Zero-Flux Boundary Condition in a Two-Probability-Parameter Random Walk Model

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***Abstract*—Zero-flux boundary condition is revisited in the context of a two-probability-parameter and a rigorous combinatorial model. The two-parameter model distinguishes partial segregation, partial absorption, and partial reflection. Both models show that vanishing flux across the barrier can be realized for non-zero gradient of the dopant distribution at the boundary.**

Keywords-component; zero-flux boundary condition; reflective diffusion barrier; random walk

I. Introduction

With the advent of nano-scale dimensions for dielectric, metal gate and semiconductor films precise knowledge of impurity, contaminants, and point defect distribution have become crucial in understanding the properties of thin and subsurface layers. The zero-flux boundary condition [1] is revisited in the context of a rigorous random walk barrier model proposed by Feller [2]. It is shown that in the more general model the zero-flux boundary condition has by no means to be associated with the vanishing gradient of the diffusing species. A special case of a totally reflective barrier leads to a strong dopant depletion at the interface.

II. Feller's Model

According to Feller an elastic barrier, situated at the location on the x axis halfway between the positions $m=0$ and $m=-1$, is defined by the rule that from position $m=0$ the particle moves with the probability p to position $m=1$; with probability δq it stays at $m=0$; and with probability $(1-\delta)q$ it moves to $m=-1$ where it is absorbed (i.e., the process terminates), with $p+q=1$, see Fig.1.

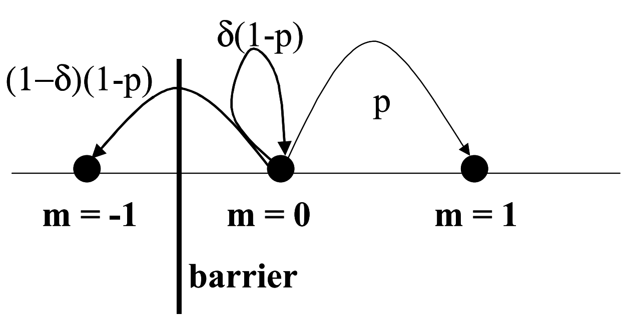

Fig.1 Two-probability parameter model of a diffusion barrier.

For $\delta=0$ we have an absorbing barrier, for $\delta=1$ a reflecting barrier. Both, the absorbing and reflecting barrier are special cases of the elastic barriers. As δ runs from 0 to 1, a whole family of partially reflective and partially absorbing barriers is generated. The case $\delta=1$ and $p=0$ corresponds to a totally segregating barrier, which has the same properties as a totally absorbing barrier, however now shifted by one unit lattice distance to the right. The cases for $\delta=1$ and $0<p<1$ can be called partially reflecting barriers. The model comprehends intermediate cases of co-existence of partial segregation, partial absorption, and partial reflection as shown in Table I.

δ \ p	p=0	0<p<1	p=1
δ=0	totally absorbing	totally absorbing	totally absorbing
0<δ <1	partially absorbing partially segregating	partially absorbing partially segregating partially reflecting	partially absorbing non-segregating partially reflecting
δ=1	non-absorbing totally segregating	non-absorbing partially segregating totally reflecting	non-absorbing non-segregating totally reflecting

Table I. Depending on the choice of δ and p probability parameters one can have various degrees of absorptivity, segregation, and reflectivity.

This paper focuses specifically on the case $\delta=1$ of a non-absorptive barrier (zero-flux across the barrier) and investigates the impact of the probability parameter p on the distribution of diffusing species. Fig.2 shows that only the choice of $p=1/2$ leaves a uniform species distribution invariant and compatible with the zero-flux boundary condition used in partial

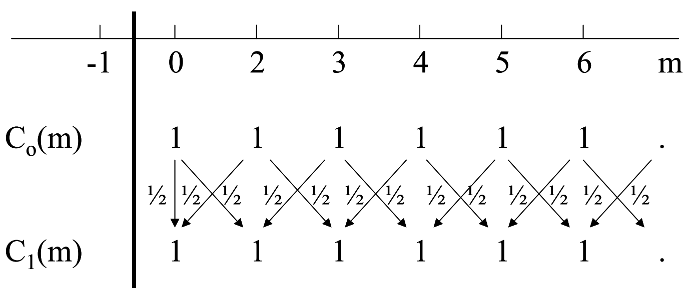

Fig.2 A uniform distribution is invariant under the random walk in presence of partially reflecting barrier with the properties d=1 and p=1/2 (first two arrows at m=0 position). All other choices of p lead to a non-uniform distribution while conforming to the zero-flux condition.

differential equations theory. All other choices of not vanishing p lead either to accumulation (p>1/2) or to depletion (p<1/2) of the diffusing species at the barrier, while still preserving the zero-flux boundary condition. For the special case of ***p=1*** an analytical combinatorial formula is derived, for the first time, showing strong dopant depletion at the interface which increases with increasing number of diffusion steps. In the case of vacancies, the depletion at the interface lowers the number of distinguishable ways of distributing vacancies among lattice sites, reducing thus the configurational entropy at the interface. The lowering of Gibbs energy at the interface is therefore less pronounced at the interface than in the bulk by virtue of the spatially non-uniform vacancy distribution.

