ge properties.

When a highly transparent (low absorbing) film is on the measurement (Raman excitation) side (i.e. Si/Ge and $\text{Si}_{1-x}\text{Ge}_x/\text{Ge}$), shorter excitation wavelength Raman measurements can probe both film and substrate materials. In the opposite configuration, with a highly opaque (or absorptive) film on the Raman measurement side (i.e. Ge/Si and $\text{Si}_{1-x}\text{Ge}_x/\text{Si}$), the most likely Raman signals from the film are measured at many excitation wavelengths. Longer excitation wavelengths, with deeper probing depths, are highly desirable for investigating the interfaces of Ge/Si and $\text{Si}_{1-x}\text{Ge}_x/\text{Si}$ heterostructures.

One other important consideration in selecting a proper Raman excitation wavelength is the luminescence or fluorescence bands (in this case, room temperature PL bands for Si, $\text{Si}_{1-x}\text{Ge}_x$ and Ge). Raman scattering yield of semiconductor crystals is typically on the order of parts per million (ppm) or less,³⁶ while PL yields can easily be on the order of percent (%), even for the indirect semiconductors such as Si

Figure 3. Log scale Raman spectra from 1.0 μm thick epitaxial Ge(100)/Si(100) wafers after thermal annealing in the temperature range of 800 ~ 875°C. Raman spectra from Si, thin (0.2 μm thick) epitaxial Ge(100)/Si(100) and Ge(100) wafers were also shown as references. (Excitation wavelengths: 457.9, 488.0 and 514.5 nm).

and Ge. When there is a PL signal from either film or substrate, the Raman signal from the specimen cannot be measured or separated. Typical room temperature PL spectra from Si and Ge are measured in the wavelength ranges of 850 ~ 1400 nm and 1200 ~ 2000 nm (Fig. 3(c)).^{37–39} The Raman excitation wavelength must not be longer than 850 nm in the case of a Ge/Si, $\text{Si}_{1-x}\text{Ge}_x$ /Ge or Si/Ge structure.

Absorption coefficients and corresponding Raman probing depths of Ge and Si, under various excitation wavelengths, are summarized in Table I. The absorption coefficient of Ge is at least one order of magnitude larger than that of Si for all excitation wavelengths.^{40–42} The Raman probing depth for Ge is almost constant at 8 ~ 9 nm, up to 532 nm excitation, while the Raman probing depth for Si increases as the excitation wavelength is increased. In the case of ultra thin epitaxial $\text{Si}_{1-x}\text{Ge}_x$ /Si, ultraviolet (UV) and/or near UV visible excitation wavelengths are frequently used.^{34,43,44}

The similarity of multiwavelength Raman spectra shown in Fig. 3(a) ~ 3(c) and 3(d) ~ 3(f) can be explained by the constant probing depth of ~8 nm in Ge film under 457.9, 488.0 and 514.5 nm excitation. To effectively detect Ge/Si intermixing in epitaxial Ge/Si with Ge film thickness greater than 50 nm, the Raman excitation wavelength must be longer than 650 nm and shorter than 850 nm (to avoid interference from PL signal from Si). It is not easy to detect Ge-Si intermixing near the Ge(100)/Si(100) interface, if the Ge film thickness

is in the range of microns, due to the high absorption coefficient of Ge. Any Si contamination and/or Ge-Si intermixing near the as grown surface of Ge(100)/Si(100) can easily be detected under all excitation wavelengths listed in the Table I.

Raman characterization of Ge(100)/Si(100) interface.— To prove the effectiveness of Raman measurements in detecting Si contamination and/or Ge-Si intermixing in epitaxial Ge(100)/Si(100), an as-grown 1.0 μm thick Ge/Si wafer was characterized under for different excitation wavelengths (457.9, 488.0, 514.5 and 785 nm). The same specimen was measured after removing ~ 0.8 μm of Ge epitaxial layer by CMP. The remaining epitaxial film thickness was ~ 0.2 μm . Figure 5 shows schematic illustrations of samples (a) and (b), linear scale Raman spectra from (c) as-grown 1 μm thick epitaxial Ge/Si wafer and (d) after CMP under four different excitation wavelengths.

No evidence of Si contamination and/or Ge-Si intermixing was found from the as-grown 1.0 μm thick Ge(100)/Si(100) wafer within the probing depths (~267 nm, 3 times the probing depth of 785 nm excitation, where >90% of Raman signal is originated) of all four excitation wavelengths. The ~0.2 μm thick Ge/Si wafer (after ~0.8 μm epitaxial Ge film removal by CMP) showed significant Ge-Si intermixing and Si-Ge alloy formation within the probing depths from the surface (8 nm ~ 89 nm) for all four excitation wavelengths

Figure 4. (a) absorption coefficient, (b) transmittance and (c) room temperature PL spectra of Si and Ge in the wavelength range of 0.2 μm and 3.0 μm .

after CMP. Since no Si Raman peak at $\sim 520\text{ cm}^{-1}$ was detected, even under 785 nm excitation, we may assume the excitation light did not reach the Si wafer, approximately 0.2 μm below the surface, after the CMP. The Raman intensity increase and upward shift of Ge-Ge peak $\sim 300\text{ cm}^{-1}$ and Si-Ge peak $\sim 400\text{ cm}^{-1}$, with excitation wavelength increase, strongly indicates the increase of probing vol-

ume and decrease of Ge content in the Si-Ge alloy layer toward the Ge(100)/Si(100) interface.

