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Letter

A novel theoretical model for the temperature dependence of band gap energy in semiconductors

Peiji Geng, Weiguo Li[1], Xianhe Zhang, Xuyao Zhang, Yong Deng and Haibo Kou

State Key Laboratory of Coal Mine Disaster Dynamics and Control, College of Aerospace Engineering, Chongqing University, Chongqing 400044, People's Republic of China

E-mail: wgli@cqu.edu.cn (W Li)

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Abstract

We report a novel theoretical model without any fitting parameters for the temperature dependence of band gap energy in semiconductors. This model relates the band gap energy at the elevated temperature to that at the arbitrary reference temperature. As examples, the band gap energies of Si, Ge, AlN, GaN, InP, InAs, ZnO, ZnS, ZnSe and GaAs at temperatures below 400 K are calculated and are in good agreement with the experimental results. Meanwhile, the band gap energies at high temperatures ($T > 400$ K) are predicted, which are greater than the experimental results, and the reasonable analysis is carried out as well. Under low temperatures, the effect of lattice expansion on the band gap energy is very small, but it has much influence on the band gap energy at high temperatures. Therefore, it is necessary to consider the effect of lattice expansion at high temperatures, and the method considering the effect of lattice expansion has also been given. The model has distinct advantages compared with the widely quoted Varshni's semi-empirical equation from the aspect of modeling, physical meaning and application. The study provides a convenient method to determine the band gap energy under different temperatures.

Keywords: semiconductors, temperature dependency, band gap energy, modeling

(Some figures may appear in colour only in the online journal)

1. Introduction

Band gap energy plays a very important part in semiconductors, for it will significantly affect intrinsic carrier concentration, intrinsic transition temperature and maximum withstand voltage, and then it influences the electrical properties of semiconductor materials and devices. With the increase of temperature, the band gap energy usually presents the obvious temperature dependence. Therefore, the knowledge of the band gap energy variations with temperature is necessary for semiconductors.

In the past few years, researchers obtained the band gap energy of semiconductors at the elevated temperature through experiments. Feneberg [1] measured the band gap energy of AlN through free exciton spectrum method. The band gap energy of AlN is 6.034 eV when the temperature is close to 0 K, and it reduced to 5.96 eV at near room temperature. Pejova [2] experimentally studied the band gap energy varying with temperature of ZnSe semiconductor material. A large number of experimental results [3–6] showed that the band gap energy gradually decreases with the increase of the temperature. The two main reasons are as follows [6]: one is the lattice expansion, and the other is the enhancement of electron–phonon interactions when the temperature rises. Besides, it is found

[1] Author to whom any correspondence should be addressed.

that the trend of the band gap energy with temperature will change from nonlinear to linear at a specific temperature for different semiconductors [6]. Fan [7] studied the effect of lattice vibrations in producing a shift of the energy levels which resulted in the temperature dependent variation of energy gap in semiconductors. Allen [8] attributed the effect of electron–phonon interactions to the corresponding electronic states.

In theoretical research, many theoretical models were proposed to predict the temperature-dependent band gap energy of semiconductors. Varshni [6] proposed a semi-empirical relation (see equation (1)) for the variation of the band gap energy with temperature, in which α and β are constants, and β is thought to be related to the Debye temperature.

$$E_{\mathrm{g}}(T) = E_{\mathrm{g}}(T_0) - \alpha T^2/(T+\beta). \tag{1}$$

Vina [9] suggested they can also fit the experimental data using the expression $E = a - b\coth(\theta/T)$; a and b are fitting parameters; θ is the Debye temperature. Manoogian and Leclerc [10] noted that β in Varshni's equation is negative sometimes, and they also devised their equation (see equation (2)).

$$E_{\mathrm{G}} = E_{\mathrm{D}}^0(1+AT^x) + B\left[\theta_1 \coth\left(\frac{\theta_1}{2T}\right) + \theta_2 \coth\left(\frac{\theta_2}{2T}\right)\right]. \tag{2}$$

