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Computer modelling of porous silicon formation

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Porous silicon formation has been simulated by the finite diffusion length (FDL) model. This considers a dynamic isoconcentration profile from which the aggregating particles begin their random walks. In this paper we report on the isoconcentration profile non-uniformities which increase as the finite diffusion length is increased. The implementation of the FDL model with zero diffusion length generates non-fractal structures with a fractal dimension close to 1. It is found that Eden clusters cannot be generated at zero diffusion length, due to the problem of "sinking isoconcentration profile". We conclude that these are limitations that should be considered in the FDL model for improving the understanding of physical phenomena such as formation and morphology of porous silicon.

1. Introduction

The observation of efficient visible photoluminescence from porous silicon [1] has important implications for materials research on silicon optoelectronics. In view of this, many models to explain the mechanism of formation of porous silicon are being investigated. Electrochemical anodizing can lead to porous silicon formation at lower current densities, while electropolishing occurs at higher current densities. Other factors which influence porous silicon morphology and formation are ambient light conditions, doping type and concentration in the substrate material and electrochemical anodization parameters. The origin of photoluminescence is also not established and porous silicon having morphological features of a few nanometres [2], as well as porous silicon having up to 1000-nm silicon columns have been shown to be photoluminescent [3]. The observation of photoluminescence quenching by chemical treatments suggests surface chemical species are very important for photoluminescence [4]. Several explanations for the preferential dissolution of silicon at the pore tips have been suggested. Deposition of passivating silicates on the pore walls [5] and depletion layer formation [6] are the more accepted ones. These models do not explain all the experimentally known features of porous silicon formation. The finite diffusion length (FDL) model has been suggested to be a successful model for theoretical description of porous silicon formation [7]. The nanostructured morphology of porous silicon has similarities to computer simulated patterns generated by the FDL model [8]. The simulated patterns for small values of finite diffusion length resemble the experimentally observed structure of porous silicon formed on *p*-type silicon, while for larger values of finite diffusion length the simulated patterns are similar to the experimentally observed porous silicon structures formed on *n*-type silicon.

The Eden and diffusion limited aggregation (DLA) model are being investigated for describing growth of clusters and aggregation phenomena [9, 10]. Both of these models describe non-equilibrium phenomena and the rate controlling step of aggregation differentiates between these models. The Eden model generates compact clusters and relates to phenomena which are surface reaction rate controlled, while the DLA model describes diffusion rate limited phenomenon. The FDL model has been suggested to be a more generalized model [11] by the incorporation of a finite and variable diffusion length from which the particles begin their random walk. This model considers a *n*-dimensional random walk of a particle in the presence of a concentration gradient. The time dependent diffusion equation for the one-dimensional concentration gradient is

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

where, $C(x,t)$ is the concentration, x is the distance from the interface, t is the time and D is the diffusion coefficient, which is assumed to be independent of concentration. The solution of the above differential equation can be obtained under different boundary conditions. If an infinite source of dopants diffusing into an infinite region is considered, the solution is given by

$$\frac{C(x,t)}{C_0} = \operatorname{erfc}\frac{x}{2(Dt)^{\frac{1}{2}}} \quad (2)$$

where C_0 is the concentration in the surface region. A diffusion length parameter L can be identified where the concentration is essentially the bulk concentration

$$L = 3.6(Dt)^{\frac{1}{2}} \quad (3)$$

The parameter L describes an isoconcentration profile from which there is equal probability to start a particle on its random walk towards the cluster. The mathematical equivalence between the spatial diffusion and electric fields leads to similarity in the

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diffusion-based and depletion layer-based explanation of phenomena such as porous silicon formation. The equivalent of the diffusion length parameter L is the Debye length in electrostatics.

In this paper we discuss the non-uniformities present in the isoconcentration profile from which particles are released in the FDL model. These non-uniformities are observed even at small finite diffusion lengths. The FDL model has been implemented in the limit of zero finite diffusion length and the results are compared with compact Eden clusters generated by another algorithm.