III. Combinatorial Model of a Totally Reflecting Barrier

In the unrestricted one-dimension case, the probability that particle arrives at the point m after N unit displacements is well-known and given by the number of paths arriving at m divided by the total number of paths, i.e. $W(m,N)= C(N, \frac{1}{2}(N+m))/2^N$, where $C(n,m)$ is the binomial coefficient. In case of a diffusion barrier at m=0, particle diffusion is restricted to the positive axis. The conventional treatment postulates for this case the reflection principle [3], which leads indeed to a probability formula predicting uniform dopant distribution at the boundary. If we assume that a barrier is at m_b, the argument is made that any path which in absence of the barrier would have ended at $m^*<m_b$ is merely reflected at the plane $m=m_b$. Thus the image point of m* lies on the other side of the barrier at $2m_b-m^*$. [3]. It is then concluded that the effect of the reflecting barrier is taken into account by adding to W(m,N) the reflected probability $W(2m_b-m,N)$. Thus the resultant probability is: $W(m,N;m_b)=W(m,N)+W(2m_b-m,N)$ **.** It can then be shown [3, 4] that in the limit of large N:

$$\frac{dW(m,N,m_b)}{dm}\bigg|_{m=m_b} = 0 \qquad for \qquad N \to \infty.$$

This condition is reproduced by the choice ***p=1/2*** in the case of the rigorous two-probability-parameter model shown in Fig.1.
The case of totally reflective barrier can be also considered within a rigorous combinatorial model. As an example, consider all paths for N=4 for a particle starting its random walk at m=0 at the barrier. In presence of the barrier, the allowed and disallowed paths are summarized in Table II. (+) denotes a step to the right and (-) a step to the left. Obviously, the first step allowed is only (+). The number of allowed paths is 6. All other paths such as (+--+) have to be excluded. The total number of excluded paths is 10. Thus the probabilities to find the particle at *m=0,2,4* is $W_o(0,4)=1/3$, $W_o(2,4)=3/6=1/2$, $W_o(4,4)=1/6$, respectively. The same probabilities given by the textbook formula given according to the formula for $W(m,N,m_b)$ are: $W(0,4;0)=2W(0,4)=3/4$, $W(2,4;0)=1/2$, $W(4,4;0)=1/8$ respectively, which, besides not being properly normalized at the origin (double counting of paths), give clearly a markedly different probability distribution.

For the general case, a convenient bookkeeping scheme to keep track of all allowed paths originating from and arriving at arbitrary location can be found considering a "truncated" Pascal's triangle shown in Fig.3. Fig.3 shows the evolution of the path tree for a particle staring random walk at m=0. Similar truncated Pascal's triangles can be constructed for particles departing from arbitrary locations.

Allowed Paths	Paths excluded by the barrier	
(+ + + +)	(- - - -)	(- + + -)
(+ + + -)	(- - - +)	(- + + +)
(+ + - +)	(- - + -)	(+ - - -)
(+ + - -)	(- - + +)	(+ - - +)
(+ - + +)	(- + - -)	
(+ - + -)	(- + - +)	

Table II. Allowed and disallowed random walk paths for N=4 steps starting at (just right of) the reflecting barrier.

m

N	Σ	−1	0	1	2	3	4	5	6	7	8	9	10	11	12
1				1											
2	2		1		1										
3				2		1									
4	6		2		3		1								
5				5		4		1							
6	20		5		9		5		1						
7				14		14		6		1					
8	70		14		28		20		7		1				
9				42		48		27		8		1			
10	252		42		90		75		35		9		1		
11				132		165		110		44		10		1	
12	924		132		297		275		154		54		11		1

Reflecting barrier

Fig.3. The truncated Pascal's triangle is designed to count number of paths at a particular location for a particle starting its random walk at m the barrier (m=0) and proceeding through the first 12 diffusion steps.

