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Positron studies of plasma-treated silicon wafers

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Abstract

Wafers of silicon treated with rf oxygen and hydrogen plasma have been studied with the Herodotus slow positron beam. Doppler broadening measurements reveal the influence of temperature and time on defect profiles beneath the surfaces.

The continuing miniaturization of semiconductor devices emphasizes the influence lattice defects have on their electrical properties. In their construction conventional processing methods have been replaced by more advanced techniques such as ion implantation, electron and X-ray lithography and plasma treatment. At present, plasma processes are widely used for dry etching and for low temperature deposition of materials. Oxygen plasma is mainly used for stripping photoresist, surface cleaning and in multilayer lithography [1–5]. Hydrogen plasma can be effective in passivating or neutralizing electrically active defects and impurities in semiconductors [6–9]. Within a plasma environment wafers of silicon with or without a SiO_2 layer are subjected directly to the bombardment of ions, electrons and photons which often results in defects such as oxygen-vacancies, divacancies and vacancy donor complexes in the samples.

Results from deep level transient spectroscopy (DLTS) applied to Si/SiO_2 samples [10] showed that for similar conditions hydrogen and oxygen plasma create different kinds of defects. Hydrogen plasma treatment at temperatures between 20–200°C causes deep levels which are attributed to divacancies, but none has been seen at 300°C, which is in accordance with the fact that at this temperature divacancies have been annealed. Oxygen plasma treatment also creates deep levels which are so far unidentified but may arise from defects containing oxygen.

Further, it has been shown [11] that hydrogen plasma treatment for SiO_2/Si structures at increasing temperatures leads to a decrease of fixed oxide charges and interface states. The reduction increases with increasing treatment temperature. At treatment temperatures lower than 300°C, the doping in the substrate is increased towards the interface.

Ellipsometry measurements of hydrogen plasma treated Si/SiO_2 samples [12] showed that some structural defects, close to the SiO_2/Si interface, were annealed resulting in Si-bond reformation and in a release of the intrinsic oxide stress.

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In 1986 Dannefaer and Kerr [13], using positron annihilation spectroscopy, showed that oxygen in silicon gives rise to a greater Doppler broadening of the 511 keV annihilation line (i.e. a lower *S*-parameter [14]) than for pure Si. They attributed this to interstitial clusters of at least 2 oxygen atoms. The low *S*-parameter value should then be due to the core electrons of the oxygen atoms. According to a recent review [14], the SiO_2–Si interface has an *S* value smaller than that of both bulk Si and SiO_2. The low *S* value at the interface was associated with Si dangling bond sites (P_b-centers) and oxygen. The conclusion was that the positrons were annihilating at P_b-centers that were pointing into the oxide. When P_b-centers are passivated with hydrogen, the centers are still attractive to positrons, and this results in an even lower value of *S*-parameter, which is due to the increased overlap with the oxygen core electrons.

On the other hand, positron measurements performed on MOS structures treated with vacuum ultraviolet irradiation [15] showed a strong correlation of a decreasing *S*-parameter with an increasing number of interface trap states. These states are not P_b centers but could be formed by a relatively large network of interstices in the neighborhood of the interface. Positron measurements on rf hydrogen plasma treated Si [16] indicated the formation of hydrogen filled microvoids.

As the initial stage in a program designed to study the Si/SiO_2 interface, we here report findings on nominally plain silicon wafers.

For our study we have used phosphorous doped (6–9 Ω cm), Czochralski grown Si (111) wafers. The samples have a native oxide which is about 2.5 nm thick. The samples were subjected directly to the influence of hydrogen and oxygen plasma at 20, 100, 200 and 300°C for 15, 30 and 45 min. The plasma was excited in a planar reactor by a 13.56 MHz rf generator with a power density of 75 mW cm^{-2} and a gas pressure of 133 Pa. The preparation was done in Sofia.

Positron annihilation measurements were performed on the samples using the Herodotus slow positron beam. The Doppler broadening of the 511 keV annihilation γ-rays, characterized in terms of the parameter *S*, was measured by a Ge detector, placed behind the sample.