2. Computer algorithm

Two algorithms have been used in this study: the first is similar to the FDL model and the second is the algorithm for generating Eden clusters. These models require the availability of pseudo-random numbers with good statistical properties. We have generated these random numbers by the Tausworth shift generator [12] with modifications of Kirkpatrick and Stoll [13]. This method generates random numbers by performing an exclusive-OR operation (equivalent to addition in Galois field) on random numbers stored in an array.

The details of the algorithm used for generating constant density non-fractal structures are similar to the description of the FDL model [7], though in our implementation the finite diffusion length was measured from available peripheral sites rather than from occupied sites. This has more physical meaning since the diffusing particles would become part of the aggregate on contacting an available peripheral site. These details are discussed with reference to Fig. 1, which illustrates the occupied sites, available sites and unavailable sites for a diffusing particle beginning its random walk towards the cluster. The tree-like branched structures formed by the FDL simulations are similar to the pores in the morphology of porous silicon. In the case of porous silicon formation diffusion is considered to limit the necessary reactants in the bulk of silicon from reaching the growing pore. Since the anodic dissolution of silicon requires the presence of holes, they can be considered to be the necessary diffusion limited species. Though such an assumption is not required and any diffusion-limited rate controlling reactant particle can be considered to be the necessary species. The details of the algorithm are:

1. The silicon–electrolyte surface width was taken as 100 lattice units. All the locations on the first row of the lattice were considered as potential sites.
2. The lattice was arranged in a horizontal "wrap around" configuration. This is important for generating uniform clusters.
3. The growth of porous silicon was simulated by releasing a particle from a distance of predetermined finite diffusion length L from the silicon–electrolyte interface.
4. The set of all the lattice points at a vertical distance of L from the available peripheral sites of the growing aggregate were termed as the "isoconcentration profile". The farthest peripheral site was chosen when more than one peripheral site was in consideration.
5. The starting location of the particle was chosen at random from the set of all the available lattice points on the isoconcentration profile.
6. The particles then executed a random walk on this two-dimensional lattice. If a peripheral site was encountered during the random walk, this site was occupied and became part of the growing aggregate. If the occupied site was not in the interior of porous structure, then the isoconcentration profile was extended by one lattice unit. If the particle wandered away to more than twice the diffusion length from the isoconcentration profile, the random walk of the particle was terminated without any effect on the aggregates. Another particle was then released.
7. This process of release of particles from random locations from the isoconcentration profile was continued till 1000 to 10 000 particles were added to the aggregate.

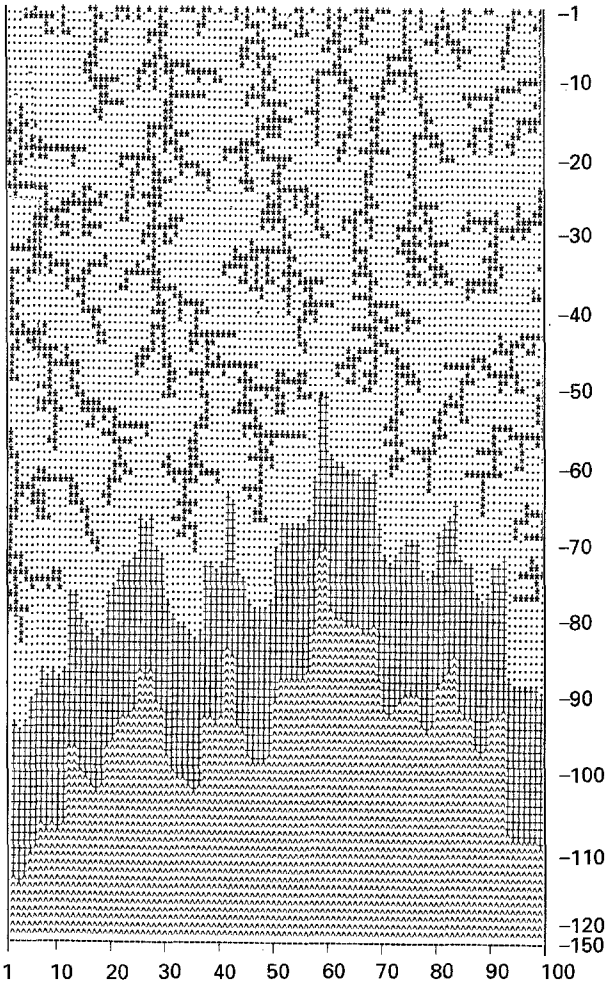


Figure 1 Illustration of aggregation pattern generated by the FDL algorithm. The finite diffusion length was chosen to be 10. The clusters grow from top to bottom. * occupied sites; · unoccupied sites; + permitted sites; ^ forbidden sites; # particle position.

