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Oxygen in Ge:Sn

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The effect of doping with tin on the ν_3 vibrational mode of oxygen in Ge has been studied. The appearance of three new series of absorption lines besides the ν_3 oxygen vibration spectra was found. The spectrum structure in each series of lines found is similar to the ν_3 oxygen spectrum structure in Ge. But unlike the ν_3 mode, the fine structure due to rotational–vibrational interaction of the ν_3 and ν_2 modes is not observed and the spectrum structure remains up to temperatures of 130 K. The found three sets of absorption lines are ascribed to the ν_3 vibration of interstitial oxygen disturbed by tin atoms located in the nearest environment. The assumption has been made that no rotation of oxygen around a Ge–Ge bond for a Ge–O–Ge quasi-molecule disturbed by a neighbour Sn atom occurs.

1. Introduction

In recent years Ge attracts the attention of researchers as a material alternative to Si, which can be used for the creation of 22 nm CMOS (complementary metal–oxide semiconductor) devices. The main advantage of Ge is a higher mobility than in Si. So, the electron mobility in Ge is nearly three times higher as that in Si, and Ge is characterized by the highest hole mobility of all known semiconductors. It is expected that the carrier mobility in Ge can be increased still more by creating conditions in the matrix for occurrence of compression stresses. Such conditions can be created e.g. by doping Ge with Sn or Si.

To obtain a material with specified parameters, identification of defects and knowledge of their fundamental properties and possible interaction channels are required first of all. However, in spite of a great interest in Ge, the structure and fundamental characteristics of the defects resulting from growth and external actions (heat treatment, irradiation) remain undetermined to date. So, the properties of oxygen-related defects in Ge are studied scantily.

When oxygen is incorporated into Ge, it breaks the bond between the neighboring atoms and forms with them a bent Ge–O–Ge quasi-molecule [1–3]. This quasi-molecule must have three normal vibrational modes. However, only two modes have been identified for certain in Ge: the band near 860 cm^{-1} (ν_3 vibration) has been found in absorption spectra, and the low energy rotational ν_2 mode has also been detected by phonon spectroscopy [3–8].

The absorption spectrum of oxygen (O_i) in the ν_3 vibration region at low temperatures in Ge is known to have a complex structure and to consist at low temperatures of more than 25 lines [3,7]. The structure in the absorption spectrum arises from two effects: owing to different combinations of isotopes in a quasi-molecule

(natural Ge is known to consist of five isotopes) and rotational–vibrational interaction of the ν_3 and ν_2 modes. Near the helium temperature in addition to the ground rotational state, three excited states, which are at distances of 0.18, 0.67 and 1.37 meV from the ground state, are highly occupied [6–8]. Therefore, four absorption lines are observed for each isotopic composition [9,10].

In the present work, the effect of doping with tin on the absorption of oxygen in the Ge lattice has been studied.

2. Experimental details

We have studied *n*-type of O and Sn doped Ge grown by the Czochralski technique (Cz-Ge). The oxygen concentration in the samples was determined at room temperature from the peak absorption near 862 cm^{-1} using the conversion factor $1.05 \cdot 10^{17}\text{ cm}^{-3}$ [11] and was $(1.7\text{--}2.76) \cdot 10^{17}\text{ cm}^{-3}$. The Sn content in the samples was changed from $1 \cdot 10^{19}$ to $4 \cdot 10^{19}\text{ cm}^{-3}$. The sample Ge:Sn grown by floating zone method and the undoped with tin Ge sample with the oxygen content of $1.1 \cdot 10^{17}\text{ cm}^{-3}$ were also studied.

Absorption spectra in the range of the ν_3 vibrational mode of oxygen have been studied. The spectra were recorded by Bruker Fourier-transform spectrometer IFS-113v. The measurements were performed in the temperature interval 8–300 K with the spectral resolution of $0.06\text{--}0.1\text{ cm}^{-1}$.

3. Experimental results and discussion

Doping of Ge with tin gives rise to a number of peculiarities in the ν_3 vibration region of oxygen. Fig. 1 shows the O_i absorption spectra in the ν_3 vibration region registered at 8 K for Ge (curve 1) and Ge:Sn (curve 2).

