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## DETERMINATION OF BAND GAP OF SEMICONDUCTOR MATERIAL IN END PRODUCT


#### Abstract

The paper puts forward a method for determination of semiconductor activation energy in end product. It is illustrated that band gap can be calculated at cutoffs on both axes of graphs $\ln (I) \div U$, measured at different temperatures. Minimum temperature interval is determined depending on measuring accuracy. A new method for determination of value $E_{g}$ without VAC (volt-ampere characteristics) extrapolation is put forward.


## 1. INTRODUCTION

Classic method for determination of band gap of semiconductor crystal is a study of temperature dependence of its conductivity [1,2]. Among optical methods the most widely used is determination of excitation light wavelength at maximum photosensitivity and extrapolation of spectral distribution of absorption coefficient [3,4].

However, in some cases, such as identification of semiconductor material, it is required to determine matter activation energy in end product. Simple thermal methods cannot be applied for this purpose, since crystal has already undergone a series of complementary technological operations, such as contact etching, annealing and oxide coating, etc.

Optical methods cannot be used for the same reason. In case of photoconverters measuring results are distorted due to protective coatings, transparent layers of $\mathrm{SnO}_{2}$ applied as a front window, etc. Frequently photocells are fabricated on a hard opaque surface obstructing the passage of penetrating light. This excludes measurement of absorption coefficient.

In this case temperature variations of voltampere characteristics (VAC) are studied. There are two methods [5]. The first one implies study of temperature variations of saturation current $I_{s}$ in VAC reverse-bias region. However, not to get into junction region, it is necessary to apply fairly
large reverse voltages of tens of Volts. For many photocells this is beyond their operating parameters. And in that case rectification of VAC forward biases in semi-log plot is applied to operating region below open circuit voltage - usually a few tenths of a Volt (Fig. 1).

## 2. RESULTS, DISCUSSION

Photoconverters operate due to potential barrier between p - and n -semiconductors. Effect of relatively insignificant barriers on ohmic contacts in this case is negligible.

Here is the expression for photodiode VAC lines without photo-excited carriers [5]:

$$
\begin{equation*}
I=I_{s}\left[\exp \left(\frac{e U}{k T}\right)-1\right] \tag{1}
\end{equation*}
$$

where $I_{s}$ - reverse saturation current of $\mathrm{p}-\mathrm{n}-$ junction, created by carriers flowing from the barrier. Its value is in proportion to concentration of minor carriers in p-region

$$
\begin{equation*}
n_{p}=N_{c} \exp \left(-\frac{E_{g}}{k T}\right) \tag{2}
\end{equation*}
$$

and n -region

$$
\begin{equation*}
p_{n}=P_{v} \exp \left(-\frac{E_{g}}{k T}\right) \tag{3}
\end{equation*}
$$

In case of fairly large forward bias, where
eU»kT
unit (1) can be disregarded. Then, taking into account (2) and (3), the expression (1) can be as follows:

$$
\begin{equation*}
I=A \exp \left(-\frac{E_{g}-e U}{k T}\right) \tag{5}
\end{equation*}
$$

where A-weakly temperature-dependent coefficient. Taking logarithm (5), we obtain:

$$
\begin{equation*}
\ln I=\ln A-\frac{E_{g}-e U}{k T} \tag{6}
\end{equation*}
$$

It follows that the set of characteristics $\ln (\mathrm{U})$ at different temperatures is represented by tem-perature-dependent slope intercept form of a line

$$
\begin{equation*}
\operatorname{tg} \alpha=\frac{\Delta \ln I}{\Delta U}=\frac{e}{k T} \tag{7}
\end{equation*}
$$

and meeting at some point with abscissa $\mathrm{E}_{\mathrm{g}} / \mathrm{e}$. This enables to calculate band gap of material by measuring diode VAC lines at two different temperatures (Fig. 1).


Fig.1. Standard direct current-voltage dependence for silicon diodes in semi-log plot.