The results of the implementation of this algorithm, taking the finite diffusion length as 10 lattice units, are shown in Fig. 1. The occupied lattice positions are shown by *. Note that the centre of the * is shifted up by half line spacing. The unoccupied lattice points

within the porous structure and contained by the isoconcentration profile are marked by . . The region shown by + extends 2×10 lattice units from the isoconcentration profile into the unoccupied lattice. The particle released from the isoconcentration profile is permitted to execute its random walk within the region marked by . or + . If a peripheral site (these are unoccupied sites around * and are also marked .) is encountered, it is occupied. The unoccupied lattice is represented by the symbol ^ . If the randomly walking particle encounters a ^ the walk is terminated and a new particle is released. The symbol # shows the position of a particle that is about to be released.

The algorithm for generating Eden clusters is different from the above description and the main points are listed below:

1. The lattice size was 100×150, but no "wrap around" was implemented in this lattice.
2. The first row of the lattice was stored in an array of potential sites. The location to be occupied was chosen randomly from this array. The unoccupied peripheral sites were added to this array (avoiding duplication), while the occupied site was removed from the array. The next site to be occupied was again chosen randomly from the sites stored in the array. This procedure was repeated until a large aggregate is formed.

This procedure is slightly different from the more established Eden algorithm where the starting site is at the centre of the lattice and the aggregate is away from the edges. In our case we start with all the surface sites as the potential starting locations so that a closer representation of porous silicon formation beginning from silicon–electrolyte interface can be achieved. This choice of potential starting sites also allows comparison with the FDL model in the limit of zero finite diffusion length.

