# FORMATION OF THIN $SiO_XN_Y$ FILMS ON Si BY ION IMPLANTATION

**Sashka Petrova Alexandrova, Vania Encheva Mikhailova, Rumen Georgiev Kobilarov and Elena Jordanova Halova**

Department of Applied Physics, Technical University, 8 Kl. Ohridski Blvd., 1797Sofia, Bulgaria, phone + 359 2 975 3112, e-mail: salex@tu-sofia.bg

**Keywords:** Silicon, Silicon oxynitride, Ion implantation, Thermal oxidation)

*In this study the possibility of thin $SiO_xN_y$ films formation on Si by $N^+$ implantation followed by thermal oxidation is discussed. The nitrogen profiles in the silicon substrate are evaluated through Monte Carlo simulations. The energy, ion fluence and implantation angle are varied in order to obtain films with different thicknesses. The energy was chosen in the range of 5 to 25 keV. The fluence was varied in the range of $10^{13}$ to $10^{16}$ $cm^{-2}$. The implantation profile during the oxidation is modeled using standard diffusion equations. The oxidation temperature was taken to be $1000^oC$. The role of the defects formed during implantationin the oxidation process is discussed.*

## 1. INTRODUCTION

Recently rapid downscale of the MOS device dimensions requires development of dielectric layers of higher dielectric constant for replacement of the conventional thermal $SiO_2$ layers. Special attention have gained the silicon oxynitride ($SiO_xN_y$) thin films which offer advantages like precise composition variability, resistance to oxidation and low mechanical stress [1]. The most important among these is its compatibility to the contemporary silicon-based electronics. In addition, oxynitrides are a key component in nonvolatile memory such as flash memory. Studies of $SiO_xN_y$ films indicate performance enhancement in devices. Even introducing of small amounts of nitrogen is known to improve certain properties of the devices [2].

$SiO_xN_y$ films can be formed on Si through different methods. Among these are deposition from gaseous phase, or nitridation of thermally formed $SiO_2$ layers. Another possibility is to implant $N^+$ in Si followed by standard thermal oxidation which is the aim of the present study. Nitrogen implantation is known to retard oxidation. The retarding effect of incorporated N on oxidation kinetics is utilized to result in a thinner oxide in the N implanted areas.

## 2. PROBLEM STATEMENT

The most important advantage of using $N^+$ implantation in Si is the ability to obtain best control and precision over the formation of the $SiO_xN_y$ films in all three dimensions.

The implantation process occurs through multiple cascade processes before the implanted ion comes to rest. This process in envisaged in Fig.1. It can be seen that the implanted atoms are spread over extended depth range into the Si substrate. The thickness of the subsequently formed $SiO_xN_y$ film will be determined by the spread of the implanted nitrogens. Therefore, their profile in the Si substrate has to be modeled

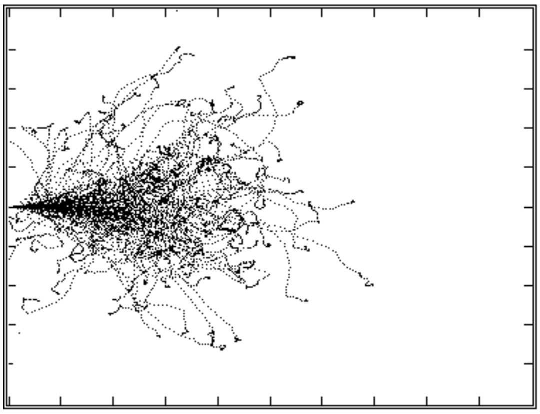

Fig.1. Cascades of $N^+$ ions into Si substrate.

before the oxidation. During implantation also defects are being created through recoil of host Si atoms from their regular positions. By the subsequent oxidation, which proceeds at elevated temperatures the implanted N ions are being built-in the crystal lattice forming bonds to Si and O atoms. The N and O atoms move during oxidation taking their equilibrium sites. Therefore, it is desirable to obtain the profile of all atoms in the Si substrate. This would contribute to our understanding of the way N atoms retard the oxidation process, an issue that has not been clarified in literature so far. Also the equivalent $SiO_2$ thickness can be estimated.

## 3. RESULTS

### 3.1 Implantation conditions

The depth in the Si substrate, which the implanted ions reach during implantation, is very important for the formation of the $SiO_xN_y$, since this implanted region will serve as a base for the subsequent $SiO_xN_y$ film formation. For that reason a detailed modeling has been performed based on Monte Carlo simulations to extract the exact distributions of the implanted ions depending on ion energy, ion type (single or double ionized) and tilt angle of implantation.