In Fig. 1a and b we show results for silicon

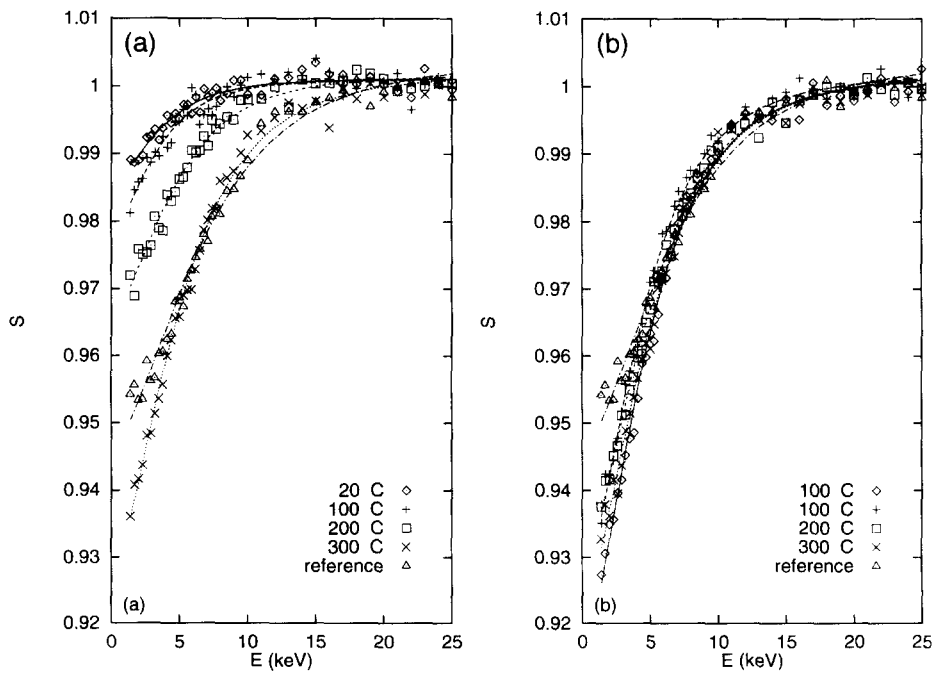

Fig. 1. The Doppler *S*-parameter as a function of the positron injection energy for (a) hydrogen and (b) oxygen, plasma treatments.

treated for 30 min at different temperatures in hydrogen and oxygen plasma, respectively. The values for untreated samples are also recorded. Other measurements (not shown) for treatments of 15 and 45 minutes gave similar curves.

At the high positron injection energies all the samples yielded the same value for S, this corresponding to annihilation deep in the material. The values of S_s at the lowest energies correspond to annihilation at the surfaces and it is seen that, whereas there are only small variations for oxygen treated samples, large variations occur for hydrogen.

It is tempting to suggest that oxygen atoms are attaching themselves to the sample surface and consequently reducing the values of the surface value of S, S_s. However, we note in Fig. 1a that after hydrogen treatment at 300°C a very similar curve is obtained, with a lower S_s than for the untreated sample, which suggests that the surface traps have been modified in the same manner in both treatments. One sensible explanation is that this modification is damage promoted by UV photons from the plasma.

Fig. 1a, with hydrogen, demonstrates that the surface parameter is affected by the treatment temperature. It is seen that hydrogen raises S_s but that treatment at the higher temperatures reduces this effect. We note that Ref. [16] reports a rise in S_s for hydrogen plasma treatment on Si at 275°C, but at 300°C we find that S_s has declined to below its original value. The differences may be due to the relatively low power density used in our plasma.

In Fig. 1, the lines represent the best fits derived from the diffusion program VEPFIT [17]. In the case of oxygen satisfactory fits are obtained using an accepted value for the positron diffusion length L_+ in silicon, with no electric field, of 220 nm. The hydrogen curves (Fig. 1a) corresponding to the treatment at 20 and 100°C yield shorter diffusion lengths of about 130 nm, but the 200 and 300°C cases revert to 220 nm. The likely explanation is the that positive surface charges have been built up [11] causing internal electric fields that will tend to drive the positrons into the interior of the sample. Relying, to a first approximation, on a uniform field (E) best fits are obtained with $E \sim 10^5$ V m^{-1} for the 20 and 100°C cases. The fields seem to disappear with the higher temperature treatments. Other possibilities are conceivable but these will be addressed in later work.

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