However, this method is difficult to apply in practice. Standard potential barrier height at p-$n$-junction for the most popular silicon diodes is
0.1-0.15 eV. At forward biasing the barrier reduces. That is why beyond the above voltage diode current loses its diode nature and is limited to series resistance only, whereas VA characteristics become linear. This means that experimentally measured points applicable for calculation in the given method, are located as shown in Fig. 1, in the lower quadrant outside voltage $\sim 0.2 \mathrm{~V}$ (solid graphs).

One should note that $\ln \mathrm{I}=0$ at amperage $\sim 1$ A. In real low-power diodes direct current is milliampere units or even fractions. Which is equivalent to $\ln \mathrm{I} \sim-5.0$. All points on a graph above this value on current axis can be only extrapolationbased. In other words, a large number of points near both axes disappears, narrowing actual rectification region even more.

Silicon band gap is 1.1 eV . Thus, intersection of graphs should be expected at voltage bias $\sim 1.1$ V on voltage axis, i.e. extrapolation (dotted lines) is applied to $90-95 \%$ of graph length. Clearly, at this arm intersection of lines is extremely sensitive to two factors. Firstly, it is measuring accuracy, i.e. spread of points with confidence interval $\Delta$. And secondly, temperature interval applied at measuring, i.e. difference in slopes of graphs. These values are interconnected. At a large value of confidence interval and insufficient temperature difference graphs may not intersect at all, as shown in Fig. 2 for lines CN and DG.

VAC measuring pattern is the following. Exact applied rectification is specified. Then error current flowing at a given voltage is measured. Value $\Delta$ means vertical spread of points on a graph $\operatorname{lnI} \div \mathrm{U}$.

Graphs $\operatorname{lnI} \div \mathrm{U}$ are plotted within a few confidence bands, as shown in Fig. 2. In general, width of these bands differs. It is determined by band slope

$$
\begin{equation*}
\Delta_{1}=2 \Delta \cdot \cos \alpha \tag{8}
\end{equation*}
$$

Inclination angle according to (7) depends on measuring temperature.

However, in reality temperature difference is not too large. Lower limit is correlation (4). Naturally, it is assumed that room temperature is the lower. The upper limit is maximum rated temperature of the product (for silicon it is around $+60{ }^{\circ} \mathrm{C}$ ), when contribution of intrinsic carriers
becomes more obvious due to region-region junction. At this temperature interval for the sake of simplicity we assume that confidence band width in both graphs is the same.


Fig. 2. Operating region for method of VAC intersecting lines.

We can obtain criterion for minimum temperature interval at a given spread of points $\Delta$, subject to parallelism of CN and DG (Fig. 2). Line equation EH y $=a_{1} x+b_{1}$, where according to (6)

$$
\begin{equation*}
a_{1}=\frac{e}{k} \frac{1}{T_{1}} \quad b_{1}=\ln A-\frac{E_{g}}{k} \frac{1}{T_{1}} \tag{9}
\end{equation*}
$$

Value $b$ is negative, since operating region of flowing current is I $<1 \mathrm{~A}$. Thus, both summands for a constant term are less than zero.

Then FG line equation is given by $\mathrm{y}=\mathrm{a}_{1} \mathrm{x}-$ $\left(/ b_{1} /+\Delta\right)$, remembering that values $b_{1}$ are negative and $F$ point ordinate increases in comparison with point E . It follows that G point coordinate at $\mathrm{y}=0$ is $\mathrm{x}_{\mathrm{G}}=\frac{\left|b_{1}\right|+\Delta}{a_{1}}$. D point coordinate decreases by confidence interval value: $-\mathrm{y}_{\mathrm{D}}=-\left(/ \mathrm{b}_{1} /-\Delta\right)$. It gives the lowest possible slope for DG graph within confidence band:

$$
\begin{equation*}
\operatorname{tg} \beta_{1}=\frac{\left|b_{1}\right|-\Delta}{\left|b_{1}\right|+\Delta} a_{1} \tag{10}
\end{equation*}
$$

Note that numerator modulo is less than denominator, so $\operatorname{tg} \beta_{1}<\mathrm{a}_{1}$, i.e. angle $\beta_{1}$ is less than angle $\alpha_{1}$.

