PHYSICAL REVIEW B VOLUME 52, NUMBER 15 15 OCTOBER 1995-I

Fluctuation tail of valence bands in hydrogenated amorphous silicon

A.A. Klochikhin
Petersburg Nuclear Physics Institute, Gatchina,1888350 St. Petersburg, Russia
(Received 31 January 1995; revised manuscript received 30 May 1995)

A theoretical approach to the problem of the valence-band tail of hydrogenated amorphous silicon is developed. A quantitative description of experimental data on the density of states (DOS) in the region of the valence-band tail is attempted. A single-band three-dimensional version of the Brodsky model complemented by an assumption of the random size distribution of potential wells and barriers was used in the calculation. This model corresponds to a solid solution where the regions of amorphous silicon and those saturated by hydrogen play the role of constituents. The Brodsky model restricts the depth of potential wells for holes by the difference between the valence-band tops of the crystal and hydrogenated amorphous silicon. The experimental total-yield photoemission data on the DOS of hydrogenated amorphous silicon for various samples were compared with theoretical calculations. The results show that a good quantitative agreement can be achieved with the DOS for both undoped and doped samples. The random potential characteristics deduced from a comparison with experimental data mainly on undoped and B-doped samples, show no dependence on the level of doping, and, in fact, describe well the DOS of P-doped samples as well. Earlier, a similar conclusion was drawn from the data on hole drift mobility. However, we obtain the best coincidence with experimental data when the depth of the fluctuation wells is approximately two times that assumed in the simplest version of the model. The possible reasons for this divergence seem to be an additional fluctuation potential obeying the Gaussian statistics and (or) the shallow B-acceptor states neglected in our calculations. We obtain also general and simplified expressions for the D-center band contour due to the interaction with a fluctuation potential. It is shown that the band contour of these centers is a source of supplementary information about the fluctuation potential, which is in qualitative agreement with data derived from comparison with the DOS of the host band tail.

I. INTRODUCTION

Amorphous semiconductors of the group IV as well as $A_{III}B_{V}$ and $A_{II}B_{VI}$ compounds (Refs. 1–3 and references therein) represent a wide class of systems where disorder follows from structural damages. That distinguishes them both from solid solutions and strongly doped crystals and from liquid and glassy formations.

Amorphous silicon itself and its hydrogenated form has attracted the attention of researchers[1,2,4–14] (and references therein) for a long time. This is due to a technical application of this substance and a general interest in the amorphous state. One of the major tasks of theory is qualitative and quantitative explanation of the electronic structure of these complex systems within the framework of models of amorphous network acceptable from the point of view of the structural analysis data.[1,2,4,5,15–21] A separate but rather important aspect of this problem is one concerned with the origin of fluctuation localized states of the hydrogenated amorphous silicon valence bands.

An approach to the quantitative description of the valence-band tail is presented in this work. The first question is whether we can find the only reason which is mainly responsible for the localization phenomenon in this complex system. It is also important that the model Hamiltonian has to be both physically meaningful and tractable enough to be applicable to calculations in the region of localized states where neither a perturbation theory nor a coherent potential approximation are applicable. Different mechanisms creating the localized fluctuation states in the α-Si and α-Si:H valence-band tails have been studied in many papers[18–25] (and references therein).

The short-range order is preserved[1,2] in amorphous silicon at least up to the second coordination sphere, while the long-range order is completely broken because of the relatively large number of dangling bonds ($\approx 10^{20}$ cm^{-3}). The mean valence bond length appears to be close to the crystal Si value, and the relative root-mean-square deviation was estimated to be about $2-4\,\%$.[1,2,4,5] The valence bonds are oriented along directions close to tetrahedral ones, and the angle root-mean-square deviations do not exceed 0.2 rad.[1,2,4,5] It was shown by Joannopoulos[18] that the local bond angle distortions having the magnitude of the order of their dispersion give rise to resonant states near the top of valence bands, while at a larger perturbation the localized states split off.

The distribution of bond length and bond angle deviations from their mean values in various models of amorphous network[26–31] (and references therein) is assumed to be Gaussian at a relatively small dispersion. This circumstance allows us to suggest that the random potential arising from these deviations should be characterized by Gaussian statistics. The dependence of the density of fluctuation states on the localization energy is

 ©1995 The American Physical Society

determined by statistical properties of the random potential. As it follows from Refs. 32–35, the random potential obeying the Gaussian law leads to the density of states (DOS) decrease described by the exponential root square dependence on energy. That is far enough from both the well known Urbach behavior[36–38] and a more complex experimental dependence.[13]

Stern[22] has assumed that the random potential in the amorphous silicon obeys modified Gaussian statistics with a finite correlation radius. Later, a detailed study of random potential of such a kind was performed[39–41] and it was shown that the model provided explanation of the Urbach form dependence of the density of localized states in the relatively narrow energy range, however, the results are insufficient for description of experiment in a more wide range. We can conclude that the Gaussian fluctuations and the corresponding random potential cannot be considered as a principal reason for the tail states.

The valence bands of amorphous and crystalline silicon are formed by the sp^3-hybrid orbital of Si atoms, and the valence-band top consists primarily of p components. According to Weaire and Thorpe,[15–17] this is due to the by preservation of the short-range order.

Such a characteristic as the valence-band full width is preserved approximately, while the band gap width demonstrates some growth as compared with the crystal and is found to be about 1.5 eV.[1,2,4–6] The DOS of the valence bands preserves the characteristic maximum belonging to the p states, however, the structure of the DOS in the depth of the valence bands inherent to the crystal Si disappears.[1,2,4,7,8] This fact is likely to result largely from the topological disorder of the amorphous network, which leads to the disappearance of the regular sixfold ring structure of the diamond lattice. From this point of view, it is demonstrative that the DOS of the Bethe-lattice model[18–21] describes the valence bands of α-Si fairly well.

Of interest for our consideration is the result following from the calculations of the model DOS of the Bethe lattice,[21] which has shown that at the same parameters as the crystalline Si, the Bethe-lattice DOS appears to have a smaller electron bandwidth. Therefore, the α-Si valence-band edge shift, as compared with c-Si, can be attributed at least partly to the destruction of the sixfold ring structure.

Inhomogeneous distribution of structural damages can create a considerable random potential relief for a hole. Mathematical simulation of disordered systems widely used for the description of α-Si and α-Si:H (Refs. 26–31) assumes such possibilities.

A mechanism responsible for the random potential connected with a dihedral angle random distribution was considered by Singh.[24] The dihedral angle distribution in amorphous silicon models appears to be continuous resulting in continuous and limited in the definite energy range distribution of the random potential.[24,29] The calculations of the random potential are given in the paper,[24] however, its possible role in the formation of fluctuation states has not been treated in detail so far.

Appreciable changes in the density of valence-band states occur after the saturation of amorphous silicon by hydrogen. As a result, hydrogenated amorphous silicon includes in the network a large quantity of hydrogen. Its top limit of content has been estimated to be larger than 30 at.%. Only a small fraction of hydrogen saturates the dangling bonds and, as a result, their concentration lowers in good quality (device class) samples down to 10^{16} cm^{-3} or even less.

Further displacement of the valence-band top occurs as a result of hydrogenation and, because of this, the increase in the band gap width takes place. This can be described approximately by the linear law[6] $E_g = 1.5 + 1.5C_H$, where C_H is the relative concentration of hydrogen. At $C_H = 0.3$, the width of the band gap, according to this equation, reaches a value about 2 eV, which agrees with experimental data. We notice that the largest possible value of the valence-band top displacement following from this formula is equal to 1.5 eV, which can be achieved in areas where $C_H \approx 1$. This value agrees with the estimation of the maximum band gap in α-Si equal to 3 eV obtained by Allan and Joannopoulos.[20]

The shift of the valence-band top is followed by the occurrence of the structure in the depth of α-Si:H valence-bands DOS,[1,2,7,8] which demonstrates the hydrogenation effect on the valence-band electrons. We note here two variants of explanation of the α-Si:H DOS structure suggested by Allan, Joannopoulos, and Pollard,[21] which highlight also the possible reasons of the random potential occurrence. The major features of the DOS structure, according to Allan, Joannopoulos, and Pollard,[21] can be equally well explained in two cases. First, it is possible that the hydrogenation leads to partial relaxation of structural distortions resulting in the restoration of the role of sixfold rings in some part of the volume and hydrogen saturates the dangling bonds of the sixfold rings. Second, perhaps no recrystallization occurs, but hydrogen saturates surfaces of internal voids of α-Si:H or ones of the small regions of crystalline order.[42] In both cases, the system was supposed to be highly inhomogeneous. Allan and Joannopoulos[20] and Brodsky[23] have supposed that the random potential in α-Si:H is produced by inhomogeneous distribution of the hydrogen over the volume of the network.

This model has been described in detail by Brodsky,[23] who has assumed that hydrogenated amorphous silicon represents the inhomogeneous system consisting of regions containing only silicon (α-Si) divided by barriers where Si-H bonds are placed. Taking into account the different values of the band gaps, it is possible to suppose that in areas containing α-Si, the band gap is restricted by the crystal silicon value equal to 1.1 eV, while its value in barriers, according to Ref. 23, can reach 2.5 eV and even 3 eV as it was estimated by Allan and Joannopoulos.[20] The α-Si:H band gap width is equal to about 2 eV and, therefore, neglecting the fluctuations of the conductivity band bottom, we estimate both the potential well depth and the barrier height measured from the mobility edge level to be equal to 1 eV and 0.5–1 eV, respectively.

