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Kinetic Monte Carlo Study of Low Pressure Chemical Vapor Deposition SiN_x Thin Films Deposit Phase

Bouhadiche A* and Benghorieb S

Research Unit in Optics and Photonics (UROP), University of Setif 1, Algeria

***Corresponding author:** Adil Bouhadiche, Research Unit in Optics and Photonics, Center for Development of Advanced Technologies, University of Setif1 Campus El-Bez, 19000 Setif, Algeria, Tel: 00213797371501; Email: a.bouhadiche@gmail.com

Research Article

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Abstract

In the present study, we use a simulation program based on the kinetic Monte Carlo method able to describe the deposition process of nitrogen doped silicon films obtained by low-pressure chemical vapor deposition technique with a mixture of disilane and ammonia. A new pattern describing the ammonia molecules distribution in the simulation matrix allowed us via the kinetic Monte Carlo method to simulate the deposit phase of layers. The obtained results describe well the different stages of the nitrogen doped silicon deposition process. Indeed, an increase in the gas flow ratio leads to the formation of a high density of small amorphous silicon clusters.

Keywords: Kinetic Monte Carlo; Amorphous Silicon Cluster; Cluster Density

Abbreviations: CMOS: Complementary Metal Oxide Semiconductor; PECVD: Plasma-Enhanced Chemical Vapor Deposition; LPCVD: Low-Pressure Chemical Vapor Deposition; Cat-CVD: Catalytic Chemical Vapor Deposition; KMC: Kinetic Monte Carlo.

Introduction

The SiN_x thin films are widely used for the production of silicon nanocrystals (Si-nc) [1-3], because the optical and electrical properties of this material are compatible with complementary metal oxide semiconductor CMOS technology. Indeed, silicon nanocrystals have attracted a great deal of attention owing to its potential nanoelectronic and optoelectronic device applications as well as their interesting physical properties [1]. Various fabrication techniques, such as plasma-enhanced chemical vapor deposition (PECVD) [4,5], low-pressure chemical vapor deposition (LPCVD) [2,3] and catalytic chemical vapor deposition (Cat-CVD) [1] have been examined for the fabrication of Si-nc in SiN_x thin films. Moreover, the physical properties of these films [1,2,4] depend strongly on their deposition parameters (temperature, total pressure, gas flow ratio…). Consequently, the simulation of the deposit step plays an important role in defining the required properties of the obtained films. In this work, we investigate the influence of deposition parameter, namely gas flow ratio on the deposition process of SiN_x thin films obtained by LPCVD technique by using a mixture between disilane (Si_2H_6) and ammonia (NH_3) via the kinetic Monte Carlo (kMC) method. To simulate this process, we propose a new pattern for the distribution of the $NH_{3\ molecules\ in\ the\ simulation\ matrix}$ that can model the formation of small amorphous silicon clusters.

Simulation Procedure

The deposition process of SiN_x thin films has been simulated in the present work using the kinetic Monte Carlo method via a two-dimensional triangular lattice representing

the surface structure of the film, as shown in Figure 1. We suppose that deposited molecules must have discrete positions in the simulation matrix. A fixed number of sites (N = 40,000) is available in the system. The diameter of the silicon atom is around 0.25 nm [6]. In the simulation, empty sites are chosen randomly from the matrix for the deposition of molecules. The deposition rate of each molecule is calculated as follows [7]:

$$V_d = V_{d_0} \exp\left(-\frac{E_a}{K_B T}\right) \quad (1)$$

Where the V_{d0} parameter depends only on the deposition total pressure P and on the wafer-to-wafer distance δ, and the deposition activation energy E_a was estimated to be 2.25 eV [8]. K_B is the Boltzmann's constant and T is the deposition temperature.

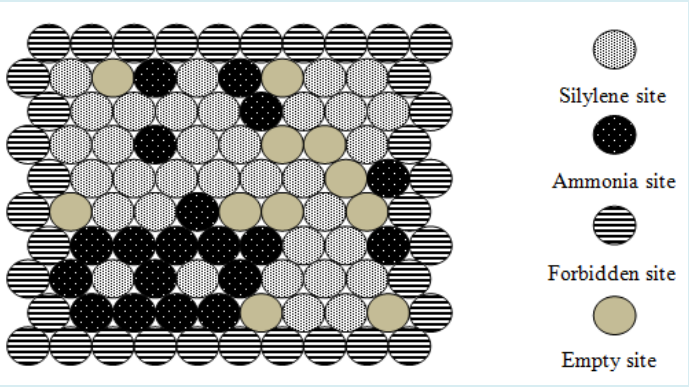

Figure 1: Schematic illustration of the SiN_x thin film deposition process on a triangular lattice.

