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Analytical expression for concentration and sensitivity of a thin film semiconductor gas sensor



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Abstract In this paper, a mathematical model for gas sensing thin film semiconductor at an internal diffusion limitation for non-steady-state conditions is discussed. The model is based on diffusion equations containing a linear term related to the reaction processes. Analytical expressions for concentrations are derived using Laplace transformation. The gas sensitivity for both actual and equivalent models has been reported for all the values of reaction parameters such as rate constant and film thickness. Furthermore, in this work a complex inversion formula is employed to solve the boundary value problem. An excellent agreement with simulation data is observed. The dependence of sensitivity on temperature, film thickness and time are discussed for both actual and equivalent models.

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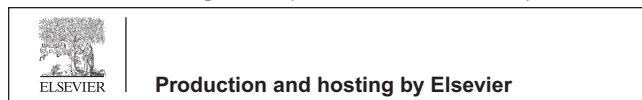
1. Introduction

Gas sensor technology has already been grown as in dispensable practice in various aspects in our life. Yet further advancements in the technology are required in order to improve sustainability of our society and quality of human life. Gas sensors play vital role in detecting, monitoring and controlling the presence of hazardous and poisonous gases in the atmosphere. It is well known fact that the gas adsorption

on the surface of a semiconductor can influence its electrical conductivity [1].

Semiconductor based gas sensor can be fabricated into three types of devices, i.e., sintered block, thick film and thin film, of these sintered block and thick film devices are commercialized successfully [2]. Even though thin film devices are brought into practical use, they have remarkable characteristic features such as, fast response, low fabrication cost, ease of miniaturization, and compatibility with microelectronic circuitry [3]. Thong et al. [4] have compared gas sensor performance of SnO₂ nanowires and their hierarchical nanostructures. Every semiconductor gas sensor is provided with a porous sensing layer (resistor) of a semiconducting oxide. Under the steady-state condition, the gas concentration inside the sensing layer would decrease with increasing diffusion depth, resulting in a gas concentration profile which depends on the rates of diffusion and surface reaction [5]. Semiconductor sensors can be produced in arrays to allow sensing of

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<i>Symbol</i>		<i>r</i>	pore radius, nm
<i>a</i>	sensitivity coefficient, ppm ⁻¹	<i>R</i>	gas constant, J K ⁻¹ mol ⁻¹
<i>a</i> ₀	pre-exponential constant, ppm ⁻¹	<i>R</i> _a	resistance of the film in air, none
$A = \left(\frac{3k_0}{4r}\right)^{\frac{1}{2}} \left(\frac{\pi M}{2R}\right)^{\frac{1}{4}}$	constant, nm ⁻¹ K ^{1/4}	<i>R</i> _g	resistance of the film in gas, none
<i>C</i>	concentration of target gas, ppm	<i>S</i>	sensitivity, none
<i>C</i> _s	target gas concentration outside the film, ppm	<i>t</i>	time, s
<i>D</i>	diffusion coefficient, nm ² s ⁻¹	<i>u</i>	dimensionless concentration, none
<i>D</i> _k	Knudsen diffusion coefficient, g/mol	<i>x</i>	depth from the film surface, nm
<i>E</i> _a	apparent activation energy, kJ mol ⁻¹	<i>x</i>	distance, nm
<i>E</i> _k	activation energy, kJ mol ⁻¹	<i>Greek symbols</i>	
<i>k</i>	rate constant, s ⁻¹	χ	dimensionless distance, none
<i>k</i> ₀	pre exponential constant, none	τ	dimensionless time, none
<i>L</i>	film thickness, nm	$\sigma(x)$	sheet conductance under exposure to the gas, none
<i>M</i>	molecular weight, Amu	σ_0	sheet conductance normalized in air, none
$m = L\sqrt{k/D}$	Hatta number, none		

multiple species simultaneously with advances in sensitivity and detection limits which approaches parts-per-million (ppm) levels for some species. Tin oxide semiconductor gas sensors patented in 1962 by Taguchi [6]. Korotcenkov and Cho [7] analyzed the influence of film thickness of SnO₂ films deposited by a spray pyrolysis method on the operating characteristics of gas sensors. Since then stannic oxide gas sensors have undergone extensive research and development. Nowadays, Tin dioxide (SnO₂) is the most important material for use in gas sensing applications [8].

Gas sensor technology has played an important role in various fields such as in the automation of industrial processes, emission control for automobiles, and gas leakage detection in home and workplace. Specifically, the research work done on gas sensors based semiconducting metal oxides has made remarkable progress in detecting various kinds of gas molecules such as H₂, CO, hydrocarbons, NO_x, SO_x, CO₂, VOCs, and odors [9,10]. The pioneering works of Taguchi [6] in the early 1960s supported the same. Among semiconducting metal oxides, the gas sensing properties and sensing mechanism of SnO₂ have been well studied by many workers due to their excellent ability for gas sensing [11–15]. However, the understanding of working principles needs further exploration in order to develop high-performance semiconductor gas sensors required for practical applications.