This model can be considered as a phenomenological description of the topological disorder effect together

with the effect of hydrogenation. It is of interest, first of all, because it contains the assumptions of the inhomogeneous structure of α-Si:H compatible with those taken for the explanation of the structure in the depth of valence-band DOS.[21] On the other hand, the model has the doubtless similarity with a two-component solid solution for which the behavior of the density of localized fluctuation states[43,44] has qualitatively agreed with experimental data on α-Si:H.[13]

The amorphous silicon as well as the hydrogenated amorphous silicon are characterized by the smeared valence-band edge.[1,2,4,6–14] At present, it is established that the valence-band edge is a result of the superposition of two constituents. The first is the fluctuation state tail of the silicon host bands and the second is the dangling bond bands (D_0- and D_- centers) contiguous to the tail. Reliable separation of these two contributions is possible perhaps only in the case of the hydrogenated silicon, where the deep center concentration is not too high. The most detailed experimental information about behavior of the density of states in the region of the valence-band tail and in the band gap is available for hydrogenated amorphous silicon[1,2,9–14] and hereinafter just this case is considered.

The mobility edge of the α-Si:H valence bands is placed at the density of electronic states equal to about $(2\text{–}4)\times10^{21}$ eV^{-1} cm^{-3} and minimum values of DOS, which can be related surely enough to the tail states is about 10^{16}–10^{17} eV $^{-1}$ cm^{-3}. These values were observed in the band gap at the depth about 0.6–0.5 eV below the mobility edge.[13]

The number of localized states in the tail is equal to $(3\text{–}5)\times10^{20}$ cm^{-3}, in other words, to only about 0.3% of the total number of p states in valence silicon bands. This value shows that the random potential effect on the valence-band electron states is relatively weak. In our calculations, we use the three-dimensional single-band version of the Brodsky model[23] complemented for a mathematical definiteness by the law of the random distribution of the potential well and barrier sizes.

For the last purpose, we divide the volume of the amorphous network into artificial cells containing an arbitrary number of $\kappa \geq 1$ atoms. Then we admit that every cell can be characterized by one of two possible values of the potential for the hole in the valence band. The amorphous network is considered then as a solid solution, which consists of the fracture c cells, where the potential for the hole has the attractive character and of the remaining fracture $(1-c)$ cells, where the potential has the opposite sign.

Assuming the random distribution of these cells over a volume of the network, we can obtain wells and barriers of arbitrary sizes consisting of κ, 2κ, ..., $n\kappa$ atoms. Probabilities of their occurrences decrease as c^n or $(1-c)^n$ with n increasing.

As a result, the model at $\kappa = 1$ coincides with classical model of an ideal two-component solid solution. At $\kappa > 1$, the minimum cell size κ is an additional parameter of the theory. It influences such characteristics of the model as the critical depth of the potential and the critical size of the potential well. The first of these characteristics is the amplitude of the potential, which is necessary for splitting off the localized state from the border of the continuous spectrum when perturbation is concentrated within the volume of one cell. The second one is the size of the potential well, which gives the same effect when the amplitude of a model fluctuation potential is less then the critical value.

The fluctuation well can split off the localized state at a fixed magnitude of the attractive potential if its size exceeds the critical one. Therefore, the number of wells in the unit volume satisfying this criterion gives immediately[43,44] an estimation of the total number of the localized fluctuation states. As far as the crystal silicon valence-band top is placed at the energy higher than the tops of both amorphous and hydrogenated silicon the valence-band top of crystal silicon will coincide with the Lifshitz border that restricts the spectrum of a disordered system.

The Gaussian fluctuations of the potential, due to a small bond length, and angle deviations can be included into the model. They can play a significant role at least in those areas where the potential has the attractive character for the hole.

In this work, we also consider the form of the band produced by the dangling bonds remaining unsaturated by hydrogen. The band of the dangling bonds overlaps with the fluctuation tail of the valence bands at a concentration equal to about 10^{16} cm^{-3} on the depth approximately 0.3 eV below the mobility edge as it follows from the experimental data.[13]

Considerable interest in the deeply localized states in both doped and undoped α-Si:H is concerned with studies of the thermal equilibration in amorphous silicon[45–51](and references therein).

Local centers embedded in the inhomogeneous environment exhibit the broadening of the band, because of their interactions with an environmental random potential. We suppose that in distinction to the tail fluctuation states, the wave function of a local deep center is largely concentrated within the volume of its own deep potential well, where fluctuations are not present and only the exponentially decreasing tail of the wave function of the center penetrates beyond the limits of this well. Because of a small value of the wave function beyond the deep well, the broadening of the deep center band is conditioned by those fluctuations that have the largest probability within the volume restricted by the radius of the deep center wave function. These are mainly the single-cell fluctuations that lead to the Gaussian broadening of the band, despite the fact that the random potential obeys the binary statistics. However, the more complex statistics of the proposed random potential makes the deviation of the fluctuations from the Gaussian statistics quite reliable, which can result in a more complex form of the band. Indeed, the observed bands in α-Si:H (Ref. 13) have the forms distinguishable from the Gaussian ones. As it is shown in our work, the band asymmetry depends on the parameter c in the considered model. Therefore, it is connected with the ratio between fractures of the volume occupied by potential wells and barriers. In our band contour calculation, the deviation of the fluctua-

tions from the Gaussian statistics is taken into account.

The structure of the paper is as follows. In Sec. II of the paper, the model Hamiltonian in question is described at an arbitrary value of κ and the main results of the theory[43,44] in the more transparent form are presented. The third section is devoted to the investigation of the form of the deep center band. Further, in Sec. IV, we present the simple equations enabling us to express the main parameters of the theory through observable characteristics of DOS. In Sec.V, we present the results of the numerical analyses and the comparison of the theory with the experiment at the minimum value of the minimum cell size, i.e., at $\kappa = 1$. The discussion of results is presented in the last section of the paper.

II. RESULTS OF THEORY

A. Model Hamiltonian

We suppose that amorphous medium is divided into microscopic cells of size κv_0, where v_0 is a volume per one atom in the silicon lattice and κ is an integer. We present the fluctuation potential in the form of the sum over the cells,

$$V_{\rm FL}(r) = \sum_n V_n(r) \,. \qquad (1)$$

Here, n enumerates the cells and $V_n(r)$ is the potential defined within the cell with the number n. Further, we assume that the value of the potential within a cell of one kind is equal to $V_n(r) = V^A$, and within a cell of the other kind it is equal to $V_n(r) = V^R$ and suppose inequality $V^R > V^A$, so that cells of the first kind have the attractive potential, while cells of the second kind possess the repulsive one. Concentrations of cells of the first and second kinds are taken to be equal to c and $(1-c)$, respectively . The mean value of the potential at a random filling within any cell in the whole considered volume is equal to

$$\bar{V}_n = \bar{V} = cV^A + (1-c)V^R \,. \qquad (2)$$

We accept this value as a point of reference for an energy. Then the depth of the attractive potential well $\bar{V} - V^A$ and the height of barriers $\bar{V} - V^R$ are equal to

$$\bar{V} - V^A = (1-c)\Delta \,, \quad \bar{V} - V^R = -c\Delta \,, \qquad (3)$$

respectively, where

$$\Delta = V^R - V^A \,. \qquad (4)$$

The random filling of each of the cells is described by function of distribution

$$P(V_n(r)) = P(V_n) = c\delta[V_n - (1-c)\Delta] + (1-c)\delta(V_n + c\Delta) \,, \qquad (5)$$

for a value of r within the cell with number n.

We assume a continual description that is acceptable in the case of a weak scattering limit.[43,44] The weak scattering limit supposes that the single cell is not able to split off the bound state and actual potential wells have sizes considerably exceeding the minimum cell.

The single band Hamiltonian in the effective mass approximation can be written in the form

$$H = -\frac{\hbar^2}{2M}\nabla^2 - V_{\rm FL}(r) \,, \qquad (6)$$

where M is the effective mass of the particle. The statistical properties of the random potential according to Eq. (5) are described now by the continual distribution function,

$$P(V_{\rm FL}(r)) = c\delta[V_{\rm FL}(r) - (1-c)\Delta] + (1-c)\delta[V_{\rm FL}(r) + c\Delta] \,. \qquad (7)$$

B. Halperin-Lax conception

Using results,[43,44] we write the averaged expression for the imaginary part of the Green function of the particle as

$$\frac{1}{\pi}\langle {\rm Im}G(\omega)\rangle = \frac{1}{2\pi}\int_{-\infty}^{\infty} d\tau \int \frac{d^3r}{\kappa v_0}\varphi_{\rm tr}^2(r) \times\langle \exp\{-i(\tau - it)[\omega + H]_{\varphi_{\rm tr}\varphi_{\rm tr}}\}\rangle \,, \qquad (8)$$

where

$$[\omega + H]_{\varphi_{\rm tr}\varphi_{\rm tr}} = \int \frac{d^3r}{\kappa v_0}\varphi_{\rm tr}(r)[\omega + H]\varphi_{\rm tr}(r) \,.$$

Here, ω is the localization energy counted from the mean level of the potential $V_{\rm FL}$, $\varphi_{\rm tr}$ is the so-called trial wave function of the localized state introduced by Halperin and Lax[33,34] for an approximate calculation of the DOS in a disordered system, and angular brackets designate averaging with distribution functions like (7) taken at every point of the volume considered. This means summarizing all possible configurations. The Halperin-Lax conception supposes that there is only one wave function, within the small interval of energies $d\omega$ near any localization energy ω, which possesses the spherical symmetry and describes well enough the overwhelming majority of the solutions really existing in this energy interval in a disordered system. If such wave function exists, it does not depend on the configuration and, therefore, summarizing all possible configurations is possible.[43,44]

The norm of $\varphi_{\rm tr}$ is chosen in such a way that the integral over the whole volume

$$\int \varphi_{\rm tr}^2(r)\frac{d^3r}{\kappa v_0} = \sum_n \varphi_{\rm tr}^2(r_n) = 1 \,, \qquad (9)$$

is equal to unit. The normalization integral is preserved in Eq. (8) for convenience.

