East European Journal of Physics. **2.** 187-190 (2026)

DOI:10.26565/2312-4334-2026-2-19 ISSN 2312-4334

THE EFFECT OF TEMPERATURE ON THE ENERGETIC POSITION OF THE FERMI LEVEL IN POROUS SILICON

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Received January 5, 2026; revised March 26, 2026; accepted April 3, 2026

This paper presents the theoretical investigation of the temperature-dependent shift of the Fermi level in porous silicon (por-Si). The study is based on the charge-state distribution model originally proposed for hydrogenated amorphous silicon (a-Si:H), while accounting for the unique physical and chemical properties of porous silicon (por-Si). The temperature dependence of the parameters in the charge-state density within the bandgap is accounted for in both simplified and advanced models. For each model, the Fermi-level shift behavior was calculated using numerical methods based on integral-differential equations. The results are presented in graphical form, and the physical mechanisms underlying the Fermi level shift across different temperature ranges are discussed. The conclusions obtained can be applied to explain carrier transport processes, reduce surface recombination, and improve the efficiency of por-Si/c-Si heterostructure-based solar cells.

Keywords: *Fermi level; Amorphous silicon; Porous silicon; Bandgap; Density of states; Gaussian distribution; Electrical conductivity*

PACS: 71.23.Cq, 71.10.Ca, 73.61.Cw, 72.40.+w, 78.20.-e

INTRODUCTION

The increasing demands on the performance and efficiency of various electronic devices based on semiconductor materials have been consistently noted in the scientific literature for many years. The development of multi-component (heterostructure-based) devices using different modifications of semiconductor materials has been expanding. In accordance with the principles of HIT technology, to enhance the efficiency of crystalline silicon (c-Si)-based solar cells, heterostructure devices comprising three or more layers are being developed using modified forms of silicon such as hydrogenated amorphous silicon (a-Si:H), microcrystalline silicon (μc-Si:H), nanocrystalline silicon (nc-Si:H), or porous silicon (por-Si) [3,4,5].

Due to the low physicochemical stability and rapid degradation of hydrogenated silicon layers, extensive research in recent years has focused on improving the efficiency of heterostructure solar cells based on porous silicon (por-Si) layers [6,7]. Over the past decade, the fabrication of heterostructure-based solar cells has been recognized as one of the most rapidly advancing technologies. Among the most promising and efficient approaches for producing solar cells with crystalline silicon (c-Si)-based heterostructure layers is the HIT technology (heterojunction with intrinsic thin layer) [1,2].

One of the key advantages of heterojunction-based solar cells is their ability to effectively reduce surface recombination. In particular, when a thin layer of n^+-type hydrogenated silicon (Si:H) modification is deposited on the surface of p-type crystalline silicon, the resulting valence band offset (ΔE_v) significantly suppresses surface recombination [3]. Compared to materials such as a-Si:H, μc-Si:H, and nc-Si:H, porous silicon (por-Si) possesses a larger specific surface area as well as additional physicochemical properties, which can substantially contribute to enhancing the efficiency of heterojunction solar cells based on por-Si. One of the main challenges in heterojunction solar cells is the formation of theoretical potential barriers for majority charge carriers in either the conduction or valence band. An increase in the magnitude of such potential barriers negatively affects the carrier transport process, ultimately leading to a reduction in the fill factor (FF).

It is well known that the primary cause of potential barrier formation between layers is the difference in the Fermi level positions of the semiconductor materials composing the layers, as well as the sensitivity of the Fermi level's energetic position to external influences. Moreover, the transport process of charge carriers is significantly affected by the average lifetime of both majority and minority carriers [8]. Therefore, the present study aims to theoretically analyze the temperature dependence of the Fermi level and the average carrier lifetime.

The bandgap width and charge carrier transport parameters of porous silicon (por-Si) are significantly influenced by the size of its crystallites. In por-Si, crystallite sizes can range from a few nanometers to several hundred nanometers [9]. Considering the crystallite size is crucial when selecting theoretical research methods, since, as noted earlier, the electrical conductivity of por-Si can vary widely with porosity.

Studies have shown that when the porosity is in the range of 50–70%, the electrical conduction mechanism and bandgap width of por-Si become similar to those of hydrogenated amorphous silicon (a-Si:H).