Several attempts have been made to analyze/improve semiconductor gas sensors based on diffusion equations by many researchers [16–25]. Need of a sensing body with the well-defined geometry and porous structure with proper initial and boundary conditions are found to be important from the existing analysis reports [5]. Gas diffusion dynamics of a thin film semiconductor gas sensor is investigated by solving the relevant diffusion equation using the explicit finite difference method [26]. Liu et al. [27] proposed the probable application of the modified expression on explaining response of thin films to various reducing and oxidizing gases. Hosein-Babaei and Orvatinia [28] presented a mathematical model for simulation of the steady state gas sensitivity ($s = G_g/G_a$) of a thin film resistive gas sensor. Yamazoe and Shimano [29] discussed the gas response of oxide semiconductor film devices under control of gas diffusion and reaction effects. It is found that

no rigorous analytical expressions for the concentrations of target gas and sensitivity inside the thin film semiconductor gas sensor for all values of reaction parameters have been reported so far. Hence an attempt has been made, in this paper to come up with, approximate analytical expressions for the concentrations and sensitivity of both actual and equivalent models using Laplace transformation method. In addition the dependence of gas sensitivity on film thickness and temperature is also reported.

2. Mathematical modeling

A thin film semiconductor gas sensor is usually fabricated by depositing a porous thin layer of a semiconducting oxide on a dense substrate. The target gas molecules diffuse in the thin layer while reacting with the surface oxygen of the oxide grains. Generally, Scanning electron micrographs (SEM) demonstrate information about the surface homogeneity, surface morphology like crack free nature, pinholes, grain size, nature of the film and smoothness of the films. In optimized conditions, Metal oxide (Tin oxide thin films) illustrates a well defined and smooth uniform surface with uniform grain distribution or high crystalline nature. It provides good sensing behavior. As the layer thickness is far smaller than the layer width, the gas diffusion can be taken as one-dimensional along the direction of depth, as illustrated in Fig. 1(a) for actual

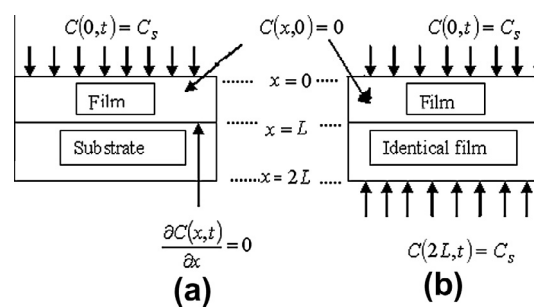


Figure 1 Modeling of thin film device: (a) for actual model (b) for equivalent model.

model and Fig. 1(b) for equivalent model. In equivalent model, the film is twice as thick as the original film, but it has no substrate to attach on, allowing the gas diffusion from both sides. For both models of the first order kinetics, diffusion equation is expressed as follows [5]:

$$\frac{\partial C(x, t)}{\partial t} = D \frac{\partial^2 C(x, t)}{\partial x^2} - kC(x, t). \quad (1)$$

Here the target gas concentration $C(x, t)$ is a function of depth from surface (x) and time (t), D is diffusion coefficient, and k is reaction constant. The initial and boundary conditions for both models (actual and equivalent) are as follows:

$$C(x, 0) = \varphi(x) = 0 \quad (2a)$$

$$C(0, t) = \psi_1(t) = C_s \quad (2b)$$

The another boundary condition for the actual model is

$$\frac{\partial C}{\partial x} = \psi_2(t) = 0 \quad \text{at} \quad x = L. \quad (2c)$$

But for the equivalent model this boundary condition is replaced by

$$C(2L, t) = \psi_3(t) = C_s. \quad (2d)$$

Here suffixes 1 to 3 denote the upper and lower surfaces of the film, for both actual and equivalent models respectively. $\varphi(x)$, $\psi_1(t)$, $\psi_2(t)$ and $\psi_3(t)$ are introduced as general conditions for the convenience of mathematical treatments before they are specified to be as indicated in the later stage of derivation. Due to the symmetry of boundary conditions, the solution based on equivalent model should be also symmetric with respect to a mirror located at $x = L$. Only the upper half ($0 \leq x \leq L$) of the solution is reduced to the solution based on actual model. These models give the same solution under steady-state conditions. Under non-steady-state conditions, however, the actual model fails to give a solution of diffusion equation because the boundary conditions are not sufficient. The linear differential equation can be made dimensionless by defining the following parameters:

$$u = \frac{C}{C_s}; \quad \chi = \frac{x}{L}; \quad \tau = \frac{Dt}{L^2}; \quad m = L\sqrt{k/D}; \quad (3)$$

where u and χ represent dimensionless concentration and distance respectively. Here τ and m represent dimensionless time and Hatta number respectively. Eq. (1) can be reduced to the following dimensionless form:

$$\frac{\partial u}{\partial \tau} = \frac{\partial^2 u}{\partial \chi^2} - m^2 u. \quad (4)$$