The implanted profiles are illustrated in Fig.2 for three different ion energies. It can be seen that depending on ion energy the profiles extend to a different depth. Varying the energy from 5 up to 25 keV films films with thickness from 20 up to 100 nm can be obtained as illustrated in Fig.3. It can be seen that even at the lowest energy of 5 keV the N profile extends up to about 40 nm.

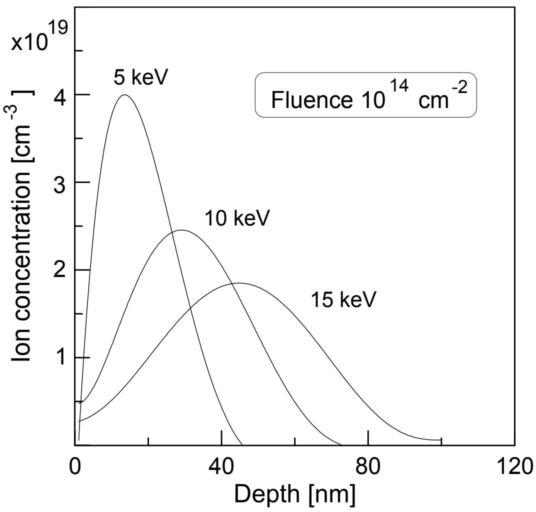


Fig.2 Ion distribution profiles at different ion energies.

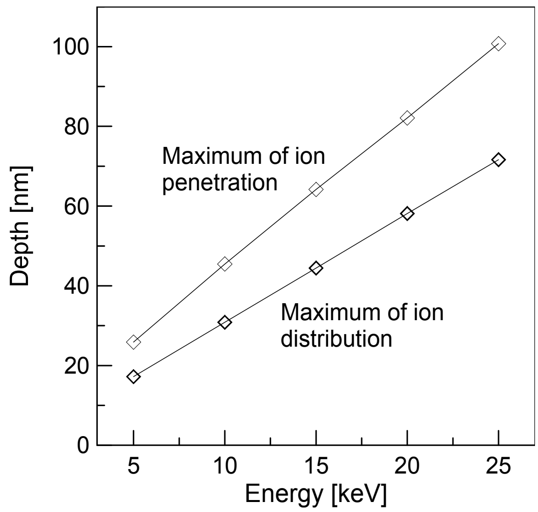


Fig.3 Ion penetration depth at different ion energies.

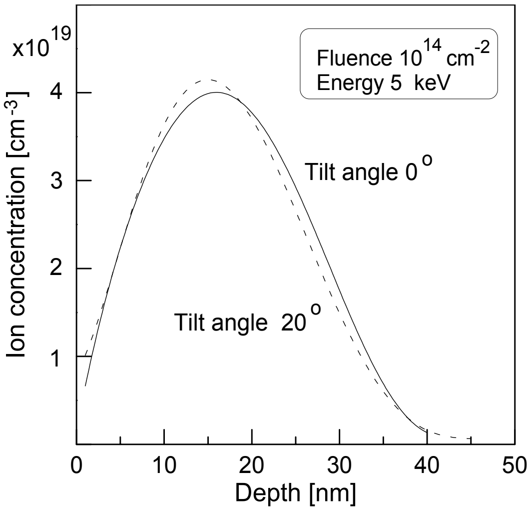


Fig.4. Implantation at different tilt angle to the Si surface.

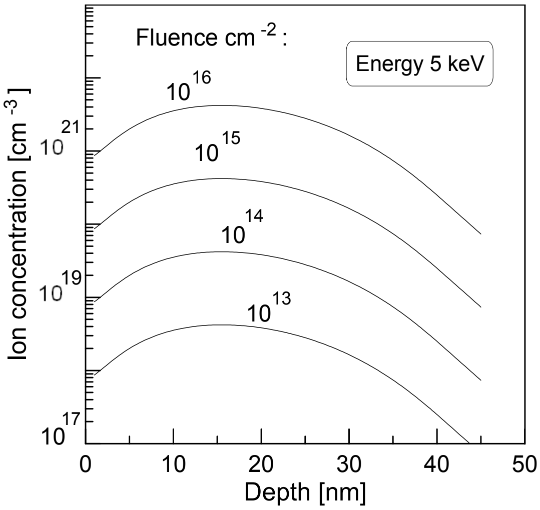


Fig.5. Ion distributions for different ion fluences at a constant ion energy.