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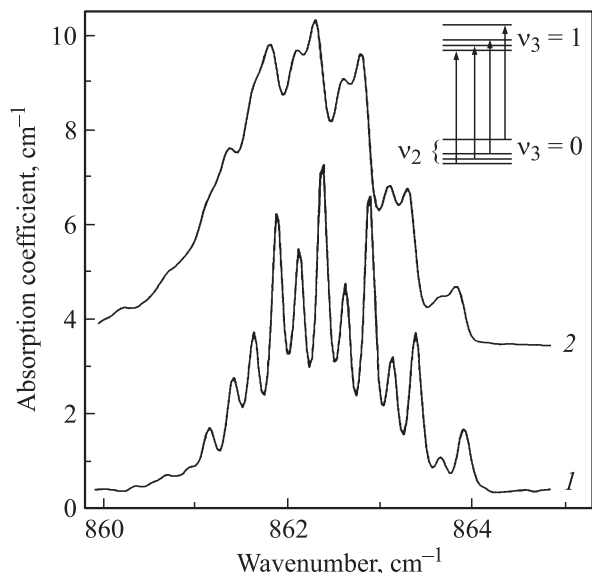


Fig. 1. Absorption spectra of oxygen in Ge (1) and Ge:Sn (2) in the ν_3 mode region. In the insert the scheme of transitions is shown. The spectra were registered at 8 K with resolution of 0.1 cm^{-1} . $N_{\text{Sn}} = 4 \cdot 10^{19} \text{ cm}^{-3}$.

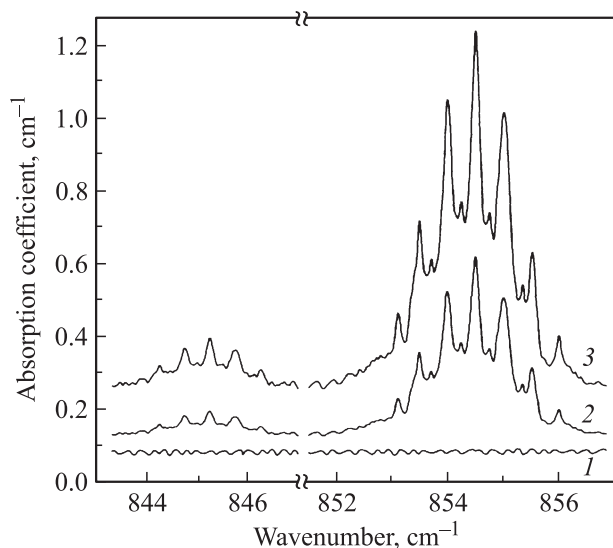


Fig. 2. Series of lines observed in Cz-Ge doped with Sn. The spectrum was registered at 8 K with resolution of 0.1 cm^{-1} . N_{Sn} , cm^{-3} : 1, 3 — $4 \cdot 10^{19}$, 2 — $1 \cdot 10^{19}$. 1 — the sample was grown by the floating zone process.

It is seen that in Ge doped with Sn lines broaden that results in overlap of closely components and disappearance of the fine spectrum structure. A small shift of bands towards the low-frequency spectral region is also observed. Besides, the appearance of two new series of lines is observed in the wavenumber ranges $852\text{--}856$ and $843\text{--}847 \text{ cm}^{-1}$. Fig. 2 shows the absorption spectra found. The investigation of samples with various Sn content have shown that the intensity of series of lines found rises with increasing Sn

content and no absorption is observed in the Ge:Sn samples grown by floating zone process (Fig. 2).

The spectrum structure in each found series is similar to the structure of the ν_3 mode in Ge, appearing owing to different combinations of Ge isotopes in a quasi-molecule Ge–O–Ge. The distance between the components in each set of lines is equal to the distance between the lines corresponding to different isotopic Ge combinations in the ν_3 mode region in Ge undoped with Sn, and the frequency spaces, in which the ν_3 vibration and the spectra found are observed, are equal. As distinguished from the ν_3 oxygen mode structure in Ge, the fine structure due to rotational–vibrational interaction of the ν_3 and ν_2 modes is not observed for individual lines in each found series even at resolution of 0.03 cm^{-1} . The structure in found series of lines differs also from the ν_3 modes in Ge: the lines do not overlap one with other.

In addition to the found two series of lines, an additional absorption with weak structure is also observed in the low-frequency wing of the ν_3 mode (Fig. 3). This spectral region is known to be determined by absorption due to quasi-molecules with the isotopic composition $^{76}\text{Ge}\text{--O--}^{76}\text{Ge}$. If to decompose this part of the spectrum into components and to subtract the absorption corresponding to $^{76}\text{Ge}\text{--O--}^{76}\text{Ge}$ quasi-molecules with taking into consideration the shift and broadening of lines in Ge:Sn, one can single out a part of additional absorption (Fig. 3), which is analogous to the two series of lines observed in the low-frequency spectral region. It is impossible to single out fully the additional absorption in this spectral region because of

