FTIR Studies of buried silicon oxynitride layers synthesized by sequential oxygen/nitrogen ion implantation in silicon

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Abstract: The silicon-on-insulator (SOI) structures were synthesized by separation by implanted nitrogen-oxygen (SIMNOX) process. Silicon oxynitride ($Si_xO_xN_x$) buried insulating layers of different structures were synthesized by $^{14}N^+$ and $^{16}O^+$ ion implantation sequentially in the ratio 1:1 to different fluence levels at 150 keV into single crystal silicon wafers. The structural modifications of the SOI structures synthesized by implantation of nitrogen and oxygen in silicon at 150 keV are characterized by the FTIR techniques. The FTIR spectra show single broad absorption band in the wavenumber range 1250-600 cm^{-1} which indicates the formation of silicon oxynitride. The FTIR studies show that the structure of the SOI is strongly dependent on the sequence of the implantation. It is found that the formation of nitrogen-rich silicon oxynitride layers for nitrogen and then oxygen implantation sequence and oxygen-rich silicon oxynitride layers for oxygen and then nitrogen implantation sequence at high fluence levels. It is found that the rapid thermal annealing (RTA) introduces significant structural transformations in the ion implanted layers. The intensity of the absorption band was found to increase for all fluence levels with increase in annealing temperature.

Keywords: Buried, FTIR, Silicon Nitrate, Implantation.

I. INTRODUCTION

The silicon oxynitride films are being examined as potential materials in re-placing silicon oxide (SiO_2) in metal-oxide semiconductor (MOS) devices [1]. The main advantages of SiO_2 are high electrical resistivity, low interface state density and high dielectric strength. However, it has limitation of being susceptible to alkali ion diffusion and radiation damage effects. On the other hand, the silicon nitride (Si_3N_4) films have very low permeability to alkali ions and other impurities, high radiation resistance and high dielectric constant but it refers from the undesirable features of high interface states. Moreover, the Si_3N_4 films exhibit high tensile stress that led to cracking of the films on some substrates, notably after post deposition heat treatments. In view of the above, silicon oxynitride ($Si_xO_yN_z$) layer seems to be a potential candidate for the incorporation of the positive features of both silicon dioxide (SiO_2) and silicon nitride (Si_3N_4). It may be possible to preserve the excellent electronic characteristics of the SiO_2 and the alkali ion diffusion barrier properties of the Si_3N_4 in silicon oxynitride by choosing the proper composition. Silicon oxynitride has the advantage that it does not crystallize even after high temperature annealing. The dielectric constant is found to increase from 3.9 for SiO_2 (SiO_2N_0) to 7.5 for Si_3N_4 ($Si_3O_0N_4$) almost linear with the nitrogen content in the oxynitride [2]. The diffusion suppressing properties of oxynitrides are also of interest [3]. The silicon oxynitride ($Si_xO_yN_z$) thin films are of great importance for the development of integrated devices and sensors in the microelectronics and opto-electronic industries due to the wide range of variation of their stoichiometric properties. These films are transparent in the visible range and their refractive index (RI) can be varied from 1.46 (silicon oxide) to 2 (silicon nitride) by changing their stoichiometry. These interesting properties of ($Si_xO_yN_z$) films are required for the optical applications. The large variation of the refractive index of silicon oxynitride ($Si_xO_yN_z$) films, is useful for the design of a large variety of waveguide structures.

In these paper silicon oxynitride ($Si_xO_yN_z$) buried insulating layers of different structures were synthesized by $^{14}N^+$ and $^{16}O^+$ ion implantation sequentially in the ratio 1:1 to different fluence levels at 150 keV into single crystal silicon wafers. The structural modifications of the SOI structures synthesized by implantation of nitrogen and oxygen in silicon at 150 kV are characterized by the FTIR techniques.