Equation (13) was solved numerically. Parameter value $\ln A=29.77$ is taken from experimental measurement for a sample of one of Si-diodes. $a_{1}$ and $a_{2}$ slope values were determined from the formulae (9) and (11) at given temperatures. Room temperature was used as reference temperature $\mathrm{T}_{1}$. Point of graph intersection occurred at $x_{0}=\frac{E_{g}}{e}$ [See dependence (6), silicon band gap $1.1 \mathrm{eV}]$. Then cutoffs $\mathrm{b}_{\mathrm{i}}$ were determined from the equation of the pencil of lines, going through that point $\ln A=a_{i}(T)\left(\frac{E_{g}}{e}\right)+b_{i}(T)$.

By solving equation (13) two roots were obtained, different by a large ratio - either tenths or hundreds of units. Here $b_{i}$ values fell in the interval of 12-25 units. For the sake of rationality the larger value $\Delta$ was discarded as having no physical content. Calculation result is shown in Fig. 3.

The more operating temperatures $\mathrm{T}_{1}$ and $\mathrm{T}_{2}$ are different, the more accurate the results are. However, there is a limit for lower temperature. At large errors $\Delta$ confidence bands are too wide, and it is necessary to increase minimum temperature interval for graphs to intersect $\ln \mathrm{I} \div \mathrm{U}$.

As shown in Fig. 3, the more spread points are obtained at current measurement, i.e. the larger value $\Delta$ is and the wider confidence bands are, the more temperature interval should be applied to measurement of graphs. Here high-temperature band is more sloped, which compensates divergence of lines. However, the problem of determination accuracy of intersection coordinate persists.

To determine diode band gap, there is no need to extrapolate VAC lines at a huge arm till their intersection, as it is recommended in the classic method. This parameter can be obtained with more accuracy at cutoffs on axes.

For current axis those are values $\ln \mathrm{I}_{1}$ and $\ln \mathrm{I}_{2}$, i.e. values $b_{1}$ and $b_{2}$ from the formulae (9) and (11). As shown in Fig. 4, length of the respective interval is

$$
\begin{equation*}
\ln I_{1}-\ln I_{2}=\frac{E_{g}}{k}\left(\frac{1}{T_{1}}-\frac{1}{T_{2}}\right) \tag{14}
\end{equation*}
$$

Since temperatures $T_{1}$ and $T_{2}$ applied for measurement are given, and values on the left are de-
termined directly on the graph, formula (14) enables to calculate value $\mathrm{E}_{\mathrm{g}}$.


Fig. 4. VAC lines at different temperatures.

Similarly, for voltage axis intersection points (Fig. 4) from equation (6) it is true that

$$
-\ln A=-\frac{E_{g}}{k T_{1}}+\frac{e U_{1}}{k T_{1}}=-\frac{E_{g}}{k T_{2}}+\frac{e U_{2}}{k T_{2}}
$$

from which

$$
\begin{equation*}
\frac{E_{g}}{e}\left(\frac{1}{T_{1}}-\frac{1}{T_{2}}\right)=\frac{U_{1}}{T_{1}}-\frac{U_{2}}{T_{2}} \tag{15}
\end{equation*}
$$

which also enables to determine parameter $\mathrm{E}_{\mathrm{g}}$, given values $U_{1}$ and $U_{2}$ from the graph.