Initial and boundary conditions (Eqs. (2a), (2b)) for both the models are reduced to

$$\tau = 0, \quad u = 0 \quad (5a)$$

$$\chi = 0, \quad u = 1 \quad (5b)$$

Another boundary condition as in Eq. (2c) for actual model can be reduced to

$$\chi = 1, \quad \frac{\partial u}{\partial \chi} = 0. \quad (5c)$$

Similarly the boundary condition Eq. (2d) for the equivalent model is reduced to

$$\chi = 2, \quad u = 1. \quad (5d)$$

3. Analytical expression of concentration profile for actual and equivalent model

The partial differential equation (4) and the boundary conditions (Eqs. (5b) and (5c)) in Laplace space becomes as follows:

$$\frac{d^2 \bar{u}}{d\chi^2} = (s + m^2) \bar{u}. \quad (6)$$

where \bar{u} denotes the Laplace transform of a function u . Now, the boundary conditions for actual model becomes,

$$\chi = 0, \quad \bar{u} = \frac{1}{s} \quad (7a)$$

$$\chi = 1, \quad \frac{\partial \bar{u}}{\partial \chi} = 0. \quad (7b)$$

The analytical solution for Eq. (6) (Appendix A) is

$$u(\chi, \tau) = \frac{\cosh((1-\chi)m)}{\cosh(m)} - \sum_{n=1}^{\infty} \frac{(-1)^{-n} (2n+1) \pi \exp \left[- \left(m^2 + \frac{(2n+1)^2 \pi^2}{4} \right) \tau \right] \cos \left(\frac{(2n+1)\pi}{2} (1-\chi) \right)}{\left(m^2 + \frac{(2n+1)^2 \pi^2}{4} \right)}. \quad (8)$$

Now, the boundary conditions for equivalent model become,

$$\chi = 0, \quad \bar{u} = \frac{1}{s} \quad (9a)$$

$$\chi = 2, \quad \bar{u} = \frac{1}{s} \quad (9b)$$

Similarly the analytical solution of Eq. (6) for equivalent model is as follows:

$$u(\chi, \tau) = \frac{\sinh(m\chi) - \sinh[m(\chi-2)]}{\sinh(2m)} - \sum_{n=1}^{\infty} \frac{(-1)^{-n} n \pi \left[\sin \frac{n\pi}{2} (\chi-2) - \sin \left(\frac{n\pi}{2} \chi \right) \right] \exp \left[- \left(\frac{n^2 \pi^2}{4} + m^2 \right) \tau \right]}{2 \left(\frac{n^2 \pi^2}{4} + m^2 \right)}. \quad (10)$$

4. Analytical expression of sensitivity for actual model

Let us consider that the thin film is a uniform stack of infinitesimally thin sheets, the electric conductance of each of which is given by $\sigma(x)$, where x is depth from the film surface. The conductance of the whole film is then derived by integrating $\sigma(x)$ over the whole range of x ($x = 0 - L$). Also we can assume that [5].

$$\sigma(x) = \sigma_0(1 + aC). \quad (11)$$

Here a is sensitivity coefficient and σ_0 is conductance in air. The resistance in air (R_a) and resistance in the air containing target gas (R_g) can be expressed as follows:

$$\frac{1}{R_a} = \int_0^1 \sigma_0 d\chi, \quad \frac{1}{R_g} = \int_0^1 \sigma_x d\chi. \quad (12)$$

Gas sensitivity (s) is defined as the ratio of resistance in air (R_a) to resistance in the air containing target gas (R_g). This can be obtained using Eq. (12) as follows:

$$s(m, \tau) = \frac{R_a}{R_g} = \frac{\int_0^1 \sigma_x d\chi}{\int_0^1 \sigma_0 d\chi} = 1 + a \int_0^1 C(\chi, \tau) d\chi$$

$$= 1 + a \left[\frac{\tanh(m)}{m} + \frac{\sum_{n=1}^{\infty} 2(2n+1)\pi e^{-\left(m^2 + \frac{(2n+1)^2 \pi^2}{4}\right)\tau}}{\left(m^2 + \frac{(2n+1)^2 \pi^2}{4}\right)} \right]. \quad (13)$$

5. Analytical expression of sensitivity for equivalent model

For equivalent model the resistance in air (R_a) and resistance in the air containing target gas (R_g) can be expressed in the following form:

$$\frac{1}{R_a} = \int_0^2 \sigma_0 d\chi, \quad \frac{1}{R_g} = \int_0^2 \sigma_x d\chi \quad (14)$$

Using Eq. (14), the analytical expression of sensitivity for equivalent model is obtained as,

$$s(m, \tau) = \frac{R_a}{R_g} = \frac{\int_0^2 \sigma_x d\chi}{\int_0^2 \sigma_0 d\chi} = 1 + a \int_0^2 C(\chi, \tau) d\chi$$

$$= 1 + a \left[\frac{2}{m} \left[\frac{1}{\tanh(2m)} - \frac{1}{\sinh(2m)} \right] - 2 \sum_{n=1}^{\infty} (-1 + (-1)^n) \frac{\exp\left(-\left(m^2 + \frac{n^2 \pi^2}{4}\right)\tau\right)}{\left(m^2 + \frac{n^2 \pi^2}{4}\right)} \right] \quad (15)$$

