NITROGEN CONTAINING ULTRA THIN SiO_2 FILMS ON Si OBTAINED BY ION IMPLANTATION

Sashka Petrova Alexandrova[1], **Evgenia Petrova Valcheva**[2], **Rumen Georgiev Kobilarov**[1]

[1]Department of Applied Physics, Technical University, Blvd. Kl. Ohridski 8, 1797Sofia,
Bulgaria, + 359 2 965 3112, e-mail: salex@tu-sofia.bg

[2]Faculty of Physics, Sofia University, Blvd. Bourchier 5, 1126 Sofia

In the present study the formation of nitrogen containing ulrtathin films on Si is discussed using ion implantation by two technological schemes: implantation of N^+ *into Si followed by thermal oxidation and* N^+ *implantation in already formed* SiO_2 *is discussed. The nitrogen profiles in the silicon structures are evaluated through Monte Carlo simulations. The energy implantation was chosen in the low range of 5 to 10 keV. The fluence was* 10^{14} cm^{-2}*. The implantation profile during thermal processing (annealing and oxidation) was modeled using standard diffusion equations. The temperature was taken to be* 650^oC*. The role of the defects formed during implantation in the thermal process is discussed.*

Keywords: Silicon, Silicon oxynitride, Ion implantation, Thermal oxidation.

1. INTRODUCTION

In recent years special attention have gained nitrogen containing ultrathin SiO_2 films on Si. For application as electronic components these films offer beneficial properties such like precise composition variability, resistance to oxidation and low mechanical stress. 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 [1]. The most important advantage of these films is their compatibility to the contemporary silicon-based electronics [2]. Moreover, nitrided oxides have improved radiation hardness than pure thermal oxides [3]. Quite recently experimental results have shown that the implantation of nitrogen into the buried oxide layers (BOX) can increase the BOX hardness to total-dose irradiation [4]. In the case of oxynitrides technology, the prime importance is to control the atomic concentration in the thin SiO_xN_y layers. Using implantation allows the oxide thickness to be varied across the Si wafer, which is especially useful for technology that requires multiple gate oxide thickness on the same wafer [5], by appropriate choose of energy and fluence of the implanted nitrogen.

In the present study the formation of thin nitrogen containing ultrathin SiO_2 films on Si through ion implantation is discussed. The most important advantage of using N^+ implantation in Si in comparison to oxide growth in NO or N_2O ambients is the ability to obtain best control and precision over the formation of SiO_xN_y films in all three dimensions. To produce nitrogen containing films on Si also N^+ implantation in already formed SiO_2 has been considered.

2. PROBLEM STATEMENT

Ion implantation can be used to produce nitrogen containing ultrathin SiO_2 films on Si, further denoted as SiO_xN_y films. This can be achieved mainly by two different approaches. One possibility is to implant N^+ in Si followed by standard thermal oxidation. Another possibility is to implant nitrogen in already oxidized silicon, i.e. in thermal SiO_2 layers. In both cases control of concentration, position and bonding of N atoms is very crucial, because a certain amount of incorporated N atoms may degrade the reliability of devices due to negative bias instability [6].

The implantation is a complicated process involving formation of defects and complexes in the target, such as vacancies, substitutional and interstitial atoms, nitrogen dimmers and nitrogen-vacancy pairs. Any further technology step at elevated temperature will influence the defect centers due to diffusion of atoms and reaction processes. The properties of the subsequently formed SiO_xN_y film will be determined to a higher extent by the profile of the implanted nitrogens and the defects as well. Modeling of the positions of the different defect centers can contribute to our understanding of the physical and chemical processes that determine and help in developing technological schemes for high performance devices. 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, fluence and subsequent diffusion.

3. RESULTS

3.1 Implantation of nitrogen into silicon substrate

In the present section the formation of SiO_xN_y film is supposed to be performed by N implantation into Si wafer followed by low temperature oxidation (below 900°C). Nitrogen incorporation is known to retard oxidation [7]. The retarding effect of incorporated N atoms on oxidation kinetics is utilized to result in a thinner oxide

