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Infrared vibrations of interstitial oxygen in silicon-rich SiGe alloys

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Abstract

We report on the infrared spectra of the antisymmetric stretching vibration of O_i in Si-rich $Si_{1-x}Ge_x$ alloys. The shift of its frequency is obtained as a function of the germanium content x below ~0.5. We present a decomposition of the low-temperature spectra using Gauss–Lorentz profiles. A low-lying broad band is found for $x = 0.08$, and assigned tentatively to the vibrations of Si_2O units with the nearest sites occupied by several Ge atoms. We compare our experimental findings with results of a recent ab initio study of the phonon modes.

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1. Introduction

The infrared active local vibrations of interstitial oxygen (O_i) in silicon-germanium alloys have been studied several times, see, e.g., Refs. [1–4] and references therein. In particular, the recent ab initio study [4] of the electronic structure and phonon spectra for Si-rich alloys is appealing because it aims at a deeper understanding of the changes introduced into the vibrations of the Si_2O quasimolecules by nearby Ge atoms.

The background lattice absorption, due to the multiple-phonon as well as single-phonon ("Si–Si" and "Si–Ge", allowed due to the loss of symmetry in the alloys) transitions, has been reported and analyzed in our previous work [5]. Here, we focus on the infrared absorption due to the antisymmetric stretching vibration of O_i causing the "$1106\,cm^{-1}$" room temperature band in Si, for the Si-rich alloys. We have selected the three following aspects of the fairly complex behavior of this band: (i) the shift of its position as a function of the germanium content x in $Si_{1-x}Ge_x$ for x below ~0.5, (ii) the composite structure of the spectrum for $x = 0.019$, and (iii) a low-lying satellite which appears in the spectra for higher values of x. We discuss the data in terms of the occupation probabilities of the lattice sites, and compare the results with the recent calculations.

2. Experiment

The samples were 1–2 mm thick slices of Czochralski-grown $Si_{1-x}Ge_x$ alloys, single crystalline for $x \leqslant 0.02$ and polycrystalline beyond. They were not intentionally doped; however, the typical concentration of $\sim 10^{15}$ free holes per cm^3 leads to a weak, Drude-like contribution to the absorption. A spurious decrease of transmittance due to the scattering of light, preventing a part of the transmitted light from reaching the detector, has also been observed occasionally. This effect is the strongest near $x = 0.5$, and results probably from the fluctuations of the refractive index due to spatial fluctuations of the composition. However, the two spectrally flat contributions can be easily accounted for and do not influence our results. The alloy compositions were determined from the spectroellipsometric data in the visible and the ultraviolet [6]. The oxygen content was not controlled during the growth and was of the order of $10^{18}\,cm^{-3}$.

The transmittance has been measured with a BRUKER IFS55 and 66 spectrometers, equipped with a liquid

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nitrogen and liquid helium cryostats. The resolution was set to 0.25 wavenumbers for the sharpest low temperature spectra.

3. Results and discussion

3.1. Band position as a function of alloy composition

The lowering of the band position with increasing Ge content resulting from our data is plotted in Fig. 1. The Si_2O unit has 6 nearest neighbors and 12 next-nearest neighbors, as shown in the inset. We use the notation of Ref. [4] for the lattice sites within the Si_2O unit (A), the next- (B) and second-nearest (C) neighbors, respectively. According to Ref. [4], the downward shift of the resonance frequency is partly due to the heavier Ge atom substituting for Si on the sites B and C; however, changes in chemical bonding are also found to be important. The all-^{28}Si cluster of Ref. [4] resonates at $1107.2\,\mathrm{cm}^{-1}$, while one Ge atom substituted in position B results in a lower value of the frequency of $1046.3\,\mathrm{cm}^{-1}$; this shift seems to contradict the measured data. Assuming the binomial distribution of the occupation probabilities,

$$P_N(m) = \frac{N!}{m!(N-m)!}\, x^m (1-x)^{N-m}, \quad m = 0, \ldots, N, \tag{1}$$

the probability of all six sites B occupied by Si for the center $x = 0.5$ of the composition range is as low as $P_6(0) = 0.016$. All remaining configurations should have vibration frequencies lower by at least $60\,\mathrm{cm}^{-1}$, much more than the actually observed value of about $15\,\mathrm{cm}^{-1}$. The computed downward shift due to one Ge atom in position C (next-nearest neighbor) is $46\,\mathrm{cm}^{-1}$; the discrepancy extends to this coordination ($P_{12}(0) = 0.00024$). For the $x = 0.5$ alloy, the absence of a significant number of the Ge atoms adjacent to the Si_2O unit or in its second coordination sphere seems to be highly improbable. Note that the linear shift of $17.5\,\mathrm{cm}^{-1}$ between pure Si and Ge reported in Ref. [3] is significantly smaller compared to our slope for the Si-rich alloys.