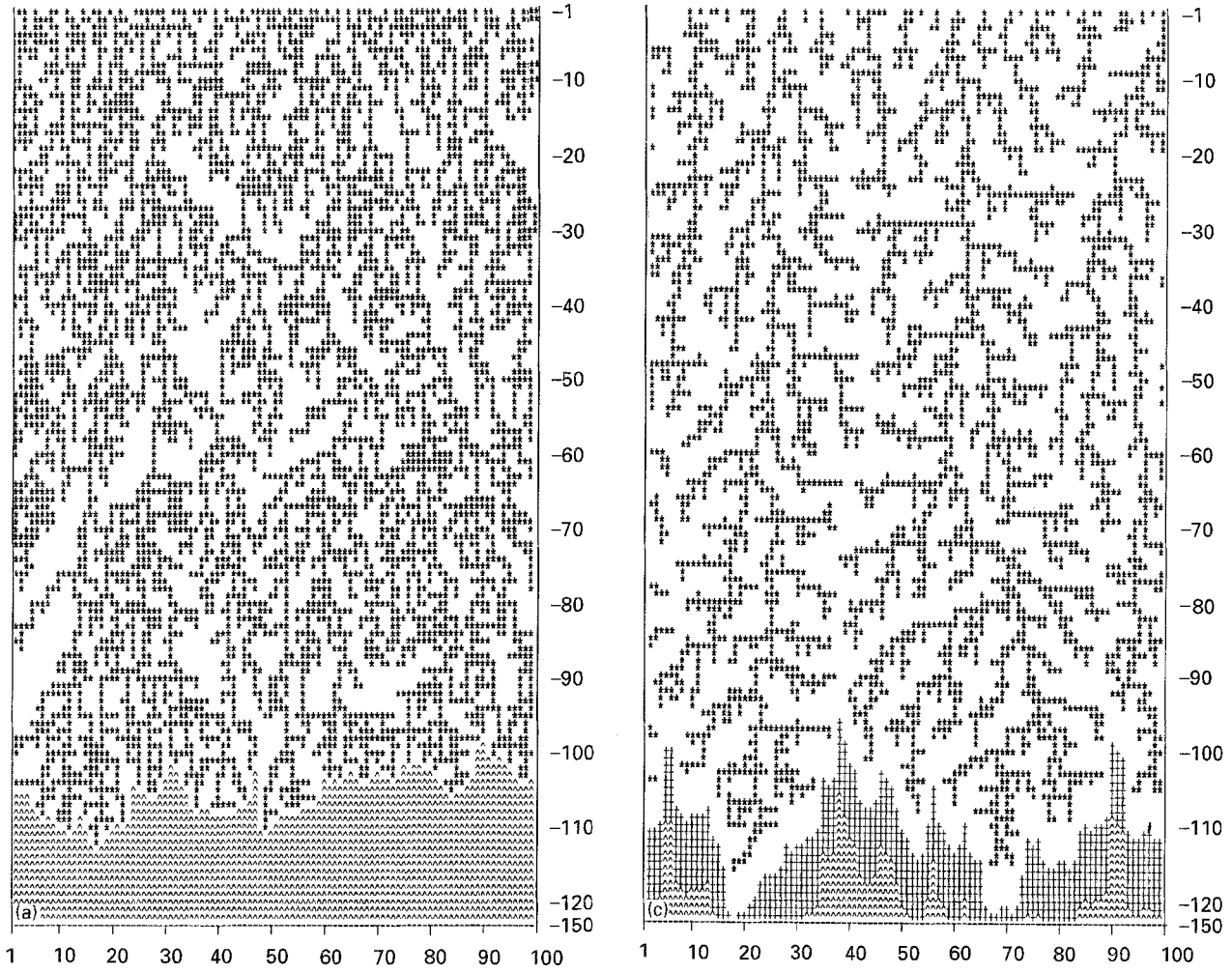
3. Results and discussion

The generation of porous structure by the FDL model is dependent on the processes of random selection of particle release site on the isoconcentration profile and the nature of the random walk of the particles. The other factor is the magnitude of the finite diffusion length which also decides the morphology and the density of the resultant patterns, and it is this parameter which can be selected before starting the simulation. The qualitative description of porous silicon growth by this simulation model can be obtained by studying the random motion of the particles in the lattice after being released from the isoconcentration profile. As the particle begins its random walk towards the aggregate, it is more likely to contact an available peripheral site that is near the tip of the growing aggregate. These sites near the tip have a much higher probability of occupation compared to sites that are deep within the porous structure. The porous silicon structure is then characterized by an "active zone", where a large number of particles contact an unoccupied peripheral site and a "frozen zone", which is the constant porosity region behind the active zone. The morphology of the stable porous silicon structure is decided in the active zone. Hence, the width of the active region is an important parameter and can be measured by techniques that have been reported previously [11].

The structure of aggregates generated by our simulations of the FDL model are shown in Fig. 2(a–e). These patterns are generated for finite diffusion lengths of 0, 2, 5, 10 and 20. The patterns are filamentary in nature and appear to occupy the lattice uniformly. The isoconcentration profile in all cases is non-uniform. In several cases "abrupt discontinuities", which are a few columns wide and many rows long, are present. The presence of such discontinuities does not appear representative of physical phenomenon such as porous silicon formation and seems to be a limitation of the FDL model. A qualitative explanation for the presence of non-uniformities is that the release of particles from random locations on the dynamic isoconcentration profile and their subsequent random walk to the aggregate, promotes clustering near the aggregate tip, which leads to formation of valleys that are more difficult to fill. In extreme cases the non-uniformities can be narrow and sharp and have been called "abrupt discontinuities". Fig. 3 shows the compact structure that is formed on implementing the Eden algorithm. Note that the occupied lattice sites are shown by *, which displaced up by half a lattice unit. Due to this the top portion of the * overlaps with . , the symbol for the unoccupied lattice site of the upper row. The appearance of compact Eden cluster in Fig. 3 is clearly different from Fig. 2(a), which shows patterns generated for zero finite diffusion length and suggests that the FDL model cannot generate such compact clusters and hence cannot be considered as a generalized model which incorporates both the Eden and the DLA model. Fig. 4 shows the density profiles for the patterns in Fig. 2. The computation of the density was performed by using the scaling relationship for constant density structures [11]