Compare accuracy of two offered options with the classic method (Fig. 5). Obviously, for current axis parameter spread is

$$
\begin{equation*}
\pm 2 \Delta \tag{16}
\end{equation*}
$$

To determine spread of axis intersection points, it is necessary to determine band width projection from (8) on X-axis:

$$
\begin{equation*}
\pm \Delta \cdot\left(\operatorname{ctg} \alpha_{1}+\operatorname{ctg} \alpha_{2}\right)= \pm \Delta \cdot\left(\frac{1}{a_{1}}+\frac{1}{a_{2}}\right) \tag{17}
\end{equation*}
$$

Formula (17) gives general change of confidence interval when determining coordinates $\mathrm{U}_{1}$
and $\mathrm{U}_{2}$ on voltage axis (Fig. 4), i.e. for the right member of dependence (15). However, extension of this interval is not symmetrical, since now it depends on angles $\alpha_{1}$ and $\alpha_{2}$, which are different for temperatures $T_{1}$ and $T_{2}$. According to (7), for higher temperature $T_{2}$ slope $\alpha_{2}$ is lower. Segment $\mathrm{U}_{1}-\mathrm{U}_{2}$ spreads more to the right (See Table).


Fig. 5. In the same ratio, as in Fig. 1. Error for axis intersection points and graph convergence point (illustrated by one of dependences in the same ratio as in Fig.1).

It is well to bear in mind that, though absolute error at determining cutoffs $\mathrm{U}_{1}$ and $\mathrm{U}_{2}$ on voltage axis is much lower (See Table), absolute magnitude of these values is also an order less than cutoffs $b_{1}$ and $b_{2}$ for current axis. So it is not possible to say, which method is more accurate.

Define error in the coordinate of VAC graph convergence point. If temperature interval is set correctly based on dependence (13), abscissa of intersection peint of lines DM and EH (See Fig. 1-2) shall be $\underline{E_{g}}$. Then its ordinate from the equation (6) shall Be y=lnA (horizontal line in Fig. 5).

Maximum deviation from it to the right can be determined as intersection point of line DG with highest possible slope to the right within confidence interval at temperature $T_{1}$ (See Fig. 2). Taking into account (10), we obtain
from here

$$
\ln A=\frac{\left|b_{1}\right|-\Delta}{\left|b_{1}\right|+\Delta} a_{1} x-\left(\left|b_{1}\right|-\Delta\right)
$$

$$
\begin{equation*}
\Delta x_{1}=\frac{\left[\ln A+\left(\left|b_{1}\right|-\Delta\right)\right] \cdot\left(\left|b_{1}\right|+\Delta\right)}{\left(\left|b_{1}\right|-\Delta\right) \cdot a_{1}}-\frac{E_{g}}{e} \tag{18}
\end{equation*}
$$

Highest possible deviation to the left can be obtained by extending line CN to intersection. According to (12), we obtain
$\ln A=\frac{\left|b_{2}\right|+\Delta}{\left|b_{2}\right|-\Delta} a_{2} x-\left(\left|b_{2}\right|+\Delta\right)$,
from which

$$
\begin{equation*}
\Delta x_{2}=\frac{E_{g}}{e}-\frac{\left[\ln A+\left(\left|b_{2}\right|+\Delta\right)\right] \cdot\left(\left|b_{2}\right|-\Delta\right)}{\left(\left|b_{2}\right|+\Delta\right) \cdot a_{2}} \tag{19}
\end{equation*}
$$

Numerical values of parameter spread are given in the Table. Values used for calculation: $\mathrm{T}_{1}=300 \mathrm{~K}, \mathrm{~T}_{2}=360 \mathrm{~K}, \Delta=0.2$ (mid segment Fig. 3). Other parameters are the same as for equation calculation (13).

|  | Inward departure | Outward <br> departure |
| :--- | :--- | :--- |
| Determination <br> of $\mathrm{E}_{\mathrm{g}}$ at cutoff on <br> Y-axis | 0.2 | 0.2 |
| Determination <br> of $\mathrm{E}_{\mathrm{g}}$ at cutoff on <br> X-axis | 0.04 | 0.031 |
| Classic method of <br> graph intersection | 0.39 | 0.96 |

As shown in Fig. 5, classic method error is a few times higher, which is accounted for by extremely large extrapolation arm.