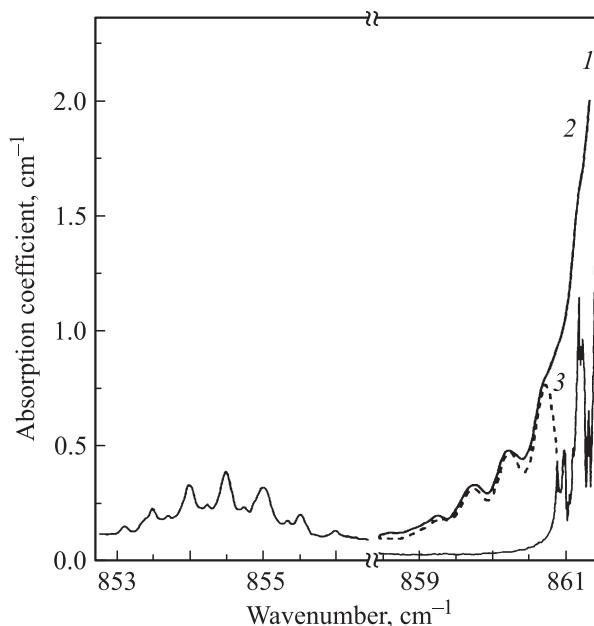


Fig. 3. Additional absorption in the range of the ν_3 oxygen vibration in Ge:Sn. N_{Sn} , cm^{-3} : 1 — 0; 2 — $4 \cdot 10^{19}$. 3 — component of additional absorption in Ge:Sn. The spectra were registered at 8 K with resolution of 0.06 cm^{-1} .

The positions (in cm^{-1}) of the lines for ν_3 oxygen mode in Ge and for two found series of lines in Ge doped with tin and comparison with average Ge mass (M_{aver}) in Ge–O–Ge quasi-molecule

Line	M_{aver}	Ge	Ge:Sn(2)	Ge:Sn(3)
1	70	863.89	856	
2	71	863.37	855.49	846.23
3	71.5	863.13	855.24	845.98
4	72	862.88	854.99	845.73
5	72.5	862.62	854.73	845.48
6	73	862.37	854.48	845.23
7	73.5	862.12	854.23	844.98
8	74	861.88	853.98	844.73
9	74.5	861.63	853.73	844.47
10	75	861.39	853.48	844.23
11	76	860.88	853.1	

the superposition of intense absorption from other isotopic combinations in Ge–O–Ge quasi-molecules.

In our view, the absorption detected cannot correspond to Ge–O–Sn quasi-molecules, because in this case the appearance of only one series of lines would be observed, the spectrum structure would consist of only five components, and a larger shift towards the low-frequency spectral region must be observed due to a considerable increase in the quasi-molecule mass. The similarity of the spectra structure found in Ge:Sn to that of the ν_3 mode in Ge undoped with Sn and their dependence on the tin content of the samples allow the assumption to be made that the absorption detected corresponds to the ν_3 mode of Ge–O–Ge quasi-molecules perturbed by neighboring Sn atoms. Like the effect which was observed earlier in silicon doped with isovalent impurities [12], we assume that the three sets of absorption lines found correspond to the ν_3 vibration of Ge–O–Ge quasi-molecules perturbed by tin atoms that are situated in the first, the second and the third coordination environments. The positions of the lines observed for the ν_3 oxygen mode in Ge and for two found series of lines in Ge doped with tin and comparison with average Ge mass (M_{aver}) in a Ge–O–Ge quasi-molecule are listed in Table.

Assuming the random distribution of Sn atoms in the Ge lattice, the amount of quasi-molecules with Sn atoms in the nearest coordination environment may be estimated using the probability theory. The probability that i Sn atoms are in the j -th coordination sphere containing m atoms is defined by the following expression:

$$P(i, j) = c_m^i x^i (1-x)^{m-i}, \quad (1)$$

where c_m^i is the number of i -combinations of m elements, x is the Sn content in Ge.

