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Nitrogenation of Amorphous Silicon: Reactive Molecular Dynamics Simulations

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ABSTRACT

Since silicon nitride (SiN_x) film is more stable than SiO_2, silicon nitride, thus it is widely used in semiconductor industry as an insulator layer. The study of nitrogenation process of a-Si was performed using molecular dynamics simulations to determine the properties of the bonds created in the structure of a-SiNx. Reactive force field (Reaxff) was used as potential in this molecular dynamic simulation owing to its ability to describe charge transfer as well as breaking and formation of atomic bonds. The structure of a-Si is obtained by melting the crystalline silicon at temperature of 3500 K followed by quenching to room temperature. The nitrogenation process was carried out by randomly distributing 900 N atoms over the a-Si surface for 60 ps at temperature varied from 300 K, 600 K, 900 K, and 1200 K. The higher the temperature nitrogenation ~~is~~ applied in the system, the more number of N atoms adsorbed, resulting in a deeper penetration depth of Nitrogen atom. Amorphization and nitrogenation changed the distribution of coordination number of Ni, Si, and O atoms. Transfer of electrons from silicon to nitrogen occurs only in the nearest nitrogen atom with silicon atom.

Key word: Nitrogenation, Amorphous, Silicon, Molecular Dynamic

INTRODUCTION

Silicon nitride have wide applications owing to its good mechanical properties, electrical properties, oxidation resistance, and biocompatibility [1]. For instant, Si_3N_4 ceramics which have light weight, high abrasion resistance and excellent corrosion resistance, can make environmentally friendly engine parts that help complete the combustion [2]. Si_3N_4 is also attractive as a substitute of SiO_2 insulating layer due to its higher dielectric constant and its resistance of contamination [3]. Moreover, amorphous SiNx is a very important material application in the field of memory and optoelectronics. An application in the field of memory devices used in the manufacture of EEPROMs (erasable programmable read only memories). EEPROM is a type of semiconductor memory that is non-volatile. The main component of the EEPROM is a thin layer of SONOS (polysilicon-oxide-nitride-oxide-semiconductor). SONOS is one of the floating gate transistors that serve as an electron trap on a memory device. The electrons are trapped in the ONO (oxide-nitride-oxide) structure, resulting in a change in the threshold voltage across the transistor. This change in threshold voltage causes the bits in the program cell to change to logic 1, "the state where electrons are trapped in the floating gate" or logic 0, i.e. conditions in which electrons are not trapped in floating gates [4,5,6].

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In 2011, Ippolito and Meloni performed a molecular dynamics simulation on the atomic structure of a-SiNx. According to Ippolito and Meloni, one of the reasons for trapping electrons in the silicon nitride and ONO structure is the result of a defect in the bonds of these materials. In amorphous silicon nitride, the higher concentration of bond defects causes more trapped electrons. This makes a-SiNx a suitable material for the production of non-volatile storage media [7].

Defect in the bonds of a-SiNx should be related to diffusion of Nitrogen atoms in Silicon substrate. Diffusion of nitrogen atom into silicon has been investigated experimentally [8,9,10] and theoretically [11, 12]. They discussed activation energies for diffusion of nitrogen and describe reaction path which pass through an intermediate metastable pair structure so called Humble form [10] and metastable structure called Low Symmetry (LS) configuration [11]. Even though previous studies have studied the diffusion of nitrogen into silicon but none of them simulated the process of nitrogenation of silicon and gave detail information about distribution of nitrogen atoms on silicon as well as coordination number of both atoms.

In this study, a molecular dynamics simulation was performed on nitrogenation process of the amorphous silicon by applying different temperature variations to investigate the effect of thermal conditions on a-SiNx system. Distribution of nitrogen atoms on silicon and bonding between them were also explored.

COMPUTATIONAL METHOD

In this simulation, Reactive Force Field (ReaxFF) made by Van Duin *et.al* was used due to its capability to handle forming and breaking of atomic bonding as well as its ability to represent charge transfer [13]. Molecular Dynamic Simulations were performed by means of LAMPS simulator [14]. Mixed boundary condition*, i.e* combination of periodic boundary condition (PBC) along *x* axes and *y* axes, and Isolated boundary condition (IBC) in z axis direction. The Si substrate of diamond structure was built with the size of 38.4 A x 38.4 A x 76.0 A. Initially, silicon system was created in the form of crystalline silicon with diamond structure. The length of lattice constant is 5.4307 Å. The c-Si amorphization process was performed in the simulation in this study using the melting-quenching method. This procedure was done by heating the c-Si structure from room temperature to its melting point of 3500K for 10 ps, then let it for 1 ps to equilibrate by applying the NVT ensemble. Continue with quenching process to return it to room temperature of 300K. The quenching process was performed with a high cooling rate of 2.13×10^{15} K/s for 1.5 ps by applying the NVE ensemble, then the system was left in equilibrium for 4 ps until the a-Si phase was stable.

