Experimental identification of nitrogen-vacancy complexes in nitrogen implanted silicon

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Nitrogen implantation is commonly used in multigate oxide thickness processing for mixed signal complementary metal-oxide-semiconductor and System on a Chip technologies. Current experiments and diffusion models indicate that upon annealing, implanted nitrogen diffuses towards the surface. The mechanism proposed for nitrogen diffusion is the formation of nitrogen-vacancy complexes in silicon, as indicated by *ab initio* studies by J. S. Nelson, P. A. Schultz, and A. F. Wright [Appl. Phys. Lett. **73**, 247 (1998)]. However, to date, there does not exist any experimental evidence of nitrogen-vacancy formation in silicon. This letter provides experimental evidence through positron annihilation spectroscopy that nitrogen-vacancy complexes indeed form in nitrogen implanted silicon, and compares the experimental results to the *ab initio* studies, providing qualitative support for the same. © *2001 American Institute of Physics.*
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Nitrogen implantation has been used to retard gate oxide growth.[1] The extent of the retardation of gate oxide growth depends on the dose of implanted nitrogen. Therefore, by varying the dose of the nitrogen implant, we can vary the thickness of the gate oxide across the wafer and hence the device characteristics. This ability to vary the gate oxide thickness across the wafer is of particular importance in mixed signal complementary metal-oxide-semiconductor (CMOS) and System on a Chip technologies.

Previous experiments reported that nitrogen diffuses towards the surface.[2] Based on these experimental results, a physical diffusion model was developed that fits measured nitrogen profiles at elevated temperatures.[3] The model uses a series of reactions, in which the location of nitrogen is interchanged among interstitial, substitutional, and tied-to-a-vacancy sites. The *ab initio* calculations predict the binding energy of the nitrogen-vacancy (NV) complex (consisting of nitrogen at a lattice site with a vacancy adjacent to it) of 1.73 eV.[4] Considering the vacancy formation energy of about 3.7 eV, the corresponding value of the formation energy is about 2 eV for the NV complexes,[5] a value indicative of the good probability of formation of the NV complex. However, the *ab initio* calculations indicate that the migration energy for the NV complex is 4.4 eV, which is very high.[4] Hence, for all practical purposes we can assume that the NV complex is immobile. Nevertheless, in the series of reactions used in the model, NV can be converted to interstitial nitrogen that is mobile. In the interstitial state, the only mobile state of nitrogen used in the model, nitrogen moves towards the sur-

face due to the presence of its concentration gradient, determined by the rates of reactions mentioned above and accumulation of nitrogen at Si/SiO_2 interface. This shifts the entire nitrogen profile towards the surface as time elapses. The presence of the NV complex is quite important in the series of reactions used in the model. In this letter, using methods of positron annihilation spectroscopy, PAS, we provide experimental evidence for the formation of NV complexes in nitrogen implanted Si. PAS was selected based on its sensitivity to vacancy-type defects.