The number of nearest neighbors of a deposited particle ranges from zero to six in the triangular lattice. A particle with six nearest neighbors is considered stable. This particle cannot migrate because it is fully surrounded by other particles in all directions. However, a particle having less than six nearest neighbors is considered unstable and it becomes subject to migration. This particle jumps to its most stable neighboring unoccupied site. The expression of the migration rate of the ith particle is defined as follows [6]:

$$r_{m,i} = \upsilon_0 \exp\left(-\frac{n_i E_0}{K_B T}\right) \quad (2)$$

Where υ_0 is a pre-exponential factor, n_i the number of the nearest neighbors of the ith particle, and E_0 the contribution to the activation energy barrier. In this paper, the pre-exponential factor and the activation energy barrier contribution take the following values $\upsilon_0 = 10^{13}\ s^{-1}$ and E_0 = 0.6 eV [9].

Noticing that deposition and migration events are executed instantaneously upon selection and sites for both events are chosen randomly from the simulation matrix.

The technique of KMC is used to simulate the deposit step of SiN_x thin films on a matrix of (200 x 200) sites. All molecules are assumed to occupy discrete lattice sites. During the simulation, the NH_3 molecules distribution in the matrix of simulation does not take a random aspect. In our approach, each of the NH_3 molecules must occupy one random nearest neighbor site of each silylene (SiH_2) site, as it is illustrated in Figure 1. Thus, two neighbor SiH_2 molecules become isolated from each other that allow the SiN_x thin film growth. As a result, a nitrogen compound is created with the formation of strong Si-N bonds. Furthermore, by increasing the number of NH_3 molecules introduced into the simulation matrix; the SiH_2 sites become increasingly isolated from each other preventing the coalescence phenomenon (the NH_3 molecules will occupy all the nearest neighbor sites of each SiH_2 site). Consequently, the deposition of amorphous silicon clusters with small sizes can be simulated using KMC method. Noticing that, hydrogen atoms are omitted from the matrix during the simulation.

Results and Discussion

We applied our approach to simulate the deposit step of SiN_x thin films obtained by LPCVD technique. A mixture between Si_2H_6 and NH_3 was used as the source gas. The films were deposited at low temperature (723 K), while the total pressure P was set constant at 26.66 Pa [2]. The gas flow ratio R (defined as $R = f(NH_3) / f(Si_2H_6)$ where $f(NH_3)$ is NH_3 flow and $f(Si_2H_6)$ is Si_2H_6 flow) was chosen to be the main influent parameter ranging from 0.18 to 4. All films were deposited at total surface coverage.

The evolution of the surface structures of the SiN_x thin films prepared at R = 0.18, 1, 2 and 4, respectively, is shown in Figure 2. Thus, an increase in the gas flow ratio values provokes an increase in the amorphous silicon clusters density combined with a decrease in their sizes, as shown in Figure 3, in good agreement with the experimental results [2].

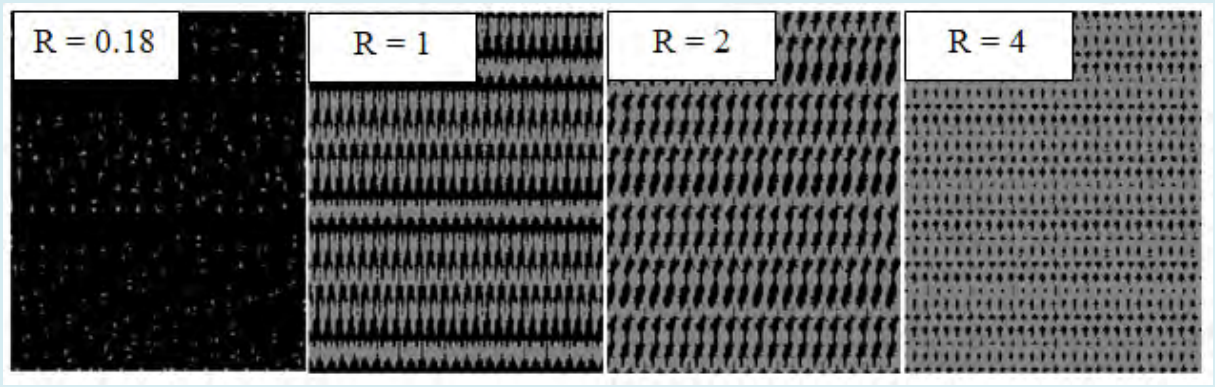

Figure 2: Surface structure evolution of SiN_x thin films as a function of the gas flow ratio R with fixed 100% surface coverage, N = 40000, P = 26.66 Pa, T = 723 K. Gray color represents nitrogen regions while black color is for the amorphous silicon clusters.

