

# Quantum interactions of optical radiation with the defect centres in the tails of the forbidden band of amorphous materials

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In this paper, the model approach that describes the quantum interaction of optical waves with the polycrystalline and amorphous semiconductor films is proposed. The absorption coefficient for active layers of semiconductor films is represented as the sum of pseudo-crystalline and amorphous components. Based on the proposed theoretical approach, we considered the long-wavelength optical absorption spectra of amorphous silicon in 1500–4000 cm<sup>-1</sup> range. The resonant absorption centres were identified and were associated with V-V, I-V, V-V defect centres in a silicon gap with energies of 0.20–0.45 eV.

Keywords: resonant absorption centres, quantum interaction, semiconductor film, polycrystalline and amorphous silicon.

## 1. Introduction

The integral part of modern optoelectronics are thin-film converters whose efficiency is compatible with an efficiency of monocrystalline devices [1]. They are based on amorphous and polycrystalline materials, which are used as a receiving and transforming matrix for photoelectric elements [2–4]. However, obtaining strictly disordered semiconductors with optimal optical properties is a difficult practical task.

Nevertheless, the realization of this problem is important because the use of these materials is significantly expanding functional properties of modern devices. Thus it is necessary to solve a number of problems which are associated with deep understanding of the processes which occur in the atomic structure of the material [5–7].

The purpose of this paper is to describe the quantum structure of active layers of optoelectronic devices by determining the energy spectrum in the tails of the bandgap

and by determining the absorption coefficient of a non-monocrystalline atomic structure. The theoretical relationship between the micro- and macro-parameters was presented with further experimental analysis. To explain the optical and electrical processes in amorphous structures, we proposed a model for describing the optoelectronic characteristics of the disordered matrix, based on stoichiometric and structural parameters.

## 2. Absorption in the tails of the bandgap

Abstracting from intersymmetric interaction allows the representation of the most general form of the total absorption coefficient  $\alpha_{\Sigma}$  as a sum:

$$\alpha_{\Sigma} = \alpha_{pc} + \alpha_d \quad (1)$$

where the first of them,  $\alpha_{pc}$ , is responsible for transitions in quasi-crystalline periodicity. The second,  $\alpha_d$ , gives the opportunity to describe the broadband absorption material on the defective part of material.

To identify each of the components, it is necessary to understand the impact of the formation of the fine structure, when it is grown, especially in the initial moment when the basic geometry of the atomic structure of the semiconductor is laid. The defective component of the amorphous material is more diverse and interesting.

Localization of a separate defect (Fig. 1a) in an isotropic material can be described by macroperiodicity over the entire sample [8, 9]. Consequently, the energy landscape

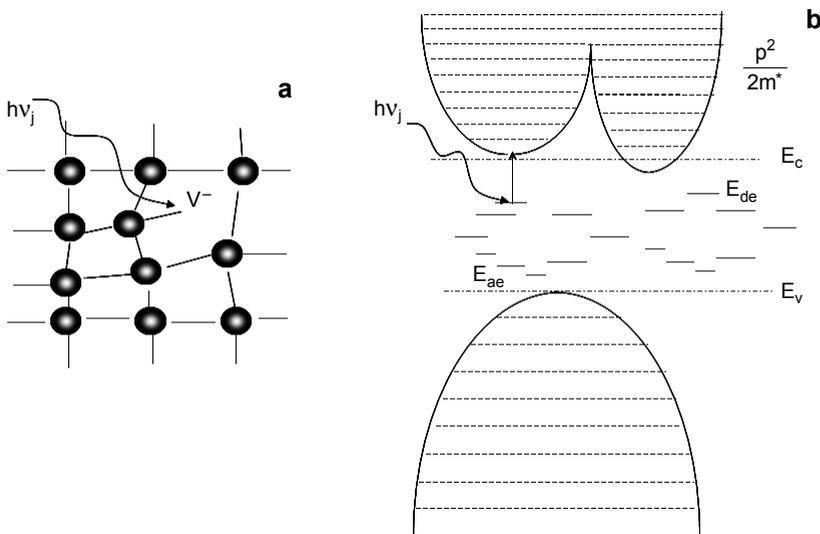


Fig. 1. The presentation of defects in amorphous and polycrystalline materials: dangling bond is a negatively charged vacancy (a). Energy band diagram; pseudozone formation and defective periodicity (b).