The result of averaging the imaginary part of the Green

function can be presented in the form of the Laplace transformation,[43,44]

$$\frac{1}{\pi}\langle \mathrm{Im}G(\omega)\rangle = \frac{1}{2\pi}\int_{-\infty}^{\infty} d\tau \frac{\int d^3r\varphi_{\rm tr}^2(r)}{\kappa v_0} \times \exp\left\{ -\int \frac{d^3r}{\kappa v_0}\left[i(\tau - it)\frac{\hbar}{2M}(\nabla\varphi_{\rm tr}(r))^2 + \omega\varphi_{\rm tr}^2(r) - \ln\mathcal{R}(\tau - it)\right]\right\}, \tag{10}$$

where t is the free parameter of the Laplace transformation and $\mathcal{R}(\tau - it)$ represents the result of averaging the exponents with the distribution function (7),

$$\begin{aligned}\mathcal{R}(\tau - it) &= \int dV_{\rm FL}(r)P(V_{\rm FL}(r)) \times \exp\{i(\tau - it)V_{\rm FL}(r)\varphi_{\rm tr}^2(r)\} \\ &= c\exp\{i(\tau - it)(1-c)\Delta\varphi_{\rm tr}^2(r)\} + (1-c)\exp\{-i(\tau - it)c\Delta\varphi_{\rm tr}^2(r)\}.\end{aligned} \tag{11}$$

Therefore, the introduction of the trial function $\varphi_{\rm tr}(r)$ identical for all variants of cell filling makes it possible to obtain an approximate but closed expression for the imaginary part of the Green function.

C. Density of states

To find the number of states at localization energy ω, it is necessary to take into account the fact that the point of reference of r for $\varphi_{\rm tr}(r)$ is arbitrary. Therefore, there are $(\kappa v_0)^{-1}$ of ways to choose $\varphi_{\rm tr}(r)$. As the valence-band top is formed by triply degenerated p states, we have also to multiply the expression for the density of states by $(2l+1)$,

$$\rho(\omega) = \frac{(2l+1)}{\pi\kappa v_0}\langle \mathrm{Im}G(\omega)\rangle, \tag{12}$$

where $l = 1$.

Equation (12) together with (10) and (11) allows us to determine the density of states if the function $\varphi_{\rm tr}(r)$ and the parameter t are known.

We transform the expression $\ln\mathcal{R}(\tau - it)$ in the manner

$$\ln\mathcal{R}(\tau - it) = \ln\mathcal{R}(-it) + \ln\left[\frac{\mathcal{R}(\tau - it)}{\mathcal{R}(-it)}\right]. \tag{13}$$

Then the second item of Eq. (13) can be presented as

$$\ln\left[\frac{\mathcal{R}(\tau - it)}{\mathcal{R}(-it)}\right] = \langle\langle \exp\{i\tau V_{\rm FL}(r)\varphi_{\rm tr}^2(r)\}\rangle\rangle, \tag{14}$$

where double brackets denote the averaging with the weight factor

$$\langle\langle\cdots\rangle\rangle = \frac{\langle E(-it)\cdots\rangle}{\langle E(-it)\rangle} \tag{15}$$

and

$$E(-it) = \exp\{tV_{\rm FL}(r)\varphi_{\rm tr}^2(r)\}.$$

Substituting Eqs. (13) and (14) into Eq. (10), we present the imaginary part of the Green function as

$$\frac{1}{\pi}\langle \mathrm{Im}G(\omega)\rangle = \exp\{-A[-it]\}\int \frac{d^3r\varphi_{\rm tr}^2(r)}{\kappa v_0}\frac{1}{2\pi} \times \int_{-\infty}^{\infty} d\tau\,\exp\{-\mathcal{A}[\tau]\}, \tag{16}$$

where

$$A[-it] = \int \frac{d^3r}{\kappa v_0}\left\{ t\left[\frac{\hbar^2}{2M}(\nabla\varphi_{\rm tr}(r))^2 + \omega\varphi_{\rm tr}^2(r)\right] - \ln\mathcal{R}(-it)\right\}, \tag{17}$$

and

$$\mathcal{A}[\tau] = \int \frac{d^3r}{\kappa v_0}\left\{ i\tau\left[\frac{\hbar^2}{2M}(\nabla\varphi_{\rm tr}(r))^2 + \omega\varphi_{\rm tr}^2(r)\right] - \ln\langle\langle \exp\{i\tau V_{\rm FL}(r)\varphi_{\rm tr}^2(r)\}\rangle\rangle\right\}. \tag{18}$$

The demand of the action $A[-it]$ extremum leads to the equation of the particle motion,

$$\left\{-\frac{\hbar^2}{2M}\nabla^2 + \omega - U_{\rm tr}(r)\right\}\varphi_{\rm tr}(r) = 0, \tag{19}$$

where

$$U_{\rm tr}(r) = \frac{\partial}{\partial t\varphi_{\rm tr}^2(r)}\ln\mathcal{R}(-it) \equiv \langle\langle V_{\rm FL}(r)\rangle\rangle \tag{20}$$

is defined by means of the self-consistent solution $\varphi_{\rm tr}(r)$ of nonlinear Eq. (19), which gives also the value of the parameter t. Function (20) describes a smoothed potential well that is created by the fluctuations of the cell concentration.

The potential well is formed within some volume when there appeared an excess of the attractive cells as compared with the mean concentration. As a result, the potential within this volume has an attractive character. The localized state in the three-dimensional case appears when the potential well exceeds the power of the critical cluster. This is, in a general case, a cluster with an excess of attractive cells which results in splitting off the localized state with nearly zero localization energy.

It follows from Eqs. (20) and (11), that the function $U_{\rm tr}(r)$ is restricted in such a manner that its value does not fall out of the interval,

$$(1-c)\Delta \geq U_{\rm tr}(r) \geq -c\Delta. \tag{21}$$

When the description of the fluctuation potential in the model is exact, only the limiting values $(1-c)\Delta$ and $-c\Delta$ are allowed. The intermediate values of $U_{\rm tr}(r)$ have

appeared after the averaging procedure, as a result of approximate solution of the problem.

D. Critical cluster

Equation of motion (19) has too wide a class of the solutions and we have to constrain the trial function by means of restrictions,[43,44] which make the trial function more similar to the real solutions of the model system described by the Hamiltonian of Eq. (6).

The additional restriction introduced in Refs. 43 and 44 constrains the behavior of the trial function $\varphi_{\rm tr}(r)$ in the region of a small r. It is concerned with a behavior of the wave function of the localized state within the region occupied by a critical cluster. Equation (19) coincides within the critical cluster with the linear Schrödinger equation, which completely defines a behavior of $\varphi_{\rm tr}(r)$ there and makes it identical to the solution of the problem in a virtual crystal approximation for the same localization energy.

To reach an accordance with the Halperin-Lax conception, we have to suppose that there exists the uniquely defined and most probable critical cluster in this problem. There is a wide region of the concentration where the most probable critical cluster is the sphere compacted by the attractive cells. It is possible to find analytically the critical size for such compact clusters in the virtual crystal approximation. The noncompact critical clusters[52] represent a more general case. In the region of concentrations c actual for hydrogenated amorphous silicon, the compact clusters are more probable.