Suggested methods enable to obtain band gap of material without VAC graph extrapolation. Based on formula (6), distance between VAC lines $/ \ln \mathrm{I}_{01}-\ln \mathrm{I}_{02} /$ in operating region at some fixed voltage $\mathrm{U}_{0}$ will be:
$-\left|\ln I_{01}-\ln I_{02}\right|=\frac{E_{g}}{k}\left(\frac{1}{T_{2}}-\frac{1}{T_{1}}\right)+\frac{e U_{0}}{k}\left(\frac{1}{T_{1}}-\frac{1}{T_{2}}\right)$.
from here

$$
\begin{equation*}
E_{g}=e U_{0}+\frac{k\left|\ln I_{01}-\ln I_{02}\right|}{\left(\frac{1}{T_{1}}-\frac{1}{T_{2}}\right)} \tag{20}
\end{equation*}
$$

By contrast, for a section of horizontal graph system for a certain value $\ln I_{0}$ in operating region the following is true:
$\ln I_{0}-\ln A=-\frac{E_{g}}{k T_{1}}+\frac{e U_{01}}{k T_{1}}=-\frac{E_{g}}{k T_{2}}+\frac{e U_{02}}{k T_{2}}$.
from here

$$
E_{g}\left(\frac{1}{T_{1}}-\frac{1}{T_{2}}\right)=\frac{e U_{01}}{T_{1}}-\frac{e U_{02}}{T_{2}} .
$$

or

$$
\begin{equation*}
E_{g}=\frac{\frac{e U_{01}}{T_{1}}-\frac{e U_{02}}{T_{2}}}{\frac{1}{T_{1}}-\frac{1}{T_{2}}} \tag{21}
\end{equation*}
$$

where $T_{1}<T_{2}-$ temperatures, at which graphs were measured, and $U_{01}>U_{02}$ are abscissas of section points.

Energy accuracy $\mathrm{E}_{\mathrm{g}}$ obtained remains $\pm 2 \Delta$ for a section along voltage axis by the formula (20) and error (17) for the expression (21).

Note that there is no value $\ln \mathrm{A}$ in the above dependences (20), (21), i.e. it is not required for determination of value $\mathrm{E}_{\mathrm{g}}$ by given method.

## 3. CONCLUSION

Thus, determination of band gap based on volt-ampere characteristics becomes simpler and more accurate, using cutoffs on current and volt-
age axes or vertical or horizontal sections of VAC graphs instead of extrapolation. It is necessary to bear in mind dependence of required temperature interval on amperage measurement error.

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Key words: determination of band gap, semiconductor material, activation energy.

# ВИЗНАЧЕННЯ ШИРИНИ ЗАБАРОНЕНОЇ ЗОНИ НАПІВПРОВІДНИКОВОГО МАТЕРІАЛУ В ГОТОВОМУ ВИРОБІ 

## Резюме

Запропоновано метод визначення енергії активації напівпровідника в готовому виробі. Показано, що ширину забороненої зони можливо розрахувати по відсічкам на обох осях графіків $\ln (I) \div U$, виміряних при різних температурах. Визначений мінімальний температурний інтервал в залежності від точності вимірювань. Вказано новий засіб визначення $E_{g}$ без екстраполяції BAX.

Ключові слова: ширина забороненої зони, енергія активації, напівпровідник.

## ОПРЕДЕЛЕНИЕ ШИРИНЫ ЗАПРЕЩЁННОЙ ЗОНЫ ПОЛУПРОВОДНИКОВОГО МАТЕРИАЛА В ГОТОВОМ ИЗДЕЛИИ

## Резюме

Предложен метод определения энергии активации полупроводника в готовом изделии Показано, что ширину запрещённой зоны можно рассчитать по отсечкам на обеих осях графиков $\ln (I) \div U$, измеренных при разных температурах. Определён минимальный температурный интервал в зависимости от точности измерений. Указан новый способ определения величины $E_{g}$ без экстраполяции BAX.

Ключевые слова: ширина запрещенной зоны, энергия активации, полупроводник.