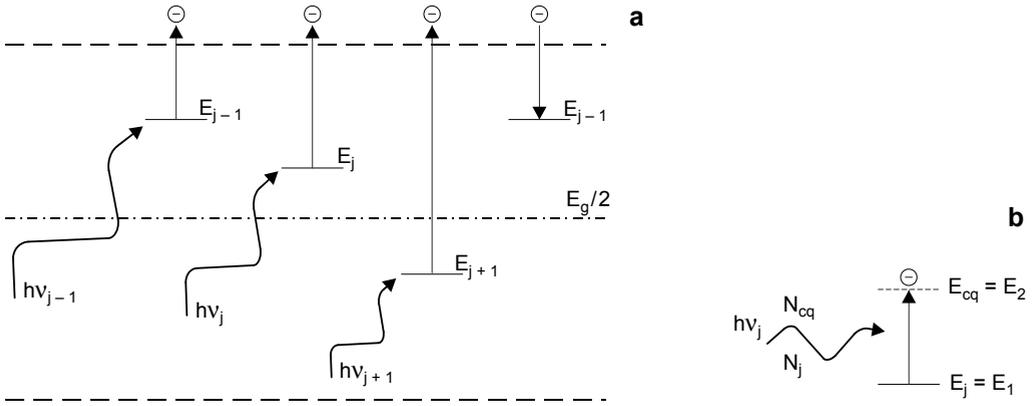


Fig. 2. Defective spectrum allocation of amorphous material: defective absorption spectrum (a); representation of negatively charged two-level vacancy by the Einstein approximation (b).

of amorphous or polycrystalline semiconductors can be described as quasi-zones (valence conduction) and macroscopic periodicity of localized centres (Fig. 1b).

Such representation allows us to represent non-crystallinity of material as a set of symmetries of various irregularities (Fig. 2a). Localization of each of the centres allows us to represent them in the form of the Einstein approximation of the two-level energy system with concentrations  $N_c = N_m$  and  $N_j = N_n$  (Fig. 2b).

In the bandgap of the amorphous material, in particular silicon, there are energy levels of various defects (Fig. 2a): single, multiple vacancies, inclusions of impurity atoms, foreign atoms (Fig. 2b), etc. If the electromagnetic wave is incident on an amorphous material, a certain absorption of this material can be observed. This is due to the fact that there will always be a defective centre with respect to the conduction band energy equal to the energy of the absorbed photon. As a result of the absorption of a photon, an electron moves into the conduction band and can participate in transfer charges. The frequency of the absorbed photon is determined by [10, 11]

$$\nu_{nm} = \frac{E_2 - E_1}{h} \tag{2}$$

The energy levels are labelled as  $E_2$  and  $E_1$  (accordingly, the upper and lower),  $h$  is the Planck's constant.

Considering the incident electromagnetic waves [12] to determine the absorption coefficient a model was used, which is based on the idea of atoms absorbing as dipoles. Positive charge is a charge of the nucleus with an inner electron shell, negative one is a charge of the outer electron. Consequently, the atom has a certain dipole moment, which we may denote as  $D_{nm}$ , and

$$D_{nm} = ex \tag{3}$$

On this basis, we can write the differential equation for forced oscillations of the electron in this dipole [11]

$$m_0 \ddot{x} + m_0 \gamma^* \dot{x} + m_0 \omega_{nm}^2 x = e E_0 e^{i\omega t} \quad (4)$$

where  $\gamma$  is a coefficient characterizing the attenuation which is determined by the lifetime of the photogenerated electron-hole pair. And after we substitute the dipole moment,

$$\ddot{D}_{mn} + \gamma^* \dot{D}_{mn} + \omega_{nm}^2 D_{mn} = \frac{e^2 E_0 e^{i\omega t}}{m_0} \quad (5)$$

Solution is the expression:

$$D_0 = \frac{\frac{e^2}{m_0} E_0}{\omega_{nm}^2 - \omega^2 + i\omega\gamma^*} \quad (6)$$

where  $D_0$  is the integrated dipole moment per unit volume of the substance.

Further, using the relationship between  $D$  and  $E$ , we move on to the absorption coefficient  $\alpha$ .

