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LOCALIZED VIBRATIONAL MODES OF INTERSTITIAL OXYGEN IN $\text{Si}_x\text{Ge}_{1-x}$ ALLOYS

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We study infrared-active vibrations of interstitial oxygen in Czochralski-grown samples of $\text{Si}_x\text{Ge}_{1-x}$ alloys with the silicon content from 0 to 1 between room and liquid nitrogen temperature. The measurements were performed on a large series of samples including single crystals of Si and Si-rich alloys, and polycrystalline samples of alloys with a higher Ge content. We focus on quantitative data on the compositional and temperature evolution of the strongest absorption band above 1100 cm^{-1} , related to the asymmetric stretching of the Si_2O pseudomolecule. We have also observed a pronounced Fano-like resonance centered at 520 cm^{-1} .

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In Czochralski-grown silicon, germanium, and $\text{Si}_x\text{Ge}_{1-x}$ alloy crystals, oxygen exists primarily as an interstitial defect (O_i). The infrared-active vibrations of O_i in Si and Ge have been studied many times. Recently, the structure, dynamics and infrared polarizability have been revised for both Si:O and Ge:O, see Refs. [1–3] and references therein.

In this paper, we report the basic characteristics of the most prominent O_i absorption bands in the alloys. The results are obtained from a comprehensive set of measurements on 19 samples, covering the whole compositional range from pure Si to pure Ge, performed in the temperature range of 85–300 K. Our main aim is to provide quantitative data on the compositional and temperature evolution of the strongest, localized-vibration band related to the asymmetric stretching of the Si_2O pseudomolecule. This band is located at *ca.* 1106 cm^{-1} in Si at room temperature, and is known to exhibit a composite structure at low temperatures [4–6]. We also report on the structure related to the lower-frequency infrared-active mode, occurring at about 520 cm^{-1} in pure Si.

The measurements have been performed on single-crystal and polycrystalline samples grown by Czochralski (CZ) method. The samples were not intentionally doped; the free-hole concentration at room temperature was typically *ca.* 10^{15} cm^{-3} . The oxygen concentration was about 10^{18} cm^{-3} throughout the

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whole compositional range. The sample thickness ranged from 1 to 2 mm. Transmission measurements have been performed with a FTIR spectrometer Bruker IFS55, with the spectral resolution of 1 cm^{-1} . The background of two- and three-phonon absorption of the defect-free silicon lattice has been measured on a float-zone (FZ) sample, having a negligible concentration of O_i . Another source of the absorption background is the free-hole plasma, which can be easily identified due to its monotonic Drude-like increase towards lower frequencies.

Fig. 1. Low-temperature (85 K) spectra of several silicon-rich samples in the range of symmetric (lower panel) and asymmetric (upper panel) stretching vibrations of interstitial oxygen.

In Fig. 1 there is an overview of the spectra of absorption coefficient for silicon-rich alloys in two separate frequency ranges at 85 K. The band above 1100 cm^{-1} shifts towards lower frequencies with increasing Ge content, becomes broader, and its fine structure is almost completely lost for $x \geq 10$ atomic % Ge. It is related to the asymmetric stretching of the Si_2 unit; the resonance frequency is expected to decrease with the substitution of at least one of the six adjacent silicon atoms with the heavier atom of Ge. We were able to identify this band for the Ge content up to *ca.* 80 at.%. The peak positions extracted from the data taken at several temperatures are listed in Table. Note the monotonic changes of the peak positions and their temperature coefficients, α_1 , with changing the alloy composition.

The multiple-component spectra of the high-frequency band are shown in Fig. 2 for silicon and the 2.2 at.% Ge alloy. In order to quantify the influence of alloying, we have fitted the spectra with a sum of Gauss-Lorentz (G-L) oscillators. The Gaussian and Lorentzians profiles of variable widths were convoluted and their parameters adjusted to the measured data. Besides the increase in the

TABLE

Observed compositional dependence of the asymmetric stretching vibration of interstitial oxygen in $\text{Si}_x\text{Ge}_{1-x}$ alloys. Parameters of the best-fit linear regression, $\nu(T) = a_0 + a_1(300 [\text{K}] - T)$, in the 85–300 K range.