6. Analytical expression of sensitivity on operating temperature for actual and equivalent models

The dependence of sensitivity on temperature is considered here. It is obvious that Knudsen diffusion coefficient D_k , the rate constant k and sensitivity coefficient a can be represented in terms of temperature as follows:

$$D_k = \frac{4r}{3} \sqrt{\frac{2RT}{\pi M}} \quad (16)$$

$$k = k_0 \exp\left(-\frac{E_k}{RT}\right) \quad (17)$$

$$a = a_0 \exp\left(-\frac{E_a}{RT}\right) \quad (18)$$

Combining Eqs. (16)–(18) with Eq. (13), the following analytical expression of sensitivity for actual model can be obtained as,

$$s(m, \tau) = 1 + a_0 \exp\left(-\frac{E_a}{RT}\right) \left[\frac{\tanh(m)}{m} + \frac{\sum_{n=1}^{\infty} 2(2n+1)\pi \exp\left(-\left(m^2 + \frac{(2n+1)^2 \pi^2}{4}\right)\tau\right)}{\left(m^2 + \frac{(2n+1)^2 \pi^2}{4}\right)} \right] \quad (19)$$

where $m = ALT^{-0.25} \exp(-E_k/2RT)$. By combining Eqs. (16)–(18) with Eq. (13), followed by rearranging, the analytical expression of sensitivity for equivalent model can be obtained as,

$$s(m, \tau) = 1 + a_0 \exp\left(-\frac{E_a}{RT}\right) \left[\frac{2}{m} \left[\frac{1}{\tanh(2m)} - \frac{1}{\sinh(2m)} \right] - 2 \sum_{n=1}^{\infty} (-1 + (-1)^n) \frac{\exp\left(-\left(m^2 + \frac{n^2 \pi^2}{4}\right)\tau\right)}{\left(m^2 + \frac{n^2 \pi^2}{4}\right)} \right] \quad (20)$$

7. Numerical simulation

The diffusion equation (Eq. (6)) for the boundary conditions (Eqs. (7a), (7b), (9a), (9b)) are solved by numerical methods. The function `pdx4` in Matlab software, which is a function of solving the initial boundary value problems for partial differential equations, is used to solve these equations. Numerical solution obtained from this function is compared with the analytical results which are depicted in Fig. 2. An excellent agreement for all values of time τ is observed. The corresponding Matlab program is made available in Appendix B.

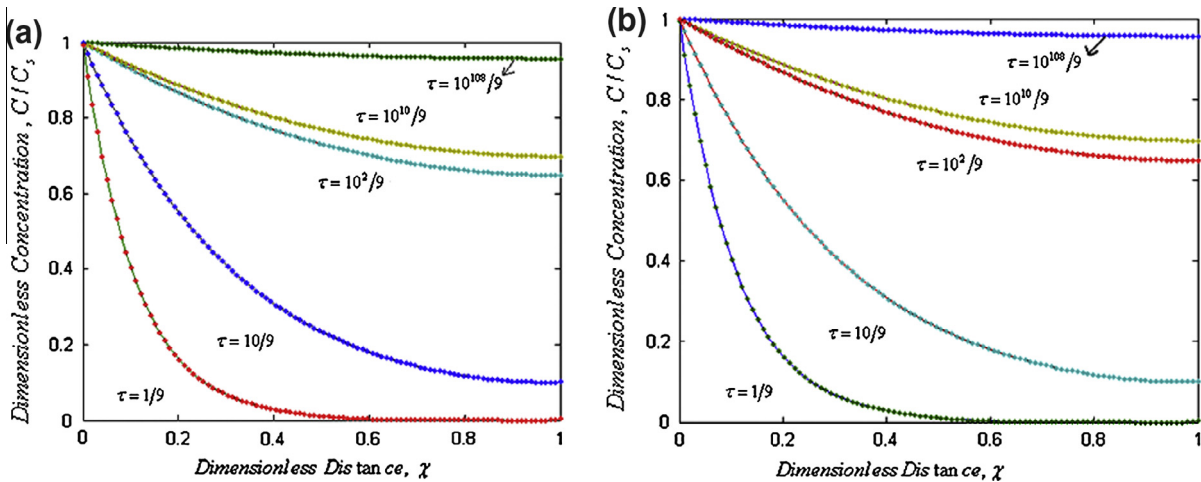


Figure 2 Dimensionless concentration versus the dimensionless distance for various values of τ and for the fixed value of $m=9$, $L = 300$ nm, $D = 10^{12}$ nm² s⁻¹, $k = 9 * 10^8$ s⁻¹. (–) represents analytical results and (···) represents numerical results. (a) For actual model (Eq. (8)); (b) for equivalent model (Eq. (10)).

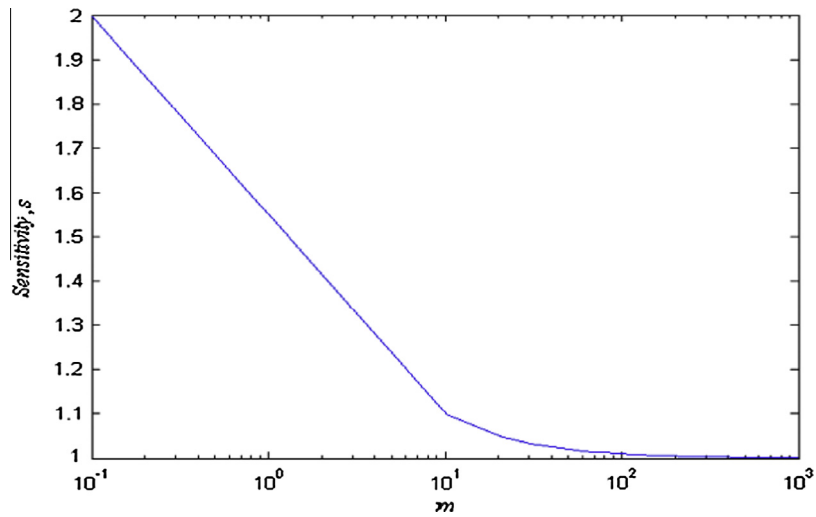


Figure 3 Generalized expression of the gas sensitivity of thin films versus non-dimensional parameter, ($m(= L\sqrt{k/D})$) for actual model using Eq. (13) at $\tau = 1$.