Cite as: U.S. Babakhodzhaev, M.A. Usmanov, I.Sh. Vokhobjonov, S.M. Shamsiddinova, East Eur. J. Phys. 2, 187 (2026), https://doi.org/10.26565/2312-4334-2026-2-19

Accordingly, the temperature dependence of electrical conductivity exhibits an activation character and can be expressed as:

$$\sigma = \sigma_0 exp\left(\frac{\Delta E}{kT}\right)$$

where the quantities σ_0 and ΔE vary in accordance with the Meyer–Neldel rule, a fact confirmed by experimental results. It has also been established that for por-Si with 50–70% porosity, the bandgap width (E_g) lies within the range of 1.7-2 eV [10].

Based on the above considerations, the model proposed in [11] for the bandgap of a-Si:H material was employed to investigate the temperature dependence of the Fermi level. According to this model, the charged states arising from broken bonds within an energy width Δ around the Fermi level are distributed according to a Gaussian distribution.

The electrons in these charged states are redistributed with temperature in accordance with the function $f(\varepsilon, \varepsilon_F, U, T)$, which leads to a temperature-dependent shift of the Fermi level $\varepsilon_F(T)$.

To determine the temperature dependence of this shift, the law of electric charge conservation is applied:

$$\int_{\varepsilon_v}^{\varepsilon_c} f(\varepsilon, \varepsilon_F, U, T)\, N(\varepsilon)\ d\varepsilon \tag{1}$$

where: ε_v — upper energy state of the valence band; ε_c — lower energy state of the conduction band; ε_F — Fermi level; U — correlation energy (temperature-independent); N(ε) — energy density of charged states.

By taking the derivative of expression (1) with respect to temperature, the following equation for the function $\varepsilon_F(T)$ is obtained:

$$\frac{d\varepsilon_F}{dT} = \frac{\int y^2 \frac{\partial f}{\partial y}\ N(\varepsilon)\ d\varepsilon}{\int \frac{\partial f}{\partial \varepsilon_F} N(\varepsilon)}, \qquad y = \frac{1}{T} \tag{2}$$

The integral-differential equation (2) can be solved using a step-by-step (iterative) method, which can be written as:

$$\varepsilon_{F_{i+1}} = \varepsilon_{F_i} + \frac{d\varepsilon_F}{dT}\ \sigma T$$

where σT is the calculation step size, and the value of $\frac{d\varepsilon_F}{dT}$ is obtained from equation (2).

The function N(E), which describes the density of charged states in equation (2), is expressed in the following analytical form according to the model adopted from [12]:

$$N(E) = N_{ct}(E) + N_{vt}(E) + N_G(E) \tag{3}$$

Now, let us examine each term in expression (3) separately. $N_{ct}(E)$ represents the density of charged states located near the bottom of the conduction band within the energy width ε_{c0} and follows the relation $N_{ct}(E) = N_{ct0}\exp\,[(\varepsilon - \varepsilon_g)/\varepsilon_{c0}]$, where $N_{ct0} = 10^{21} - 10^{22}\ sm^{-3}\ eV^{-1}$ [12,13], ε_g is the bandgap width of porous silicon (por-Si), and ε_{c0} is the width of the energy range over which the charged states are distributed, taking values in the range 25-30 meV [11]. The second term, $N_{vt}(E)$, corresponds to the density of charged states located above the valence band. This function is distributed within the energy width ε_{v0} and follows the relation $N_{vt} = N_{vt0}\exp\,(-\varepsilon/\varepsilon_{v0})$, where $N_{vt0} = (1-3)\cdot 10^{21}$ $sm^{-3}\ eV^{-1}$, and ε_{v0}, unlike ε_{c0}, is temperature-dependent, with the temperature dependence expressed as follows:

$$\varepsilon_{v0}(T) = \sqrt{[\varepsilon_{v0}(T^{\star})]^2 - (kT^{\star})^2 + (kT)^2}$$