The concentration  $N_{nm}$  can be estimated using the density of states in the conduction band and the valence band. For example, for the crystalline silicon their values are on the order of  $10^{-19} \text{ cm}^{-3}$ .

Parameter  $\Delta N_{nm}$  is the population difference between the levels  $n$  and  $m$ , which is determined,

$$\Delta N_{nm} = N_m - \frac{g_m}{g_n} N_n \quad (7)$$

where  $g_m$  and  $g_n$  are statistical weights of level populations.

Therefore, a single resonator will have the absorption coefficient for a two-level system [11]. Assuming that the number of resonators is due to the defective elementary structure, the  $nm$ -th resonator of the  $j$ -th energetic level (Fig. 2) is determined as a defect. For each of defective centres  $N_c \gg N_j$ , that shows that the number of defects is much lower than ordered matrix atoms. This condition effectively limits the number of transitions by the defect centres. And, therefore, we can assume that the maximum number of transitions  $N_{nm}$  will be limited  $N_j$ , then  $N_j = \Delta N_{nm}$  in the absorption coefficient

$$\alpha_{aj}(\lambda) = \frac{4\pi e^2 \Delta N_j \omega^2 \gamma_j}{cm \left[ (\omega_{nmj}^2 - \omega^2)^2 + \omega^2 \gamma_j \right]} \quad (8)$$

here  $\omega_j = \omega_{nm}$  is the transition frequency.

Overall absorption coefficient of the amorphous component is the sum of the absorption of each of the defects,

$$\alpha_a(\lambda) = \sum_{j=1}^K \alpha_{aj}(\lambda) \quad (9)$$

where  $K$  is the number of points in the absorption of the amorphous component. Combining Eqs. (8) and (9) we obtain

$$\alpha_a(\lambda) = \sum_{j=1}^K \frac{4\pi e^2 \Delta N_j \omega^2 \gamma_j}{cm \left[ (\omega_{nmj}^2 - \omega^2)^2 + \omega^2 \gamma_j^2 \right]} \quad (10)$$

It is convenient to tie the quantitative assessment of defects to the density of states of the basic atoms  $N_c$ . However, the description of defects remains difficult due to their amorphous nature, or, in other words, the disorder. The introduction of the assumption of uniform distribution of defects in the structure can serve as a methodological solution to this [9]. It allows to enter two parameters  $b_j$  and  $\xi_j$ . Therefore, the total number of defects can be described as the product of the total number of atoms and the repetition frequency of defects. In this case, the absorption coefficient takes the following form:

$$\alpha_a(\lambda) = \sum_{j=1}^K \frac{4\pi e^2 N_c b_j \omega^2 \gamma_j}{cm \left[ (\omega_{nmj}^2 - \omega^2)^2 + \omega^2 \gamma_j^2 \right]} \quad (11)$$

Also, using the model representation of transitions between the energy levels  $\xi_j$  of a film defective part [9], the absorption coefficient can be expressed as

$$\alpha_a(\lambda) = \sum_{j=1}^K \frac{4\pi e^2 N_c b_j \omega^2 \gamma_j}{cm_0 \left\{ \left[ \left( \frac{E_g}{2\hbar} - \frac{\xi_j}{\hbar} \right)^2 - \omega^2 \right]^2 + \omega^2 \gamma_j^2 \right\}} \quad (12)$$

In this formula, the transition frequency  $\omega_{nmj}$  was painted over the defect energy parameter  $\xi_j$ , which represents the energy of the defect in relation to the mid-bandgap of the considered amorphous semiconductor. This count was taken due to the curvature of the boundaries of the bandgap with the valence and the conduction bands;  $\hbar$  is the Dirac constant.

### 3. Experimental observation of absorption spectra at a-Si thin films

The above theoretical curves show a greater complexity in the description of the spectrum of amorphous films. However, despite the complexity of the theoretical representation of the absorption coefficient of the amorphous material, the spectrum

passing the amorphous silicon can be decoded and the defect spectrum can be determined in band tails with successive approximations. The attractiveness of a-Si as a promising material in optoelectronics is its high-bandwidth, which is provided not only by increasing the optical bandgap, but with the help of the presence of a large amount of defect centres (Fig. 1b), giving multiple quantum transitions (Fig. 2b). Therefore, we considered the IR spectrum of the amorphous silicon in the long wavelength part of the spectrum (Fig. 3).