Using eq. (1) we have estimated the dependence of the probabilities (W) that Sn atoms fall into the first, the second and the third coordination arrangements relative to the Ge–O–Ge quasi-molecule on the concentration

of Sn (N_{Sn}). Fig. 4 shows the obtained values of the probabilities of 1 Sn atom to be located in the first, the second and the third coordination environments of a quasi-molecule at Sn concentrations in the interval $4.5 \cdot 10^{17} \leq N_{\text{Sn}} \leq 10^{20} \text{ cm}^{-3}$. It can be seen that the probability of a Sn atom appearing in the nearest coordination arrangements relative to a Ge–O–Ge quasi-molecule increases with increasing the Sn content, and at a given content the probability of a Sn atom appearing in more distant spheres exceeds that for nearer spheres. The respective intensities of absorption components should then be proportional to the probabilities of Sn atom arrangement in the corresponding spheres. As the disturbance should be maximum for Ge–O–Ge with Sn atom in the first coordination neighbourhood and should decrease with increasing distance between the quasi-molecule and the source of disturbance, we may suppose that absorption appearing in Ge with Sn in the ranges 843–847, 852–856 and near 860.5 cm^{-1} corresponds to Ge–O–Ge quasi-molecules disturbed by Sn atoms located in the first, the second and the third coordination neighbourhood, accordingly.

The behavior of the absorption spectra found as the measurement temperature is increased appears to be interesting. In Ge undoped with Sn, as the temperature rises from the helium temperature the absorption lines in the ν_3 mode region broaden, the individual structural components merge gradually and whole spectrum shifts towards low frequencies. This happens because the excited states of ν_2 rotational sublevels are filling with rising of temperature. Besides, as the temperature rises the probability of transitions to higher excited ν_3 vibrational states increases [3,7]. As a result of these two effects, a considerable part of the ν_3 spectrum structure disappears at as low temperature as 20 K.

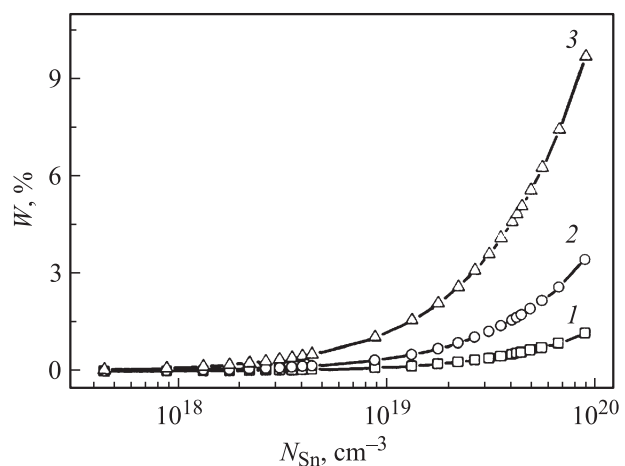


Fig. 4. Dependencies of probability (W) of Sn atom positions in the first (1), in the second (2) and in the third (3) coordination arrangement relative to Ge–O–Ge quasimolecule on Sn content in Ge.

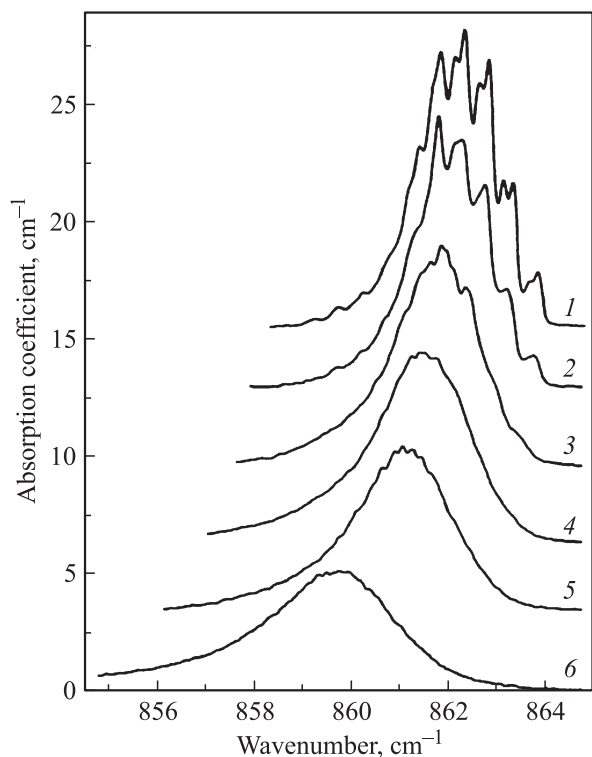


Fig. 5. Temperature dependence of the ν_3 mode for Ge:Sn. T , K: 1 — 8, 2 — 20, 3 — 50, 4 — 70, 5 — 100, 6 — 160. $N_{\text{Sn}} = 4 \cdot 10^{19} \text{ cm}^{-3}$. The spectra were registered with resolution of 0.1 cm^{-1} .