$T^{\star}$=500 K represents the equilibrium temperature, which varies within the range of 0.04 eV to 0.15 eV depending on the degree of disorder in the material, i.e., the extent of amorphization [12,13]. For porous silicon (por-Si), $\varepsilon_{v0}(300)$ typically lies within 40–45 meV, whereas $\varepsilon_{v0}(500)$ is in the range of 51–56 meV. In constructing the graphs, the value of $\varepsilon_{v0}(300)$ was selected within the interval of 20–50 meV. The term $N_c(E)$ in expression (3) represents the distribution function of charged states arising from the breaking of Si–Si bonds during the formation of microcrystallites, follows a Gaussian distribution and is expressed as follows:

$$N_G(\varepsilon) = \frac{N_c}{\sqrt{2\pi\sigma^2}} exp(-(\varepsilon - \varepsilon_F)^2/2\sigma^2)$$

where σ represents the maximum potential energy of defects formed due to bond breaking, and it is determined by the relation $\sigma = (\varepsilon_{v0}(T)\cdot(\Delta + U))^{1/2}$ [12,13]. In this expression, Δ and U are energetic parameters associated with defect states, where Δ=0.44 eV is the energy separation, and U=0.2÷0.3 eV denotes the correlation energy of defect electrons.

The magnitude N_G is obtained from experimental results and varies in the range $N_G = 10^{17} - 10^{18}\ eV^{-1} sm^{-1}$ [11]. In [14], when determining the temperature dependence of the Fermi level, a simplified model of N(E) — namely the approximation $N(\varepsilon) \approx N_G(\varepsilon)$ — was used. However, in that approach, the temperature dependence of the parameters in the Gaussian function was not accounted for.

In the present study, the temperature dependence of certain parameters in the charge state distribution function within the bandgap of porous silicon (por-Si) was taken into account. Accordingly, two models were considered:

1. Simplified model:

$$N(\varepsilon) = \frac{N_G}{\sqrt{2\pi\sigma^2}} exp(-(\varepsilon - \varepsilon_F(T))^2/2\sigma^2) \tag{4}$$

2. Complex model:

$$N(\varepsilon) = N_{ct0}\exp\left(\frac{\varepsilon-\varepsilon_g}{\varepsilon_{c0}}\right) + N_{vt0}\exp\left(-\frac{\varepsilon}{\varepsilon_{v0}}\right) + \frac{N_G}{\sqrt{2\pi\sigma^2}} exp\left(-\frac{(\varepsilon-\varepsilon_F)^2}{2\sigma^2}\right) \tag{5}$$

For both models, graphs illustrating the temperature-dependent shift of the Fermi level were constructed using numerical computation methods.

RESULTS AND DISCUSSION

The temperature-dependent variation of the Fermi level was calculated using Equation (4), and the results are shown in Figure 1. As can be seen from the graph, when the temperature is T<100 K, the shift of the Fermi level shows a negligible change, depending on the parameters of the function describing the charge states. This behavior can be explained by the fact that the thermal energy kT is insufficient to excite electrons into the charge states.

When the temperature exceeds T>100 K, the difference becomes much more pronounced, and a sharp temperature-dependent shift of the Fermi level is observed. This result is consistent with the graphs presented in [14], but does not fully agree with the conclusions in [15] and [16]. According to the interpretations in [15] and [16], as the temperature increases, electrons located in charge states below the Fermi level become almost fully activated. In addition, electrons in the valence band are also activated, and their transition to the conduction band can occur through the charge states under consideration. All these processes contribute to a decrease in the Fermi level shift.

Furthermore, in [16], the shift of the Fermi level was studied in relation to the Stabler–Wronski effect, and it was emphasized that in undoped a-Si:H materials, the Fermi level shift is not monotonic and tends to approach a certain limiting value.

In Figure 2, the graph of the Fermi level shift is calculated using formula (6). This expression shows that the Fermi level shift value, $\Delta\varepsilon_F$, changes within certain limits. Such a variation can be explained as follows: with increasing temperature, the concentration of broken Si–Si bonds increases, and in the charge exchange process between these defect states, electrons from both the valence band tail and the valence band itself participate. Since the density of these charge states is greater than that of the charge states distributed around the mid-gap according to the Gaussian distribution, their activation slows down the Fermi level shift.