II. EXPERIMENTAL DETAILS

Single crystal silicon wafers (p-type, 10 - 50 Ω-cm resistivity and <100> orientation) were used as substrate material. The silicon wafers were thoroughly cleaned adopting standard RCA-I and RCA-II cleaning procedures using electronic grade chemicals and distilled deionized (DI) water. These wafers were then cut into sizes of 1cm × 1cm samples for loading onto the sample holder of the implanter. To synthesize the silicon oxynitride insulating layers, samples were implanted with $^{16}O^{2+}$ and $^{14}N^{2+}$ in the ratio 1:1 into silicon at room temperature to total fluence level of 1.0×10^{17} cm^{-2} to 2.0×10^{18} cm^{-2} at 150 keV energy. The samples with oxygen to nitrogen ratio of 1:1 was prepared using the 150 keV energy using low energy ion beam facility (LEIBF) at IUAC, New Delhi. For uniform implantation over 1 cm^2 area and to reduce the ion-beam heating effects, magnetic field scanning of the ion beam was employed. Dry O_2 and N_2 high-purity gases were used as the ion source feed-in material. The Fourier transform infrared (FTIR) measurements were performed on FTIR JASCO model 610 spectrometer available at the Department of Physics, University of Mumbai (in the range (7800 cm^{-1} to 350 cm^{-1}).

III RESULTS AND DISCUSSION

Silicon oxynitride buried layers synthesized by ion implantation of nitrogen and oxygen at 150 keV for different fluence levels were characterized with FTIR measurement techniques to study the structural changes.

3.1 Fourier transform infrared (FTIR) studies

The FTIR spectra of the buried silicon oxynitride layers implanted with nitrogen and oxygen in the ratio of 1:1 to fluence levels 1.0×10^{17}, 2.5×10^{17}, 5.0×10^{17}, 7.5×10^{17} and 1.0×10^{18} cm^{-2} are shown in Fig. 1. The FTIR spectra show single broad absorption band in the wavenumber range 1250-600 cm^{-1} confirming the formation of silicon oxynitride. The IR main absorption bands for ion beam synthesized SiO_2 and Si_4N_4 have been observed at 1050 and 800 cm^{-1} respectively [5,6]. The integrated absorption band intensity is found to increase with increasing ion fluence. As the fluence level increases the band position shifts towards lower wavenumber and band becomes sharper. Thus, the samples implanted at lower fluence levels, $1.0\times10^{17}$and 2.5×10^{17} cm^{-2} show the formation of homogeneous silicon oxynitride ($Si_xO_yN_z$) structure while the sample implanted with higher fluence ($5\times10^{17}cm^{-2}$) shows sharper peak centered at 830 cm^{-1} indicating the formation of nitrogen-rich silicon oxynitride structure.

Fourier transform infrared spectroscopy measurements are carried out to study the effect of change of sequence of implantation of oxygen and nitrogen at 150 keV on the structure of ion beam synthesized silicon oxynitride layer. Fig. 2 shows the FTIR spectra of the buried silicon oxynitride layers formed by implantation of first oxygen and then nitrogen (SiON) in the ratio of 1:1 at different fluences. The FTIR spectra show single broad absorption band in the wavenumber range 1250-600 cm^{-1}. The IR main absorption bands for ion beam synthesized SiO_2 and Si_4N_4 have been observed at 1050 and 800 cm^{-1} respectively [7]. The FTIR spectra observed in the present work indicates the formation of silicon oxynitride. As the fluence increases, it is observed that the IR band sharpening occurs and the peak position shifts towards higher wave number showing increase in oxygen and nitrogen content in the growing layer. The integrated absorption band intensity is found to increase with increasing ion fluence.

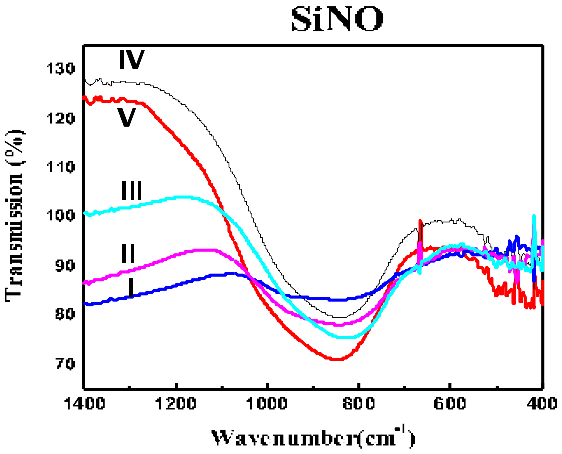

Figure 1: FTIR spectra of silicon samples implanted at 150 keV with nitrogen and oxygen in 1:1 ratio at

different fluence levels i) 1.0×10^{17} (ii) 2.5×10^{17}, (iii) 5.0×10^{17}, (iv) 7.5×10^{17} and (v) 1.0×10^{18} cm^{-2}