The initial state of the simulations performed in this study is shown in Figure 1 (a): In Figure 1 (a), a simulated box of silicon atoms is regularly arranged to form a crystal structure, with a substrate treated with a lower fixed layer-Si structure (shown in red). Then Figure 1 (b) shows the conditions after the amorphization process completed. The silicon atoms which previously bound regularly in the form of crystals are converted into irregular or commonly referred to as amorphous forms.

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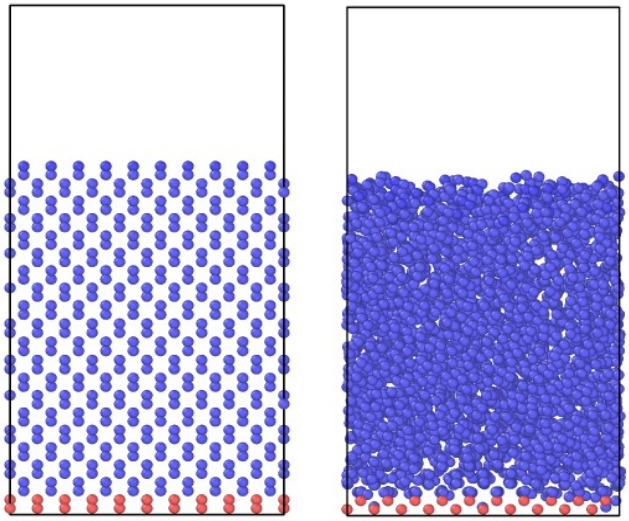

Figure 1. (a) Crystalline silicon structure before the amorphization process, (b) The structure of amorphous silicon after amorphization process.

When the c-Si amorphization process was completed and produced an a-Si material, the results of the amorphous silicon in the nitrogenation process were randomly distributed over an a-Si surface of 300 atoms, up to three times, over nitrogen atoms (see Figure 2) so that the total given nitrogen atom is 900 atoms. This nitrogenation step was carried out for 20 ps (400,000 Δt) with the time step $\Delta t = 0.05$ fs.

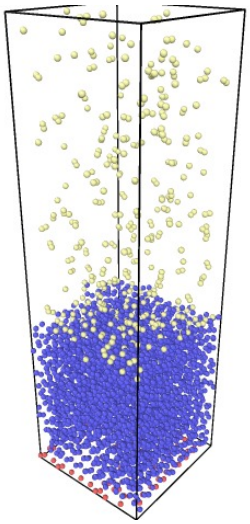

Figure 2. Nitrogenation in the form of amorphous silicon nitride (a-SiNx).

RESULT AND DISCUSSION

Simulations of molecular dynamics to produce a structure of amorphous silicon, previously described by many researchers such as Stich, Auto and Parinello [15], who used the process amorphization of silicon with the approach of first-principle. While Ishimaru, *et al*. [16,17] performed molecular dynamic simulations with Tersoff potential [18]. Molecular

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dynamic simulations of amorphization of crystalline silicon in this study was performed by reactive force field (ReaxFF) which include bond forming and breaking as well as charge transfer. The melt-quench method used in these simulations could be divided into two phases: i) the heating process (melting) of crystalline silicon to become liquid phase ii) followed by quenching process to obtain amorphous silicon structures. In this heating process, the initial temperature of 300 K system increases until the melting point of silicon (about 3500 K) for 10 ps, which then allows the system to reach equilibration processes by keeping the system at a constant temperature of 3500K with applying NVT ensemble.

The melting process with a temperature of 3500 K induces the displacement of silicon atoms from their original positions. This causes the position of silicon atoms to be randomly distributed throughout the system. The equilibration process maintains the system at 3500K by applying the NVT ensemble, the equilibration process does not cause a peak site changes and the minimum part (valley) of curve to the X axis. After the heating and equilibration processes, the liquid silicon structure was cooled very rapidly from 3500 K to 300 K, then the system was subjected to an equilibration process to keep the system temperature constant at 300K.