$$N^{\upsilon} = W \rho x \tag{4}$$

where N is taken as the total number of particles contained at a distance x. The parameter W is the lattice width, ρ is the density and x is measured from the silicon–electrolyte interface. The parameter $\upsilon = 1/D$ where D is the fractal dimension. The density profiles shown in Fig. 4 are for finite diffusion lengths of 0, 2, 5, 10 and 20. The region of constant density is towards the middle portion of each curve and corresponds to the "frozen zone" of constant porosity in porous silicon formation. The interface at surface shows higher density, which is due to the high lattice occupancy in this region because of the planar starting profile. As the aggregate starts growing the probability of further growth near the tips increases causing shadowing of lattice sites in the interior. Thus the site occupancy for each row declines resulting in a lower constant density region. The value of the constant density decreases as the finite diffusion length is increased. This suggests that at larger finite diffusion lengths the occupation of sites near the tips is


(a)
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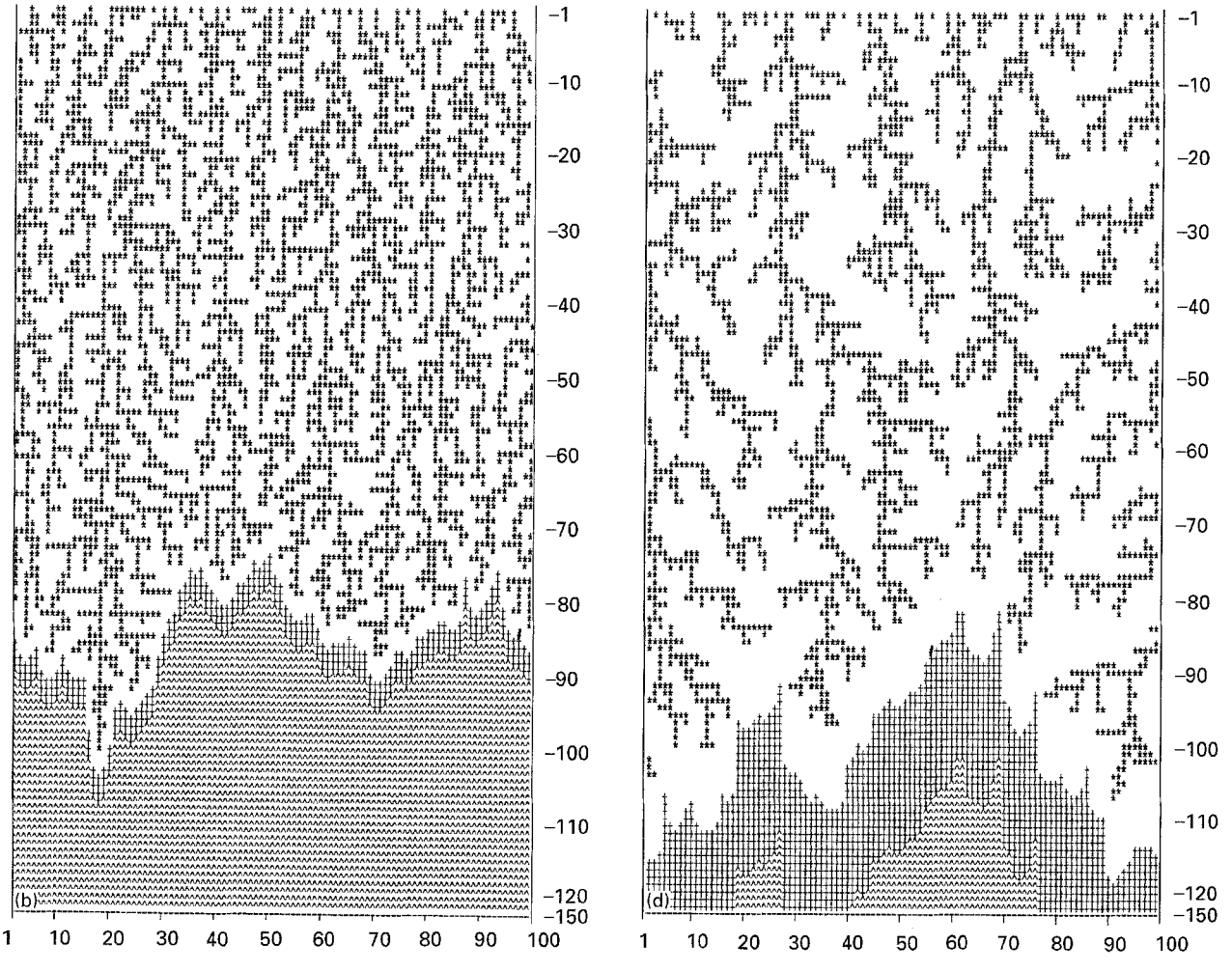
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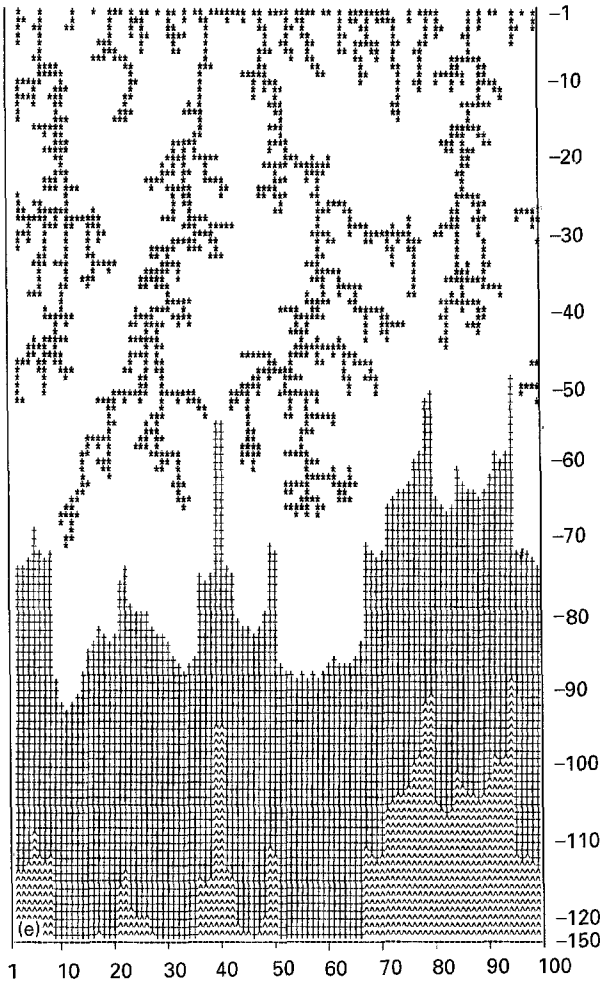

Figure 2 Aggregation patterns generated with a finite diffusion length of (a) 0, (b) 2, (c) 5, (d) 10, (e) 20. The clusters grow from top to bottom.

