The effect of oxygen impurity on the emission by bound excitons in silicon

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The dependence of the shape of the emission band of excitons bound to phosphorus atoms in silicon on the oxygen concentration has been investigated. It is shown that the dependence observed can be explained quantitatively by an increase in the width of the forbidden band as a result of random extension of the crystal lattice on introducing interstitial oxygen.

It has been found[1] that the width of the emission band of excitons bound to phosphorus atoms in silicon containing less than 10^{15} cm^{-3} oxygen, is not more than 5 μeV, while for a concentration $\approx 10^{18}$ cm^{-3} this band broadens to ≈ 100 μeV. The quantitative relations between the shape of the emission band of bound excitons and oxygen concentration N is established in the present work. Silicon specimens containing phosphorus as the principal or residual impurity, with concentrations 10^{13}–10^{15} cm^{-3} were studied. The oxygen concentration was determined by the standard method from the attenuation of radiation in the region of 9 μm (see, for example, Aleksandrova *et al.*[2]). The shape of the zero-phonon emission band of excitons bound to phosphorus atoms was analyzed using a Fabry-Perot etalon, in which the optical path difference is changed by changing the air pressure in the etalon chamber.[3] Luminescence of the silicon was excited at 4.2 K by radiation from an argon laser, focussed onto a spot with dimensions about 0.1 mm. The spectrum was recorded on a chart tape and simultaneously fed to a computer memory.

Three such spectra are shown in Fig. 1, and in Fig. 2 the dependence of the shift in the position of the maximum of the emission band and of the half width of this band on oxygen concentration. For this, the half-width was determined as the ratio of the area enclosed by the spectral curve to its amplitude. A number of specimens contained, apart from oxygen, carbon in concentrations comparable and even exceeding N, which, however, produced no additional change in the form of the band.

A characteristic feature of the spectral bands is their shift and broadening in the region of larger energies compared with the band in "oxygen-free" silicon. Such an effect can be produced by a random increase in the forbidden band E_g, which is only possible for an isotropic dilatation of the silicon lattice. The increase in the lattice constant of silicon containing oxygen at a concentration $N = 1.8\times 10^{18}$ cm^{-3} was observed experimentally in x-ray pictures,[4] but was not accompanied by an increase in the volume of the crystal as a whole. On the basis, the authors concluded that the oxygen is an interstitial impurity. Since the Si–O bond length (1.6 Å) is less than the Si–Si bond length (2.3 Å), the oxygen impurity atom must attract the nearest silicon atom, which produces a deformation of the isotropic dilatation in regions not belonging to the cells in which the interstitial oxygen is introduced. According to Bond and Kaiser,[4] the effective change in the specific volume of silicon $\Delta V/V = 2\times 10^{-5}$, which for a silicon compressibility $\chi = 10^{-6}$ cm^2 kg^{-1} is equivalent to a pressure $P \approx 20$ kg cm^{-2}. By taking account of the change in width of the forbidden band in silicon for hydrostatic compression $\partial E_g/\partial P = (-1.5 - -3.8)\times 10^{-6}$ eV/(cm^2 kg^{-1}) (see, for example, Barenskiĭ *et al.*[5]), it can be seen that the characteristic increase in the width of E_g is of the order of 30–80 μeV for $N = 1.8\times 10^{18}$ cm^{-3}, i.e., of the same order as both the characteristic broadenings and the shift in the maximum of the emission band of bound excitons for high oxygen concentrations, in Fig. 2.

There is a fundamental difficulty in a quantitative description of the experimental results. First, the mean distance between oxygen atoms r_0 ($\sim N^{-1/3}$) for $N \approx 10^{18}$ cm^{-3} is of the order of the characteristic dimensions of a bound exciton ($\approx 10^{-6}$ cm). We note, however, that the shape of the zero-phonon emission band was investigated, emitted as a result of the transfer of quasimomentum by a phosphorus atom in an indirect band gap semiconductor. This is only possible on recombination of an electron and hole in a bound exciton in the immediate proximity of an impurity center. A bound exciton can therefore be regarded as a point center. Second, the dependence of deformation on distance r to an interstitial atom is unknown. However, it can be assumed that for relatively large r, the shift of silicon atoms takes place as in an isotropic medium, i.e. $\propto r^{-2}$. In this case the change is width of the forbidden band, proportional to the

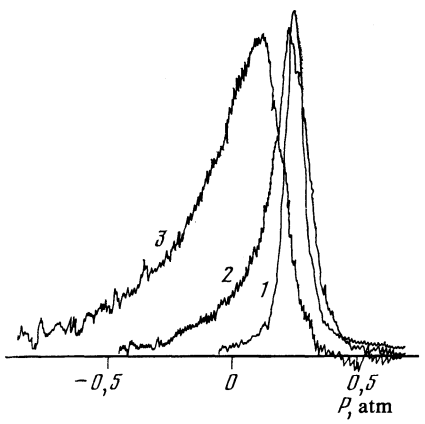

FIG. 1. Spectral dependence of the intensity of zero-phonon components of the emission of excitons bound to phosphorus atoms in silicon, on air pressure P in the interferometer chamber for different oxygen concentrations (cm^{-3}); 1) $< 10^{15}$; 2) 4.2×10^{17}; 3) 1.04×10^{18}.

