Shallow buried SiN_x layers

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High dose nitrogen implantations have been performed at an energy of 30 keV. After high temperature annealing, 1200 °C, a buried layer composed mostly of silicon nitride is formed leaving an overlayer with a high fraction of crystalline silicon. The lattice constant of the overlayer and the region below the SiN_x are reduced in 0.13% and 0.089%, respectively. The substitutional N seems to be responsible for this reduction. © *2000 American Institute of Physics.*
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Separation by implantation of oxygen is a well established technology for a variety of applications such as ultralow scale integration, high voltage devices, and micromachining of sensors and actuators. Nitrogen implantation has also been proposed to synthesize silicon-on-insulator (SOI) layers because of the better stability, the lower doses required, and the excellent barrier against impurity diffusion of the Si_3N_4 compared to SiO_2.[1–4] More recently the use of SOI layers as compliant substrates has been reported.[5–8] For these applications, O^+ ions, for instance,[6] are implanted in silicon wafers. After implantation a high temperature annealing leads to the growth of a SiO_2 buried layer and a good crystalline quality Si overlayer. If the buried layer is close enough to the surface, it might be possible to grow thicker layers without degradation because most of the stress is expected to be absorbed on the thin substrate.[9,10]

In this communication we report the formation of a shallow buried SiN_x layer by low energy N^+ ion implantation and subsequent annealing.

N type float zone (FZ) ⟨100⟩ silicon wafers were used in these experiments. These wafers have a resistivity over 50 Ω cm and oxygen content below 0.3 ppm. Implantations were carried out in a modified Varian Extrion ion implanter. Different doses of $^{14}N^+$, 1×10^{16}, 1×10^{17}, and 6.7×10^{17} cm^{-2}, well over the critical amorphization dose for these ions in silicon (of about 10^{15} cm^{-2}), at an energy of 30 keV were implanted. The sample holder used for the implantations was maintained at room temperature by means of a closed cycle circuit, and the slight increase of the sample temperature only allowed some relaxation of the amorphous network. The highest dose was chosen to obtain a concentration of nitrogen in about 0.1 μm similar to the bulk silicon concentration. Afterwards the samples were annealed in nitrogen gas. Two of the samples of each dose were rapid thermal annealed (RTA) for 1 min at 600 and 1200 °C and a third one furnace annealed for 15 min at 1200 °C.

Fourier transform infrared (FTIR) spectroscopy, spectroscopic ellipsometry, x-ray diffraction (XRD), and spreading resistance techniques were used for characterization.

IR measurements in transmission mode, shown in Figs. 1(a) and 1(b), were performed in Bruker equipment to identify the chemical bonds present in the samples. An unimplanted silicon wafer has been used as reference and no baseline correction has been done. The antireflecting behavior of the implanted layer leads to an overestimation of the sample transmittance, specially apparent in the lowest dose sample because of its low absorption. Figure 1(a) shows the measured spectra of samples with several implantation doses 600 °C RTA annealed. They showed the characteristic band of amorphous silicon nitride (the large band centered in 820 cm^{-1}) (see, for example, Ref. 11) and a small peak at about 950 cm^{-1} probably due to substitutional N in silicon.[12] In the lowest dose the concentration of Si–N bonds seems to be too small to be detected. The spectra of the 1200 °C RTA annealed samples, not shown here, were quite similar to the 600 °C ones, but no traces of the characteristic N substitutional band were detected probably because it is masked by the high intensity of the amorphous Si_3N_4 band.

Figure 1(b) shows the spectra of the 1200 °C furnace annealed samples. A band structure similar to that of crystalline Si_3N_4,[13,14] with the main lines about 850, 890, and 930 cm^{-1}, can be seen. It seems to be a mixture of α and β crystalline phases. The bowing of these spectra around 1000 cm^{-1} is probably due to free carrier absorption because of the high nitrogen doping. Also in this case, the high intensity of the amorphous Si_3N_4 band may have masked the substitutional N band.

High resolution XRD was performed in a SIEMENS D 5000 diffractometer. XRD rocking curves of the highest-dose samples around the (400) reflection are shown in Fig. 2.

In the 1200 °C RTA annealed sample the main peak is broadened compared to that of an unimplanted sample indicating that the crystallinity is not completely recovered. At the right side of this peak two broad bands appear, suggesting the presence of two disordered layers with lattice constants 0.089% and 0.13% smaller than the silicon one. The substitutional N might be responsible for this reduction. Using Vegard's law and half the size of the Si–Si (1.17 Å),[15] and Si–N (0.86 Å) bonds[14] as atomic radii we have estimated the concentration of N in silicon lattice sites. The

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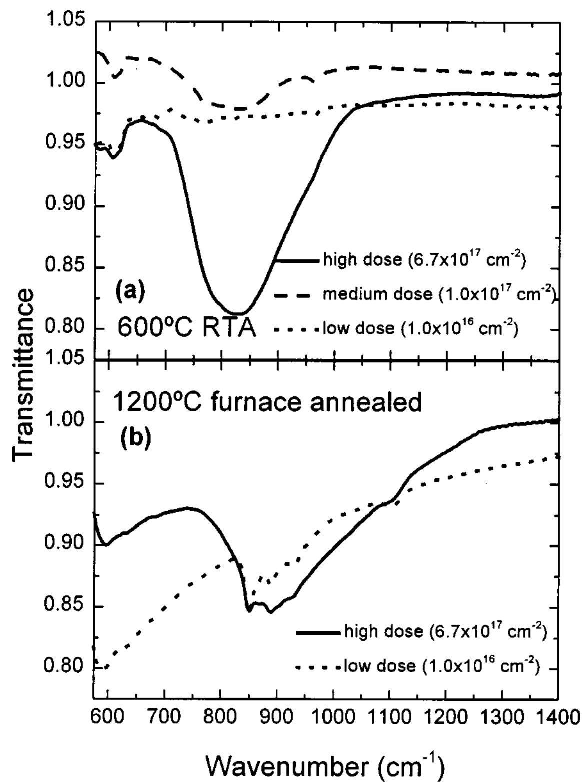