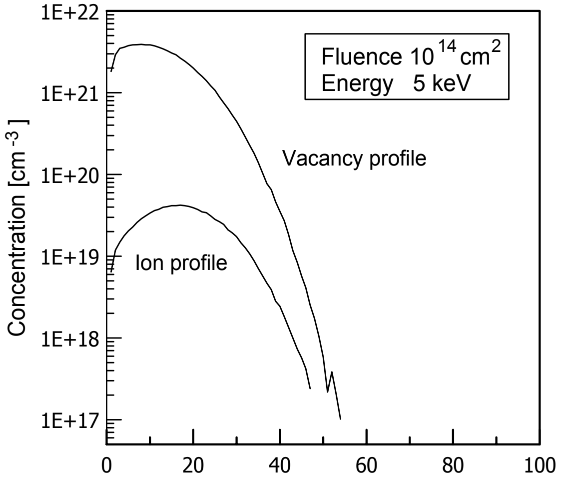

Fig.1 Ion and vacancy defect profiles for implantation energy of 5 keV

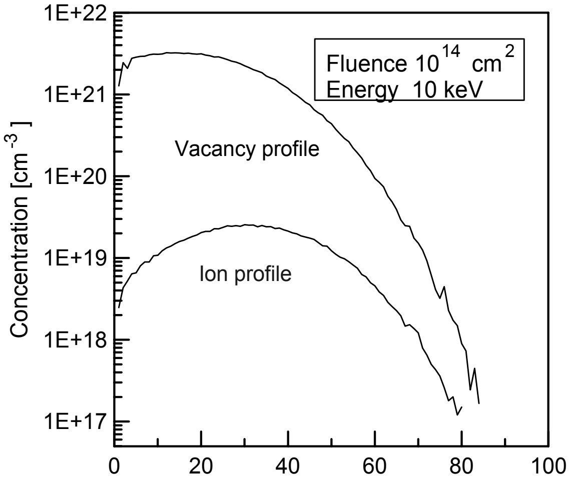

Fig.2 Ion and vacancy defect profiles for implantation energy of 10 keV

in the N implanted areas. Although the retardation effect has been a subject of many studies [7-10], the mechanism is not well understood yet.

In fig.1 and 2 the implantation profiles of nitrogen ions and the vacancies are illustrated for two implantation energies, respectively. The vacancies are result of cascade process, namely direct collision with incoming implant or with recoil. It is obvious from fig.1 and fig.2 that the concentration of vacancies is much higher than the concentration of the implanted nitrogen atoms. It can be seen in fig.3 that the local concentration ratio of vacancies and implanted nitrogen (V/N) varies with depth being higher near Si surface. However, it should not be forgotten that the self-interstitials in substantial concentration are also present, generated during implantation process through collisions and recoils. The importance of this point will be lightened later.