We consider the spherical form fluctuation well containing in its center the critical cluster compacted by attractive cells. Then the expression for $\mathcal{R}(-it)$ can be written as

$$\mathcal{R}(-it) = \begin{cases} c\,\exp[(1-c)\Delta t\varphi_{\rm tr}^2(r)], & r \le R_c \\ c\,\exp[(1-c)\Delta t\varphi_{\rm tr}^2(r)] + (1-c)\exp[-c\Delta t\varphi_{\rm tr}^2(r)], & r > R_c, \end{cases} \tag{22}$$

where

$$R_c = \frac{\pi}{2}\sqrt{\frac{\hbar^2}{2M(1-c)\Delta}}\,. \tag{23}$$

Then we have for $U_{\rm tr}(r)$,

$$U_{\rm tr}(r) = \begin{cases} (1-c)\Delta, & r \le R_c \\ (1-c)\Delta\left[1 - \dfrac{\exp\left(-t\Delta\varphi_{\rm tr}^2(r)\right)}{c + (1-c)\exp\left(-t\Delta\varphi_{\rm tr}^2(r)\right)}\right] & r > R_c. \end{cases} \tag{24}$$

For convenience, we introduce a new variable $p(r)$, which will describe a local deviation of the attractive cell concentration from its mean quantity equal to c. This variable can take its values within interval

$$(1-c) \ge p(r) \ge -c\,. \tag{25}$$

The variable $p(r)$ accepts the maximum and minimum values in areas occupied by the attractive or repulsive cells exclusively. The local values of the cell concentration of the first and second kind are now equal to $[c+p(r)]$ and $[1-c-p(r)]$, respectively. With help of $p(r)$, we rewrite $U_{\rm tr}(r)$ as

$$U_{\rm tr}(r) = -\Delta\, p(r)\,, \tag{26}$$

where

$$p(r) = \begin{cases} (1-c), & r \le R_c \\ (1-c)\left[1 - \dfrac{\exp(-t\varphi_{\rm tr}^2\Delta)}{c + (1-c)\exp(-t\varphi_{\rm tr}^2\Delta)}\right], & r > R_c. \end{cases} \tag{27}$$

Then we can find that

$$\exp\{-t\Delta\varphi_{\rm tr}^2\} = \frac{c}{c+p}\frac{1-c-p}{1-c}\,, \tag{28}$$

where the reduced notation $p \equiv p(r)$ is used. Taking into account Eqs. (19), (26), (28) and the notation introduced, we present $A[-it]$ in the form

$$A[-it] = -\int \frac{d^3r}{\kappa v_0}\left[\ln\left(\frac{c}{c+p}\right)^{c+p} + \ln\left(\frac{1-c}{1-c-p}\right)^{1-c-p}\right]. \tag{29}$$

The integrand of Eq. (29) at $r \le R_c$ when $p = (1-c)$

is equal simply to $\ln(c)$.

Adding and subtracting function $i\tau U_{\rm tr}(r)\varphi_{\rm tr}^2(r)$ in the integrand of Eq. (18), we present this expression as

$$\mathcal{A}[\tau] = \int \frac{d^3r}{\kappa v_0}\left\{ i\tau\left[-\frac{\hbar^2}{2M}\varphi_{\rm tr}(r)\nabla^2\varphi_{\rm tr}(r) + \omega\varphi_{\rm tr}^2(r) - U_{\rm tr}(r)\varphi_{\rm tr}^2(r)\right] - \ln\langle\langle\exp\{-i\tau[V_{\rm FL}(r) - U_{\rm tr}(r)]\varphi_{\rm tr}^2(r)\}\rangle\rangle\right\}. \tag{30}$$

With the help of Eqs. (27) and (28), averaging with the weight factor identical to Eq. (15) can be written as

$$\langle\langle\cdots\rangle\rangle \equiv \int_{-\infty}^{\infty} dV_{\rm FL}(r)\tilde{P}(V_{\rm FL}(r))\cdots , \tag{31}$$

where the auxiliary distribution function

$$\tilde{P}(V_{\rm FL}(r)) = (c+p)\delta[V_{\rm FL}(r) - (1-c)\Delta] + (1-c-p)\delta[V_{\rm FL}(r) + c\Delta] \tag{32}$$

is introduced.

Expanding the last item of Eq. (30) in a Taylor series in powers of $i\tau\varphi_{\rm tr}^2$, we get for $\mathcal{A}[\tau]$ the expression

$$\mathcal{A}[\tau] = \int \frac{d^3r}{\kappa v_0} i\tau\left[-\frac{\hbar^2}{2M}\varphi_{\rm tr}(r)\nabla^2\varphi_{\rm tr}(r) + \omega\varphi_{\rm tr}^2(r) - U_{\rm tr}(r)\varphi_{\rm tr}^2(r)\right] + \frac{\tau^2}{2}m_2 - \frac{i\tau^3}{6}m_3 + \cdots , \tag{33}$$

where

$$m_2 = \Delta^2 \int \frac{d^3r}{\kappa v_0}(\varphi_{\rm tr}^2(r))^2[c+p][1-c-p] \tag{34}$$

and

$$m_3 = \Delta^3 \int \frac{d^3r}{\kappa v_0}(\varphi_{\rm tr}^2(r))^3[c+p][1-c-p][1-2c-2p] . \tag{35}$$

As it follows from Eqs. (34) and (35), moments m_2 and m_3 represent the first two nonzero powers of the matrix element of the interaction of the localized state described by the wave function $\varphi_{\rm tr}(r)$ with the fluctuating environment, i.e., with the difference between statistically possible values of the random potential and its smoothed value $U_{\rm tr}(r)$. If ω is the eigenvalue of Eq. (19), then the expression in square brackets of Eq. (33) is equal to zero.

Restricting the expansion in Eq. (33) by the square item in τ powers and substituting this into Eq. (16), we obtain the Gaussian integral, which can be easily calculated. As a result, we have

$$\frac{1}{\pi}\langle{\rm Im}G(\omega)\rangle = \frac{1}{\sqrt{2\pi\gamma^2(\omega)}}\exp\left\{\int\frac{d^3r}{\kappa v_0}\left[\ln\left(\frac{c}{c+p}\right)^{c+p} \times\left(\frac{1-c}{1-c-p}\right)^{1-c-p}\right]\right\}, \tag{36}$$

where

$$\gamma^2(\omega) = \frac{m_2}{\left[\int \frac{d^3r}{\kappa v_0}\varphi_{\rm tr}^2(r)\right]^2} . \tag{37}$$

The function $\gamma(\omega)$ represents the statistical deviation of the localization energy ω in the potential well of Eq. (26), due to interaction of the localized state with surrounding random potential.

E. Estimation of mobility edge position

The expression for the imaginary part of the Green function derived as a result of a variational procedure applied to the highly nonlinear functional $A[-it]$ presents, in a general case, an infinite series in cumulants due to $\mathcal{A}[\tau]$ expansion in Eq. (33). The series is created by the interaction of the localized state with fluctuation potential. The interaction is conditioned by the fact that the trial wave function $\varphi_{\rm tr}(r)$ does not coincide as a rule with an eigenfunction of any configuration of the random potential and, therefore, the problem of the stability of the solution within the chosen class of trial functions appears. We consider the problem, restricting ourselves by the first item of the series.

Quantitatively, the interaction is measured in terms of the difference between really possible values of the random potential and its smoothed value being described by $U_{\rm tr}(r)$. The value $\gamma^2(\omega)$ is expressed by the second power of the matrix element of this difference averaged over all possible configurations.

At $\omega \to (1-c)\Delta$ the value $\gamma \to 0$, which shows that near the Lifshitz border, the solution coincides with exact one. There is a wide interval of localization energies where inequality $\gamma \ll \omega$ takes place. Therefore, $\varphi_{\rm tr}(r)$ describes the stable solution of the problem and Eqs. (12) and (36) give the value of the DOS in the region of localization energy $\omega \geq \gamma(\omega)$. The next items of expansion of $\mathcal{A}[\tau]$ Eq. (33) in this region are considerably smaller and decrease with $\varphi_{\rm tr}^2(r)$ powers in the integrand increasing.

In the opposite limit, $\omega \ll (1-c)\Delta$ the dependence $\gamma(\omega)$ has the form[43,44] $\gamma(\omega) \approx \sqrt{\omega E_{\rm BE}/2}$. The value $E_{\rm BE}$ defining the $\rho(\omega)$ dependence slope in the region of the band edge can be written as

$$E_{\rm BE} \approx \frac{c\Delta}{\nu_{\rm cr}}\frac{\pi^2}{6}I_4 . \tag{38}$$

Here, $\nu_{\rm cr}$ is the number of the cells in the compact critical cluster

$$\nu_{\rm cr} = \left[\frac{E_{\rm cr}}{(1-c)\Delta}\right]^{3/2} . \tag{39}$$

The value $E_{\rm cr}$ is the critical depth of the potential in the volume of one cell in the effective mass approximation,

$$E_{\rm cr} = \frac{\pi^2}{4} \frac{\hbar^2}{2M\left(\frac{3}{4\pi}\kappa v_0\right)^{2/3}}, \tag{40}$$

and the integral I_4 is a function weakly dependent on the energy

$$I_4 = \int_0^\infty \frac{e^{-4X_{\rm cr}Y}}{(1+Y)^2}\,dY, \quad X_{\rm cr} = \sqrt{\frac{2M\omega}{\hbar^2}}\,R_{\rm cr}, \tag{41}$$

where $X_{\rm cr}$ represents the radius of the compact critical cluster in units of de Broglie wavelength. The value of I_4, at small but finite ω, is approximately equal to 0.5.

In this region, $\gamma(\omega)$ decreases slower then ω with ω decreasing. Therefore, above some energy ω, the value $\gamma(\omega)$ will exceed the localization energy.

We denote as $\omega_{\rm ME}$ the point where $\gamma(\omega)$ is equal to ω. It is defined by equation

$$\omega = \gamma(\omega)\,. \tag{42}$$

The situation described by Eq. (42) means that fluctuations of the potential are able to shift the localized state back into continuum with the probability equal to almost a unit. At small values of ω, where $\omega \ll (1-c)\Delta$, the inequality $\omega \ll \gamma(\omega)$ takes place. Therefore, the states with energies $\omega < \gamma(\omega)$ cannot be considered as localized ones any more and we can consider the solution of Eq. (42) $\omega_{\rm ME}$ as the estimation of a mobility edge position.