Indeed, the Ge-Ge peak was shifted from $\sim 300\text{ cm}^{-1}$ (the pure Ge peak) to $\sim 295\text{ cm}^{-1}$ (a $\text{Si}_{1-x}\text{Ge}_x$ peak) after $\sim 0.8\text{ }\mu\text{m}$ removal of heteroepitaxial Ge film by CMP under all Raman excitation wavelengths. Both the appearance of a Si-Ge peak $\sim 400\text{ cm}^{-1}$ and downshifts of the Ge-Ge peaks after CMP, are good evidence of Ge-Si intermixing at the Ge(100)/Si(100) interface at the beginning of Ge growth, including Ge seed layer growth at the relatively lower temperature of 600°C . It was quite surprising to observe the presence of Si-Ge alloy at the interface of as-grown Ge(100)/Si(100) with the maximum exposure temperature of 600°C , during heteroepitaxy. The estimated Ge content is $\sim 80\%$ ($x \sim 0.8$) based on the Ge-Ge peak position of Raman spectra from the $\sim 0.2\text{ }\mu\text{m}$ thick Ge(100)/Si(100) after CMP. Due to the high Ge content within the probing depth of Raman excitation wavelengths, the Si-Si peak $\sim 500\text{ cm}^{-1}$ was very weak and difficult to recognize. The Raman results are consistent with the speculated scenario from the XRD analysis, in the previous section.

Raman peak positions are impacted, not only by composition, but also by strain in the $\text{Ge/Si}_{1-x}\text{Ge}_x/\text{Si}$.^{27,28} For precise analysis, more careful interpretation is needed. Perhaps, additional information from XRD, SIMS, X-SEM and X-TEM results will be very useful, in early stages, for verification of Raman characterization results.

The intermixing of selectively grown Si dots with Ge core after 5 minutes of annealing at 800°C has been reported.⁴⁵ Thermal interdiffusion of Ge and Si in $\text{Si}_{1-x}\text{Ge}_x/\text{Si}$ after 60s rapid thermal annealing (RTA) as low as 950°C has been reported.⁴⁴ For successful integration of heterostructures of Si and Ge, very careful process monitoring and control are required to avoid surprising deviations in composition, profile and crystallinity from the designed specifications.

Due to the Ge-Si intermixing at the relatively lower Ge heteroepitaxial growth temperature of 600°C and the thickness of intermixing layer, the growth temperature and Ge film removal thickness from CMP for surface roughness reduction must be carefully monitored and controlled for successful device integration.

Proper Raman excitation wavelength selection.— Raman spectroscopy is very convenient and powerful as a non-contact and non-destructive semiconductor material characterization technique. It can be used as a complementary material characterization and process monitoring technique to the traditional techniques. However, very little attention was paid in selecting proper excitation wavelengths. Sometimes, very casual interpretations were given without considering materials/structures of specimens and probing depth of Raman measurements in the specimens. It can easily lead unrealistic conclusions. Appropriate Raman excitation wavelength(s) should be selected based on the materials/structures of specimens and properties/regions of characterization interests.

Table I. Absorption coefficients and corresponding Raman probing depths of Ge and Si under various excitation wavelengths.

Wavelength (nm) Excitation	Spectrum Category	Absorption Coefficient $\alpha\text{ (cm}^{-1}\text{)}$		Raman Probing Depth $\frac{1}{2}\delta_p\text{ (nm)}$	
		Ge	Si	Ge	Si
325.0	UV	-	1.24×10^6	-	~ 4
363.8	UV	-	9.75×10^5	-	~ 5
406.7	VIS	-	7.30×10^4	-	~ 68
441.6	VIS	-	4.63×10^4	-	~ 108
457.9	VIS	6.13×10^5	3.55×10^4	~ 8	~ 141
488.0	VIS	6.06×10^5	2.03×10^4	~ 8	~ 246
514.5	VIS	5.97×10^5	1.46×10^4	~ 8	~ 340
532	VIS	5.77×10^5	1.02×10^4	~ 9	~ 490
650	VIS	1.00×10^5	3.08×10^3	~ 50	~ 1623
785	NIR	5.59×10^4	1.12×10^3	~ 89	~ 4460
827	NIR	4.53×10^4	7.60×10^2	~ 110	~ 6578

Figure 5. Sample structure of (a) as-grown 1.0 μm thick epitaxial Ge(100)/Si(100) wafer and (b) after CMP. Linear scale Raman spectra from (c) as-grown 1.0 μm thick epitaxial Ge(100)/Si(100) wafer and (d) after CMP under four different excitation wavelengths (457.9, 488.0, 514.5 and 785 nm). Final Ge film thickness after CMP is 0.2 μm.