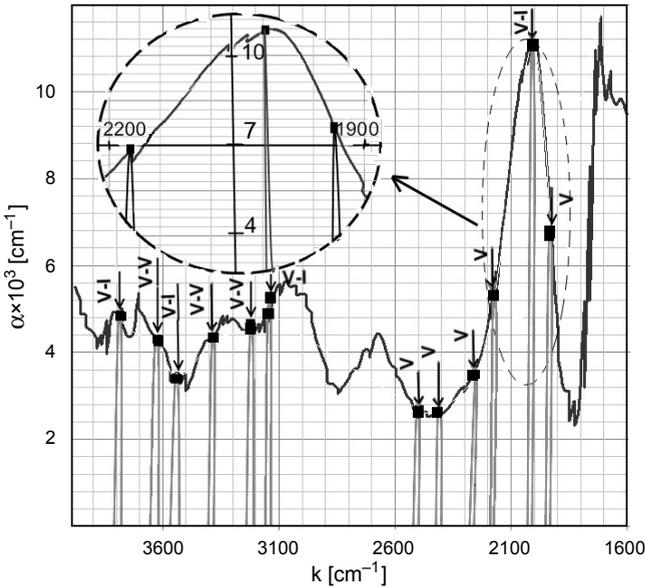


Fig. 3. Infrared absorption spectrum of amorphous silicon films in the range 1600–3900  $\text{cm}^{-1}$  wave numbers. There is a detailed examination of the peak in the range 1900–2200  $\text{cm}^{-1}$  in the inset.

The experimental film samples were hydrogenated silicon (a-Si and a-Si:H) and were obtained on a magnetron type URM3.279.014 installation at a pressure in the working chamber  $10^{-2}$ – $10^{-3}$  Pa, a voltage and a current of the target were 500–650 V and 1.5–2 A, respectively. The growth rate of the films was 0.1–0.4  $\mu\text{m}/\text{min}$  [13].

A basis of substrates used in the deposition of films were the structures of glass-ceramic (SchEO 781.001.0U, SchU 7.002-15.817, St-50-1-1-0.6) and high-quality glass. The glass substrate, having optical transparency, served as a protective screen against external influences on these thin films, in particular against the interaction with oxygen, and mechanical damage.

The very structure of silicon, due to its tetrahedral symmetry, can have many irregularities from which we can distinguish the vacancy atoms in the nodes V, interstitial I lattice (Figs. 3, 4), as well as charged and neutral divacancy ( $VV^-$ ,  $V-V^+$ , and  $V-V^0$ ) and the complex with donor and acceptor impurities [14–16].

The experimental absorption spectrum is a complex curve having a mixed picture noise (Fig. 3). For understanding the physics of the interaction, we have analyzed all possible defective components when the defect formation in silicon is possible.

According to Eq. (9) the selected continuous spectrum was represented by the sum of the absorption coefficients at fixed wavelengths (in brackets – the wavelengths in  $\mu\text{m}$ ):  $\alpha_a(\lambda) = \alpha_1(2.64) + \alpha_2(2.76) + \alpha_3(2.82) + \alpha_4(2.95) + \alpha_5(3.1) + \alpha_6(3.18) + \alpha_7(4.0) + \alpha_8(4.13) + \alpha_9(4.43) + \alpha_{10}(4.59) + \alpha_{11}(4.96) + \alpha_{12}(4.17)$ .

To determine the nature of each of the absorption coefficients, we compared the set of resonators formed by the defect centres in the bandgap (Fig. 4);  $\alpha(2.64)$ , from our point of view, belongs to a proper interstitial atom located on the level  $E = (E_c - 0.47) \text{ eV} \pm 0.04 \text{ eV}$ .