A more accurate calculation of the mobility edge position requires the solution of the quantum percolation problem for the system of interacting localized states distributed in some interval of localization energies. The DOS of the localized states is distributed in a relatively narrow energy interval in this case. Therefore, the problem is analogous to one considered by Ching and Huber,[53] where a simple relation was established between mean distance spacing the localized states and the radius of their interaction at the quantum percolation threshold. Despite a very different approach, the relationship of the same order takes place in the considered system between the mean space and the radius of a wave function of states just below $\omega_{\rm ME}$.

F. Relationship with binomial coefficients

For the best interpretation of the physical sense of Eq. (36), we consider below the case where p does not depend on r within the potential well and integrals of Eqs. (36) and (37) simplify. To find the expression for the imaginary part of the Green function, we replace the function $p(r)$ in Eq. (36) by its mean value $\bar{p}$ within the region limited by the wave function $\varphi_{\rm tr}(r)$ size, i.e., within the volume containing n cells, which in turn, we define by means of equation

$$n = \left[\int \frac{d^3r\,\varphi_{\rm tr}^2(r)}{\kappa v_0}\right]^2 \left[\int \frac{d^3r}{\kappa v_0}\varphi_{\rm tr}^4(r)\right]^{-1}. \tag{43}$$

Then the self-consistent value $\bar{p}$ can be found from equation

$$\int \frac{d^3r}{\kappa v_0}\left[\ln\left(\frac{c}{c+\bar{p}}\right)^{c+p} + \ln\left(\frac{1-c}{1-c-p}\right)^{1-c-p}\right]$$
$$= n\left[\ln\left(\frac{c}{c+\bar{p}}\right)^{c+\bar{p}} + \ln\left(\frac{1-c}{1-c-\bar{p}}\right)^{1-c-\bar{p}}\right]. \tag{44}$$

To transform $\gamma^2(\omega)$, we substitute the value $\bar{p}$ into Eq. (34). Taking into account the definition of $\gamma^2(\omega)$ following from Eqs. (34) and (37), we conclude that the value of $\gamma^2(\omega)$ can be presented as

$$\gamma^2(\omega) \approx \left[\int \frac{d^3r}{\kappa v_0}\varphi_{\rm tr}^4(r)(c+\bar{p})(1-c-\bar{p})\Delta^2\right]$$
$$\times \left[\int \frac{d^3r}{\kappa v_0}\varphi_{\rm tr}^2(r)\right]^{-2}$$
$$= \frac{\Delta^2}{n}(c+\bar{p})(1-c-\bar{p})\,. \tag{45}$$

The substitution of Eqs. (44) and (45) into Eq. (36) results in the estimation of the imaginary part of Green function

$$\frac{1}{\pi}\langle {\rm Im}G(\omega)\rangle \approx \frac{1}{\Delta}\sqrt{\frac{n}{2\pi(c+\bar{p})(1-c-\bar{p})}}\left(\frac{c}{c+\bar{p}}\right)^{n(c+\bar{p})}$$
$$\times \left(\frac{1-c}{1-c-\bar{p}}\right)^{n(1-c-\bar{p})}. \tag{46}$$

On the other hand, we find a probability of the composition fluctuation at random filling of the volume consisting of n cells by cells of two kinds under the condition that the mean composition is defined by concentration c for cells of the first kind and $(1-c)$ for cells of the other one. The probability of obtaining the configurations with $n_{c+\bar{p}} = n(c+\bar{p})$ cells of the first kind and $n_{1-c-\bar{p}} = n(1-c-\bar{p})$ cells of the other kind is proportional to the binomial coefficient and can be presented by expression

$$W_{n_{\bar{p}}}^n = \frac{n!}{n_{c+\bar{p}}!\,n_{1-c-\bar{p}}!}c^{n_{c+\bar{p}}}(1-c)^{n_{1-c-\bar{p}}}, \tag{47}$$

where the composition fluctuation is described by the excess of $n_{\bar{p}}$ cells of the first kind,

$$-n_c \le n_{\bar{p}} \equiv n\bar{p} \le n_{1-c}\,. \tag{48}$$

Factorials n, $n_{c+\bar{p}}$, and $n_{1-c-\bar{p}}$ of Eq. (47) can be transformed with help of Stirling formula,

$$n! = \sqrt{2\pi n}\,\exp(n\ln n - n). \tag{49}$$

In terms of variable $\bar{p}$ instead of $n_{\bar{p}}$, the expression for the normalized probability of the fluctuation $W_{\bar{p}}^n = n\,W_{n_{\bar{p}}}^n$ is expressed as

$$W_{\bar{p}}^{n}=\sqrt{\frac{n}{2\pi(c+\bar{p})(1-c-\bar{p})}}\left(\frac{c}{c+\bar{p}}\right)^{n(c+\bar{p})}\times\left(\frac{1-c}{1-c-\bar{p}}\right)^{n(1-c-\bar{p})}, \quad (50)$$

where

$$-c\le\bar{p}\le 1-c\,. \quad (51)$$

Now we see that the magnitude of the imaginary part of the Green function is connected with the fluctuation probability $W_{\bar{p}}^{n}$ through the equation

$$\left\langle\frac{1}{\pi}\mathrm{Im}\,G(\omega)\right\rangle\approx\frac{1}{\Delta}W_{\bar{p}}^{n}\,. \quad (52)$$

The expression is an analog of Eq. (36) when $\bar{p}n$ cells are homogeneously distributed within the volume occupied by the potential well of the localized state. It can be useful for the estimation of the imaginary part of the Green function if it is possible to find the values of n and $\bar{p}$ for the localized state with the depth ω.

G. Contour of D-center band

The D-center band contour formed as a result of fluctuations of the binding energy caused by the interaction of the localized particle with the environmental random potential represents the classical example of inhomogenous broadening. Hereafter, we shall think that the central part of the attractive potential of the deep center does not depend on the environment and does not contain a fluctuation component and the volume of this central part assume to be equal to κv_0. In this approximation, the band contour contains the information about both the value of the root-mean-square deviation and an asymmetry in the statistical distribution of the positive and negative values of the random potential.

For the ideal quantitative description of the band broadening, we need to have more realistic data on both the central part of the potential and, consequently, the wave function of the center. Nevertheless, we will show that even a semiquantitative approach to this problem gives valuable additional information about the fluctuation potential of the amorphous network.

Further, we use the results[43,44] and present the contribution into imaginary part of Green function, due to the D center like

$$\frac{1}{\pi}\langle\mathrm{Im}\,G^{D}(\omega)\rangle=\exp\{-A_D[-it]\}\frac{C_D}{2\pi}\int\frac{d^3r}{\kappa v_0}[\varphi_{\mathrm{tr}}^{D}(r)]^2\times\int_{-\infty}^{\infty}d\tau\,\exp\{-\mathcal{A}_D[\tau]\}\,. \quad (53)$$

Here, C_D is the concentration of D centers, which will be considered much less than both c and $(1-c)$. The $A_D[-it]$ and $\mathcal{A}_D[\tau]$ are defined by the equations

$$A_D[-it]=\int\frac{d^3r}{\kappa v_0}t\left[\frac{\hbar^2}{2M}(\nabla\varphi_{\mathrm{tr}}^{D}(r))^2+\omega(\varphi_{\mathrm{tr}}^{D}(r))^2\right]-t\int_0^{R_0}\frac{d^3r}{\kappa v_0}\Delta_D(\varphi_{\mathrm{tr}}^{D})^2-\int_{r>R_0}\frac{d^3r}{\kappa v_0}\ln\mathcal{R}_D(-it)\,, \quad (54)$$

$$\mathcal{A}_D[\tau]=\int\frac{d^3r}{\kappa v_0}\left\{i\tau\left[\frac{\hbar}{2M}(\nabla\varphi_{\mathrm{tr}}^{D}(r))^2+\omega(\varphi_{\mathrm{tr}}^{D}(r))^2\right]\right\}-i\tau\int_0^{R_0}\frac{d^3r}{\kappa v_0}\Delta_D(\varphi_{\mathrm{tr}}^{D}(r))^2-\int_{r>R_0}\frac{d^3r}{\kappa v_0}\ln\left[\frac{\mathcal{R}_D(\tau-it)}{\mathcal{R}_D(-it)}\right]\,. \quad (55)$$

Here, R_0 is the radius of the central part of the potential well of the deep center, Δ_D is its depth, $\varphi_{\mathrm{tr}}^{D}(r)$ is the normalized wave function of the localized state, which is a solution of the equation derived as the result of minimization of $A_D[-it]$,

$$-\frac{\hbar^2}{2M}\nabla^2\varphi_{\mathrm{tr}}^{D}(r)+\omega\varphi_{\mathrm{tr}}^{D}(r)-U_{\mathrm{tr}}^{D}(r)\varphi_{\mathrm{tr}}^{D}(r)=0\,, \quad (56)$$

where

$$U_{\mathrm{tr}}^{D}(r)=\begin{cases}\Delta_D, & r\le R_0\\ (1-c)\Delta\left[1-\dfrac{\exp\{-t\Delta(\varphi_{\mathrm{tr}}^{D}(r))^2\}}{c+(1-c)\exp\{-t\Delta(\varphi_{\mathrm{tr}}^{D}(r))^2\}}\right], & r>R_0.\end{cases} \quad (57)$$