When the c-Si amorphization process completed and produce an a-Si material, the simulation will continue with the nitrogenation process by distributing nitrogen atoms up to 300 atoms above an a-Si surface as shown in Figure 3, and repeating the process three times that the total nitrogen given is 900 atoms. This nitrogenation step was carried out for 20 ps (400,000 Δt) with the time step $\Delta t = 0.05$ fs.

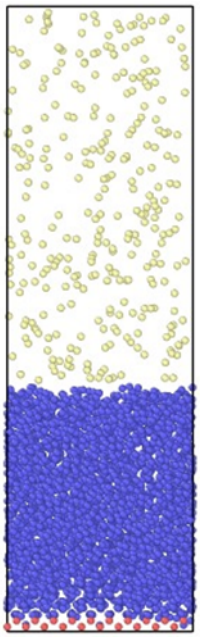

Figure 3. Initial conditions of the a-Si nitrogenation process.

After passing through amorphization, amorphous slicon a-Si was nitrogenated. The nitrogenation process was carried out by scattering random nitrogen atoms over the surface of amorphous silicon. The process was performed at four different temperatures to determine the best temperature for the nitrogenation process. The temperature in the system is 300 K, 600 K, 900 K and 1200 K. The result of this nitrogenation process is atomic coordinate data, n-fold binding of atoms and the weight of each atom in the system. It was observed that nitrogeantion

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temperature determines the number of N atoms bound to Si, the penetration depth of the N atom, as well as cordination number of silicon atoms and nitrogen atoms. Figure 4 shows an increase in the number of N atoms that bind to Si as a function of time during the a-Si nitration process. However, the increase in the number of N atoms is not completely linear, there is a decrease over time, due to the breakage of the N atom bond. It appears that the number of N atoms increases with the nitrogenation time. This can be due to two things: a larger thermal energy increases the penetration force of N atoms, in addition to higher nitrogenation temperatures, amorphous silicon structures in the system experience a higher randomness of the disorder structure, which is likely to cause more unstable Si atoms and require other atoms to fill electron defects by binding to other Si atoms as well as to N atoms in the system.

