

## Effect of Post Oxidation Anneal on VUV Radiation-Hardness of the Si/SiO<sub>2</sub> System studied by Positron Annihilation Spectroscopy

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### Abstract

The effect of a post oxidation anneal at 1000°C in a N<sub>2</sub> ambient of the thermally grown Si/SiO<sub>2</sub> system was investigated using vacuum ultraviolet irradiation for determining the generation of interface traps of the Al metallized system in combination with positron annihilation spectroscopy to characterize the structure of the oxide network. A correlation was found between the generation of interface traps and the S parameter of the positron trapping sites in the oxide close to the Si. It appears likely that the positrons are trapped in the larger near-interfacial oxide network interstices. These interstices could act as scavengers for the metastable intermediate (atomic hydrogen or excitons) involved in the generation of the interface traps.

### I. INTRODUCTION

It has been well established that the radiation-hardness of the metal-oxide-semiconductor (MOS) system is strongly affected by the details of the fabrication procedure [1,2]. Since hydrogen is a notorious intermediate in the generation of interface traps, it is quite obvious that as a rule the incorporation of this species during device fabrication should be minimized. It is also known that post oxidation anneals (POA) at temperatures above 900°C in an inert ambient should be avoided. As shown by Warren et al., such an anneal enhances positive charging of the bulk oxide and the generation of Si/SiO<sub>2</sub> interface and border traps upon exposure of the MOS system to ionizing radiation [3,4]. According to their opinion, these effects are caused by the formation of O vacancies and O vacancy-related complexes in the oxide network at or close to the Si/SiO<sub>2</sub> interface during the high temperature anneal. Such a creation of additional O vacancies would immediately explain the correlation between the positive charging of the bulk oxide and the POA treatment since the vacancies constitute trapping centers for holes [5]; however, it does not offer a straightforward explanation for the enhanced generation of interface and border traps upon irradiation.

Several techniques have been used to investigate the structure of the Si/SiO<sub>2</sub> system. Electron spin resonance studies have greatly contributed to our knowledge by resolving the microscopic structure of a number of electrically active point defects such as the O vacancy center [5,6]. The structure of the interfacial region has also been investigated by high resolution transmission electron microscopy [7] and,

indirectly, by X-ray photoemission spectroscopy [8,9]. Although the results from these latter studies have contributed to the general understanding, they have not provided specific insights in the relation between the structural and electrical properties of the interface. Positron annihilation (PA) is an alternative technique that could also provide structural information but whose possibilities have not been sufficiently explored thus far [10,11]. For the Si/SiO<sub>2</sub> system, the nature of the positron trapping centers has not been unambiguously established; however, in line with the trapping centers in metals and semiconductors one would expect that the positrons are trapped by open spaces in the oxide network thus providing information on such spaces.

In this investigation we have studied the effect of POA at 1000°C in N<sub>2</sub> of various times. On the one hand, such a treatment provides a promising test case for PA spectroscopy and in particular its sensitivity to structural changes of the Si/SiO<sub>2</sub> system. On the other hand, it could produce new insights on the effect of POA on the susceptibility for the generation of interface traps.

Like results of capacitance-voltage (C-V) measurements but unlike electron spin resonance data, the PA measurements do not provide direct structural information. The understanding and the interpretation of the results of PA measurements thus have to be derived from correlations between PA data and other system properties. Therefore, we have studied the influence of POA on the bulk oxide electron and hole traps and interface traps in the as-grown system and on the generation of interface traps by vacuum ultraviolet (VUV) irradiation [12].

Doing our PA experiments, we learned that the positrons can be preferentially driven towards the SiO<sub>2</sub> region bordering the Si substrate, thus providing valuable information on the positron trapping sites in this border region. The PA data show that already a short POA significantly changes the oxide network. This change does not correlate with the more gradual evolution observed for the interface traps and bulk oxide traps in the as-grown system, but it does correlate with the generation of interface traps by VUV radiation. In our irradiation experiments only a neutral metastable species, such as excitons or hydrogen atoms, which have to traverse the oxide layer from gate to substrate could produce the interface traps. The PA data suggest that the samples not subjected to a POA contain relatively large interstices in the oxide network near the Si substrate that account for the trapping and annihilation of the positrons. POA removes these larger interstices. Possibly, they act also as a scavenger for the metastable species that produce interface traps when arriving

at the Si/SiO<sub>2</sub> interface, which would explain the observed correlation between PA and the generation of interface traps.

In the following section we will describe the preparation of the oxides and the techniques used for their electrical characterization. Next, PA spectroscopy is briefly introduced and it is shown that this technique indeed may provide information from the oxide network near the substrate. In further sections we present the experimental results and a discussion.

## II. EXPERIMENTAL

For our studies we have used MOS capacitors on 0.05-0.2 Ωcm p-Si(100) substrates with a 105nm thick gate oxide prepared by oxidation in dry O<sub>2</sub> at 1000°C. Following the growth, the process was quenched by changing the gas flow from O<sub>2</sub> to Ar or N<sub>2</sub>, thus subjecting the oxides to POA. After a certain time, the POA time, the furnace was ramped down to 800°C, whereafter the wafers were unloaded. The system is equipped with a special unloading tube to allow the wafers to cool down in a pure N<sub>2</sub> ambient. With the aid of this tube, passivation of as-grown interface traps is avoided [12]. Transparent (15 nm) Al gates were deposited by evaporation from a resistively heated W boat. The capacitors were subjected to a 30 minute post-metallization anneal (PMA) in forming gas (10% H<sub>2</sub> and 90% N<sub>2</sub>) at 400°C.