The coefficients *a(2M,2k)* of the truncated Pascal's triangle as shown in Fig.3 conform to a recurrence relation given by :

a(2M,2M)=1, a(2M, 2(M-1))=N-1, a(0,0)=1, and a(2,0)=1
a(2M,0)=a(2(M-1),0)+a(2(M-1),2k)   for all M>1
a(2M,2k)=a(2(M-1),2(k-1))+2a(2(M-1),2k)+a(2(M-1),2(k+1))
for all k=1,…,M-1

Using generating function techniques [5] the solution of the above recurrence relation is given by:

$$a(2M,2k) = \frac{2k+1}{M+k+1}\binom{2M}{M+k} \qquad eq.(1)$$

Using mathematical induction, the above recurrence relation and its solution (eq.(1)), it can be shown that the total number of paths for N steps in a presence of a barrier is given by:

$$A^{tot}(2M) \equiv \sum_{k=0}^{M} a(2M) = \binom{2M}{M} \qquad eq.(2)$$

Thus, the total number of paths for a particle starting its random walk at the barrier is just the number of paths returning to the origin in the case of an unrestricted random walk. For particle starting from m=0 the probability $W_o(k,N)$ to find it after $N=2M$ steps is given by:

$$W_o(2k, 2M = N) = \frac{2k+1}{M+k+1}\binom{2M}{M+k} / \binom{2M}{M} \qquad eq.(3)$$

In particular, the probability to find a particle at the barrier after N steps is $W_o(0, N=2M)=1/(M+1)$, indicating that the sub-barrier region is progressively depleted with the increasing number of steps. An example of the distribution of a particle starting at the barrier after 12 steps is shown in Fig.4. It can be seen that the peak is shifted deeper into the semi-infinite medium with increasing number of steps. For a large number of steps the particle assumes uniform distribution in the bulk exhibiting pronounced depletion at the interface.

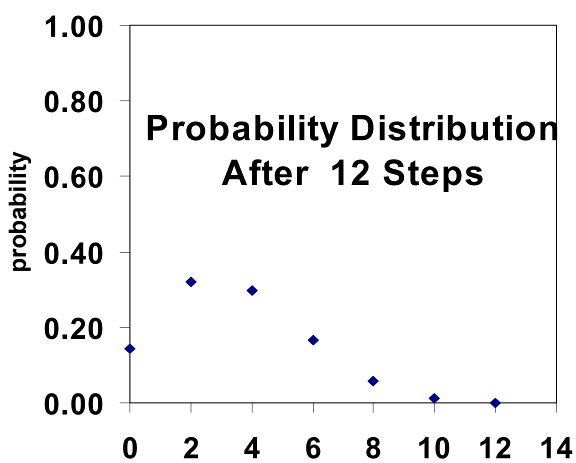

Fig.4. Probability distribution after 12 diffusion steps of a particle starting its random walk next to the totally reflecting barrier.

It is of interest to see how the location of the peak is evolving with the number of diffusion steps. To determine the location of m_{max} of the maximum of the probability distribution the difference derivative is calculated and set zero ($(a_{2m}^{2(k+1)} - a_{2M}^{2k})/2 = 0$). The solution of this equation is $m_{max}=2k_{max}=\sqrt{2(N-1)} - 2 \rightarrow \sqrt{2N}$ for large N. Hence, it can be seen that the peak is shifting rapidly into the semi-infinite medium with increasing number of diffusion steps.

The general solution of the random walk for a particle departing from any lattice site $m=2j$ near the barrier is given by the following equation (number of arrivals at m=2k after departing from m=2j):

$$a(2M, 2k, 2j) = \binom{2M}{M-j+k} - \binom{2M}{M-j-k-1} \qquad eq.(4)$$

This particular relation, in a different context, has been derived by Rosenblatt [6], however, without the proper normalization, see eq. (7). The total number of paths for every path tree originating from m=2j after N=2M steps is

$$A^{tot}(2M, 2j) \equiv \sum_{k=0}^{M} a(2M, 2k, 2j) = \binom{2M}{M} + 2\sum_{i=1}^{j} \binom{2M}{M+i}$$

eq.(5)

The probability of particle arriving at m=2k after having started its journey at m=2j is given by

$$W_{2j}(2M, 2k) = a(2M, 2k, 2j) / A^{tot}(2M, 2j) \qquad eq.(6)$$

The eq. (7) is the general solution of the diffusion of arbitrary initial distribution $c_o(2j)$ with the zero-flux condition for the case of totally reflecting barrier.

$$c_N(2k) = \sum_{j=0}^{2M+k} [W_{2j}(2M, 2k)\, c_o(2j)] \qquad eq.(7)$$

The evolution of an initially uniform distribution $c_o(i)=1$ for all integer i after $N=12$ steps is shown in Fig.5. A pronounced depletion of the surface region can be observed followed by a hump exceeding the uniform concentration before the distribution tails off into the uniform background. The formation of the hump (up-hill diffusion) is a consequence of the subsurface depletion and conservation of the dose.