The required sensitivity of PAS to vacancy-like defects originates from the distinct momentum distribution of electrons near vacancies, compared to the distribution corresponding to a defect-free specimen. Positrons injected into the sample annihilate with electrons, producing γ rays. Due to the motion of the electrons, the energy of the γ rays is Doppler shifted from 511 keV, the energy corresponding to the rest mass of electrons and positrons. The annihilation line represents information about the distribution of the electron momentum. In the vicinity of an open volume defect like a vacancy or a vacancy related defect, the probability of a positron annihilating with a high-momentum core electron is reduced. This leads to narrowing of the annihilation line in the energy spectrum. The positron annihilation data are usually reported in terms of the line shape parameter, S.[6] This parameter is defined as the ratio of the number of counts in the central region of the annihilation peak to the total number of counts in the spectral line. Similarly, other ratio-type line shape parameters may be defined by selecting other regions
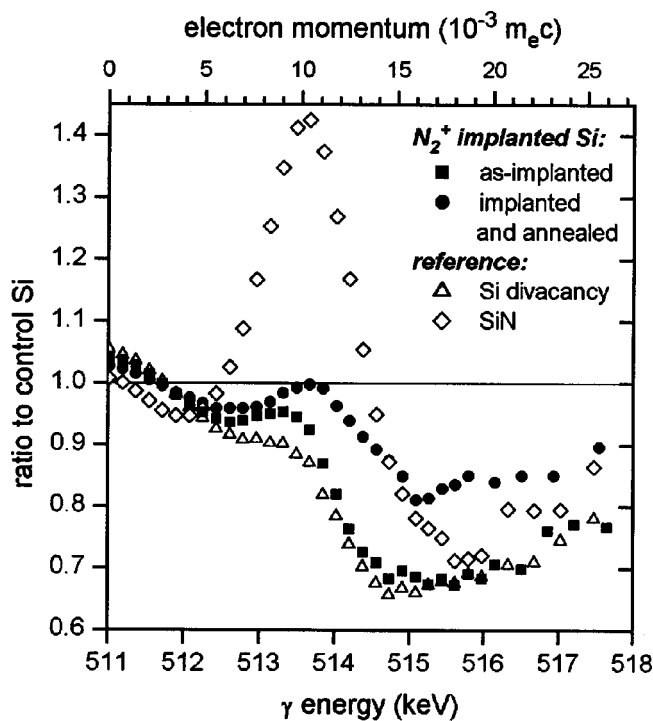
FIG. 1. Ratio curves of samples as-implanted and annealed for 12 min at 750 °C. The samples were implanted at 5×10^{13} N_2^+/cm^2, 40 keV, 25 °C. The spectrum of the as-implanted sample closely resembles that of the Si divacancy, also shown. The spectrum of the annealed sample is approximately a combination of the spectrum of the Si divacancy and of SiN, shown, indicating the nitrogen-vacancy complex to be the dominating defect.
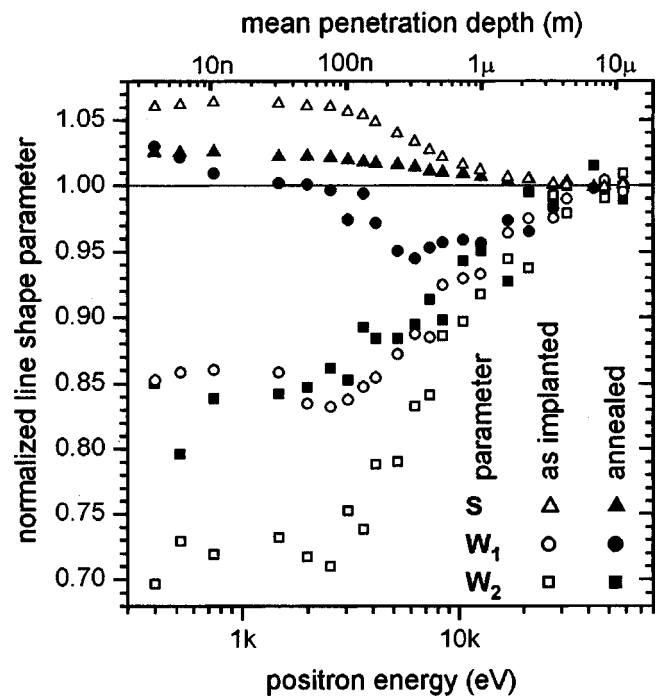

FIG. 2. Dependence of selected line shape parameters on the positron implantation energy (i.e., the distance from the surface) for samples as-implanted and annealed for 12 min at 750 °C. The values are normalized to the values found in control Si.

of the annihilation line (commonly referred to as W parameters, when the wing, not the central region of the annihilation line is analyzed). Depth resolution is accomplished through adjustments of the energy of the injected positrons. Alternatively, the data may be plotted as ratio curves, where the annihilation line, understood as a histogram of counts versus γ energy, is normalized to that of control Si for each energy channel separately. Deviations from the unity line of a ratio curve represent differences between the sample under consideration and the control sample. Analysis of the ratio curves allows chemical identification of the atoms surrounding the vacancy, as signatures of chemical elements are encoded into the ratio curves.[7,8] This feature will be used to identify complexing of nitrogen with a vacancy.

Figure 1 reports the ratio curves for Si samples [Czochralski Si(100), B-doped, 10 Ω cm] implanted at 5×10^{13} N_2^+/cm^2, 40 keV, 25 °C. This figure shows ratio curves of the as-implanted sample and the sample annealed at 750 °C for 12 min, for positron implantation energy of 2 keV. A positron implant energy of 2 keV corresponds to a probed depth of about 50 nm below the surface. The similarity of the two ratio curves and the ratio curve of the Si divacancy (see Fig. 1) for γ energies around 511 and 515 keV indicates the presence of vacancy-like defects in both samples [the divacancy-rich Si was obtained through 1 MeV proton implantation of float zone Si(P-doped, 2–4 Ω cm) at 77 K to a dose of 3×10^{17} cm^{-2}, and measured at positron energy of 35 keV]. In addition, the annealed sample exhibits a peak centered around 513.5 keV that is characteristic of nitrogen, also see Fig. 1 (obtained from chemical vapor deposited 1-μm-thick

SiN film on Si, measured at positron energy of 5 keV). Positive identification of that peak constitutes evidence of the formation of nitrogen-vacancy complexes in the annealed sample. It should be noted that such a peak would not show in a sample containing predominantly substitutional nitrogen, as opposed to nitrogen-vacancy complexes, because positrons need to be trapped at vacancies in order to detect small quantities of foreign atoms. The remnant of the peak at 513.5 keV in the ratio curve of the as-implanted sample is due to positron diffusion towards and annihilation at the $-$OH terminated surface. To minimize ambiguities associated with the similarities of the ratio curves of nitrogen and oxygen (not shown) the native oxide was chemically removed from both samples, but small amounts of oxygen were still present at the surface.