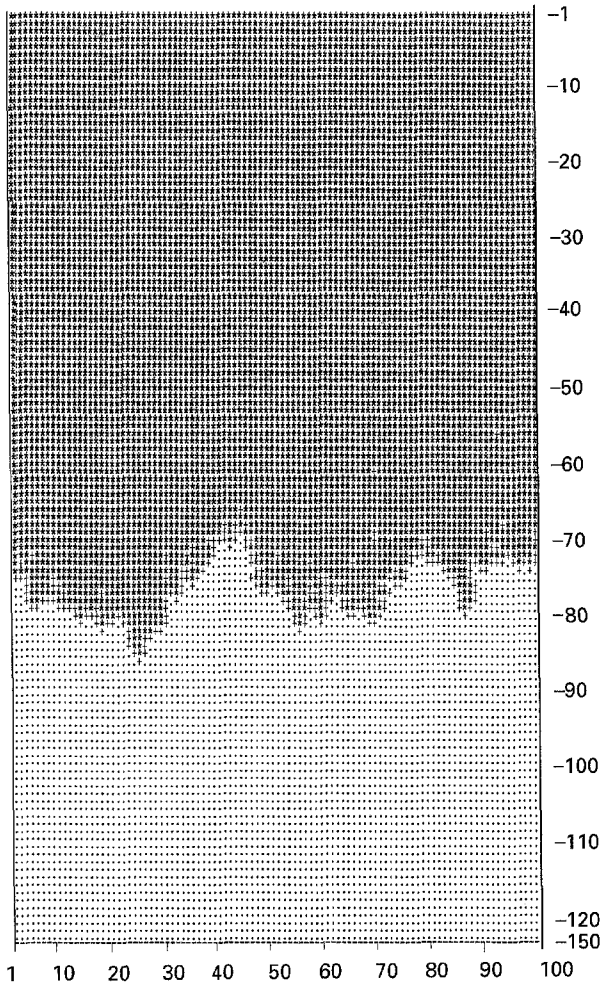

Figure 3 Pattern formed by implementing the Eden algorithm. The clusters grow from top to bottom.

preferred, leading to growth at the tips and resulting in a lower site occupancy for each row. The patterns shown in Fig. 2(a–e) illustrate this by the increase in the vacant unoccupied sites between the growing aggregates, as the finite diffusion length is increased.

The density profile for the zero finite diffusion length is very similar to the plots for other finite diffusion lengths. This curve is higher than curves for other diffusion lengths showing that there are more aggregating particles at each distance in this case. The value of the constant density is near 0.5 and clearly the corresponding pattern in Fig. 2(a) is not an Eden cluster. The formation of these clusters is shown by implementing the Eden algorithm. These results are shown in Fig. 3. To explain the differences in the morphology of Fig. 2(a) and Fig. 3, we compare the algorithms used in generating them. The FDL algorithm starts by considering all the locations of the first row as potential sites for occupation. Hence, in the case of zero finite diffusion length the starting isoconcentration profile is planar and contains all the sites in the first row. When the random location is selected on the isoconcentration profile, this location is immediately occupied and the isoconcentration profile is pushed down by one lattice unit. As the growth continues the occupied sites can shield some available sites. Since the isoconcentration profile is the

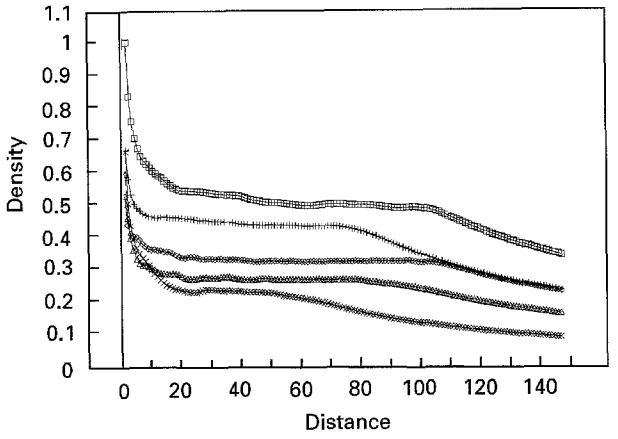

Figure 4 Density versus distance curves for finite diffusion lengths of (□) 0, (+) 2, (◇) 5, (△) 10 and (×) 20.

set of all the sites which are one lattice unit below farthest occupied sites (i.e. at a distance of zero lattice units below the farthest available peripheral site), the shielded locations are no longer in the set of sites on the isoconcentration profile. These locations have no chance of being occupied, since in the zero finite diffusion length condition no possibility of diffusing to an interior location exists and a selected site is considered immediately occupied. We call this the problem of "sinking isoconcentration profile". This is

the reason for the rarefied patterns seen in Fig. 2(a). In the case of Eden algorithm the set of initial available sites is the first row. These are stored in an array of potential sites. After the first site is occupied, all the unoccupied peripheral sites of the just occupied site are also stored in the array of potential sites, while the site that has just been occupied is removed from this array. As a result even the unoccupied sites that have been surrounded from all sides by occupied sites remain on this array of potential sites. Clearly the array of potential sites in the Eden algorithm is not the same as the isoconcentration profile in the FDL algorithm. The formation of compact clusters by the Eden algorithm is because the array of potential sites does not have the problem equivalent of "sinking isoconcentration profile" that is inherent in the FDL model.