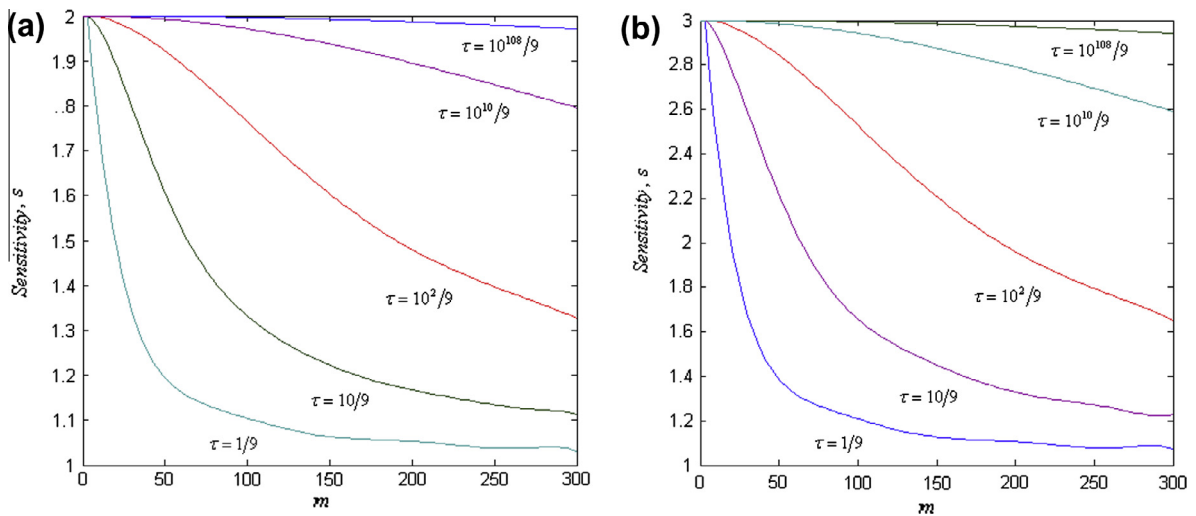


Figure 4 Non-steady state gas sensitivity versus m at various periods of time τ . (a) for actual model (Eq. (13)); (b) for equivalent model (Eq. (15)).

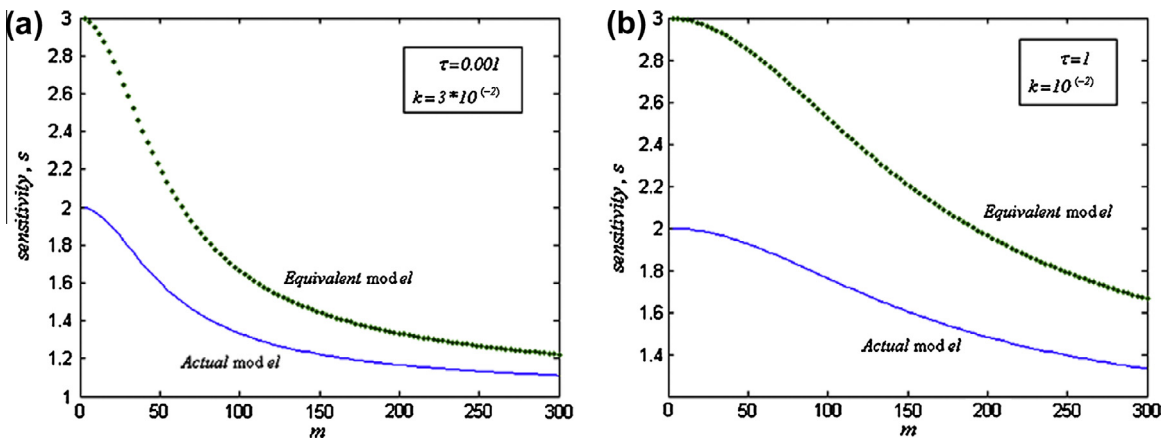


Figure 5 Non-steady state gas sensitivity versus m . (a) for actual model (Eq. (13)); (b) for equivalent model (Eq. (15)).