The first term in the bracket describes the effect of lattice expansion by means of the parameters A and x. The second term represents contributions from electron–phonon interactions, with acoustic (θ_1) and optical (θ_2) terms being averaged separately [10]. O'Donnell [4] introduced a three-parameter model (see equation (3)) as a direct replacement of the Varshni's equation. $E_{\mathrm{g}}(0)$ is the band gap energy at 0 K, S is a dimensionless constant, and $\langle hw\rangle$ is an average phonon energy.

$$E_{\mathrm{g}}(T) = E_{\mathrm{g}}(0) - S\langle hw\rangle\left[\coth\left(\frac{hw}{2kT}\right) - 1\right]. \tag{3}$$

The model is numerically better than Varshni's equation in fitting experimental data. And it is shown [4] to be compatible with reasonable assumptions about the influence of phonons on the band gap energy. However, the models above are semi-empirical equations which more or less contain fitting parameters which makes it inconvenient for application in practice.

In this letter, we report a novel theoretical model without fitting any parameters for the temperature dependence of band gap energy in semiconductors from the view of energy conservation. This model is verified by several semiconductors at low temperatures below 400 K, such as Si, Ge, AlN, GaN, InP, InAs, ZnO, ZnS, ZnSe and GaAs. Meanwhile, the band gap energies at high temperatures ($T > 400$ K) are predicted and analyzed reasonably. The advantages of the model are also discussed. The study provides a convenient method to determine the band gap energy of semiconductors under different temperatures. This may be helpful for the theoretical research of the electrical properties in semiconductors.

2. Theoretical model

From the view of energy conservation, we assume that there exists a maximum energy storage limit associated with the electron transition from valence band to conduction band, and the maximum energy is consisted of two parts: the band gap energy and the internal energy; meanwhile, the band gap energy and the internal energy could transform each other by means of an energy conversion coefficient, i.e.

$$E_{\mathrm{Total}} = kQ(T) + E_{\mathrm{g}}(T) \tag{4}$$

where E_{Total} is the maximum energy; $Q(T)$ is the increment of the internal energy due to enhancement of electron–phonon interactions as the temperature increases from 0 K; and k is the conversion coefficient between the internal energy and the band gap energy; $E_{\mathrm{g}}(T)$ is the band gap energy at temperature T. There, the conversion coefficient k is the bond of macro and micro. In virtue of the bond, the variations of micro energy (band gap energy) can be calculated by the macro energy (internal energy) indirectly.

The internal energy $Q(T)$ is related to the specific heat capacity at constant pressure $C_{\mathrm{p}}(T)$,

$$Q(T) = \int_0^T C_{\mathrm{p}}(T)\,\mathrm{d}T. \tag{5}$$

Substituting $T = T_0$ into equation (4), we obtain,

$$E_{\mathrm{Total}} = kQ(T_0) + E_{\mathrm{g}}(T_0). \tag{6}$$

When $T = T_1$, it has,

$$E_{\mathrm{Total}} = kQ(T_1) + E_{\mathrm{g}}(T_1). \tag{7}$$

Combining equations (4)–(7), it could be deduced that

$$E_{\mathrm{g}}(T) = E_{\mathrm{g}}(T_0) - [E_{\mathrm{g}}(T_0) - E_{\mathrm{g}}(T_1)]\left(\int_{T_0}^{T} C_{\mathrm{p}}(T)\,\mathrm{d}T \Big/ \int_{T_0}^{T_1} C_{\mathrm{p}}(T)\,\mathrm{d}T\right). \tag{8}$$

The relationship of the specific heat capacity at constant pressure $C_{\mathrm{p}}(T)$ and constant volume $C_{\mathrm{v}}(T)$ is given,

$$C_{\mathrm{p}}(T) \approx C_{\mathrm{v}}(T)/M \tag{9}$$

where $C_{\mathrm{v}}(T)$ is the specific heat capacity at constant volume; M is the molar mass.