x	ν (300 K) [cm^{-1}]	ν (85 K) [cm^{-1}]	a_0 [cm^{-1}]	a_1 [$10^{-3} \text{ cm}^{-1} \text{ K}^{-1}$]
1(Si)	1106.5	1127.3	1106.4 ± 1.0	100 ± 7
0.994	1107.8	1127.0	1107.7 ± 1.1	90 ± 7
0.979	1107.5	1126.4	1106.3 ± 1.3	91 ± 9
0.978	1106.3	1127.3	1107.0 ± 0.9	93 ± 6
0.920	1104.4	1120.7	1104.4 ± 0.3	74 ± 2
0.900	1102.6	1119.6	1102.5 ± 0.3	80 ± 1
0.890	1105.0	1120.7	1104.8 ± 0.4	74 ± 3
0.840	1102.6	1118.9	1102.5 ± 0.6	75 ± 4
0.790	1101.8	1116.5	1101.9 ± 0.4	71 ± 3
0.770	1100.7	1117.0	1100.2 ± 0.8	75 ± 6
0.710	1099.3	1116.1	1099.2 ± 0.3	78 ± 2
0.580	1095.9	1112.6	1095.8 ± 0.4	79 ± 3
0.510	1091.8	1111.4	1091.8 ± 0.2	96 ± 1
0.390	1091.6	1111.3	1092.0 ± 1.2	89 ± 8
0.208	1090.8	1109.8	1090.8 ± 1.0	86 ± 5

Gaussian widths with increasing Ge content, the data show an interesting behavior of the band positions. The three main components of Si are located at 1123.0 ± 0.1 , 1127.3 ± 0.1 and at $1135.6 \pm 0.1 \text{ cm}^{-1}$. Upon adding 2.2 at.% Ge, the band positions become 1120.6 ± 0.2 , 1127.3 ± 0.3 and 1134.5 ± 0.2 . In addition, we find a new weak band at $1101.5 \pm 1.0 \text{ cm}^{-1}$. While the two outer components of the strong triplet shift towards lower frequencies, the 1127 cm^{-1} band stays constant. This behavior has been confirmed by separating the individual bands by numerical differentiation of the measured spectra in a broader range of compositions. Assuming the rotational origin of the composite structure [4, 7], we are able to estimate the changes in the bonding due to the presence of Ge in Si matrix. Namely, the difference between a fundamental vibration at about 1135 cm^{-1} and the nearest lower band is 8.3 cm^{-1} in pure Si and 7.2 cm^{-1} in $\text{Si}_{0.978}\text{Ge}_{0.022}$. This corresponds to a possible decrease in Si–O–Si bond angle of about 10% due to the substitution of one Si atom by the heavier and larger Ge atom.

The low-frequency range of Fig. 1 is dominated by a strongly asymmetric spectral structure centered at 520 cm^{-1} . In some of the samples, the structure is actually an *antiresonance*, see the 2.1 at.% data of Fig. 1. We have noticed a significant correlation of this line shape with the strength of the background ab-

Fig. 2. The best fit line shapes (solid lines) of the measured spectra at 85 K (open symbols) for silicon (lower panel) and the alloy of 2.2 at.% germanium (upper panel). The arrows indicate the positions of the individual G-L bands.

sorption. Since a part of the background absorption is due to the free-hole plasma, we assign tentatively the observed spectra to a Fano-type resonance between the dipole-forbidden, one-phonon absorption in the silicon lattice and the continuum of intravalence electronic transitions. The latter spectra have been identified reliably at higher *p*-type dopings, see, e.g., Refs. [8, 9] and references therein. This assignment is further supported by the weak dependence of the resonance position on the Ge content. In fact, the oxygen-related threshold below 520 cm^{-1} in Si has been interpreted as the vibration of the Si lattice induced by the bond-breaking O_i [2]. This spectral structure shifts rather strongly to lower frequencies ($\approx 330\text{ cm}^{-1}$) in Ge:O [1].

In conclusion, we have identified the strongest effects of alloying on the infrared spectra of interstitial oxygen. Further work is conducted to extend these results.

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