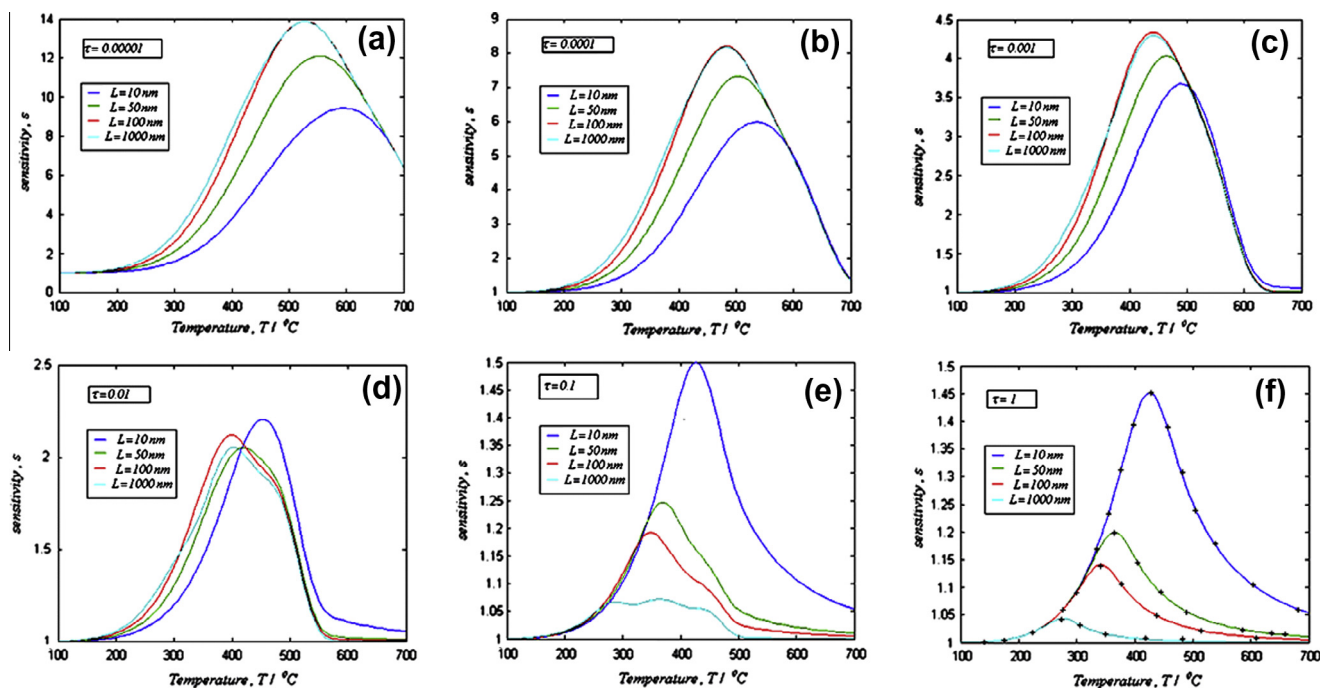


Figure 6 Actual model non-steady state gas sensitivity versus temperature for various values of film thickness, L and time, τ simulated under the conditions for $E_a = 50 \text{ kJ mol}^{-1}$, $E_k = 200 \text{ kJ mol}^{-1}$, $A = 1.7 \times 10^7 \text{ nm}^{-1} \text{ K}^{1/4}$, $a_0 = 3400 \text{ ppm}^{-1}$ (Eq. (19)). Solid line denotes the non-steady state sensitivity. In (f) '+' denotes the steady state sensitivity.