The specific heat capacity $C_{\mathrm{v}}(T)$ can be obtained by the Debye model as follows:

$$C_{\mathrm{v}}(T) = 9Nk_{\mathrm{B}}\left(\frac{T}{\theta_{\mathrm{D}}}\right)^3 \int_0^{\frac{\theta_{\mathrm{D}}}{T}} \frac{x^4 e^x}{(e^x-1)^2}\mathrm{d}x \tag{10}$$

where N is the Avogadro number; k_{B} is the Boltzmann constant; and θ_{D} is the Debye temperature. Then $C_{\mathrm{p}}(T)$ is given as follows:

$$C_{\mathrm{p}}(T) = \frac{9Nk_{\mathrm{B}}}{M}\left(\frac{T}{\theta_{\mathrm{D}}}\right)^3 \int_0^{\frac{\theta_{\mathrm{D}}}{T}} \frac{x^4 e^x}{(e^x-1)^2}\mathrm{d}x. \tag{11}$$

By plugging equation (11) into equation (8), the final form of the model is determined (equation (12)),

$$E_{\mathrm{g}}(T) = E_{\mathrm{g}}(T_0) - [E_{\mathrm{g}}(T_0) - E_{\mathrm{g}}(T_1)]\left(\int_{T_0}^{T}\left(\frac{T}{\theta_{\mathrm{D}}}\right)^3 \int_0^{\frac{\theta_{\mathrm{D}}}{T}} \frac{x^4 e^x}{(e^x-1)^2}\mathrm{d}x\mathrm{d}T \Big/ \int_{T_0}^{T_1}\left(\frac{T}{\theta_{\mathrm{D}}}\right)^3 \int_0^{\frac{\theta_{\mathrm{D}}}{T}} \frac{x^4 e^x}{(e^x-1)^2}\mathrm{d}x\mathrm{d}T\right). \tag{12}$$

Table 1. Material parameters of several semiconductors for Si, Ge, AlN, GaN, InP, InAs, ZnO, ZnS, ZnSe and GaAs.

Material parameters	T_0 (K)	$E_g(T_0)$ (eV)	T_1 (K)	$E_g(T_1)$ (eV)	θ_D (K)
Si [3, 11]	0	1.169 29	298	1.124 57	650
Ge [11, 12]	0	0.769 18	298	0.679 67	374
AlN [1]	6.9	6.033 87	290	5.960 32	558
GaN [11, 13]	14.7	3.485 85	301	3.420 08	592
InP [4]	7.4	1.420 27	301	1.3511	301
InAs [4]	16	0.4260	301	0.355 09	248
ZnS [14, 15]	9.2	3.803 98	280	3.684 87	440
ZnO [16, 17]	12	3.381 69	292	3.303 18	310
ZnSe [2]	11.9	3.227 03	301	3.121 62	340
GaAs [4, 5]	21	1.521	294	1.435	344

In the model (equation (12)), the Debye temperature of semiconductors could be found in the literature easily. The integration of Debye heat capacity can be achieved by a simple MATLAB application program. Referring to two arbitrary reference values $E_g(T_0)$ and $E_g(T_1)$, the temperature dependence of the band gap energy for semiconductors could be obtained easily. Equation (12) seems to be a complex form, but it is convenient to use because it do not contain complicated fitting process. The effect of lattice expansion is considered as follows: $\left(1+\int_0^{T_0}\alpha(T)\mathrm{d}T\right)^3/\left(1+\int_0^{T}\alpha(T)\mathrm{d}T\right)^3$. Multiply this item with equation (8) to obtain the model (equation (13)),

$$E_g(T)=\left\{E_g(T_0)-[E_g(T_0)-E_g(T_1)]\left(\int_{T_0}^{T}C_p(T)\,\mathrm{d}T/\int_{T_0}^{T_1}C_p(T)\,\mathrm{d}T\right)\right\}\times\left(1+\int_0^{T_0}\alpha(T)\mathrm{d}T\right)^3/\left(1+\int_0^{T}\alpha(T)\mathrm{d}T\right)^3 \quad (13)$$

where $\alpha(T)$ is the temperature dependent linear expansion coefficient of semiconductors. Equation (13) both considers the effect of lattice expansion and phonon-electronic interaction.