In order to confirm that the peak at 513.5 keV in the ratio curve of the annealed sample originates from NV complexes, not the $-$OH terminated surface, we examined variations of the annihilation line shape parameters as a function of the distance from the surface (through changing the energy of implanted positrons). Surface origin of the peak would induce a monotonic change of an annihilation line shape parameter towards the value of the defect-free specimen with the distance from the surface. A layer of NV complexes would show as a constant value of the line shape parameter within the defective layer. We defined several line shape parameters as the ratio of counts in the following regions of the annihilation line to the total integrated counts:

S: $510.5\ keV \leqslant E_\gamma \leqslant 511.5\ keV$,

W_1: $513.3\ keV \leqslant E_\gamma \leqslant 514.0\ keV$,

W_2: $514.9\ keV \leqslant E_\gamma \leqslant 517.0\ keV$.

The γ energies were selected for optimum sensitivity to defects in the following way: The W_1 parameter is predominantly sensitive to nitrogen or oxygen present at defects, while the S and W_2 parameters are sensitive predominantly to vacancies. The parameters are not fully decoupled, e.g., the W_2 parameter is slightly influenced by nitrogen. The variations of these line shape parameters as a function of the distance from the surface are shown in Fig. 2. The line shape parameters are normalized to the values found in control Si. For both samples, a plateau between about 10 and 100 nm in the functions describing variations of the S and W_2 parameters is indicative of the presence of layers containing open volume defects. For none of the samples, except for the near surface behavior, up to about 10 nm deep, does the W_1 parameter exhibit a monotonic change towards the defect-free value (unity) with the increase of the distance from the surface. Therefore, the contribution of the oxygen trapped at the $-$OH surface termination to the line shape parameters measured deeper than about 10 nm from the surface can be ruled out. The value of the W_1 parameter up to about 100 nm in the as-implanted sample is consistent with the value expected for a specimen containing undecorated divacancies. The corresponding value of W_1 in the annealed sample is close to unity, a value that is not characteristic of any defect in Si previously reported in literature. Since we know about the presence of nitrogen in the annealed sample from SIMS measurements,[2] we therefore assign $W_1 \sim = 1.00$ to the NV complex. Although the unity value of a line shape parameter usually indicates a defect-free specimen, it is not so for the NV complex, as the greater-than-unity contribution of nitrogen cancels the below-unity contribution of the vacancy at the complex (the value of a line shape parameter of a complex defect is approximately a superposition of the values of the individual constituents of the complex). Other line shape parameters characteristic of the NV complex plotted in Fig. 2

are not unity ($S > 1$, $W_2 < 1$), which confirms that the sample is not defect free. It should be noted that the W_1 measured further from the surface than about 100 nm in the annealed sample is below unity, indicating the presence of undecorated divacancies, probably as a consequence of their diffusion upon annealing.

As we are able to identify the NV complexes, these results support the *ab initio* calculations. The *ab initio* calculations indicate formation of NV complexes in both as-implanted and annealed samples. Although PAS failed to detect NV complexes in the as-implanted sample, it does not contradict the *ab initio* calculations. It is conceivable that the NV complexes are present in that sample too, but they are outnumbered by the undecorated divacancies, and therefore invisible to PAS. To make these results more quantitative, process models need to be used to verify the range of the binding energies of the NV complex that would be consistent with the positron annihilation results.

In summary, we have identified, using positron annihilation spectroscopy, the nitrogen-vacancy complex predicted by *ab initio* calculations of nitrogen diffusion in Si and qualitatively compared these results to *ab initio* calculations.

[1] C. T. Liu, Y. Ma, J. Becerro, S. Nakahara, D. J. Eaglesham, and S. J. Hillenius, IEEE Electron Device Lett. **18**, 105 (1997).

[2] L. S. Adam, M. E. Law, K. S. Jones, O. Dokumaci, C. S. Murthy, and S. Hegde, J. Appl. Phys. **87**, 2282 (2000).

[3] L. S. Adam, M. E. Law, O. Dokumaci, and S. Hegde, Tech. Dig. Int. Electron Devices Meet., 507 (2000).

[4] J. S. Nelson, P. A. Schultz, and A. F. Wright, Appl. Phys. Lett. **73**, 247 (1998).

[5] Florida Object Oriented Process Simulator (FLOOPS) Manual, University of Florida, Gainesville, FL, 2000, and references therein.

[6] P. Asoka-Kumar, K. G. Lynn, and D. O. Welch, J. Appl. Phys. **76**, 4935 (1994).

[7] S. Szpala, P. Asoka-Kumar, B. Nielsen, J. P. Peng, S. Hayakawa, K. G. Lynn, and H.-J. Gossmann, Phys. Rev. B **54**, 4722 (1996).

[8] U. Myler and P. J. Simpson, Phys. Rev. B **56**, 14303 (1997).