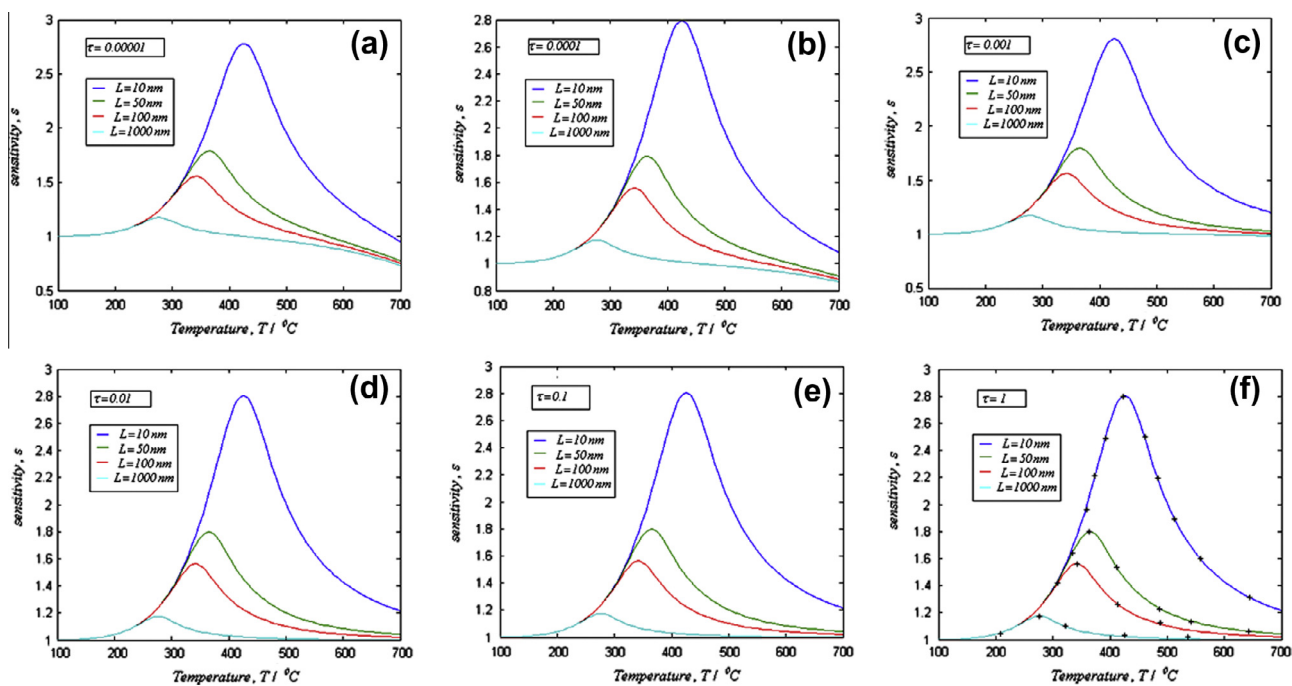


Figure 7 Equivalent model non-steady state gas sensitivity versus temperature for various values of film thickness, L and time, τ simulated under the conditions for $E_a = 50 \text{ kJ mol}^{-1}$, $E_k = 200 \text{ kJ mol}^{-1}$, $A = 1.7 \times 10^7 \text{ nm}^{-1} \text{ K}^{1/4}$, $a_0 = 3400 \text{ ppm}^{-1}$ (Eq. (20)). Solid line denotes the non-steady state sensitivity. In (f) '+' denotes the steady state sensitivity.

8. Results and discussion

Eqs. (8) and (10) are the new and simple approximate analytical expressions for the gas concentration profile calculated using Laplace transformation method. The analytical expressions of concentration $u(\chi, \tau)$ for various values of dimensionless reaction parameter m and dimensionless time τ are compared with numerical solution.

Fig. 2(a) and (b) shows the variation in dimensionless concentration versus the dimensionless distance for various values of time τ and for some fixed value of $m(=9)$. Obviously the profile changes sharply with changing time τ . From this figure, it also observed that the concentration profile of gas decreases gradually when τ decreases and the value of the concentration is uniform when $\tau \geq 10^{108}/9$ in both models.

Fig. 3 shows the generalized expression of the gas sensitivity of thin film at a fixed temperature in terms of non-dimensional parameter, m . Fig. 4(a) and (b) shows the sensitivity versus m using Eqs. (13)–(15) for various values of τ for both actual and equivalent models.

From Fig. 5 it is inferred that the sensitivity of equivalent model is always greater than actual model. Also sensitivity for both model decreases when m increases. Non-steady state gas sensitivity versus temperature for various values of film thickness, L , temperature, T and time τ is plotted in Fig. 6 (actual model) and Fig. 7 (equivalent model). From these figures it is inferred that sensitivity reaches the maximum value when $400^\circ\text{C} \leq T \leq 500^\circ\text{C}$. For actual model this maximum value decreases when time increases, whereas the maximum value is constant for equivalent model. Also in both models, sensitivity reaches the steady state value (or constant value) when $\tau = 1$ (Figs. 6(f) and 7(f)). Sensitivity always decreases when film thickness, L increases.

9. Conclusion

The time dependent reaction–diffusion equations in semiconductor gas sensor have been solved analytically and numerically. In the present study, analytical expression corresponding to the concentration profile in semiconductor gas sensor for actual and equivalent model in terms of all reaction parameter, (m) is presented. It is observed that the results obtained using the analytical expression show a good conformity with numerical simulation results. The dependency of gas sensitivity on film thickness and temperature for various values of time for both actual and equivalent models are also discussed.

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Appendix A. Solutions of Eq. (4) using complex inversion formula

The solution of Eq. (6) for the boundary condition Eqs. (7a), (7b) is

$$\bar{u}(\chi, \tau) = \frac{\cosh[(1-\chi)\sqrt{s+m^2}]}{s \cosh(\sqrt{s+m^2})} \quad (\text{A1})$$

We can find the inverse Laplace transform for the above Eq. (A1) using complex inversion formula. If $\bar{y}(s)$ represents the Laplace transform of a function $y(\tau)$, then according to the complex inversion formula we can state that

$$y(\tau) = \frac{1}{2\pi i} \int_{c-i\infty}^{c+i\infty} \exp[s\tau] \bar{y}(s) ds = \frac{1}{2\pi i} \oint_c \exp[s\tau] \bar{y}(s) ds \quad (\text{A2})$$

where the integration in Eq. (A2) is to be performed along a line $s = c$ in the complex plane where $s = x + iy$. The real number c is chosen such that $s = c$ lies to the right of all the singularities, but is otherwise assumed to be arbitrary. In practice, the integral is evaluated by considering the contour integral presented on the r.h.s of Eq. (A1), which is evaluated using the so-called Bromwich contour. The contour integral is then evaluated using the residue theorem which states for any analytic function $F(z)$

$$\oint_c F(z) dz = 2\pi i \sum_n \text{Res}[F(z)]_{z=z_n} \quad (\text{A3})$$

Where the residues are computed at the poles of the function $F(z)$. Hence from Eq. (A3) we note that:

$$y(\tau) = \sum_n \text{Res}[\exp[s\tau] \bar{y}(s)]_{s=s_n} \quad (\text{A4})$$

From the theory of complex variables we can show that the residue of a function $F(z)$ at a simple pole at $z = a$ is given by:

$$\text{Res}[F(z)]_{z=a} = \lim_{z \rightarrow a} \{(z-a)F(z)\} \quad (\text{A5})$$