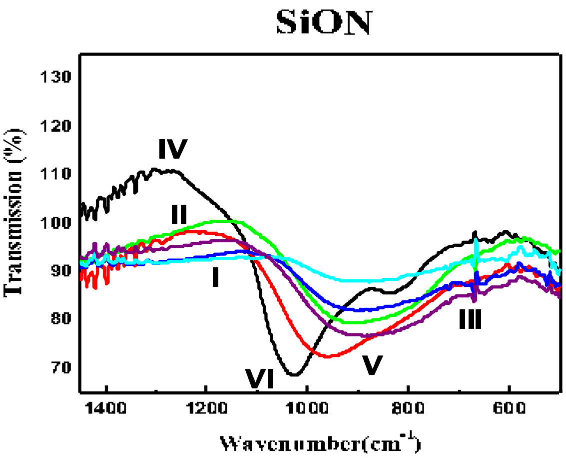

Figure 2: FTIR spectra of silicon samples implanted at 150 keV with oxygen and nitrogen in 1:1 ratio at different fluence levels i) 1.0×10^{17} (ii) 2.5×10^{17}, (iii) 5.0×10^{17}, (iv) 7.5×10^{17} (v) 1.0×10^{18} and (vi) 2.0×10^{18} cm^{-2}

For the fluence 2.0×10^{18} cm^{-2}, the double peak observed indicates the formation of separate phases of SiO_2 (1027 cm^{-1}) and Si_3N_4 (825 cm^{-1}) and some complexes composed of Si, O and N (the shoulder in the range 1000-900 cm^{-1}). The observed strong SiO_2 peak shows formation of oxygen-rich silicon oxynitride structure. The FTIR spectra are observed to be strongly dependent on the implantation sequence. The shift of the absorption band from 850 to 1025 cm^{-1} in Fig. 4.2 shows the formation of oxygen-rich $Si_xO_yN_z$ layer whereas the absorption band shift in Fig.4.1 from 802 to 850 cm^{-1} shows the formation of nitrogen-rich $Si_xO_yN_z$ layer. In both the cases, at low fluences ($1.0\times10^{17}$and 2.5×10^{17} cm^{-2}) broad band show formation of homogeneous silicon oxynitride ($Si_xO_yN_z$) structure. However, as the fluence increases 5.0×10^{17} cm^{-2}, the SION samples show the band position shift towards higher wavenumber indicating oxygen-rich silicon oxynitride layer formation and the SINO samples show the band position shift towards lower wavenumber indicating nitrogen-rich silicon oxynitride layer formation. The concentration of absorbing bonds from the FTIR spectra was calculated using the following relation [8],

$$C = C_n(cm^{-2}) \int \alpha(\omega)/\omega(cm^{-1}) \qquad (1)$$

where C is the concentration of the absorbing bonds, $\alpha(\omega)$ is the absorption coefficient of the layer, ω the wavenumber and C_n is the proportionality constant. After converting the transmission spectra into absorbance spectra, from these plots the total integrated absorption coefficients were determined and the concentration of the absorbing bonds was calculated using the above Eq. 1 as shown in Table 1. In these calculations, the thickness for buried $Si_xO_yN_z$ layer d = 1823 Å (average value of R_p for 150 keV oxygen and nitrogen in silicon) and C_n= $5.8_{\times}10^{18}$ cm^2 (average value of SiO_2 and Si_3N_4) were used. It is observed that the number of bonds increases with ion-fluence.

Table 1. Number of bonds and peak position determined from the FTIR spectra of the ion beam synthesized buried silicon oxynitride layers implanted with oxygen and nitrogen in the ratio 1:1.