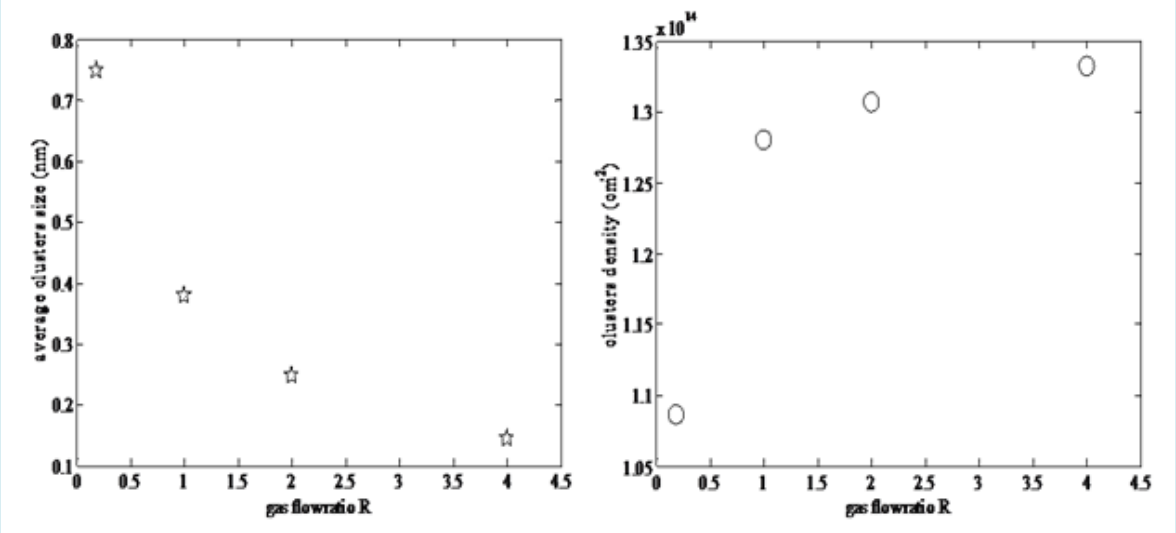

Figure 3: Variation of amorphous silicon cluster size and density as a function of the gas flow ratio R with fixed 100% surface coverage, N = 40000, P = 26.66 Pa, T = 723 K.

For these results, the corresponding amorphous silicon nanoclusters sizes were calculated to be around 0.7 nm, 0.4 nm, 0.2 nm and 0.1 nm, respectively. Therefore, the KMC simulation results suggest that the control of the source gas composition was effective in changing the amorphous nanoclusters size in the low temperature (723 K) process and that deposition of films characterized by high density of small amorphous silicon nanoclusters was possible using this size control.

During the simulation, each of the NH_3 molecules must occupy one random nearest neighbor site of each SiH_2 site preventing the coalescence between two neighbor SiH_2 molecules. Thus, by increasing the gas flow ratio values (increase in the number of NH_3 molecules introduced into the simulation matrix); the SiH_2 sites become increasingly isolated from each other leading to a reduction in the size of amorphous silicon clusters.

Noticing that, the size value represents an average size of all amorphous silicon clusters. The average size (or the average radius) is determined by dividing the sum of all amorphous silicon clusters sizes by the total number of clusters existed in the film. The size of each cluster is

obtained using the following steps:

- First, a silicon site is selected randomly from the simulation matrix.
- Then, the number of its nearest neighbors which are occupied by silicon atoms is calculated (in our approach this number varies between zero and two).
- If this number is zero, a cluster is formed by only one silicon atom and its size is equal to the radius of this silicon atom.
- However, if this number is different to zero, the Monte Carlo algorithm of grain growth is used [10] to verify which sites can ensure the minimization of the energy of the selected site.
- After, we keep only the sites verified the last condition.
- Furthermore, only sites which are in the same line with the selected site are remained (see Figure. 4).
- Moreover, each cluster is assumed to be uniform.
- Finally, the diameter of each cluster is equal to the sum of the lengths of Si-Si bonds existed in the cluster and the diameter of a silicon atom (the radius = the diameter / 2).

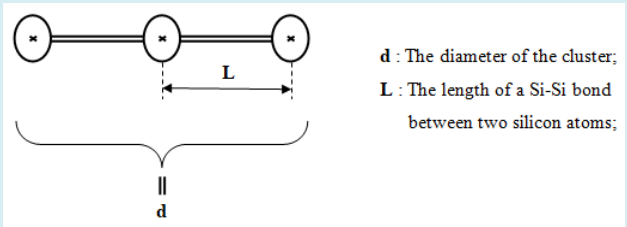

Figure 4: Schematic design of the structure of an amorphous silicon cluster. The selected site is in the middle while the other sites represent its nearest neighbors.

Conclusion

In this study, the deposit step of SiN_x thin films obtained by LPCVD technique at a temperature of 723 K using a mixture between disilane and ammonia has been simulated via the kinetic Monte Carlo method. The NH_3/Si_2H_6 gas flow ratio was chosen to be the main influent parameter. The non-coalescence between silylene molecules caused by the presence of Si-N bonds has been modeled by using a new pattern for the distribution of the $NH_{3\ \text{molecules in the simulation matrix.}}$ The size of the amorphous silicon clusters could be controlled by variation of NH_3/Si_2H_6 mixture ratio in the source gas. Indeed, an increase in the gas flow ratio leads to an increase in the amorphous silicon clusters density combined with a decrease in their sizes.

Conflicts of Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Credit Authorship Contribution Statement

Adil Bouhadiche: Investigation & Writing.
Soulef Benghorieb: Investigation.

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