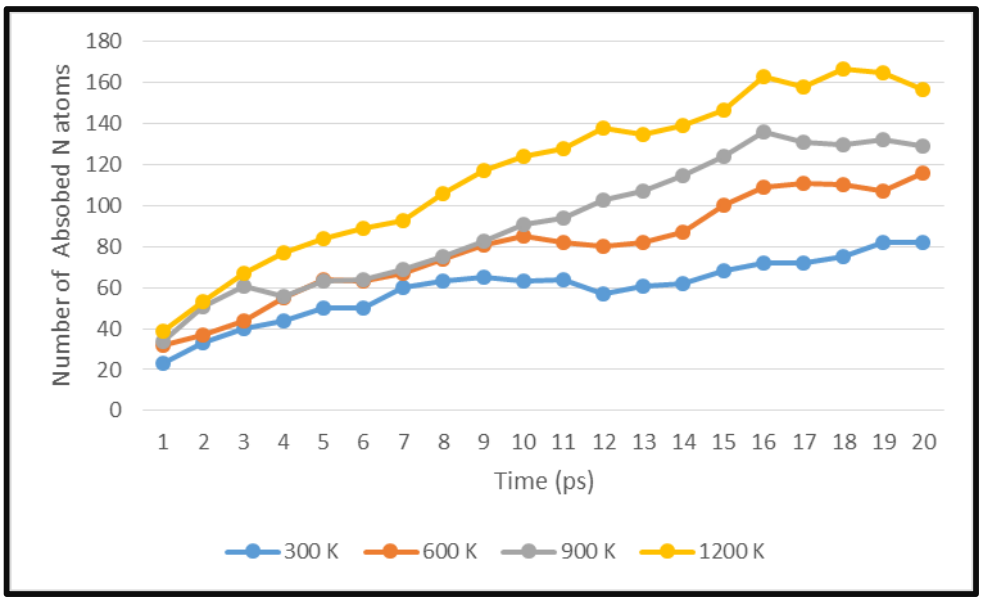

Figure 4. The number of N atoms as function of time

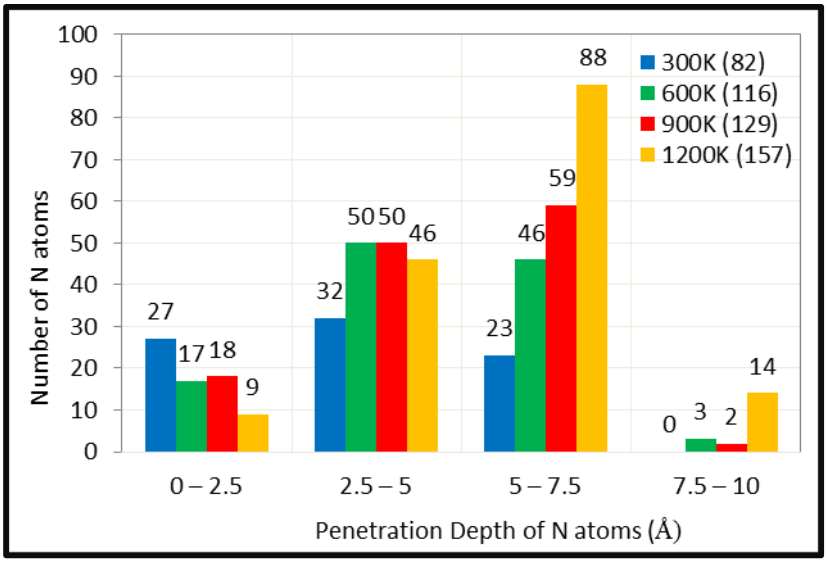

Figure 5. Distribution Number of N atoms at a given depth

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It can be seen at 300 K, the final number of N atoms bound by a-Si is smaller than that at 600 K. Similarly, the final amount of N at higher temperature, indicating an increase in the number of N atoms with the increase of temperature. Number of N atoms adsorbed in amorphous silicon increases as time increased. However, at certain time interval, there is a decrease in the number of N atoms in a-Si surface as we can observe after 16 ps at 900 K. This is due to the breaking of bonds between N atoms and other atoms in the system leads to decrement of number of N atoms in the a-Si structure. As shown by Figure 5, The penetration depth N atoms is also influenced by the nitrogenation temperature and the duration of the nitrogenation process.

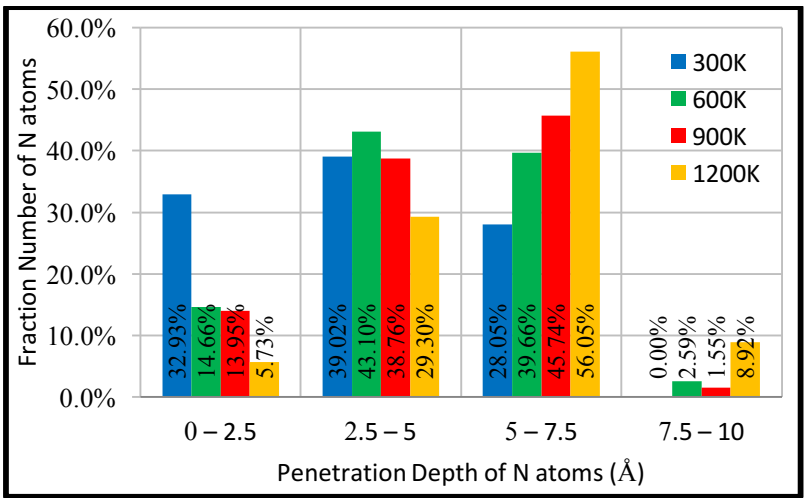

Figure 6. The fraction of N atoms in an nitrogenated amorphous silicon for 20 ps

It can also be expressed in the fractional graph of the number of N atoms according to its depth as follows. According to Figure 6, fraction number of N atoms at each temperature indicates that N atoms was distributed at different depths. At a temperature of 300 K, the number of N atoms dominates in the first and second depths (0 - 2.5 Å and 2.5 - 5 Å). While, at 600 K, the penetration of the number N occurs at most at the second depth (2.5 Å - 5 Å), while at 900 K more N atoms penetrate to the third depth (5 Å - 7.5 Å). Likewise for the nitrogenation temperature of 1200 K, the number of N atoms at third depth (5 Å - 7.5 Å) is the most. It shows that the higher the nitrogenation temperature, the more the nitrogen atom absorbed into the a-Si structure. Even, 8.92% of N atoms can penetrate into fourth depth at 1200K. The nitrogenation temperature causes penetration of N atoms in the amorphous silicon structure. This inevitably leads to changes in atomic coordination number of the entire structure in the system.

