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Short Note

Raman Investigation of the Localized Vibrational Mode of Carbon in Strain-Relaxed $Si_{1-x}Ge_x$:C

Ken MORITA[1], Kohei M. ITOH[1,*], Lone HOFFMANN[2], Brian B. NIELSEN[2], Hiroshi HARIMA[3] and Kohji MIZOGUCHI[4]

[1]Faculty of Science and Technology, Keio University, Yokohama 223-8522, Japan
[2]Institute of Physics and Astronomy, Aarhus University, DK-8000 Aarhus C, Denmark
[3]Department of Applied Physics, Osaka University, Osaka 565-0871, Japan
[4]Department of Applied Physics, Osaka City University, Osaka 558-8585, Japan

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The localized vibrational mode (LVM) of carbon in strain-relaxed $Si_{1-x}Ge_x$:C samples with $x = 0$, 0.05, 0.35, and 0.5 have been investigated by Raman spectroscopy at room- and liquid-nitrogen-temperatures. The position of the Raman peaks due to LVM of carbon shifts linearly to lower frequencies with increasing x from 0 to 0.5. The LVM frequencies of carbon obtained by Raman measurement agree very well with those determined by Hoffmann *et al.* in infrared (IR) absorption recently.

KEYWORDS: $Si_{1-x}Ge_x$:C, localized vibrational mode of carbon, Raman-spectroscopy, infrared absorption

$Si_{1-x}Ge_x$ layers grown on Si substrates have been studied extensively for the development of ultra-fast electronic devices.[2)] However, a sever limitation on the $Si_{1-x}Ge_x$ device performance is often imposed by the misfit dislocations arising from the 4% mismatch between Si and Ge lattice constants.[3)] The lattice mismatch can be compensated if some of the Ge and Si atoms in $Si_{1-x}Ge_x$ are replaced by C atoms, i.e., by forming carbon-doped $Si_{1-x}Ge_x$, which we denote $Si_{1-x}Ge_x$:C or $Si_{1-x-y}Ge_xC_y$ alloys. The fabrication of the lattice mismatched $Si_{1-x}Ge_x$:C layers requires nonequilibrium techniques such as molecular beam epitaxy (MBE) and chemical vapor deposition (CVD).[4–6)] The typical thickness of layers prepared by these techniques is very small: of the order a hundred nanometers. Hence, analytical techniques that are capable of treating such thin films may be valuable to characterize the amount and properties of carbon atoms in the material.

The vibrational spectrum of carbon is one parameter that can be used to characterize the nature and quality of $Si_{1-x}Ge_x$:C. Because carbon is significantly lighter than Si and Ge, a carbon sitting substitutionally in the $Si_{1-x}Ge_x$ lattice exhibits localized vibrations with higher frequencies than the $Si_{1-x}Ge_x$ phonons. These localized vibrational modes (LVMs) of carbon in $Si_{1-x}Ge_x$ have been investigated systematically with IR absorption by Hoffmann *et al.*[1,7,8)] Their studies have shown that substitutional carbon in $Si_{1-x}Ge_x$ binds to its four-neighboring Si and Ge and that the LVM frequency is determined mainly by the specific combination of silicon and germanium neighbors as well as the composition x of the material. However, IR absorption requires relatively thick samples in order to obtain signal intensities that are detectable. For this reason, IR absorption may not always be suitable for the characterization of thin $Si_{1-x}Ge_x$:C films.

Raman-spectroscopy, on the other hand, allows for characterization of thin films with high spatial resolution at room temperatures. Several groups have reported on Raman spectroscopy studies of $Si_{1-x}Ge_x$:C.[9–12)] Two Raman peaks, one at 607 cm^{-1} and the other at 560 cm^{-1}, have been identified as carbon LVMs in $Si_{1-x-y}Ge_xC_y$[11)] and their frequencies depends only on the Ge composition x when $y \ll 0.01$, and on both x and y when $y \gg 0.01$.[12)] The microscopic origin of the two peaks at 607 cm^{-1} and 560^{-1} have been revealed by IR absorption studies performed by Hoffmann *et al.*[1,7,8)] In this paper we report on Raman investigations of ^{13}C LVM in $Si_{1-x}Ge_x$:C samples.