The expression for the well depth beyond the limits of its central part can be written in the form similar to Eq. (26),

$$U_{\mathrm{tr}}^{D}(r)=\Delta\,p_D(r)=\Delta\,p_D\,,\qquad r>R_0, \quad (58)$$

where $p_D(r)\equiv p_D$ is now defined by the relation

$$p_D(r)=(1-c)\left[1-\frac{\exp[-t\Delta(\varphi_{\mathrm{tr}}^{D}(r))^2]}{c+(1-c)\exp[-t\Delta(\varphi_{\mathrm{tr}}^{D}(r))^2]}\right].$$

After the transformations analogous to ones fulfilled in Eqs. (26) to (29), we obtain for $A_D[-it]$ and $\mathcal{A}_D[\tau]$ expressions,

$$A_D[-it] = -\int_{r>R_0} \frac{d^3r}{\kappa v_0} \ln\left\{ \left[\frac{c}{c+p_D}\right]^{c+p_D} \times \left[\frac{1-c-p_D}{1-c}\right]^{1-c-p_D} \right\}, \tag{59}$$

$$\mathcal{A}_D[\tau] = -\int_{r>R_0} \frac{d^3r}{\kappa v_0} \ln\langle\langle \exp\{i\tau(\varphi^D_{\rm tr}(r))^2[V_{\rm FL}(r) - U^D_{\rm tr}(r)]\}\rangle\rangle_D \,, \tag{60}$$

where the double brackets mean averaging with a new auxiliary distribution function

$$\tilde{P}_D(V_{\rm FL}(r)) = (c+p_D)\delta[V_{\rm FL}(r) - (1-c)\Delta] + (1-c-p_D)\delta[V_{\rm FL}(r) + c\Delta]\,. \tag{61}$$

Substituting Eqs. (59) and (60) into Eq. (53), we obtain the contribution to the imaginary part of the Green function of the states localized in deep centers. For the calculation of the band contour, it is necessary to know the solution of Eq. (56) for each value of the localization energy ω. The solution of this equation also gives the function p_D and, therefore, the self-consistent configuration of the potential well beyond the limits of its central part. At the localization energies near the band maximum, we use the simplified expression for Eq. (53), which is deduced as a result of expanding Eq. (55) in the vicinity of the eigenvalue of Eq. (56), when $U^D_{\rm tr}(r) = 0$ at $r > R_0$,

$$-\frac{\hbar^2}{2M}\nabla^2\varphi^0(r) - \omega_0\varphi^0(r) - \Delta_{D|_{r\le R_0}}\varphi^0(r) = 0\,. \tag{62}$$

The eigenvalue of Eq. (62) corresponds to the energy of localization, due to the central part of the potential. It coincides with the center of gravity of the band and is denoted as ω_0. For this value of the localization energy $A_D[-it] = 0$, and for $\mathcal{A}_D[\tau]$, we have

$$\mathcal{A}[\tau] = -i\tau(\omega-\omega_0) + \frac{\tau^2 m_2^0}{2} - \frac{i\tau^3 m_3^0}{6} + \cdots\,, \tag{63}$$

with

$$\int \frac{d^3r}{\kappa v_0}(\varphi^0(r))^2 = 1\,,$$

where only the first two nonzero items of the expansion in powers of $i\tau(\varphi^0)^2$ are preserved. Substitution of Eq. (63) into Eq. (53) leads to the expression of the band contour suitable in the vicinity of its maximum in the form of integral

$$\frac{1}{\pi}\langle {\rm Im}G^D(\omega)\rangle = \frac{C_D}{2\pi}\int_{-\infty}^{\infty} d\tau \exp\left\{ i\tau(\omega-\omega_0) - \frac{\tau^2 m_2^0}{2} + \frac{i\tau^3 m_3^0}{6}\right\}, \tag{64}$$

where

$$m_2^0 = c(1-c)\Delta^2 \int_{r>R_0} \frac{d^3r}{\kappa v_0}(\varphi^0(r))^4\,, \tag{65}$$

$$m_3^0 = c(1-c)(1-2c)\Delta^2 \int_{r>R_0} \frac{d^3r}{\kappa v_0}(\varphi^0(r))^6\,. \tag{66}$$

Equations (64)–(66) result in the fact that the value and the sign of D-center band asymmetry depends on the third moment given by Eq. (66). The analogous results can be also obtained from more accurate expression (53) by expansion of $\mathcal{A}[\tau]$ in series of cumulants. As follows from Eq. (66), the sign of m_3 changes at $c = 0.5$. In the region $c > 0.5$, the maximum value of the density of states shifts towards $\omega < \omega_0$, while at $c < 0.5$, the deformation of the contour of opposite sign takes place. Thus, the form of the band contour within the framework of the performed consideration contains information about the fluctuation potential and defines the region of the model parameter c that gives the attractive cell concentration.

III. RELATIONSHIP OF THEORY PARAMETERS WITH EXPERIMENTAL DATA

Experimental data on the valence-band tail have a number of characteristics that can be used to find parameters of the theory. For this purpose we can exploit, in particular, the value of the density of states at the mobility edge, the slope of the linear dependence of $\rho(\omega)$ in the region of the valence-band edge, and the slope of $\ln\rho(\omega)$ in the Urbach region, i.e., the parameter of the Urbach rule.

The purpose of this section is to obtain theoretical expressions for mentioned characteristics in the form convenient for determination of the theory parameters from the data on the density of states. Equations (12) and (36) give the value of the density of states at ω larger then the value of the localization energy dispersion $\gamma(\omega)$. The estimation of the mobility edge position by means of Eq. (37) leads to the value[43,44] $\omega_{\rm ME} = E_{\rm BE}/2$.

The experimental value of the density of states at the mobility edge for α-Si:H is supposed to be about (2–4)$\times 10^{21}$ eV^{-1} cm^{-3}. It is easier to find the simple theoretical expression for the DOS in this point by means of extrapolation of the exponential factor dependence of the DOS from the region of small ω to $\omega = \omega_{\rm ME}$.[43,44]

The exponential factor of $\rho(\omega)$ in the region $\omega \ll (1-c)\Delta$ has the form[43,44]

$$\rho(\omega) \sim c^{\nu_{\rm cr}} \exp(-\omega/E_{\rm BE})\,. \tag{67}$$

$E_{\rm BE}$ defines the slope of the dependence $\rho(\omega)$ in the region of the band edge and is given by Eq. (38) above.

In order to reconcile the density of states below $\omega_{\rm ME}$ and above $\omega_{\rm ME}$ we take into account that the density of states dependence on energy is defined mainly by the exponential factor of Eq. (67) and that the density of states has no discontinuities at $\omega = \omega_{\rm ME}$. Then, present-

ing $\rho(\omega)$ in the region $\omega \leq \omega_{\rm ME}$, in the form

$$\rho(\omega) \approx \frac{2l+1}{\kappa v_0} \frac{c^{\nu_{\rm cr}}}{\sqrt{2\pi\omega_{\rm ME}^2}} \exp\left(-\frac{\omega}{E_{\rm BE}}\right) , \tag{68}$$

we obtain the satisfactory extrapolation of $\rho(\omega)$ into the region of small ω. Taking into account that $\omega_{\rm ME} = E_{\rm BE}/2$, the DOS value at the mobility edge is estimated by the expression

$$\rho(\omega_{\rm ME}) \approx \frac{2l+1}{\kappa v_0} \frac{c^{\nu_{\rm cr}}}{\sqrt{2\pi\omega_{\rm ME}^2}} \exp\left(-\frac{1}{2}\right) . \tag{69}$$

The expression for the DOS at the mobility edge gives us the first equation for the determination of theory parameters. The second equation can be deduced from comparison of the value of the Urbach parameter E_U and $E_{\rm BE}$. The theoretical value E_U is given by expression[43,44]

$$E_U \approx \frac{(1-c)\Delta}{8\nu_{\rm cr}\ln(1/c)} . \tag{70}$$

Thus,

$$\frac{E_{\rm BE}}{E_U} = \frac{c\ln(1/c)}{1-c} \frac{4\pi^2}{3} I_4 . \tag{71}$$

The value of $E_{\rm BE}$ can be found from experimental data on the slope of $\rho(\omega)$ in the region of the band edge.

The experimental data[13] give the value of $E_{\rm BE}$ approximately equal to (5–6)E_U. As it follows from Eq. (71), the theoretical value of the relationship depends mainly on the concentration c. The function given by Eq. (71) accepts the value suitable for the description of the experimental data[13] in the region $c > 0.5$, however, in interval $1 > c > 0.5$, its variation is rather small and errors of determination of the relationship from experimental data exceed this variation. Therefore, in this region of c, Eq. (71) only restricts the interval of c from below, but it does not enable us to indicate the unique acceptable value. Equations (69) and (71) and one of two Eqs. (38) or (70) permit us to find the quantities of parameters Δ and $E_{\rm cr}$, while the size of the cell κ remains undefined.