3. Results and discussions

In this section, the temperature dependence of the band gap energies of Si, Ge, AlN, GaN, InP, InAs, ZnO, ZnS, ZnSe and GaAs are calculated by the model (equation (12)), which are proposed above. Also, the model (equation (12)) is verified by the comparisons between the theoretical results and experimental results at low temperatures below 400 K. At the same time, the band gap energies at high temperatures are also predicted reasonably. The required parameters are as shown in table 1.

From figures 1–4, we can find a good agreement between the theoretical predictions and experimental results. Our model and Varshni's one both work very well at low temperatures. However, Varshni's equation contains three fitting parameters, and the determination of three fitting parameters need three reference points (six input parameters) at least. Our model only need two reference points $E_g(T_0)$, $E_g(T_1)$ and Debye temperature to reproduce the experimental results without any fitting. This is essentially different with Varshni's equation. In addition, our formula seems to be a

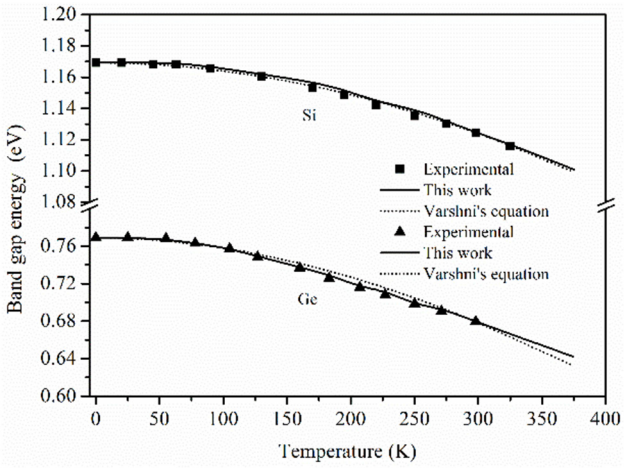

Figure 1. The temperature dependence of the band gap energy of Si and Ge.

complex form, but it is convenient to use because it does not contain complicated fitting process. Additionally, our model and Varshni's equation can both be simplified into the form: $E_g(T)=E_g(T_0)-BT$, which is in agreement with other one proposed [18]. It shows that our model could be valuable to understand the fitting parameters alpha and beta existed in Varshni's equation.

In addition, this model does not adopt one reference point like the temperature-dependent yield strength model [19]. In [19], we believe the distortion energy and heat energy per unit volume are conserved for the yielding of plastic material. According to the fourth strength theory, the distortion energy per unit volume is related to the Young's modulus, Poisson's ratio and yield strength. Through the combination of these, we establish the yield strength model in [19]. In the paper, we apply the same modeling idea as [19] to the band gap energy of semiconductors. Referring to the same derivation process of the yield strength model, if the band gap energy at T_m is equal to zero, the band gap energy model we get should rely on one reference point, $E_g(T_0)$. In fact, it is not equal to zero and difficult to obtain directly. In order to apply this model conveniently, we introduce another directly obtained reference point, $E_g(T_1)$. As thus, we only need two reference points that could be easily obtained by experiment to reproduce the measured temperature dependence of band gap energies. This is also the reason why two models adopt the same modeling thought, but require different number of reference points.