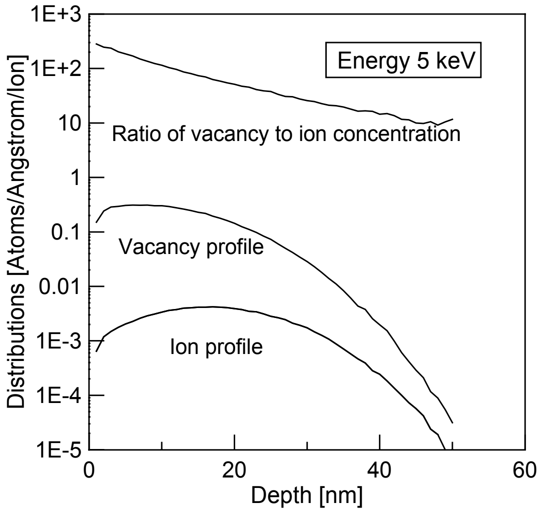

Fig. 3 Ratio of the concentrations of the vacancies and the implanted ions

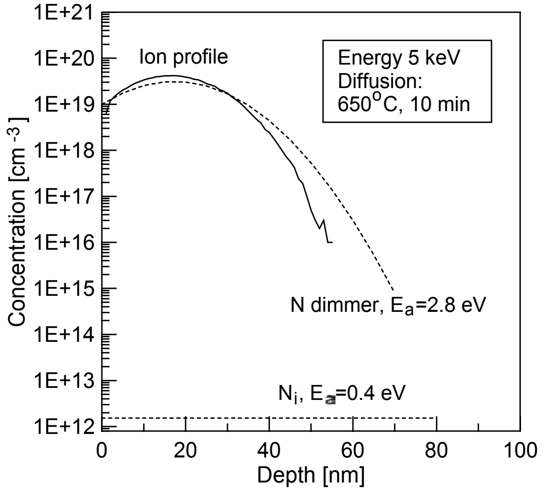

Fig. 4 Ion profiles before and after heat treatment

It is known that the implanted nitrogen can be found mostly at interstitial position directly after implantation interstitial pairs N_i-N_i (N dimer) [11, 12]. Only very small amount of N goes to substitutional Si sites [11]. During subsequent thermal oxidation different process will take place. Elevated temperatures in neutral ambient cause diffusion and formation of complex nitrogen containing defects. It has been shown theoretically that the N-V complex is highly immobile [7] due to the high activation energy of 4.4 eV. Experimental support has been found in the IR absorbtion spectra by certain bands ascribed to this defect center. The N in substitutional Si sites is also immobile [7, 11]. The N dimer was found to move with an activation energy of 2.8 eV, a value very close to the experimentally found energy for diffusion for nitrogen [13]. Migration mechanism through interstitial mediated nitrogen diffusion has been found to proceed rapidly with a barrier of only 0.4 eV [10]. The results from the simulation of the implantation profile in the Si substrate as a result of N migration at elevated temperature of 650^{o}C are plotted in fig.4. For comparison also the as-implanted ion profile is given. The simulation has been performed using standard diffusion equations with a diffusion coefficient of $D = D_o \exp(-E_a/kT))$, where $D_o = 0.87x10^{-4}$ m^{-2}s^{-1} and activation energies E_a are 2.8 and 0.4 eV as discussed above. The time of temperature treatment was taken to be 10 min. It is suggested that at the beginning of the annealing process 90% of the whole implanted amount is as N dimers and 10% as nonbonded interstitial N_i [14]. It is seen that the concentration of the nitrogen atoms decreases slightly in the whole implanted region. Also certain amount of N atoms with smaller concentration will be found farther in the Si substrate. 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. During oxidation, nitrogen will compete with the diffusing oxygen to form Si-bond. In diffusion studies [15] it has been shown that nitrogen diffuses faster in the presence of oxygen. Here a substantial influence can have the varying V/N ratio through Si depth as shown in fig.4, as well as the self-interstitials. At the very beginning of the oxidation process the highly mobile interstitial N_i will flatten through depth and moving to the silicon surface because of the concentration gradient will form N-V pairs as evident in fig.3. This process is competitive with the oxygen motion in the opposite direction. It can be suggested that that the local concentrations of the available atoms will substantially determine the reactions leading to formation of SiO_xN_y with varing x and y through depth. Since the N atoms are already in the Si substrate at the beginning of the oxidation process the already formed Si-N bonds through a reaction $NV+Si_i= N_s$, where NV, Si_i and N_s refer to nitrogen-vacancy pair, self-inetrstitial and substitutional nitrogen, respectively. Because of the high V/N concentration near the Si surface as evident from fig.3, simultaneously some of the vacancies can be taken by O atoms forming Si-O bonds. The result is thin layer of SiO_xN_y, with thickness and x/y ratio depending on N fluence and oxidation temperature. This will reduce the concentration of sites in the Si lattice available for further O-bond formation thus leading to oxidation rate decrease.

3.2 Implantation of nitrogen into SiO_2/Si structure

From fig.1 it can be seen that even by the smallest energy of 5 keV, usually available at most of the production implanters, the thickness of the obtained SiON cannot be less than 20 nm, a value relatively high for application of the SiON as active dielectric in MOSFETs. For that reason instead to implant N into Si, implantation into already oxidized Si can be attempted, i.e. in this second case it is supposed that nitrogen is implanted into a structure of ultrathin SiO_2 layer grown on crystalline Si wafer. This approach has also the advantage to benefit from the already thermally formed highly perfect Si/SiO_2 interface. Also some other advantages have to be stressed. A slightly higher SiO_2 thickness can be used (although still in the ultrathin range), since the resulting dielectric constant will be higher than 3.8 typical for the SiO_2. A better control over the nitrogen profile can be achieved, since the annealing post implantation temperature can be reduced substantially below oxidation temperature. It is known that implantation damage can be reduced substantially already by temperatures as high as 650°C, while high quality Si/SiO$_2$ interface requires much higher temperatures, at least of the order of 800-850°C.