Based on the data in Figure 7, the Si atoms are dominated by 4-fold coordinated atoms. Unlike in crystalline silicon, whose structure is tetrahedral, atoms in amorphous silicon tends to have more diverse bonds. It can be 1-fold, 2-fold, 3-fold, 4-fold, 5-fold, and 6-fold coordinated atoms. Ishimaru reported that amorphous silicon has a "coordination defect" of 3-fold (dangling bond) and 5-fold (floating bond) bonding [16] . From Figures 7 (a) and (b), It can be seen how nitrogenation change fraction of coordination number of silicon atoms. In Figure 7(a), Si bonds tend to be dominated by 4-fold bonds, whereas hydrogenated amorphous silicon (Figure 7b) is more various, number of 5-fold coordinated silicon atoms increase

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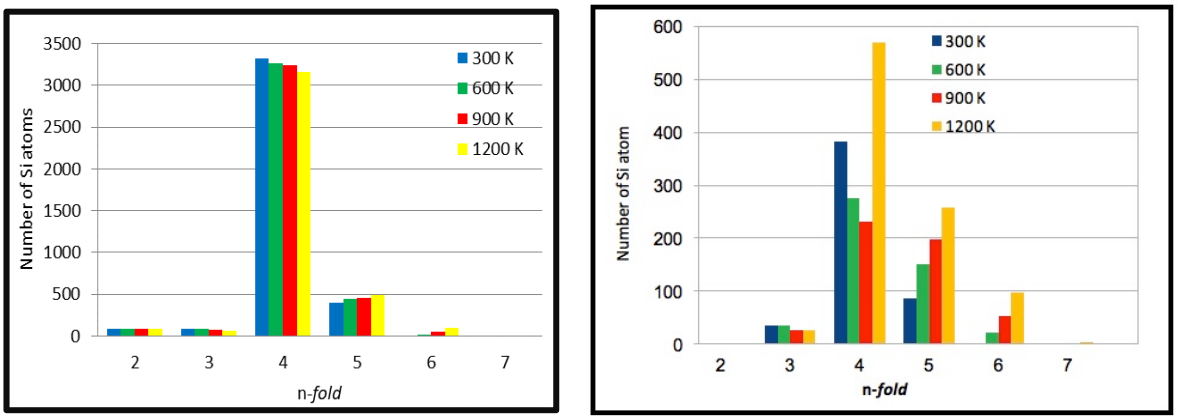
significantly, especially at 1200 K. This shows that by carrying out the nitrogenation, the properties of the Si atomic bonds change and the Si bond becomes more disorder (amorphous) as characterized by a decrease in the number of 4-fold coordinated silicon atoms and increase in the number of 3–fold, 5-fold and 6-fold coordinate silicon atoms.



(a) (b)

Figure 7. Number of n-fold coordinated Si atoms after nitrogenation in the entire silicon surface (a), and number of n-fold coordinated Si atoms after nitrogenation in the area of silicon surface which make bonding with nitrogen atoms (b).

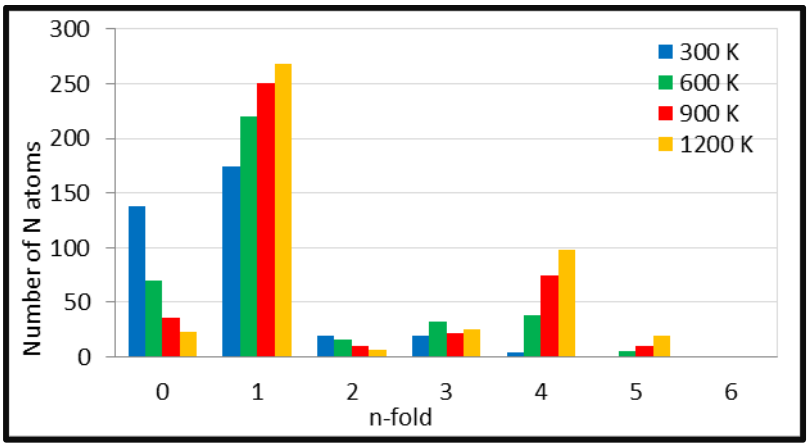


Figure 8. Number of n-fold coordinated N atoms after the nitrogenation process

In Figure 8, the highest number of coordinated atoms systems is the 1-fold. These are N atoms that do not absorbed on amorphous Si and tend to bind to other N atoms that form the N_2 gas molecule by forming a triple covalent bond. The second most common is a 4-fold bond, which shows that N atoms bind a number of four other atoms.