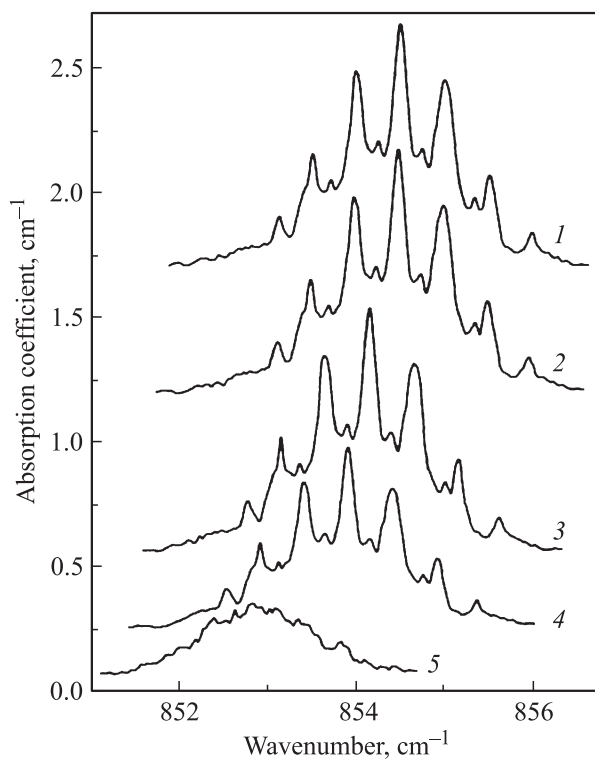


Fig. 6. Temperature dependence for the lines of the series found in Ge:Sn. T , K: 1 — 8, 2 — 20, 3 — 70, 4 — 100, 5 — 160. The spectra were registered with resolution of 0.1 cm^{-1} , $N_{\text{Sn}} = 4 \cdot 10^{19} \text{ cm}^{-3}$.

In Sn-doped Ge the absorption spectrum in the oxygen ν_3 mode region behaves in much the same way as in Ge. The temperature dependence for the ν_3 mode in Ge:Sn is demonstrated in Fig. 5. It is seen that as the temperature raises the fine spectrum structure disappears, and the spectrum shifts towards low frequencies. At $T > 20 \text{ K}$ the spectrum becomes to transform gradually into a broad structureless band with full width at half maximum comparable with that characteristic of the band of Ge undoped with Sn.

The behavior of the new series of lines found in Ge:Sn differs greatly from that of ν_3 vibration. Fig. 6 shows the temperature dependence of the spectrum for one from the found series of lines. Unlike the ν_3 mode, the spectrum structure remains up to temperatures of $T \leq 130 \text{ K}$. Besides the shift of lines to low frequencies, a difference with the ν_3 mode in Ge and Ge:Sn in the temperature range 8–20 K is practically absent for found series of lines. At $T > 20 \text{ K}$ the lines start to shift gradually to low frequencies and only at temperature $T > 130 \text{ K}$ the spectrum transforms into a broad structureless bands and the shift value relative to helium temperature approaches that for ν_3 mode in Ge and Ge:Sn.

The absence of fine spectrum structure owing to rotational–vibrational interaction and existence of the spectra structure, appearing due to different isotopic combinations of Ge atoms in Ge–O–Ge quasi-molecules, in wide temperature interval seems to indicate no rotation of the oxygen atom for a Ge–O–Ge quasi-molecule disturbed by a neighbour Sn atom. Therefore, there is apparently no structure smearing in the temperature range 4.2–130 K owing to absence of rotational–vibrational interaction. At higher temperatures, a superposition of transitions in thermally filled excited vibrational states takes place, as for the ν_3 vibration in Ge and Ge:Sn.

4. Summary

The effect of doping with tin on the ν_3 vibration of oxygen in Ge has been studied. It has been shown, that the lines in the range of the ν_3 mode broaden in Ge doped with Sn, what results in overlap of closely spaced components and disappearance of the fine spectrum structure. Besides, the appearance of the three series of absorption lines was found. The spectrum structure in each found series is similar to the structure of the oxygen ν_3 vibration spectrum in Ge appearing due to different combinations of Ge atoms in Ge–O–Ge quasi-molecules. But unlike the ν_3 mode any fine structure due to coupling of the ν_3 mode, with the low energy rotational ν_2 mode is not observed and the spectrum structure remains up to temperatures of $T \leq 130 \text{ K}$. The found three sets of absorption lines are ascribed to the ν_3 vibration of interstitial oxygen disturbed by tin atoms located in the first, the second and the third quasi-molecule environments. The assumption has been made that no rotation of the oxygen occurs for a Ge–O–Ge quasi-molecule disturbed by a neighbour Sn atom.

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