Another possibility to obtain different depths is to vary the tilt angle of implantation. A comparison between the case when the $N^+$ ions are implanted at an angle of $20^o$ and perpendicular to the Si surface is given in Fig.4. It is seen that the profile at tilt angle of $20^o$ becomes asymmetrical and the average depth remains nearly the same as for the perpendicular implantation. Moreover, although the nitrogen concentration at the maximum is somewhat less, at the inside profile part the amount becomes higher. Taking in view that the dielectric constant of the $SiO_xN_y$ can vary from 3.8 for $SiO_2$ to 6 for $Si_3N_4$, the equivalent $SiO_2$ thickness can be estimated to be between 25 to 40 nm at ion energy of 5 keV.

As mentioned in previous Section, the oxidation rate depends substantially on the amount of nitrogen at the Si surface. Simulations of implantation at different fluences ranging from $10^{13}$ to $10^{16}$ $cm^{-2}$ and at constant energy of 5 keV are illustrated in Fig.5.

### 3.2 $SiO_xN_y$ layer formation

After implantation the $SiO_xN_y$ layer can be formed by thermal oxidation of the N implanted Si substrate at high temperatures. By this technological step two issues are of great importance. First, the nitrogen implantation profile can be altered due to diffusion of N atoms because of the high temperature during oxidation, as known for different impurities in Si [3]. Also, it is known that the presence of oxygen can influence the impurity diffusion [4]. Second, oxidation is accompanied by a formation of Si-N, Si-O and O-N bonds. In the following these two processes will be treated in some more details.

Diffusion of nitrogen in Si has been extensively studied in recent years [5, 6]. Here different mechanisms have been discussed. Some authors have found that nitrogen atoms migrate in Si [7] with a diffusion coefficient of $D = D_o \exp(-E/kT))$, where $D_o = 0.87x10^{-4}$ $m^{-2}s^{-1}$ and an activation energy of $E = 3.25$ eV in the temperature interval of 1000 to 1200°C. Other authors [5, 6] have found that nitrogen atoms tend to migtate to the Si surface and to accumulate there. In order to lighten this point here simulation of the distribution of the implantation defects in the Si substrates have been performed using standard diffusion equations calculated with the values of $E$ and $D_o$ given above. The time of high temperature treatment was taken to be 30 min, a reasonable duration of e.g. oxidation process at temperature of $1000^oC$. The results are plotted in Fig.6. For comparison also the as-implanted ion profile is given. As can be expected for atoms with relatively small mass such as the N atoms, the ion distribution differs substantially from the as-implanted profile. The concentration of the nitrogen atoms decreases in the whole implanted region. This would not cause any problems since the implanted fluence can be taken high enough to obtain the desired structure. However, it should be taken into account that certain amount of N atoms with smaller concentration will be found farther in the Si substrate. It should be pointed out that this simulation resembles the oxidation process itself, if it is assumed that the presence of the oxygen atoms during oxidation does not influence considerably the diffusion of the implanted atoms. This point needs some further substantiation.

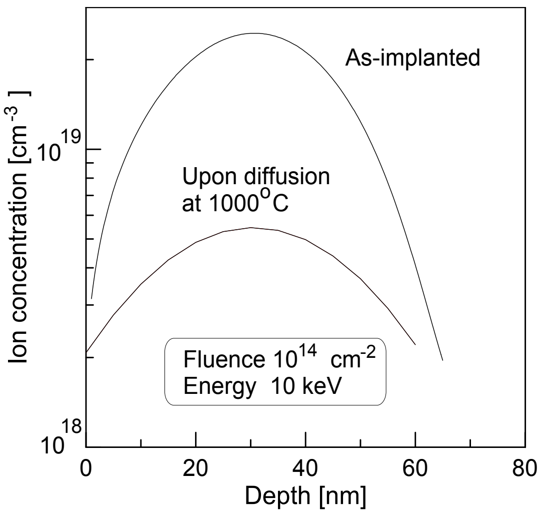


Fig.6. Ion profiles before and after high temperature treatment.

