Raman scattering in $Ge_{1-y}Sn_y$ alloys

V.R. D'Costa [a,*], J. Tolle [b], R. Roucka [b], C.D. Poweleit [a], J. Kouvetakis [b], J. Menéndez [a]

[a] Department of Physics, Arizona State University, Tempe, AZ 85287-1504, United States
[b] Department of Chemistry and Biochemistry, Arizona State University, Tempe, AZ 85287-1604, United States

Abstract

The Raman spectrum of nearly relaxed $Ge_{1-y}Sn_y$ alloys grown on Si substrates was investigated for Sn concentrations $y < 0.2$. The frequency dependence of the Ge–Ge Raman mode was re-evaluated by carrying out careful corrections for residual strain shifts. The Ge–Sn mode was observed for the first time in this type of samples. Its frequency appears to decrease monotonically as a function of the Sn concentration. This is very different from the behavior of the Si–Ge mode in $Si_{1-y}Ge_y$ alloys, but a detailed analysis suggest that there is a scaling relationship between these modes that is the analog of the scaling relationship found earlier for the Ge–Ge mode. Raman activity is also found in the spectral range where Sn–Sn modes are expected, but the polarization properties of these features suggest an overlap with disorder-activated Ge-acoustic phonons. Additional features observed in "forbidden" scattering configurations are also assigned to disorder-activated Raman scattering.
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1. Introduction

The recent development of new pathways for the growth of $Ge_{1-y}Sn_y$ and $Ge_{1-x-y}Si_xSn_y$ alloys on Si substrates has renewed the interest in Sn-containing group-IV semiconductors [1,2]. These materials enable new strain engineering solutions and offer the tantalizing perspective of becoming direct band gap semiconductors for modest Sn concentrations. From a basic physics perspective, the scaling of electronic and vibrational properties between the elementary semiconductors Si, Ge and α-Sn suggests that the properties of their alloys should be related by some type of scaling relationship. This conjecture is supported by recent experimental studies on the bowing coefficients in the compositional dependence of optical transitions [3] as well as by Raman results concerning the compositional dependence of the Ge–Ge Raman feature in $Ge_{1-y}Sn_y$ alloys, which can be predicted from the compositional dependence of the Si–Si Raman mode in $Si_{1-x}Ge_x$ alloys [4]. These Raman studies were recently extended to ternary $Ge_{1-x-y}Si_xSn_y$ alloys [5].

In this paper, we present a new Raman study of $Ge_{1-y}Sn_y$ alloys. Whereas our previous work [4] concentrated on the compositional dependence of the Ge–Ge alloy mode, we report the observation of additional alloy modes and study their compositional dependence. In addition, we reassess the compositional dependence of the Ge–Ge mode by explicitly correcting for the small residual strain present in samples grown on Si substrates.

2. Experiment

Our samples were grown directly on Si wafers using a specially developed CVD method involving reactions of Ge_2H_6 with SnD_4 in high purity H_2 (10%). This formulation provides the simplest possible CVD source of Sn atoms [1,6]. Thick and atomically flat films were grown at 250–350 °C. Dislocation densities at the film surfaces were not measured for these samples, but for material grown under identical conditions they are typically in the $\sim 10^5$ cm^{-2} range. The large lattice mismatch between $Ge_{1-y}Sn_y$ and Si is relieved by Lomer dislocations at the interface, as previously reported [1, 6]. The Sn concentrations were determined from Rutherford Backscattering experiments using the RUMP simulation

* Corresponding author.
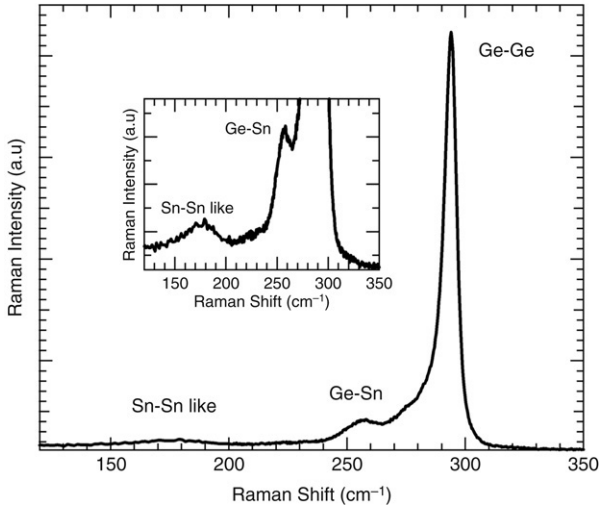 E-mail address: vijay.dcosta@asu.edu (V.R. D'Costa).

Fig. 1. Room temperature Raman spectrum for a $Ge_{0.88}Sn_{0.12}$ alloy measured with 647.1 nm excitation. The inset shows the Ge–Sn and Sn–Sn like modes in more detail. The scattering configuration was $z(x, y)\bar{z}$, as defined in the text.

code [7]. X-ray measurements were carried out using a Panalytical X'Pert MRD system. We assumed a tetragonal distortion, and determined the lattice constants $a_\perp$ and $a_\parallel$ (in the film growth direction and plane, respectively) from line scans and reciprocal space maps for the symmetric (004) and asymmetric (224) Bragg reflections. These were referenced for each sample using the corresponding reflections of the Si substrate. The relaxed lattice constant a was calculated from $a_\perp$ and $a_\parallel$ using Ge elastic constants [8].