Figure 9. shows top view of amorphous silicon nitride surface at 300 K after 20 ps. Figure 9 (a) shows the configuration of the atoms type in the system, where the silicon atoms are represented by light green ball, while nitrogen atoms with dark brown ball. Nitrogen atoms are distributed randomly during nitrogenation process of amorphous silicon. Some silicon atoms, due to the nitrogenation process, bind to nitrogen atoms. Figure 9 (b) shows an atomic color map based on the amount of charge of each atoms in the system. It can be seen that the colors of nitrogen atoms tend to be darker than the silicon atoms which shows the transfer of electrons

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from silicon to nitrogen, which makes nitrogen become more negative than silicon. However, the transfer of electrons from silicon to nitrogen occurs only between the nearest nitrogen atom and silicon atom. Figure 9 (c) shows the atomic color which corresponds to the coordination number of the atoms in the system. It can be seen that the Si atomic coordination numbers are vary from 1-fold to 7-fold (although only one atom with 7-fold observed) indicating the randomness of the Si atom's own structure. The N-atom coordination number is between 1-fold to 5-fold, although most coordination numbers are 4-fold.

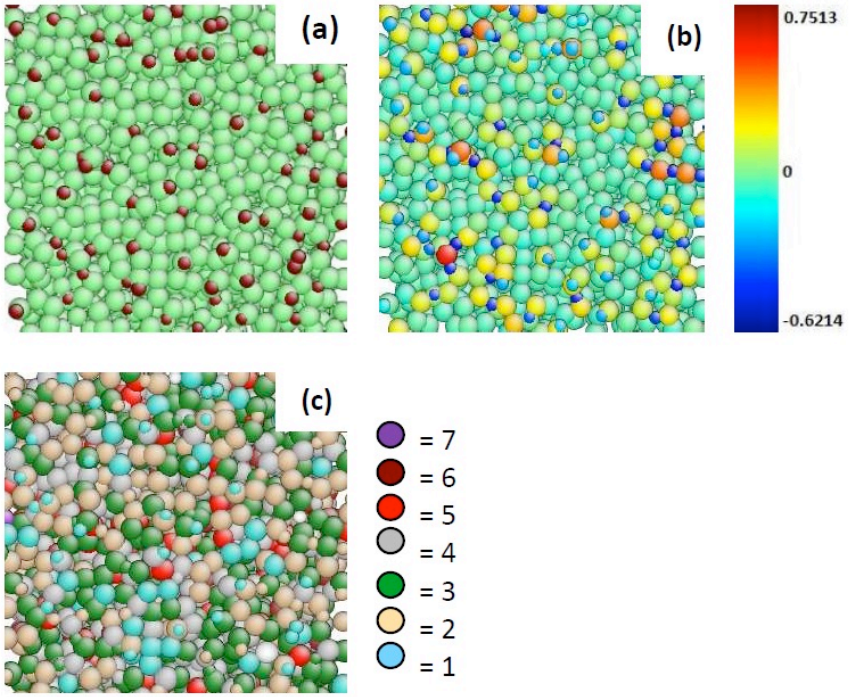

Figure 9. Top view of the surface of amorphous silicon nitride at 300 K: (a) atomic species (Si = green, N = dark brown), (b) atomic charge, (c) atom coordination number.

Figure 10, shows a picture of atomic colour analysis in the system at 600 K after 20 ps. Compared to system at 300 K (Figure 9), there is more nitrogen atoms were absorbed in the amorphous silicon system at a temperature of 600 K. Based on Figure 10 (b), it also shows that the more nitrogen atoms in the system, the more silicon atoms transfer their electrons to the next nitrogen atom. As a result, N atoms tend to be more negatively charged than Si atoms. This indicates the formation of an ionic bond between Si and N which corresponds to the nature of N atom that only can absorb electrons from a high electro-positive element or low electro-negativity element. Figure 10 (c) shows that atoms bind with five (5-fold) and three (3-fold) nearest neighbour increase.