The results from our simulation of the distributions of the implanted nitrogen in Si/SiO$_2$ structure with 10 nm thin SiO$_2$ layer are shown in fig.5. The position of the Si/SiO$_2$ interface is marked by the short straight line in the figure. The picture is markedly different for the two implantation energies. It can be seen that at 5 keV higher nitrogen concentration is observed near Si/SiO$_2$ interface due to accumulation of implanted atoms in the transitional region between the two lattices of the SiO$_2$ and Si. The increased nitrogen concentration is supposed to yield better interface characteristics and improved oxide leakage as found experimentally earlier [16]. In the case of implantation with 10 keV the maximum of the N profile is located deep in the Si substrate. It should be noted that the increased nitrogen concentration in the Si substarte could create shallow donor states.

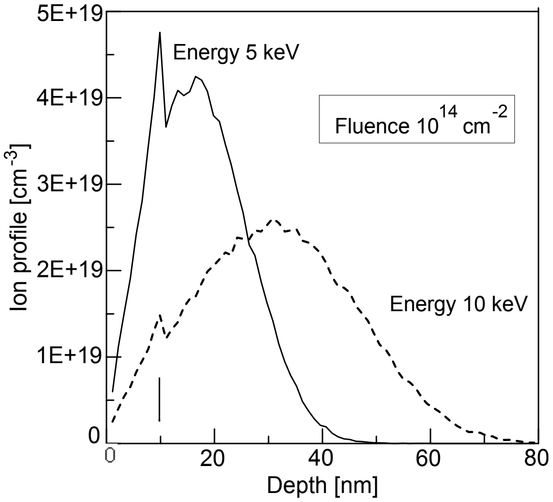

Fig.5 Profile of the implanted N atoms in SiO$_2$/Si structure at two energies.

4. CONCLUSIONS

The results of the present study have shown that based on simple simulation of N$^+$ profile in bare Si substrate after implantation and subsequent diffusion understanding can be gained about the mechanism of the oxidation rate reduction. Application of N$^+$ implantation in Si/SiO$_2$ structures leads to accumulation of implanted atoms in the interface region, which is expected to yield better electrical characteristics of the devices.

5. REFERENCES

[1] Hill W.L.,Vogel E.M., Misra V., McLarty P.K., Wortman J.J., IEEE Trans. Electron Devices, 1996, Vol. 43, pp 15-19.

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

[3] Dunn G. J., Wyatt P. W., IEEE Trans. Nucl. Sci., 1989, Vol. 36, pp. 2161-266.

[4] Zheng Z.-S., Liu Z.-L., Zhang G.-Q., Li N., Li G.-H., Ma H.-Z., Zhang E.-X., Zhang Z.-X., Wang X., Semicond. Sci. Technol., 2005, Vol. 20, pp. 481–484.

[5] Doyle B. S., Soleimani H. R., Philopossian, IEEE Electron Device Lett., 1995, Vol. 16, pp. 301-303.

[6] C. Lin,A.I.Chou, P. Choudhury, J. C. Lee, K. Kumar, H. R. Soleimani, Appl. Phys. Lett., 1996, Vol. 54, pp. 3701-3703.

[7] [5] Adam L. S., Law M.E. and Jones K.S., J. Appl. Phys., 2000, Vol. 87, pp. 2282-2284.

[8] Adam L. S., Law M. E., Dokumaci O., Hedge S., J.Appl. Phys., 2002, Vol. 91, pp. 1894-1900.

[9] Skarlatos D., Tsamis C, Tsoukalas D., J. Appl. Phys., 2003, Vol. 93, pp. 1832-1838.

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

[11] Jones R., Hahn I., Goss J. P., Briddon P. R., Oberg S., Solid State Phenomena, 2004, Vol. 95-96, pp. 93-98.

[12]Gali A., Miro J., Deak P, Ewels C., Jones R., J. Phys.: Condens. Matter, 1996, Vol. 8, pp. 7711-7722.

[13Ma] Madelung O, *Semiconductors – Basic Data*, Springer Verlag, Berlin, 1996.

[14] Voronkov V. V., Batunina A. V., Voronkova G. I., Falster R., Solid State Phenomena, 2004, Vol. 95-96, pp. 117-122.

[15] Hockett R. S., *Appl. Phys. Lett.,* 1989, Vol. 54 , pp. 1793-1795.

[16] Guo X, Ma T. P., IEEE Electron Device Lett., 1998, Vol. 19, pp. 207-209.