To clarify the role of parameter κ and to estimate its value, we have to consider the behavior of $\rho(\omega)$ in an entire observable interval. The value of κ has the heaviest influence on the behavior of $\rho(\omega)$ in the region of the deepest states. This fact is connected with the circumstance that the value of κ determines $\nu_{\rm cr}$. As long as the value $c^{\nu_{\rm cr}}$ is fixed by the experimental value of the density of states at the mobility edge, κ increasing leads to the necessity for $(1-c)\Delta$ to decrease. The $(1-c)\Delta$ decreasing means that the Lifshitz border localized on depth $(1-c)\Delta$ moves towards the mobility edge. That leads to the drastic decreasing of the DOS in the region of deep fluctuation states. For the quantitative estimation of κ value, the numerical calculations are necessary.

To get complementary information on the parameters, we can analyze the data on the D-center band. The m_3^0 of Eq. (66) defining the asymmetry of D-center band depends on the parameter c, so it is possible to answer the question whether or not the form of the band agrees with the restriction on the value c following from Eq. (71). Moreover, the fit of the form of the band with the help of Eq. (64) enables us to find both m_3^0 and m_2^0.

IV. RESULTS OF CALCULATIONS AND COMPARISON WITH EXPERIMENTAL DATA

The calculations performed have shown that the value of parameter κ resulting in the best fit of DOS to the experiment was equal to a unit. In this case, the depth of potential wells $(1-c)\Delta$ appears to be about 1.9 eV. Taking into account that the mobility edge position $\omega_{\rm ME}$ is equal to 0.15 eV, we obtain the potential well depth counted from the mobility edge equal to 1.75 eV. The total amplitude of the random potential Δ and, therefore, the barrier height depend on the value of the concentration to be chosen. The latter was taken equal to $c = 0.73$ in order to fit the D-center band broadening and the sign of its asymmetry. As a result, Δ appeared to be equal to about 7 eV and $E_{\rm cr}$ to 10 eV. All these values vary slightly at small changes of the density of states at the mobility edge within the limits $(2\text{–}4)\times 10^{21}$ eV^{-1} cm^{-3}.

The results of calculations of the function $\rho(\omega)$ at $\kappa = 1$ and at optimum values of parameters are demonstrated in Fig. 1. The straight lines representing linear approximations of $\rho(\omega)$ in the band edge and Urbach regions are also shown there. Besides, the arrow at $\omega_{\rm ME}$ is

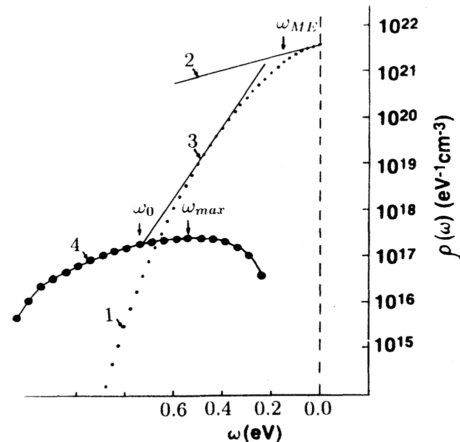

FIG. 1. Curve (1) presents the theoretical DOS in the tail region. It is calculated at values of parameters close to optimum. The line (2) presents the linear approximation of $\rho(\omega)$ dependence in the region of valence-band edge, the slope of this line is given by the value of $E_{\rm BE}^{-1}$. The Urbach region of $\rho(\omega)$ presents line (3) with slope equal to Urbach parameter E_U^{-1}. The mobility threshold $\omega_{\rm ME}$ is marked by an arrow [the value is obtained from Eq. (42)]. The dashed vertical line is the mean level of the random potential. The curve (4) gives the contour of the deep center band described by Eq. (64) at $c = 0.73$. ω_0 is the localization energy of the deep center without interaction with the fluctuation potential, and $\omega_{\max}$ is maximum of the band.

plotted, and it gives the estimated mobility edge position according to Eq. (42). In Fig. 1, the theoretical form of the D-center band also is presented. It is calculated with the same parameters of the fluctuation potential. The deep center band form given in Fig. 1 agrees qualitatively with contours presented in Fig. 7 of Ref. 13. The comparison of theoretical curves with experimental data has been fulfilled combining the experimental DOS with a theoretical curve in the mobility edge region.

In Fig. 2, a comparison of the theoretical density of states exhibited in Fig. 1 with the experimental density of states for the sample of B-doped α-Si:H (at diboran concentration in the gas phase equal to 10^{-3}) (Ref. 13) is carried out. According to Ref. 13, up to 98% of states of deep centers are eliminated in surface layer of the sample and this fact enables us to observe the deep tail of valence-bands. Experimental and theoretical curves agree in the wide range of the density of states.

To avoid the division procedure of the valence-band tail and of deep center bands, we have used for comparison two experimental spectra (Fig. 3). The first one corresponds to undoped sample and the second one to a sample grown at diboran concentration in a gas phase equal to 10^{-4} [see Fig. 4 (Ref. 13)]. Both spectra coincide at photon energies larger then 5.4 eV, while at smaller energies they show a considerably different behavior that is concerned with the larger concentration of D centers in the first sample. As a theoretical curve is used, on the one hand, the curve was like the one given in Fig. 1, which shows a good agreement with the experimental curve for the doped sample in the energy region larger than 5.1 eV. On the other hand, the curve obtained by summation of contributions of deep centers of Eq. (64) and the valence-band tail of Eq. (36) agrees well with the curve for undoped sample. It was found that the summary band describes well the experimental curve for the undoped sample at value $c = 0.73$ when $\gamma = 0.2$ eV and the relationship $(m_3^0)^{1/3}/(m_2^0)^{1/2} \approx 1$.

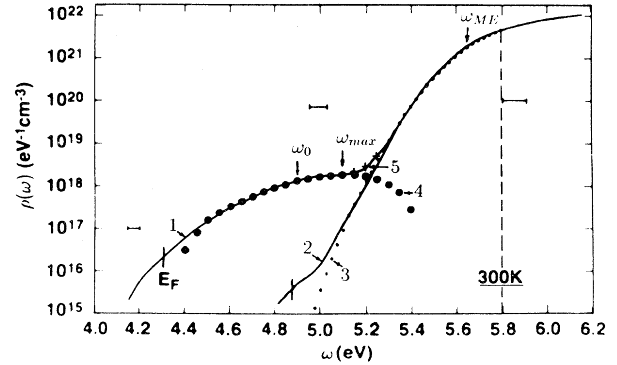

FIG. 3. Comparison of the theoretical dependence of the DOS built by addition of the fluctuation tail states and states of deep centers with experimental curve (Ref. 13). Curves (1) and (2) are the experimental data (Ref. 13) for undoped and B-doped samples, points (3) give the theoretical tail of the valence-band DOS, circles (4) present the contour of the deep center band, crosses (5) are the result of the addition of data (3) and (4). The other notations are the same as in Fig. 1.

Figure 4 shows the spectrum of the sample[13] grown at phosphin concentration in the gas phase equal to 10^{-3} and the theoretical curve built of contributions of the tail and the deep center states as well as in previous case. The localization energy ω_0 for the deep center and concentration C_D were chosen in such a way as to combine the experimental and theoretical curves in the region of the maximum value of the deep center band. The contour of the D-center band was calculated at the same value of parameter $c = 0.73$ as in the previous case. In Fig. 4, one can see that the good agreement of experimental data with the theory takes place in the wide range of energies.

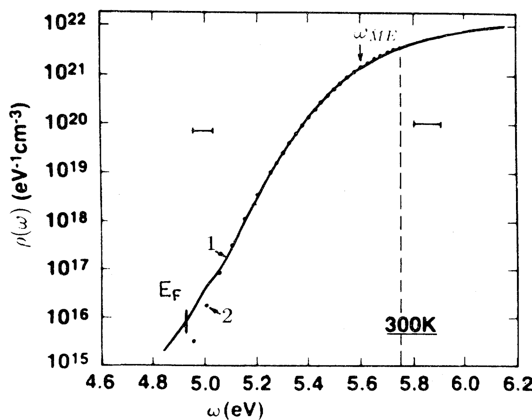

FIG. 2. Comparison of the theoretical DOS tail with experimental curve (Ref. 13) for the B-doped sample: (1) is the experimental curve, points (2) present the theoretical results. The other notations are the same as in Fig. 1.

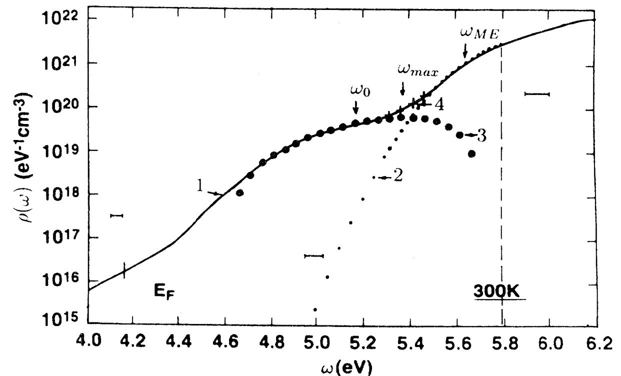

FIG. 4. Comparison of the theoretical and experimental data for the sample doped by phosphorus (Ref. 13). The curve (1) presents the experimental data, points (2) are the theoretical tail of the valence-band DOS, circles (3) give the contour of the deep center band, crosses (4) are the result of the addition of data (2) and (3). The other notations are the same as in Fig. 1.