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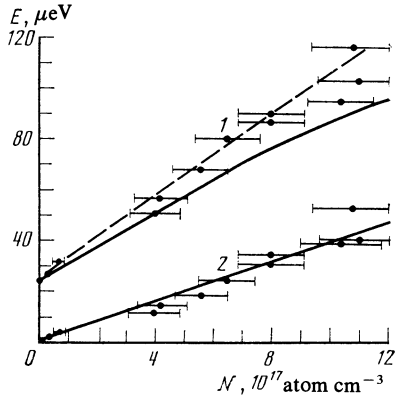

FIG. 2. Dependence of half width (1) and of shift in maximum (2) of the emission of bound excitons on oxygen concentration. The points with the indicated uncertainties in determining the oxygen concentration are experimental, the full lines are calculated, the dashed curve is an empirical linear dependence.

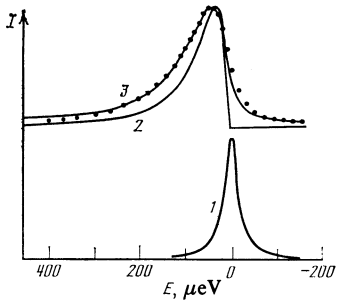

FIG. 3. Emission spectra of bound excitons: 1) in oxygen-free silicon (instrumental function of the Fabry-Perot etalon with half width 23 μeV); 2) calculated by Eq. (2) for $E_0 = 65\,\mu$eV; 3) convolution of the function of Eq. (2) with the instrumental function (1); the points are the experimental spectrum for an oxygen concentration 1.1×10^{18} cm^{-3}.

deformation should be $E \propto r^{-3}$. We considered it possible to take account of only the oxygen atom nearest to a given phosphorus atom. To such approximations, the probability that within a spherical layer of volume $4\pi r^2 dr$ there is one oxygen atom and that this atom is the closest (i.e. there are not n nearer oxygen atoms), can be written in the form

$$dW(r) \sim r^2\,dr \prod_{i=1}^{n} (1-\Omega/\Omega_n)_{n\to\infty} \to r^2 \exp(-r/r_0)^3\,dr. \quad (1)$$

Here $\Omega = 4/3\ \pi r^3$, $\Omega_n = 4/3\ \pi n r_0^3$. Substituting $E/E_0 = (r_0/r)^3$, where E_0 is the value of E corresponding to the average distance r_0, we obtain for the spectral emission density of bound excitons:

$$I(E/E_0) \sim (E_0/E)^2 \exp(-E_0/E). \quad (2)$$

The shape of the band for $N = 1.1\times10^{18}$ cm^{-3} with $E_0 = 65\,\mu$eV, calculated according to Eq. (2) is shown in Fig. 3. For checking how it corresponds to experiment, the spectral function of Eq. (2) is shown there with the instrumental function of the Fabry-Perot etalon, having half width 23 μeV (the emission band of a bound exciton in oxygen-free silicon). The satisfactory agreement between calculation and experiment can be seen from the figure. Appreciable disagreement is only observed for large E, i.e., for small r, for which the approximation $E \sim r^{-3}$ is hardly valid. Substituting $E_0 = 60\times10^{-18} N\,\mu$eV, we also calculate, taking account of the instrumental function, the dependence of the spectral position of the band maxima and their half width on oxygen concentration. The results of this calculation are shown in Fig. 2 by the continuous lines. It can be seen from this figure that the shift in the maximum is proportional to oxygen concentration, in agreement with Eq. (2). A noticeable departure from a linear dependence is observed in the calculated dependence of half width on concentration N at large concentrations. This is connected with the fact that the calculated dependence of Eq. (2) has a more linear "tail" for large E, which leads to a stronger overlap of the orders of interference in constructing the calculated dependence.

It can be seen from Figs. 2 and 3 that in spite of the approximation of the model used, it describes the experimental results fairly well. Moreover, the characteristic energy parameter E_0, dependent on oxygen concentration, is in reasonable agreement with the change in the width of the forbidden band of silicon for $N = 1.8\times10^{18}$ cm^{-3}, calculated from the change in lattice constant, determined from x-ray photographs,[4] using known values of the compressibility and of the change in width of the forbidden band of silicon for hydrostatic compression.

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