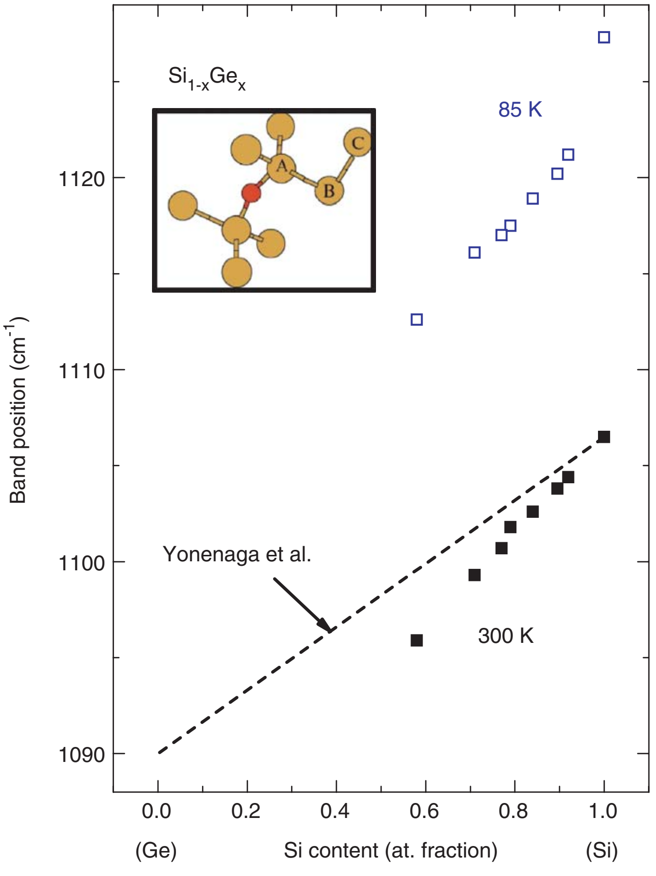

Fig. 1. Position of the main band of the asymmetric stretching vibration of the Si_2O molecule (shown in the inset) at 300 and 85 K. The linear composition dependence reported in Ref. [3] is shown as the dashed line.

3.2. Separation of bands in the spectra of alloys

We show in Fig. 2 the low-temperature spectra of three samples, including pure Si. They have been normalized to the same peak height in order to enable a better comparison of the lineshapes. Since the lowest attainable sample temperature in our cryostat was about 10 K, we can see traces of the "hot" transitions at $1128\,\mathrm{cm}^{-1}$. Our data are similar to the previously reported results of Refs. [1] and [2].

We have fitted the measured spectra with sums of the convolutions of Gaussian and Lorentzian (GL) profiles, which have been found to be efficient for representing the fundamental optical spectra of the alloys in NIR–VIS–UV in Ref. [7]. The Gaussian part of the width is indicative of independent contributions to the frequency shifts due to

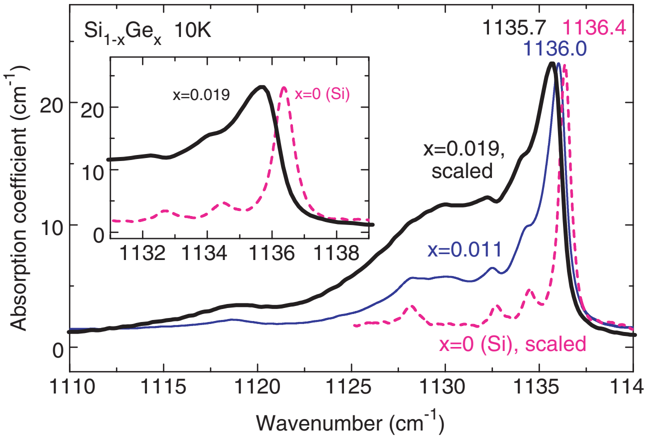

Fig. 2. Absorption spectra of Si (dashed lines) and two samples of the SiGe alloys with low Ge content (solid lines), measured at 10 K with the resolution of $0.25\,\mathrm{cm}^{-1}$. The inset shows the leading peaks on an expanded scale, to visualize the strong asymmetry of the alloy band, underlying the two low-frequency satellites of the heavier Si isotopes.