V. DISCUSSION

The demonstrated results show that the random potential parameters, deduced from a comparison with experimental data mainly on undoped and B-doped samples, show no considerable dependence on the level of doping and, in fact, describe well the DOS of P-doped samples as well. This conclusion coincides with the opinion[45] about weak dependence of the random potential on the sample nature based on measurements of the hole drift mobility.

The D-center band form (D_0 center in undoped samples and D_- center in samples doped by phosphorus[13]) also does not depend on the kind and the level of doping. This circumstance finds that the explanation in our work as the only reason for the D-center band broadening in the model is the interaction with the random potential. It is conditioned by the relatively small changes of both the mean localization energy ω_0 and the wave function when passing from one sample to the other.

There is the considerable divergence between amplitude of the random potential derived from the fit to the experimental data as compared with ones assumed in the model. Taking into account the fact that the valence-band top shift at transitions from crystal silicon to α-Si:H is equal to about 1 eV, we see that the potential well depth measured from the mobility threshold in the calculations appeared to be larger. All other energy parameters at $\kappa = 1$ are also almost twice larger then the preliminary estimations have given.

To diminish the divergency, we have examined $\kappa > 1$. The good concordance of the calculated DOS with experimental data in the energy interval $\omega > 5.3$ eV has been obtained at $\kappa = 3$, yielding the depth of the wells equal to 1.3 eV, which still exceeds the difference of the band tops of the crystal and hydrogenated amorphous silicon. Greater values of κ giving the better coincidence with model parameters lead to the deviation of the theoretical curves from the experimental data at energies approaching the mobility edge.

The value $\kappa = 1$ was chosen mainly because it gives the best fit to the experimental DOS for B-doped samples[13] in the region of photon energies 4.9–5.2 eV. If, as it was admitted by authors,[13] the band concerned with shallow acceptor states of B is situated in the region 5.25–5.43 eV, it is necessary to take the last fact into account in the fitting procedure. That could affect the value of the potential amplitude, which we need to describe the experimental data.

It is possible, however, to find the other reason resulting in analogous consequences. The model[23] supposes that in regions occupied by the amorphous silicon where the potential has an attractive character for holes, the well depth is limited by the crystal silicon band top. At the same time, fluctuations of valence bond lengths and angles in the amorphous silicon take place resulting in the random Gaussian potential.[30] These fluctuations in the fraction of wells equal to about 0.5 could increase the depth and result in the increase of the density of localized states in a region of large localization energies, which is required in this case. Then the well depth connected with that part of random potential, which is described by binary statistics, can be taken smaller and that can give the best coincidence with the initial assumption. Calculations performed have shown an almost obvious result that the root-mean-square amplitude of an additional Gaussian potential is the quantity defining the well deepening. The estimation of the amplitude of the Gaussian potential in the work[24] gave the value 0.3 eV for the potential connected with a bond angle deformation. That is approximately two to three times less than it is required to achieve the agreement with the experiment. The results of the calculations show that the model describes well the major features of the band tail and might be fruitfully used for the analysis of further experimental information.

ACKNOWLEDGMENT

The work was partially supported by the International Scientific Foundation Grant No. R4I000.

[1] *Amorphous Semiconductors*, edited by M.H. Brodsky, Topics in Applied Physics Vol. 36 (Springer, Berlin, 1979).

[2] *Hydrogenated Amorphous Silicon II*, edited by J.D. Joannopoulos and G. Lucovsky (Springer, Berlin, 1984).

[3] N.J. Shevchik, Javier Tejeda, and M. Cardona, Phys. Rev. B **9**, 2627 (1974).

[4] D. Allan and J. Joannopoulos, in *Hydrogenerated Amorphous Silicon II* (Ref. 2), Chap. 2.

[5] G. Lukovsky and T.M. Hayes, in *Amorphous Semiconductors* (Ref. 1), Chap. 8.

[6] L. Ley, in *Hydrogenated Amorphous Silicon II* (Ref. 2), Chap. 3.

[7] B. von Roedern, L. Ley, and M. Cardona, Phys. Rev. Lett. **39**, 1576 (1977).

[8] B. von Roedern, L. Ley, M. Cardona, and F.W. Smith, Philos. Mag. **40**, 433 (1979).

[9] R.S. Crandall, Phys. Rev. Lett. **44**, 749 (1980).

[10] G.D. Cody, T. Tiedje, B. Abeles, B. Brooks, and Y. Goldstein, Phys. Rev. Lett. **47**, 1480 (1981).

[11] D.V. Lang, J.D. Cohen, and J.P. Harbison, Phys. Rev. B **25**, 5285 (1982).

[12] K. Winer and L. Ley, Phys. Rev. B **37**, 8363 (1988).

[13] K. Winer, I. Hirabayashi, and L. Ley, Phys. Rev. B **38**, 7680 (1988).

[14] S. Aljishi, J.D. Cohen, Shu Jin, and L. Ley, Phys. Rev. Lett. **64**, 2811 (1990).

[15] D. Weaire, Phys. Rev. Lett. **26**, 1541 (1981).

[16] D. Weaire and M.F. Thorpe, Phys. Rev. B **4**, 2508 (1971).

[17] M.F. Thorpe and D. Weaire, Phys. Rev. B **4**, 3518 (1971).

[18] J.D. Joannopoulos, Phys. Rev. B **16**, 2764 (1977).

[19] J.D. Joannopoulos and F. Yndurain, Phys. Rev. B **10**, 5164 (1974).

[20] D.C. Allan and J.D. Joannopoulos, Phys. Rev. Lett. **44**, 43 (1980).

[21] D.C. Allan, J.D. Joannopoulos, and W.P. Pollard, Phys. Rev. B **25**, 1065 (1982).
[22] F. Stern, Phys. Rev. B **3**, 2636 (1971).
[23] M.H. Brodsky, Solid State Commun. **36**, 55 (1980).
[24] J. Singh, Phys. Rev. B **23**, 4156 (1981).
[25] C.H. Soukoulis, M.H. Cohen, and E.N. Economou, Phys. Rev. Lett. **53**, 616 (1984).
[26] D.E. Polk and D.S. Boudreaux, Phys. Rev. Lett. **31**, 92 (1973).
[27] A.N. Connel and R.J. Temkin, Phys. Rev. B **9**, 5323 (1974).
[28] P. Steinhardt, R. Alben, and D. Weaire, J. Non-Cryst. Solids **15**, 199 (1974).
[29] D. Beeman and B.L. Bobbs, Phys. Rev. B **12**, 1399 (1975).
[30] W.Y. Ching, C.C. Lin, and L. Guttman, Phys. Rev. B **16**, 5488 (1977).
[31] L. Guttman and C.Y. Fong, Phys. Rev. B **26**, 6756 (1980).
[32] B.I. Halperin and M. Lax, Phys. Rev. **148**, 722 (1966).
[33] B.I. Halperin and M. Lax, Phys. Rev. **159**, 802 (1966).
[34] J.L. Cardy, J. Phys. C **11**, L321 (1978).
[35] E. Brezin and G. Parizi, J. Stat. Phys. **19**, 269 (1978).
[36] F. Urbach, Phys. Rev. **92**, 1324 (1953).
[37] W. Martienssen, J. Phys. Chem. Solids **2**, 257 (1957).
[38] M.V. Kurik, Phys. Status Solidi A **8**, 9 (1971).
[39] W. Sritakool, V. Sa-Yakanit, and H.R. Glyde, Phys. Rev. B **33**, 1199 (1986).
[40] S. John, C. Soukoulis, M.H. Cohen, and E.N. Economou, Phys. Rev. Lett. **57**, 1777 (1986).
[41] A.A. Klochikhin, O. Kühn, and S.G. Ogloblin, Phys. Status Solidi B **160**, 211 (1990) .
[42] J.C. Philips, Phys. Rev. Lett. **42**, 1151 (1979).
[43] A.A. Klochikhin and S.G. Ogloblin, Zh. Eksp. Teor. Fiz. **103**, 1676 (1993) [Sov. Phys JETP **76**, 825 (1993)].
[44] A.A. Klochikhin and S.G. Ogloblin, Phys. Rev. B **48**, 3100 (1993).
[45] R.A. Street, M. Hack, and W.B. Jackson, Phys. Rev. B **37**, 4209 (1988).
[46] Y. Bar-Yam, D. Adler, and J.D. Joannopoulos, Phys. Rev. Lett. **57**, 467 (1986).
[47] R.A. Street, J. Kakalios, and T.M. Hayes, Phys. Rev. B **34**, 3030 (1986).
[48] Z.E. Smith and S. Wagner, Phys. Rev. Lett. **59**, 688 (1987).
[49] R.A. Street and K. Winer, Phys. Rev. B **40**, 6236 (1989).
[50] K. Winer, Phys. Rev. B **41**, 12 150 (1990).
[51] S.C. Deane and M.J. Powell, Phys. Rev. Lett. **70**, 1654 (1993).
[52] A.A. Klochikhin and A.N. Reznitsky (unpublished).
[53] W.Y. Ching and D.L. Huber, Phys. Rev. B **25**, 1096 (1982).