In figure 5, the temperature dependence of the band gap energy of GaAs is also calculated by the model (equation (12)). It can be found that it almost overlaps with Varshni's equation and experimental results at low temperatures. But the predicted results of our model is higher at high temperatures. The reason is that our model ignores the effect of lattice expansion on the band gap energy. Our tentative idea considering the effect of lattice expansion is in the final model equation (13). However, the quantitative verification of the final model (equation (13)) encounters difficulties because we cannot find the temperature dependent linear expansion coefficient. Maybe there is a little research about semiconductor materials at high temperatures. Moreover, our model

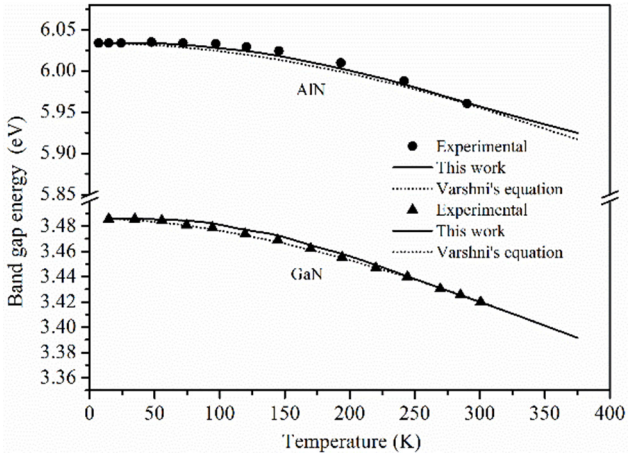

Figure 2. The temperature dependence of the band gap energy of AlN and GaN.

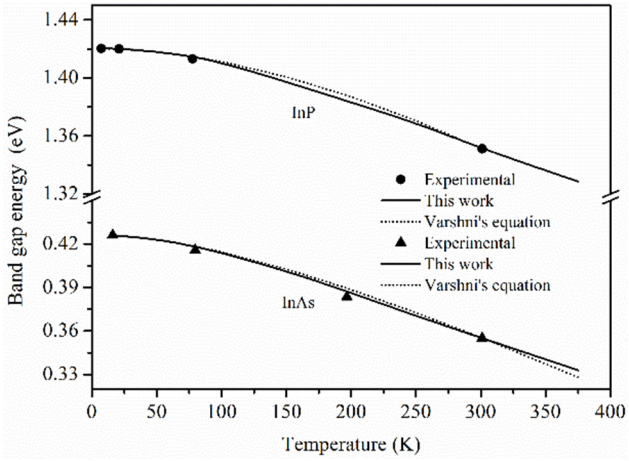

Figure 3. The temperature dependence of the band gap energy of InP and InAs.

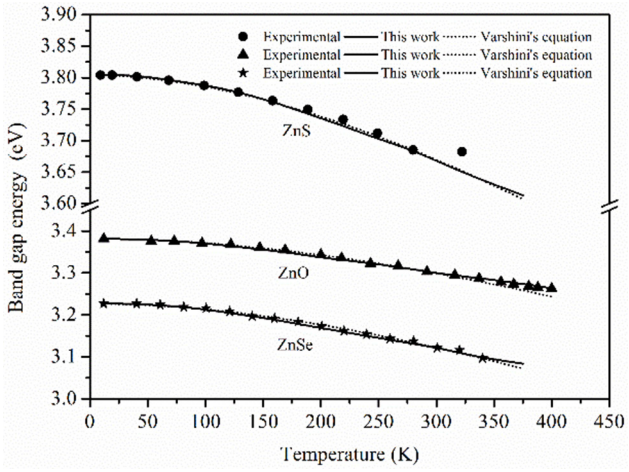

Figure 4. The temperature dependence of the band gap energy of ZnS, ZnO and ZnSe.

is mainly used to predict the measured band gap energies at low temperatures, and the effect of lattice expansion could be ignored because of its weak temperature dependence. In addition to the two major factors above, optical phonons also have definite effects. These will be completed as the subsequent

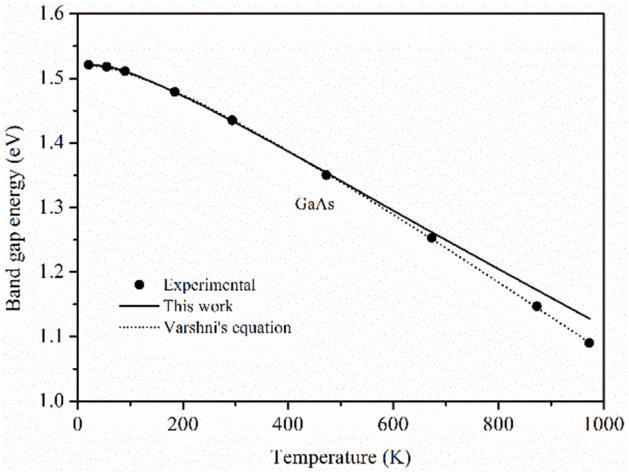

Figure 5. The temperature dependence of the band gap energy of GaAs.