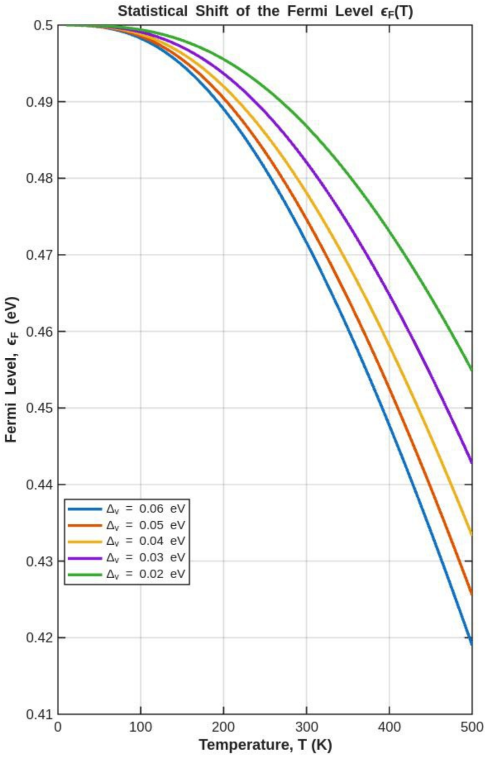

Figure 1. Temperature dependence of the Fermi level calculated using equation (4)

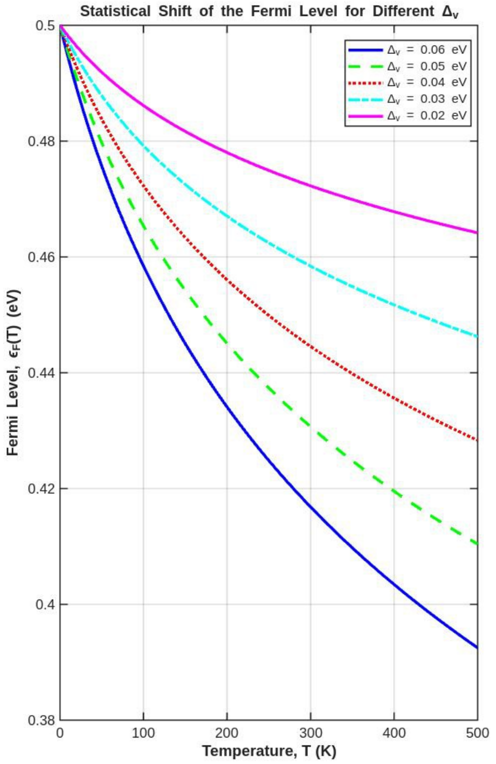

Figure 2. Temperature-dependent Fermi level shift calculated using equation (6)

CONCLUSIONS

As noted earlier, according to [9], in certain types of porous silicon samples, the electrical conductivity exhibits an activation character, following the law $\sigma = \sigma_0 exp\left(-\frac{\Delta\varepsilon}{kT}\right)$, where $\Delta\varepsilon = \varepsilon_c - \varepsilon_F$. Thus, the, $\Delta\varepsilon(T)$ dependence should also be valid, and this relationship should manifest in the temperature dependence of electrical conductivity. Indeed, the $j\left(\frac{1}{T}\right)$ dependence shown in [16] for the temperature range T>150 K confirms the correctness of this approach.

The obtained results indicate that this model and its outcomes can be applied to study the temperature dependence of parameters in devices based on por-Si/c-Si structures.

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ВПЛИВ ТЕМПЕРАТУРИ НА ЕНЕРГЕТИЧНЕ ПОЛОЖЕННЯ РІВНЯ ФЕРМІ В ПОРИСТОМУ КРЕМНІЇ

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У цій статті представлено теоретичне дослідження температурно-залежного зсуву рівня Фермі в пористому кремнії (por-Si). Дослідження базується на моделі розподілу зарядових станів, спочатку запропонованій для гідрогенізованого аморфного кремнію (a-Si:H), з урахуванням унікальних фізичних та хімічних властивостей пористого кремнію (por-Si). Температурна залежність параметрів густини зарядових станів у межах забороненої зони враховується як у спрощених, так і в розширених моделях. Для кожної моделі поведінка зсуву рівня Фермі була розрахована за допомогою числових методів, заснованих на інтегрально-диференціальних рівняннях. Результати представлені в графічній формі, а також обговорюються фізичні механізми, що лежать в основі зсуву рівня Фермі в різних температурних діапазонах. Отримані висновки можуть бути застосовані для пояснення процесів переносу носіїв заряду, зменшення поверхневої рекомбінації та підвищення ефективності сонячних елементів на основі гетероструктур por-Si/c-Si.

Ключові слова: *рівень Фермі; аморфний кремній; пористий кремній; заборонена зона; густина станів; розподіл Гауса; розподіл Гауса*