Hence in order to invert Eq. (4), we need to evaluate $\text{Res}[\cosh(1-\chi)(\sqrt{s+m^2})/s \cosh(\sqrt{s+m^2})]$. Now the poles are obtained from $s \cosh(\sqrt{s+m^2}) = 0$. Hence there is a simple pole at $s = 0$ and there are infinitely many poles given by the solution of the equation $\cosh(\sqrt{s+m^2}) = 0$ and so $s_n = -\left[\frac{(2n+1)^2\pi^2}{4} + m^2\right]$ with $n = 1, 2, \dots$. Hence we note that:

$$\begin{aligned} S(\chi, \tau) &= \text{Res} \left[\frac{\cosh(1-\chi)(\sqrt{s+m^2})}{s \cosh(\sqrt{s+m^2})} \right]_{s=0} \\ &\quad + \text{Res} \left[\frac{\cosh(1-\chi)(\sqrt{s+m^2})}{s \cosh(\sqrt{s+m^2})} \right]_{s=s_n} \\ &= \lim_{s \rightarrow 0} (s-0) \left\{ \exp(s\tau) \frac{\cosh(1-\chi)(\sqrt{s+m^2})}{s \cosh(\sqrt{s+m^2})} \right\} \\ &\quad + \lim_{s \rightarrow s_n} (s-s_n) \left\{ \exp(s\tau) \frac{\cosh(1-\chi)(\sqrt{s+m^2})}{s \cosh(\sqrt{s+m^2})} \right\} \quad (\text{A6}) \end{aligned}$$

The first residue in Eq. (A6) is given by

$$\begin{aligned}
& \text{Res} \left[\frac{\cosh(1-\chi)(\sqrt{s+m^2})}{s \cosh(\sqrt{s+m^2})} \right]_{s=0} \\
&= \lim_{s \rightarrow 0} \left\{ \exp(s\tau) \frac{\cosh(1-\chi)(\sqrt{s+m^2})}{s \cosh(\sqrt{s+m^2})} \right\} \\
&= \frac{\cosh[(1-\chi)m]}{\cosh(m)} \tag{A7}
\end{aligned}$$

The second residue in Eq. (A6) can be evaluated as follows. It is established that if $F(z)$ can be expressed as $F(z) = f(z)/g(z)$, where the functions f and g are analytic at $s = s_n$ and $g(s_n) = 0$ while $g'(s_n) \neq 0$ and $f(s_n) \neq 0$. Then, $\text{Res}[F(z)]_{s=s_n} = \sum_{n=0}^{\infty} \frac{f(s_n)}{g'(s_n)} \exp[s_n \tau]$. Hence we can show that:

$$\begin{aligned}
& \lim_{s \rightarrow s_n} e^{s\tau} \frac{\cosh(1-\chi)(\sqrt{s+m^2})}{s \frac{d}{ds} \cosh(\sqrt{s+m^2})} \\
&= \lim_{s \rightarrow s_n} e^{s\tau} \frac{\cosh(1-\chi)(\sqrt{s+m^2})(2\sqrt{s+m^2})}{s_n \sinh(\sqrt{s+m^2})} \\
&= \frac{2 \exp \left[- \left\{ \frac{(2n+1)^2 \pi^2}{4} + m^2 \right\} \tau \right] \cosh \left[\frac{i(2n+1)\pi}{2} (1-\chi) \right] \sqrt{s+m^2}}{- \left(\frac{(2n+1)^2 \pi^2}{4} + m^2 \right) \sinh \left(\frac{i(2n+1)\pi}{2} \right)}, \\
&n = 1, 2, \dots \tag{A8}
\end{aligned}$$

Using $\cosh(i\theta) = \cos(\theta)$ and $\sinh(i\theta) = i \sin(\theta)$ the above results becomes

$$\begin{aligned}
& \lim_{s \rightarrow s_n} e^{s\tau} \frac{\cosh(1-\chi)(\sqrt{s+m^2})}{s \cosh(\sqrt{s+m^2})} = \\
& - \sum_{n=1}^{\infty} \frac{(-1)^{-n} (2n+1) \pi \exp \left[- \left(\frac{(2n+1)^2 \pi^2}{4} + m^2 \right) \tau \right] \cos \left[\frac{(2n+1)}{2} (1-\chi) \right]}{\left(\frac{(2n+1)^2 \pi^2}{4} + m^2 \right)} \tag{A9}
\end{aligned}$$

Adding Eqs. (A7) and (A9) we obtain Eq. (8) in the text.

Appendix B. The Matlab program to find the numerical solution of Eq. (8)

```

function pdex1
m = 0;
x = linspace(0,1);
t = linspace(0, (1/9));
sol = pdepe(m,@pdex1pde,@pdex1ic,@pdex1bc,x,t);
u1 = sol(:, :, 1);
figure
plot(x,u1(end,:))
title('u1(x,t)')
function [c,f,s] = pdex1pde(x,t,u,DuDx)
m1 = 300 * 3 * 10^(-2);
c = 1;
f = 1. * DuDx;
F = -m1^2 * u(1);
s = F;
function u0 = pdex1ic(x);
u0 = 0;
function [pl,ql,pr,qr] = pdex1bc(xl,ul,xr,ur,t)
pl = ul(1) - 1;
ql = 0;
pr = 0;
qr = 1;

```

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