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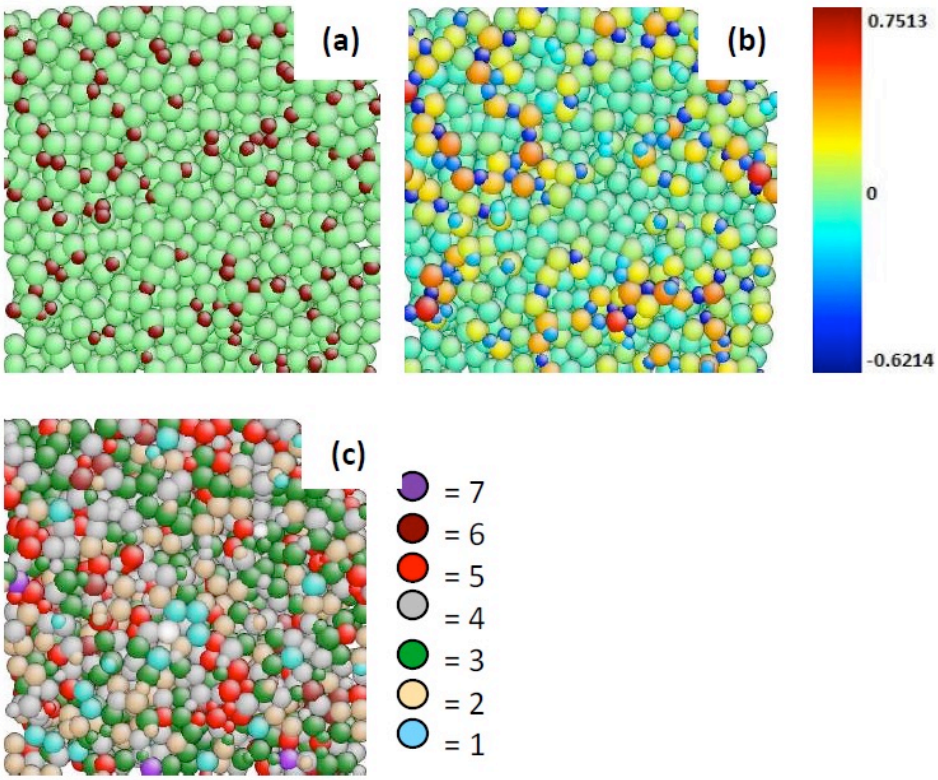

Figure 10. Top view of amorphous silicon nitride at 600 K surface: (a) atomic species (Si = green, N = dark brown), (b) atomic charge, (c) atom coordination number.

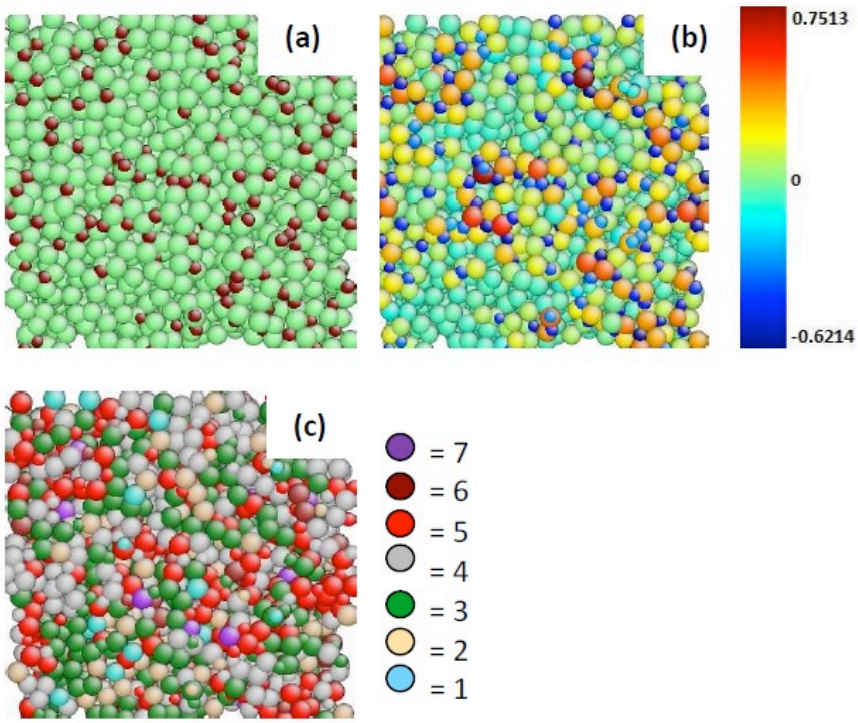

Figure 11. Top view of amorphous silicon nitride surface at 900 K. (a) atomic species (Si green atoms and N dark brown atoms), (b) atomic charge, (c) atom coordination number.