To facilitate the comparison between our spectra and those obtained previously by IR absorption,[1,7,8)] an equivalent series of ^{13}C-doped $Si_{1-x}Ge_x$:C samples was studied in this work. Extensive descriptions of sample preparations are given in ref. 1, 13, and 14, and only a brief account will be given here. For all samples a 1-μm-thick Si buffer layer, a graded SiGe buffer layer, and a 4-μm thick $Si_{1-x}Ge_x$ top-layer were grown on highly resistive, (100) Si wafers by molecular-beam-epitaxy (MBE). In order to incorporate carbon atoms uniformly into the top $Si_{1-x}Ge_x$ layers, a multi-energy implantation of ^{13}C isotopes has been carried out in a sequence starting from 450 keV and going down to 50 keV in steps of 25 keV. The dose at each implantation step has been adjusted to obtain a uniform C concentration of 10^{20} cm^{-3} ($y \approx 0.002$ in $Si_{1-x-y}Ge_xC_y$) in the region between 0.1 and 1.0-μm from the surface. Raman scattering measurements have been carried out at 80 K and 300 K with a spectral resolution of 1 cm^{-1} in the backscattering geometry using the Ar$^+$ 514.5 nm line for excitation.

Figure 1 shows the Raman spectra of ^{13}C LVM in $Si_{1-x}Ge_x$ samples with $x = 0$, 0.05, 0.35, and 0.5 recorded at temperatures (a) 300 K and (b) 80 K in the frequency range between 500 and 650 cm^{-1}. The spectra obtained at the two temperatures [Figs. 1 (a) and 1(b)] are very similar with only

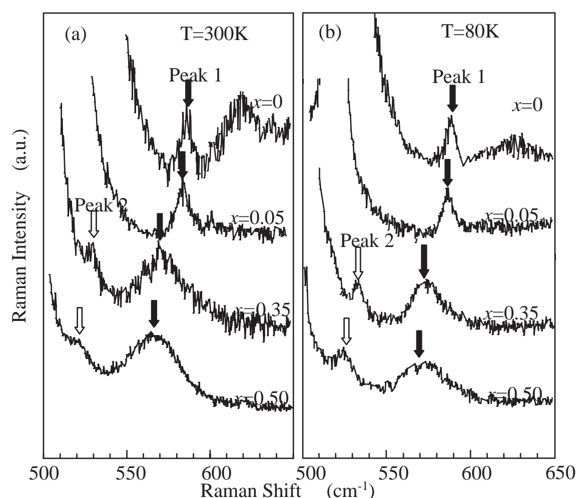

Fig. 1. Raman spectra representing LVMs of ^{13}C (Peak 1 and 2) in $Si_{1-x}Ge_x$:^{13}C recorded at (a) 300 K and (b) 80 K. From top to bottom: $x = 0$, 0.05, 0.35, and 0.5.

*E-mail address: kitoh@appi.keio.ac.jp

Table I. Vibrational modes of carbon in $Si_{4-n}Ge_n$–C molecules.

n	Point group	Mode	Peak 1	Peak 2
0	T_d	T_2	T_2	
1	C_{3v}	A_1, E	E	A_1
2	C_{2v}	A_1, B_1, B_2	A_1, B_1	B_2
3	C_{3v}	A_1, E	A_1	E
4	T_d	T_2		T_2