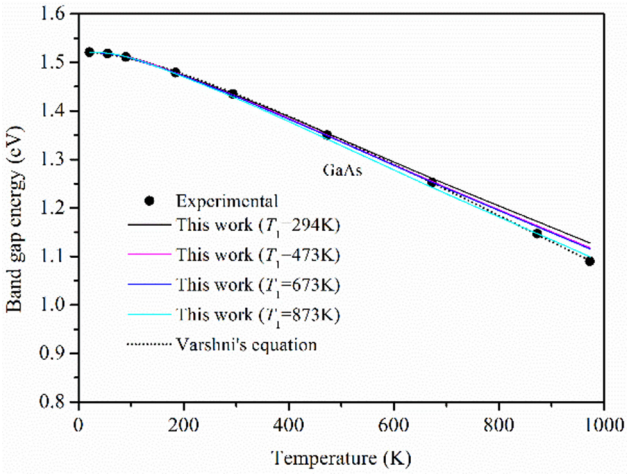

Figure 6. The sensitivity analysis of the model accuracy for GaAs.

work. Even so, qualitative analysis can support our idea. As is well known, the linear expansion coefficient of materials change little when the temperature span is very small. The large span change of the temperature will result in evident variations of the linear expansion coefficient. Therefore, considering the effect of lattice expansion in equation (13) should be reasonable. And the prediction results may be closer to the experimental value.

We also carry out the sensitivity analysis of the model (equation (12)) shown as figure 6 in this article. It could be seen that the accuracy of prediction results will be improved as T_1 varies from 294 K to 673 K. When the temperature is closer to 873 K, the accuracy begins to reduce. For GaAs, the appropriate T_1 is between 673 K and 873 K. In fact, the effect of lattice expansion still needs to be considered because we initially do ignore it in the model (equation (12)) on account of its weak temperature dependency at low temperatures, but it will work at high temperatures. Based on the above situation, a few suggestions are noted as follows: on the premise that the linear expansion coefficient could not be found, we can select T_1 at a little higher temperature to achieve accurate prediction by model (equation (12)). If the linear expansion coefficient could be obtained directly and considered using

the model (equation (13)), the selection of T_1 will not affect the accuracy of the prediction results.

In the present model, we have considered the main factors contributing to the band gap energy. And the model has showed great progress compared with the original semi-empirical models. The effect of other factors such as optical phonons will also be considered in subsequent work.

4. Conclusions

In summary, based on the authors' previous temperature-dependent modeling thoughts, a novel theoretical model without any fitting parameters for the temperature dependence of band gap energy in semiconductors is established based on the authors' previous temperature-dependent modeling thoughts. The developed model relates the band gap energy at the elevated temperature to that at the arbitrary reference temperature and Debye heat capacity. To test this new model, the band gap energies of the semiconductors of Si, Ge, AlN, GaN, InP, InAs, ZnO, ZnS, ZnSe and GaAs from approximate 0 K to 400 K were calculated and compared with those from the previous theories and experiments. It turns out that our model can well predict the temperature dependence of the band gap energies of the semiconductors at low temperatures. At high temperatures, the lattice expansion will make a significant contribution and cannot be ignored. Besides, this model shows its obvious advantages compared with the widely quoted Varshni's semi-empirical equation from the aspect of physical meaning, derivation process and application. The study provides a convenient method to determine the band gap energy of semiconductors under different temperatures.

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