Raman experiments were performed at room temperature in the backscattering $z(x, y)\bar{z}$ and $z(x, x)\bar{z}$ directions, where x, y, and z correspond to the $\langle 100 \rangle$, $\langle 010 \rangle$, and $\langle 001 \rangle$ crystal directions, respectively. We used the 514.5 nm line of an Ar$^+$ laser and the 647.1 nm line of a Kr$^+$ laser. The light was focused on the sample with a $100\times$ objective and analyzed with a single-stage monochromator equipped with a 2400 lines/mm grating. A nitrogen-cooled charge coupled device (CCD) was used as a detector. A typical spectrum obtained with 647.1 nm excitation is shown in Fig. 1. In analogy with the well-studied $Si_{1-x}Ge_x$ alloys, we expect to observe Raman features corresponding to Ge–Ge, Ge–Sn, and Sn–Sn modes. Since our samples are Ge-rich, the strongest peak can be easily associated with Ge–Ge vibrations. Its frequency approaches the Raman frequency of pure Ge, which we determine to be 301 cm^{-1} at room temperature. The second peak near 255 cm^{-1} is assigned to Ge–Sn vibrations. The lowest-energy structure near 175 cm^{-1} is the closest to the Raman-active mode in α-Sn (197 cm^{-1}) and could therefore be assigned to Sn–Sn vibrations. The validity of these assignments is discussed in detail below.

We analyze the Raman lineshapes using a model developed by Lockwood and Walisewski for $Al_xGa_{1-x}As$ alloys [9]. The peaks are written as $I(\omega) = I_{back}(\omega) + I_{EMG}(\omega)$. The background intensity $I_{back}(\omega)$ is taken as $b_1 + b_2\omega^{-m}$, and the Exponentially Modified Gaussian (EMG) function $I_{EMG}(\omega)$ is

defined as

$$I_{EMG}(\omega) = \frac{a}{2s} \exp\left(\frac{w^2}{2s^2} + \frac{\omega_0 - \omega}{s} \right)$$
$$\times \left[\text{erf}\left(\frac{\omega - \omega_0}{\sqrt{2}w} - \frac{w}{\sqrt{2}s} \right) + \frac{s}{|s|} \right], \quad (1)$$

where a is the peak area, ω_0 the mode frequency, w is the width and s is the so-called asymmetry parameter. We thus have four EMG parameters per peak in addition to the parameters b_1, b_2 and m for the background function. These parameters are obtained from a fit to the experimental data. We then plot the resulting I_{EMG} function for each *individual* peak and use the frequency ω_{max}, at which this function has a maximum, as the peak position that is subsequently graphed as a function of composition. This agrees with the conventional definition of peak frequencies in semiconductor alloys. This procedure is necessary because the mode frequency parameter ω_0 does not coincide with the maximum of the EMG function when the peak is asymmetric.

A tetragonal lattice distortion splits the triply-degenerate zone center optical phonons in diamond structure semiconductors into a doublet – polarized in a plane parallel to $a_\parallel$ – and a singlet – polarized parallel to $a_\perp$. For the standard Raman backscattering configuration at the (001) face, only the singlet is observable, and its frequency shift is approximately given by [10,11]

$$\Delta\omega = -2\omega_0 \left[\gamma \left(1 - \frac{C_{12}}{C_{11}} \right) + \frac{a_s}{3} \left(1 + \frac{2C_{12}}{C_{11}} \right) \right] \varepsilon_\parallel = b\varepsilon_\parallel, \quad (2)$$

where ω_0 is the unstrained Raman frequency, C_{11} and C_{12} are elastic constants, γ is the Grüneisen parameter, a_s the shear phonon deformation parameter, and $\varepsilon_\parallel$ the in-plane strain $\varepsilon_\parallel = (a_\parallel - a)/a$. The Grüneisen and shear phonon deformation parameters are related to the phonon deformation potentials p and q introduced by Ganesan et al. [10] by $\gamma = -(p + 2q)/6\omega_0^2$ and $a_s = (p - q)/2\omega_0^2$. For Ge, Cerdeira et al. found $p/\omega_0^2 = -1.47$ and $q/\omega_0^2 = -1.93$ (Ref. [12]). Using $C_{12}/C_{11} = 0.376$ (Ref. [8]) and $\omega_0 = 301 \text{ cm}^{-1}$, we obtain a strain shift coefficient $b_{Ge} = -415 \text{ cm}^{-1}$. The value of the square bracket in Eq. (2) is approximately the same for all group-IV semiconductors, and therefore we use Ge-values for our Ge-rich $Ge_{1-y}Sn_y$ films. The strongest contribution to the compositional dependence of the parameter b originates from the compositional dependence of the unstrained frequency ω_0. For the Ge–Ge mode we simply use the pure Ge value, since the correction is within the experimental error of the parameters in Eq. (2) For the Ge–Sn mode we use $b_{Ge-Sn} = 356 \text{ cm}^{-1}$. We emphasize that the strain corrections are relatively small, the largest value of strain in our samples being $|\varepsilon| \sim 0.004$. Therefore, including the possible compositional dependence of the strain shift parameters amounts to a small correction which should have a negligible impact on the compositional dependence of the frequencies studied in this paper.