Fluence (cm^{-2})	SINO		
	Position of band (cm^{-1})	Peak Position (cm^{-1})	No. of bonds (cm^{-3})
1.0×10^{17}	1050-670	830	1.34×10^{21}
2.5×10^{17}	1060-710	830	2.28×10^{21}
5.0×10^{17}	1050-670	843	5.63×10^{21}
7.5×10^{17}	1080-680	832	4.40×10^{21}
1.0×10^{18}	1130-710	949	6.67×10^{21}
2.0×10^{18}	1250-750	830	9.74×10^{21}

Fluence (cm^{-2})	SION		
	Position of band (cm^{-1})	Peak Position (cm^{-1})	No. of bonds (cm^{-3})
1.0×10^{17}	1050-600	801	3.78×10^{21}
2.5×10^{17}	1120-610	826	7.29×10^{21}
5.0×10^{17}	1120-660	810	9.61×10^{21}
7.5×10^{17}	1100-600	832	9.85×10^{21}
1.0×10^{18}	1160-670	830	1.32×10^{22}

3.1.2 Rapid Thermal Annealing Effects

To study the rapid thermal annealing (RTA) at 400 ^{0}C and 800 ^{0}C in nitrogen ambient in the samples implanted with ration N: O for fluence levels 1.0×10^{17}, 2.5×10^{17} and 5.0×10^{17} cm^{-2}, the FTIR measurements were carried out. The intensity of the absorption band was found to increase for all fluence levels with increase in annealing temperature and the peak position shifted towards higher frequency on annealing at higher temperature. For the annealing behaviour, representative FTIR spectra of the sample implanted with different implantation fluence are shown in the Fig. 3. The increase in the peak intensity on annealing indicates more and more nitrogen and oxygen atoms present in the implanted layer in unreacted or trapped form participate in the formation of bonds with silicon as the annealing temperature increases. The absorption peak position shift results on annealing show the reduction of bond strain, lattice disorder and defects present in the ion beam synthesized layer as annealing progresses.

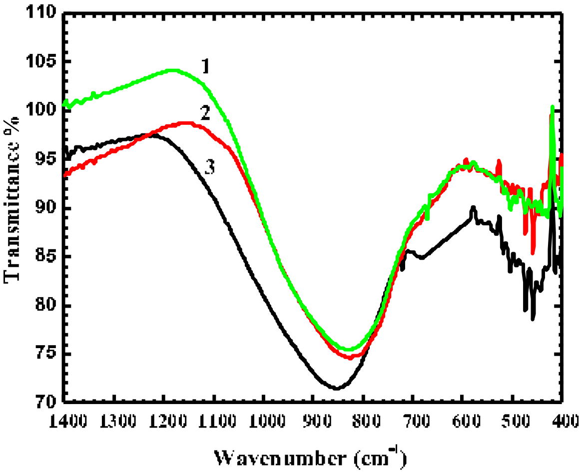

Figure 3: Rapid thermal annealing effect for silicon implanted with nitrogen and oxygen with fluence 5.0×10^{17}cm^{-2} for 1) As Implanted, 2) 400 ^{0}C annealed and 3) 800 ^{0}C annealed.

CONCLUSION

Silicon oxynitride ($Si_xO_xN_x$) buried insulating layers of different structures were synthesized by $^{14}N^+$ and $^{16}O^+$ ion implantation sequentially in the ratio 1:1 to different fluence levels at 150 keV into single crystal silicon wafers. The FTIR spectra show single broad absorption band in the wavenumber range 1250-600 cm^{-1} which indicates the formation of silicon oxynitride. The FTIR studies show that the structure is strongly dependent on the sequence of the implantation. It is found that the formation of nitrogen-rich silicon oxynitride layers for nitrogen and then oxygen implantation sequence and oxygen-rich silicon oxynitride layers for oxygen. The redistribution of implanted oxygen and nitrogen at different temperatures and the recrystallization of silicon on annealing is found that the rapid thermal annealing (RTA) introduces significant structural transformations in the ion implanted layers. The intensity of the absorption band was found to increase for all fluence levels with increase in annealing temperature.

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