In the discussion of the profiles after high temperature treatment the distributions of the defects (mostly Si vacancies) created during implantation process can play a significant role. For that reason simulation of the vacancy generation by the ions and the recoils has been performed. The results are plotted in Fig.7. In the figure also the as-implanted ion profile is given. It can be seen that the maxima of the vacancy and ion distributions are located at different depths. This result can be helpful in understanding of the experimentally measured nitrogen implanted profiles made by other authors [5, 6] where accumulation of nitrogen atoms near the Si surface has been observed. From the simulations in the present study this can be explained by migration of the implanted atoms to the vacancy reach reason nearer to the Si surface where they can come to rest taking the vacancy sites in the Si network. It can clearly be seen that the defects (vacancies) formed during implantation point to diffusion process limited by motion of interstitial nitrogen atoms, which are the only mobile species [6]. Obviously, this point has been

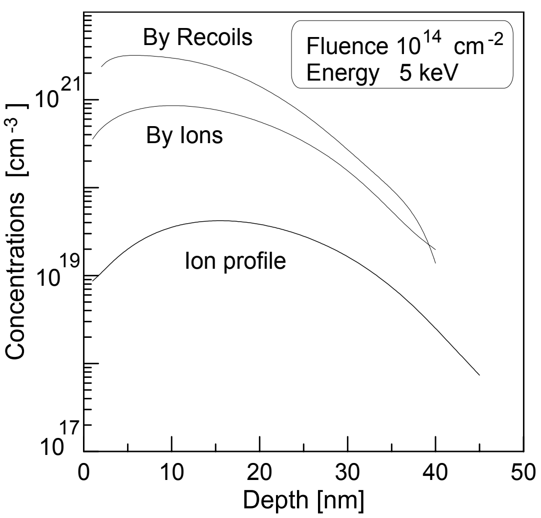


Fig.7. Vacancy and ion profiles.

overviewed by the previous authors leading to the necessity of development of complicated diffusion/oxidation models [8].

The settlement of the nitrogen atoms at vacancy places implies formation of N-related bonds, which is a complicated process. This process will be highly fluence-dependent. The presence of oxygen atoms diffusing through the same Si region during oxidation also can play a significant role. Here the bond formation energies have to be taken into account [4]. At low nitrogen fluences a competition process of Si-O and Si-N bonds formation will take place. Predominant formation of low energy bonds can be expected, resulting in $SiO_xN_y$, x/y ratio depending on the fluence and oxidation conditions. Increasing the nitrogen fluence, active formation of N-O bonds can be expected. At high nitrogen fluence the diffusion of oxygen will be entirely hindered and even formation of $SiO_xN_y$ becomes impossible.

## 4. CONCLUSION

The results of the present study have shown that $SiO_xN_y$ films with predetermined properties can be formed in Si through nitrogen ion implantation. By varying the ion fluence films with varying composition (various x/y ratio) can be obtained. By varying of the ion energy films can be obtained with different thicknesses. At energy of 5 keV films with thickness corresponding to $SiO_2$ thickness of the order of 25 nm is possible, which is important for device applications. Subsequent oxidation can result in decrease of the nitrogen concentration, which can however, be kept in reasonable values for $SiO_xN_y$ formation. :

## 5. REFERENCES


[1] Gusev E. P., Lu H. C., Garfunkel E. L., Gustafsson T., Green M. L., IBM J. Res. Dev.,1999, Vol. 43, pp. 265-288.

[2] Hill W.L.,Vogel E.M., Misra V., McLarty P.K., Wortman J.J., IEEE Trans. Electron Devices, Vol. 43, No 1, p.p 15-19.

[3] Francios-Saint-Cyr H. G., Stevie F. A. , McKinley J. M., Eishot K., Chow .L., Richrdson K. A., J. Appl. Phys., Vol. 94, No 12, pp. 7433-7439.

[4] A. H. van Ommen, Appl. Surf. Sci., 1987, Vol. 30, pp. 244-263.

[5] Adam L. S., Law M.E. and Jones K.S., J. Appl. Phys., 2000, Vol. 87, No 5, pp. 2282-2284.

[6] Adam L. S., Law M. E., Dokumaci O., Hedge S., J.Appl.Phys., 2002, Vol. 91, No 4, pp. 1894-1900.

[7] Madelung O, *Semiconcturs – Basic Data*, Springer Verlag, Berlin, 1996.

[8] Schultz P.A., Nelson J. S., Appl. Phys. Lett., 2001, Vol.78, No 6, pp.736-738.