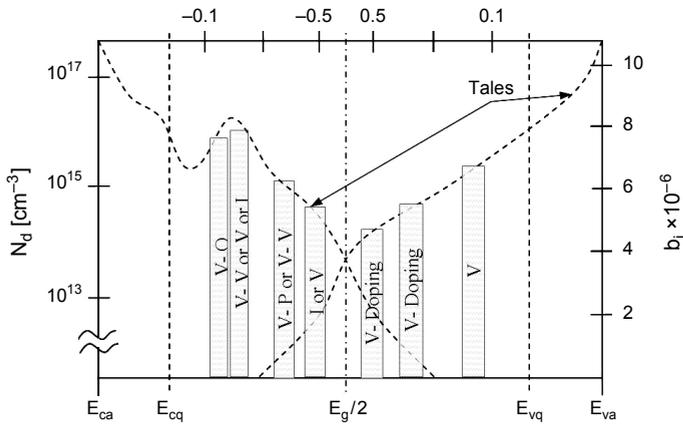


Fig. 4. Contribution of major defect levels in the wave number range  $1600\text{--}3800 \text{ cm}^{-1}$  to the absorption spectrum of amorphous silicon.

An absorption coefficient at  $2.95 \mu\text{m}$  vacancy was caused by the interaction with the impurity atom of phosphorus. Being an acceptor level, it forms the energy centre at  $E = (E_c - 0.44) \text{ eV} \pm 0.04 \text{ eV}$ . More complicated is the energy centre at the level of  $0.4 \text{ eV}$ . The physics of its formation is very ambiguous, and depending on the nature of forming the semiconductor structure may be different. On the one hand, it can be represented by self-interstitials located in the split dumbbell state of the electron, which can be interpreted as a double interstitial. On the other hand, the same energy level has a complex vacancy with a hydrogen atom having acceptor properties or a vacancy combined with a similar one which forms a divacancy. Almost merging with the energy centre at  $0.39 \text{ eV}$ , the vacancy combining with interstitial centre on  $3145 \text{ cm}^{-1}$  forms the next absorption peak.

The next group of defect centres lies in the region of  $1900\text{--}2200 \text{ cm}^{-1}$ . The vacancy in this spectral region forms the energy centre  $E = (E_c - 0.27) \text{ eV} \pm 0.03 \text{ eV}$ , whereas the defective interstitial silicon atom is located at  $0.25 \text{ eV}$  below the conduction band.

T a b l e 1. Values of  $b_j$  and  $\xi_j$  for defects peak on 1900–2200  $\text{cm}^{-1}$ .

| Type of defect    | $k$ [ $\text{cm}^{-1}$ ] | $b_j, \times 10^6$ | $\xi_j$ [eV] |
|-------------------|--------------------------|--------------------|--------------|
| Vacancy           | 2177                     | 3.8                | 0.63         |
| Interstitial atom | 2016                     | 7.7                | 0.65         |
| Dual divacancy    | 1936                     | 1.5                | 0.66         |

Resonant absorption at the centre with the wavelength of 5.17  $\mu\text{m}$  is either a vacancy or divacancy.

A contact of the centres with microscopic parameters of the silicon structure according to formula (12) is accomplished by the choice of the coefficients  $b_j$  and  $\xi_j$ , characterizing amorphous materials. The description of the whole spectrum requires a long calculation and is a subject of our further research. To test the efficiency of the approach, we have attempted to describe the peak interval at 1900–2200  $\text{cm}^{-1}$ , which is shown in more detail in the insert in Fig. 3. This single peak of absorption, from our point of view, is formed by three defect levels: vacancies, resting on a loss of 0.27 eV from the conduction pseudozone, interstitial silicon atoms lying at 0.25 eV, and the double divacancy at 0.24 eV. Qualitative and quantitative model calculations of given values  $b_j$  and  $\xi_j$  were presented in Table 1.

## 4. Conclusions

Thus, the above model representation shows that the absorption coefficient of amorphous semiconductors to be used as active layers in optoelectronic devices can be represented as the sum of pseudocrystal and amorphous components. When the disordered components are considered, we need to integrate a wide variety of modes of oscillations arising in connection with violation of bonds in the structure (the formation of vacancies, divacancies) and impurity components (hydrogen, oxygen, *etc.*). Using the localization and frequency of each of the defects, their description can be represented as a two-level resonant system described by two parameters –  $\xi_j$  and  $b_j$ . Model representations regarding the amorphous component were tested in the infrared spectral range of wave numbers of 1600–3900  $\text{cm}^{-1}$ . Based on these results, oscillation modes were identified, coinciding with both vacancies and divacancies, allowing to determine the energy distribution in the tails of the bandgap ( $\xi_j$ ) and to determine the frequency of each of the types of defects ( $b_j$ ), which reveal the internal structure of the material.

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