Figure 6 shows four examples of schematic cross-sectional diagrams of typical specimens with different materials and structures. Relative probing depths of Raman excitation wavelengths in the UV~NIR region in the four example specimens are schematically illustrated. By selecting proper excitation wavelengths, weighted average properties up to the Raman probing depths can be characterized. Depending on the properties/regions of characterization interests, one or more Raman excitation wavelengths can be selected.

For opaque materials with higher absorption coefficients such as Ge, Raman probing depths are very shallow even under NIR wavelength region. It is difficult to characterize the interface of Ge/Si samples from the Ge (opaque) side of surface unless Ge film is very thin (<0.2 μm) (Fig. 6(a)). In case of Si/Ge samples, it is relatively easy to characterize the Si/Ge interface from the Si (translucent) side of surface unless the Si film is very thick (three times thicker than the probing depth of Raman excitation wavelength) (Fig. 6(b)). Since Si_{1-x}Ge_x has intermediate optical properties, Raman probing depths are deeper than in Ge and shallower than in Si (Fig. 6(c) and 6(d)). Multiple excitation wavelengths are always beneficial to gain weight average properties up to different probing depths.

If the wavelength of Raman signal overlaps with PL spectra, Raman signal is very difficult to separate from the PL spectra. It is because the Raman scattering yield in the semiconductor crystals are generally few orders of magnitude lower than that for PL (>900 nm) (Fig. 4(c)). Thus, a 827 nm laser line in the NIR region may be the longest excitation wavelength with deepest probing depths of ~6578 nm in Si and ~110 nm in Ge (Table I).

Recently, successful selective lateral Ge growth has been reported for local GeOI fabrication.⁹ 300 nm thick Ge(100) was laterally grown at 650°C into 1.5 μm of lateral cavity interposed by SiO₂ using checkerboard mesa structures and line/space structures with [110] and [010] oriented side walls. Strain distribution of Si and Ge of mesa structures were characterized from the sample surface by micro Raman spectroscopy under single excitation wavelength of 514.5 nm. The strains in Si and Ge were mapped for 15×15 μm². A small tensile strain of ~0.09% was measured in the Si pillar and ~0.25% to ~0.3% tensile strain was measured from the Ge around Si pillar. It was reported that the strain of the Ge layer near the edge was weaker than that near the interface to the Si pillar. However, the penetration depth of Raman excitation wavelength (514.5 nm) was not considered in the interpretation of the Raman measurement results. For 514.5 nm excitation, probing depths in Si and Ge are ~340 nm and ~8 nm, respectively (Table I). The probing depth in Si is 42.5 times deeper than in Ge. The difference in probing depths in Si and Ge should be considered for accurate interpretation. The 514.5 nm excited Raman signal from the 300 nm thick Si pillar represents average strain in entire thickness of Si pillar. On the other hand, weighted Ge strain information only up to the top ~8 nm of 300 nm thick Ge layer was measured. The Raman data may have been biased. To reduce the bias, multiwavelength Raman measurements with different probing depths may be necessary.

Multiwavelength Raman characterization techniques are very effective in detecting Si contamination and/or the Ge-Si intermixing in epitaxial Ge(100)/Si(100) wafers. The effectiveness of Raman characterization and detection sensitivity of Si contamination, and/or the

Figure 6. Schematic cross-sectional diagrams of typical specimens with different materials and structures. Relative probing depths of Raman excitation wavelengths from UV to NIR region in the specimens.

Ge-Si intermixing in epitaxial Ge(100)/Si(100) wafers, for inline process monitoring can be significantly enhanced by selecting proper excitation wavelengths considering the material and structure of specimens. As seen in Fig. 5(a) and 5(b), it is very important to understand implications and limitations of each measurement so that Raman excitation wavelengths can be selected and/or proper sample structures can be prepared.

Summary

To extend the lifespan of Si, various materials and device structures are constantly introduced. As material property enhancement techniques, combinations of Si/Ge, Ge/Si, $\text{Si}_{1-x}\text{Ge}_x/\text{Si}$ are frequently introduced in the device fabrication process to meet various physical property requirements of materials for advanced application-specific devices. Heteroepitaxy, condensation and annealing processes are commonly used in advanced device manufacturing. A small variation in composition, strain and crystallinity can result in reduced device performance or failure. The composition, structure, strain and crystallinity must be carefully monitored and controlled throughout the manufacturing process.

In this study, we have investigated a multiwavelength Raman characterization technique for detecting and monitoring Ge and Si intermixing in epitaxially grown Ge(100)/Si(100) before and after successive thermal anneals. We have demonstrated successful detection of Ge and Si intermixing before and after annealing under various temperatures. Very strong excitation wavelength and film structure dependence of signal-to-noise (S/N) ratio of Raman measurements was observed.

Appropriate Raman excitation wavelength selection guidelines for Ge, Si-Ge and Si material systems are given based on optical properties of materials. Examples of suitable excitation wavelength selection for properly detecting and characterizing Si and Ge intermixing were given based on the stacking order of epitaxial films, thicknesses and compositions.

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