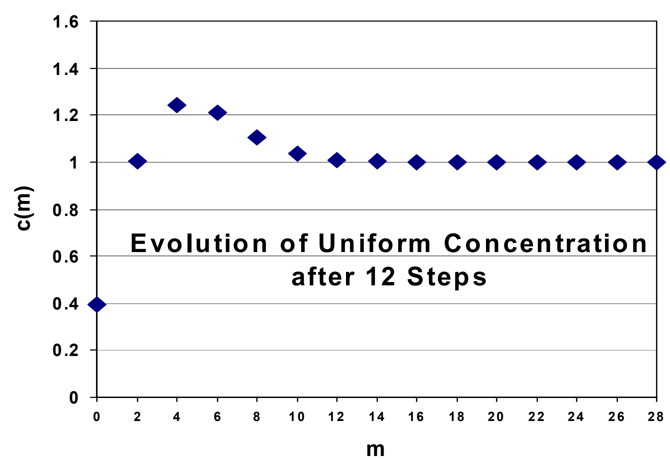

Fig.5 Concentration distribution after 12 steps of an initially uniform distribution $c_o(2j)=1$ for all j in presence of a totally reflecting barrier.

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The barrier exerts a non-local impact on the diffusion profile. The distribution affected by the barrier extends as far as m=2(M-1). In case of Fig.5, the furthest position from the barrier that is affected by the barrier is position m=22 and not m=12. A particle starting at m=10 can reach the location m=22 by only one path, consisting of a 12-tuple of exclusively forward steps $(+)^{12}$. It has also a chance of reaching the barrier at the 10-th step as it marches back by a 10-tuple of backward steps $(-)^{10}$. Hence, the total number of allowed paths is reduced from 2^{12} to $A(22)^{tot}_{12} = 2^{12} - 2$. Therefore, the probability to arrive at m=22 increases in the presence of the totally reflecting barrier from $1/(2^{12})$ to $1/(2^{12}-2)$. This is so, since the probability is not only determined by the number of arrivals at a particular location, but also by the total number of possible paths. Accordingly, given sufficiently large number of trials, one would observe more particles at the far end forward It has location in the presence of the barrier than in its absence, although the particles had never the chance to encounter the barrier in its path.

Returning to the Feller's model, it should be mentioned that the case ***p=0*** leads to a total segregation at the interface. It is easy to see that for ***½<p<1*** the dopant distribution will exhibit depletion at the interface, whereas for ***0<p< ½*** an accumulation near the interface, see Fig.2.

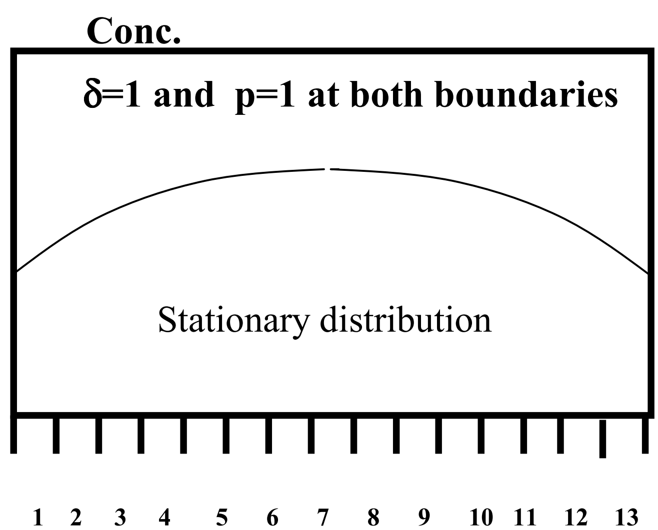

Fig. 6 Probability distribution of dopants in a thin film bounded by two totally reflective barriers. The two barriers interact and arrest the depletion at the interfaces observed in the semi-infinite plane.

This finding points to a serious limitation of the zero-flux boundary condition employed in PDE and stresses the need of better understanding of the properties of physical interfaces in terms of the parameter p.

In the case of thin layers bounded by two boundaries (as shown in Fig.6) the depletion at either barrier is brought to a halt by the presence of the other barrier at some point in time, determined by the thickness of the film, resulting in a stationary solution with a maximum probability distribution at the center of the film and decreasing concentration at the boundaries.

CONCLUSION

It has been shown that a more detailed model of a reflective diffusion barrier admits a whole range of concentration gradients while still being fully compatible with the zero-flux boundary condition. The differential equation theory postulates that the zero-flux boundary condition can be only realized for a vanishing gradient of the diffusing species at the barrier. In the two-parameter-probability model this corresponds to the particular case of δ=1 and p=1/2. The zero-gradient boundary condition designed to ensure the zero-flux condition appears therefore unduly restrictive. The present investigation indicates that a barrier, treated in the rigorous path counting model, gives rise to a driving force that is non-local in nature. The case of δ=1 and p=1 as well as the rigorous path counting method lead to a strong depletion of the subsurface region. In the case of thin films this depletion is arrested by the mutual interaction of both boundaries.

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