FIG. 1. FTIR transmission spectra of the (a) 600 °C RTA annealed samples and (b) 1200 °C furnace annealed samples.

concentrations in these two layers were less than 1.7×10^{20} and 2.4×10^{20}, respectively. The spectrum of the 1200 °C furnace annealed sample looks rather similar to the unimplanted sample except for a slight asymmetry on the right hand side. Assuming that this asymmetry is due to a reduction of the lattice constant in the near surface region, the peak may be deconvolved in two, the main peak due to crystalline silicon and a smaller one that should correspond to a N concentration of about 1×10^{19} cm^{-3}.

Spectroscopic ellipsometry measurements were performed between 1.5 and 4.5 eV with an Uvisel Jobin–Yvon ellipsometer. The experimental error in determination of the ellipsometric angles, psi and delta, is better than 0.02°. The obtained spectra were simulated as a mixture of several components of dielectric constants available from the literature.

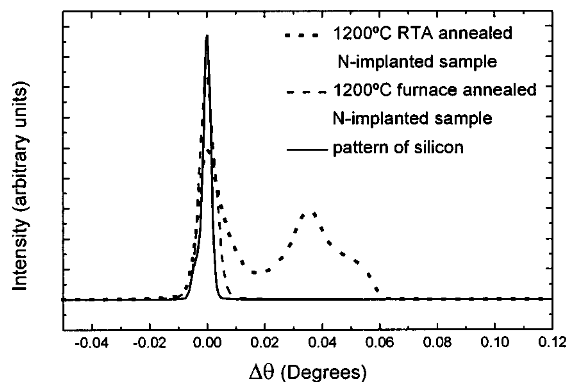

FIG. 2. The 400 rocking curve of the highest-dose implanted samples. The solid line shows the pattern of silicon.

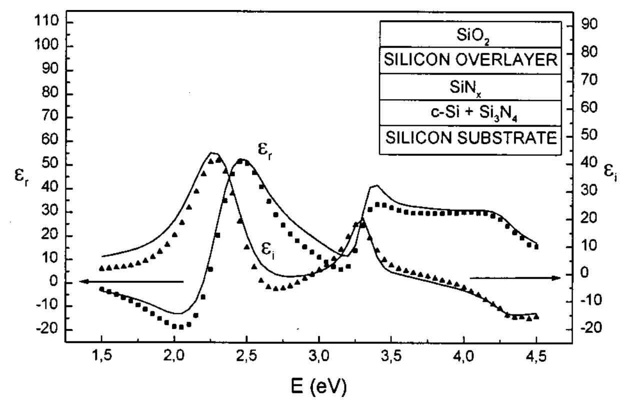

FIG. 3. Fitting of the 1200 °C furnace annealed high-dose (6.7×10^{17} cm^{-2}) implanted sample ellipsometric spectrum.

It is possible to estimate the composition and the thickness of the resulting films by fitting the experimental data. It should be noted that the technique sensitivity is limited to the outer few thousands of armstrongs. Figure 3 shows the fitting of one of the high-dose implanted samples. It has been simulated by using a structure of four layers onto the substrate (see inset in Fig. 3): a first layer of 760 Å with 84% of crystalline silicon and 16% of Si_3N_4, a second layer of 320 Å with 75% of Si_3N_4 and 25% of amorphous silicon, a third one of 366 Å with 78% of crystalline silicon and 22% of amorphous silicon, and the outer one of 49 Å of SiO_2. The spectrum fitting of the 1200 °C RTA annealed sample gave a smaller crystalline fraction in the overlayer. Below it, the fitting results in a thicker *c*-Si rich layer with a low fraction of Si_3N_4.

The 600 °C annealed sample simulation is not reliable (fitting not shown). Since the implanted dose was greater than the amorphization threshold, the damage caused by the implantation is not completely recovered at this temperature.

Spreading resistance measurements were performed in the 1200 °C annealed high-dose implanted samples. The nitride layer cannot be detected by spreading resistance probably because of an excessive contact area of the system tips. Just below the surface, the resistance measurement results were noisy, however, after a few steps the measurements were stabilized. The unstable measurements probably correspond to the crossing of the overlayer and buried nitride regions. Below this, an *n*-type N doped region extends up to 0.2 μm in the 1200 °C RTA annealed sample. Using the standard calibration a peak free carrier concentration of slightly above 1×10^{16} cm^{-3} may be deduced. Taking into account the nitrogen donor energy, 0.14 eV,[12] this free carrier concentration should correspond to a donor concentration around 3×10^{17} cm^{-3}, well below the concentration estimated from the lattice constant contraction. The mobility values in this disordered layer, well below the crystalline Si ones, may have lead to a considerable underestimation of the free carrier concentration explaining this discrepancy. The only difference in the furnace annealed samples is the quick diffusion of the N ions that widens the lower resistivity area up to 4 μm depth.

Ellipsometry measurements suggest the formation of a buried SiN_x region and an overlayer with considerable fraction of crystalline Si after annealing high dose N implanted samples. Because of the high concentration of nitrogen in substitutional sites the lattice constant of the overlayer and the region just below the buried SiN_x are slightly reduced.

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