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In addition to the temperatures of 300 K and 600 K, Figure 11 and Figure 12 represent atomic configuration at temperatures of 900 K and 1200 K, respectively. Figure 11 (a) and Figure 12 (a) show more nitrogen atoms the structure of amorphous silicon compared to that at lower temperature, this is indicated by the increasing number of dark brown in the system structure. As a result of the large number of N atoms in the amorphous silicon structure, it causes more number of silicon atoms which transfer their electrons to nearby nitrogen atoms. This is indicated by the blue color in Figure 11 (b) and Figure 12 (b). Figure 11 (c) and Figure 12 (c) show the coordination number of the silicon atoms dominated by 3-fold, 4-fold, and 5-fold (gray, green, and red). According to their coordination number, nitrogen atoms whose the numbers are decreasing indicated by sea blue color (1-fold), while nitrogen atoms whose numbers increase are indicated by green, gray and red color (3-fold, 4-fold, and 5-fold).

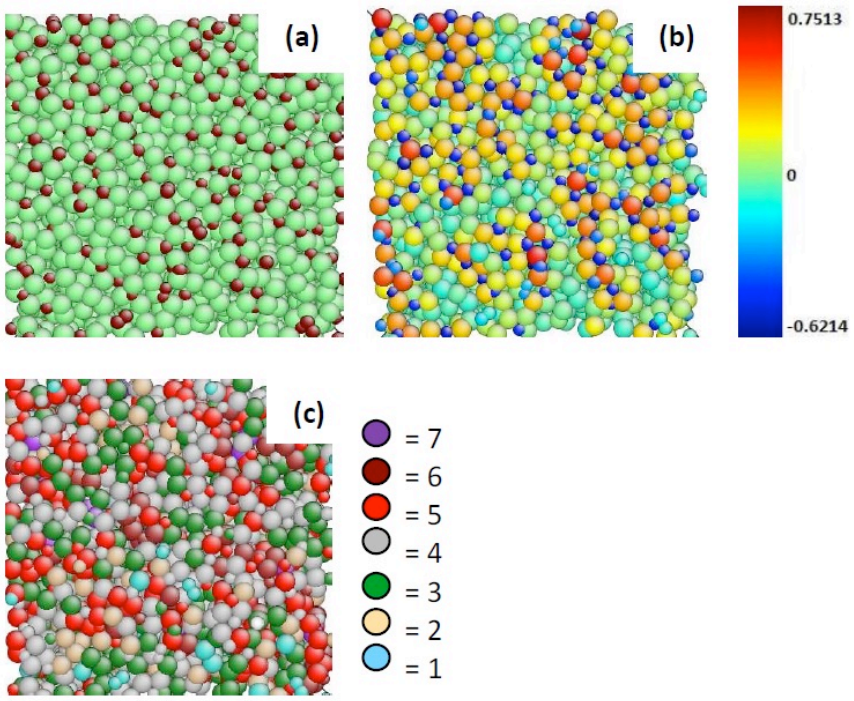

Figure 12. Top view of amorphous silicon nitride surface at 1200 K. (a) atomic species (Si green atoms and N dark brown atoms), (b) atomic charge, (c) atom coordination number.

CONCLUSION

Effects of temperatures used in nitrogenation of 300 K, 600 K, 900 K and 1200 K were clearly observed. The higher the temperature in the system, the greater the number of N atoms entering the a-Si structure and causing a deeper N atom penetration. This is indicated by the more number of N atoms in the a-Si structure at a nitrogenation temperature of 1200 K than that at lower temperature. The interaction of Si atoms with N in the nitrogenation process is indicated by the change in the n-fold bond character of silicon atoms. The Si atomic bond before nitrogenation has a coordination number between 1 and 5. While Si atoms after nitrogenation have a coordination number between 1-fold to 7-fold. However, most Si coordination numbers are 4-fold. For 1-fold bond. In addition, the formation of bonds between Si and N atoms can be represented by the ionic bonds between the two atoms.

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CONFLICT OF INTEREST
Authors declare no competing interest.

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