The density–density correlation function [14, 15] for the structures generated by DLA and other similar models is given by

$$\langle \rho(r' + r)\rho(r') \rangle \sim r^{D-d} \quad (5)$$

where ρ is the density, d is the space dimension and D is the Hausdorff dimension. The plot of number of aggregating particles versus distance is expected to be linear on a double log scale. The results shown in Fig. 5 are plots of $\log_e$ (number of particles) versus $\log_e$ (distance) for the five chosen diffusion lengths. The constant density regions of plots in Fig. 4 correspond to the central regions of constant non-zero slope on the double log plots. The slope is in the range 1 ± 0.1, in agreement with Smith and Collins [11], and corresponds to the "frozen zone" in the case of porous silicon formation. The curve for zero finite diffusion length is very interesting. It shows similar features to the curves having non-zero finite diffusion lengths, the curve for zero finite diffusion length is the result of a single stochastic process, while the curves for all other non-zero finite diffusion lengths are the outcome of two stochastic processes. These are the random selection of sites on the isoconcentration profile and the random motion of particles in the lattice. We suggest that the frozen zone slope deviations of the curves for non-zero finite diffusion lengths compared to the curve for zero finite diffusion length are due to the effect of particle diffusion in the lattice. The difference in the number of particles at the same distance inside the frozen zone is because all the released particles find available sites for occupation in the case of zero finite diffusion length condition, while for all non-zero finite diffusion lengths some particles may not reach the growing aggregate at all.

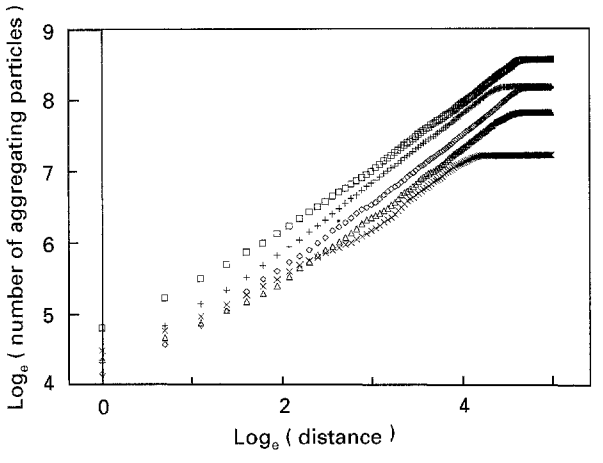

Figure 5 $\log_e$ (number of particles) versus $\log_e$ (distance) curves for the finite diffusion lengths of (□) 0, (+) 2, (◇) 5, (△) 10 and (×) 20.

4. Conclusions

We have described the details of implementation of the FDL algorithm on a 100×150 lattice. The results for all the finite diffusion lengths show that the isoconcentration profile is non-uniform and these non-uniformities increase with the finite diffusion length. In several cases abrupt discontinuities are present in the isoconcentration profile. The density profiles for all the finite diffusion lengths show similar features. The constant density portion in these curves corresponds to the frozen zone of the porous structure. The double log plots show that the slope in the frozen zone is nearly equal to 1. The clusters that are generated by the FDL algorithm for zero finite diffusion length condition are not found to be compact and the reason for this is suggested to be due to "sinking isoconcentration profile". The Eden algorithm has also been implemented and has been shown to generate compact clusters. The differences between the two algorithms have been discussed.

In view of our results we conclude that the FDL model cannot be considered to be a generalized model of aggregation, which can generate Eden clusters in the limit of zero finite diffusion length. The presence of abrupt discontinuities in the isoconcentration profile of several simulations of the FDL model appears to be a limitation of the model in describing physical phenomena such as porous silicon formation.

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