small differences in peak positions—they shift downwards by 4 cm^{-1} when the temperature is raised from 80 K to 300 K. The two Raman peaks labeled "Peak 1" and "Peak 2" in Fig. 1 represent LVMs of ^{13}C in $Si_{1-x}Ge_x$. A broad feature around 610 cm^{-1} for the $x = 0$ sample is the second-order Raman scattering of Si. As the Ge composition x increases, Peak 1 around 580 cm^{-1} broadens and its peak frequency decreases. When the Ge composition exceeds $x = 0.35$, Peak 2 appears around 530 cm^{-1}. Also the frequency of Peak 2 decreases with increasing x. An identical behavior was reported for the LVM's of substitutional carbon in the IR absorption studies, which provided the identification of the individual modes.[1] The local configuration of the substitutional carbon in $Si_{1-x}Ge_x$ can be described as a five-atom molecule in which one carbon atom is surrounded by four tetrahedrally bonded Si and Ge atoms. There are five different configuration of the molecule, $Si_{4-n}Ge_n$–C (n = 0, 1, 2, 3, and 4), and they give rise to a total of nine different carbon LVMs as listed in Table I. By inspection, it can be shown that these nine LVMs are divided into two groups as shown in the columns 4 and 5 of Table I to form Peak 1 and Peak 2 in Fig. 1, respectively. Peak 1 broadens for $x > 0$ samples because the number of available modes increases from T_2 only for $x = 0$ to E, A_1, etc. with increasing x as shown in Table I. The frequencies of Peak 1 and Peak 2 decrease with increasing x because the Ge–C and Si–C bond lengths increase with x and, hence, the effective force constants of Ge–C and Si–C bonds decrease with x. It is possible to estimate the positions of Peak 1 and 2 theoretically using the following assumptions.[1] The positions of Peak 1 and 2 depend only on the composition x of Ge and not on the composition y of C, because the concentration of carbon is very low in our samples ($y \approx 0.002$ for our $Si_{1-x-y}Ge_xC_y$). Peak 1 and 2 are formed predominantly by the T_2 mode of Si_4Ge_0–C and the A_1 mode of Si_3Ge_1–C, respectively, i.e., the peak positions of Peak 1 and 2 can be estimated simply by calculating the frequencies of the T_2 mode of Si_4Ge_0–C and the A_1 mode of Si_3Ge_1–C, respectively, as a function of the Ge composition x.

Figure 2 compares the experimentally determined LVM frequencies with the calculation for Peak 1 and Peak 2 of ^{13}C and ^{12}C in $Si_{1-x}Ge_x$:C. The positions of Peak 1 and 2 of ^{13}C found in the present Raman study (open circles) and the previous IR absorption study[1] (open triangles) agree very well with each other and with the calculation (solid and dotted lines). For comparison, we show in Fig. 2 the LVM frequencies Peak 1 and 2 of ^{12}C found by Raman spectroscopy (open rectangles[11] and diamond[12]). The open diamond agrees with calculation (dashed line) but three out of four open rectangles deviate significantly from the theory (dashed and broken lines) that has assumed that the carbon composition is small; $y \ll 0.01$. It turns out that the three open rectangles have

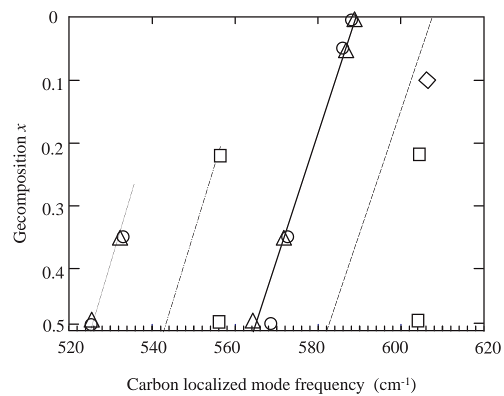

Fig. 2. Comparison of the experimentally determined LVM frequencies of ^{13}C in $Si_{1-x}Ge_x$:^{13}C obtained in the present Raman study (○) and in the previous IR absorption study[1] (△). Theoretically expected frequencies of the T_2 mode of Si_4Ge_0–^{13}C, A_1 mode of Si_3Ge_1–^{13}C, T_2 mode of Si_4Ge_0-^{12}C, and A_1 mode of Si_3Ge_1-^{12}C are shown by the solid, dotted, dashed, and broken lines, respectively. The ^{12}C LVM frequencies found by Raman are also plotted for the comparison (□ and ◇ from ref. 11 and 12, respectively).

been obtained with a sample with $y \approx 0.033$, i.e., the peak position depends not only on x but also on y.

In summary, Raman scattering spectroscopy has been applied successfully at room and liquid-nitrogen temperatures for the characterization of carbon LVMs in strain-relaxed thin-layers of $Si_{1-x}Ge_x$:C. The carbon LVM frequencies revealed by Raman in this work agree very well with the ones found in the previous work using IR absorption.[1] The frequencies of carbon LVMs have been obtained as a function of the Ge composition x for the condition $y \ll 0.01$. As we can see in Fig. 2, it is important in the future to investigate the effect of y on the LVM frequencies of substitutional carbon for samples having $y \gg 0.01$.

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