The density of interface traps was measured using combined quasi-static and high frequency C-V measurements. Avalanche electron injection was applied to study the bulk oxide electron traps. For the hole trapping experiments we used the technique of VUV hole injection: the capacitor is exposed to the irradiation from a Kr source ( $h\nu = 10$  eV,  $10^{15}$  photons cm<sup>-2</sup>s<sup>-1</sup>) while a positive gate bias is applied corre-

sponding to a 1 MV cm<sup>-1</sup> electric field in the oxide. Electron-hole pairs are generated just beneath the gate [13], the electrons being swept towards the gate whereas the holes being transported through the oxide layer towards the Si substrate, thus filling the hole traps in the oxide. For both types of injection experiments, the amount of trapped charge carriers was calculated from the midgap voltage shift ( $\Delta V_{mg}$ ).

The susceptibility for the generation of interface traps was studied by exposure of the MOS capacitors to VUV radiation at negative bias conditions. At this condition, positive charging of the oxide is avoided because the holes will not appear in the region near the Si/SiO<sub>2</sub> interface where the dominant hole trapping centers are located [5]. Bulk oxide electron trapping is also avoided since we used a rather limited exposure ( $<10^{16}$  cm<sup>-2</sup>). The oxide remains uncharged; however, large numbers of H-induced fast donor-type traps at the Si/SiO<sub>2</sub> interface are generated [12,14-16]. The number of the radiation-induced interface traps above midgap was calculated from the stretch-out of the C-V curves.

The Delft Variable Energy Positron beam (VEP) was used for the positron annihilation Doppler broadening measurements [17]. This system produces a collimated beam of monoenergetic positrons with energy ranging from 0 up to 30 keV with a typical flux of  $\approx 10^4$  cm<sup>-2</sup>s<sup>-1</sup>. The positrons are extracted from a <sup>22</sup>Na source. The  $\gamma$ -photons that result from the annihilation of the positrons are detected by a Ge detector.

## III. POSITRON ANNIHILATION

In the following we will present a brief description of the positron annihilation (PA) Doppler broadening measurements, followed by a more detailed discussion on the experimental approach developed for MOS systems. A more extended treatment of PA spectroscopy can be found in the review paper of Asoka-Kumar et al. [10].

For the PA experiments, accelerated positrons are implanted into the system [10,11]. Figure 1 gives a schematic illustration of the experimental set up. By varying their kinetic energy the positrons can be implanted at a pre-defined depth. For the lower energies they are implanted into the gate; for the higher values they are deeper implanted, into the oxide or into the substrate. After thermalization, the positrons will diffuse until being captured at a defect.

The trapped positron ultimately annihilates with an electron, thereby producing two 511 keV  $\gamma$  quanta. The energy of the  $\gamma$  quanta is slightly affected by the momentum of the annihilated particles. This variation is reflected in the spectral shape of the  $\gamma$  peak, which thus contains information about the electronic environment of the defect. The resolution of the  $\gamma$  detector is too low to obtain a detailed momentum distribution; however, it is sufficient to study the broadening of the peak. This broadening is expressed with the aid of the so-called shape parameters S and W. The definitions of S and W are given in figure 2. One should note that this figure shows an as-measured spectrum.

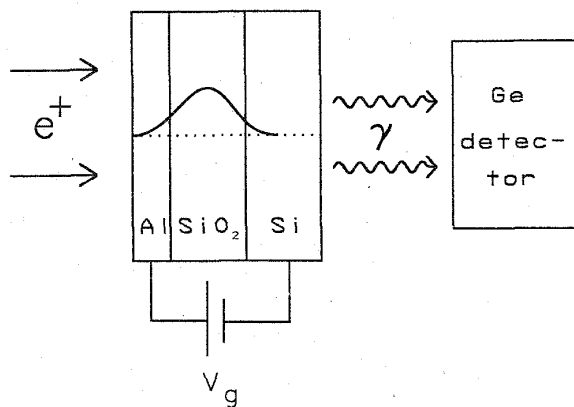


Figure 1. Schematic illustration of the experimental arrangement for PA measurements. Positrons are implanted into the MOS capacitor. After thermalization they will be trapped at defects in the system. Next, they annihilate with an electron thus producing two  $\gamma$  photons that are detected by the Ge detector. In the case of a MOS system, the thermalized positrons can be driven towards the gate or the Si substrate by applying an external gate bias.

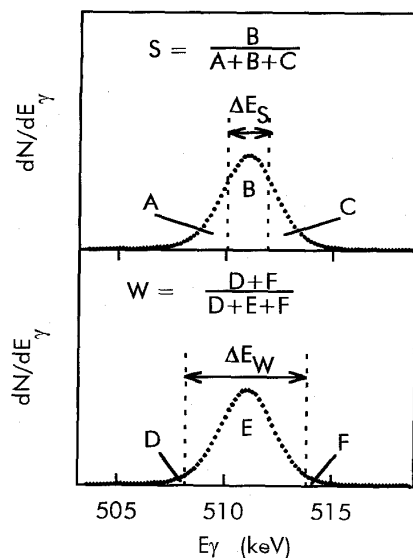


Figure 2. Definition of shape parameters  $S$  and  $W$  of the  $\gamma$ -peak. The indicated areas (A, B, ... , F) denominate sections defined with the aid of a fixed integration window ( $\Delta E_S$  and  $\Delta E_W$ ). The figure shows a typical experimental spectrum.

The introduction of these particular definitions of  $S$  and  $W$  to parameterize the  $\gamma$  peak offers the advantage of a linear formalism: if annihilation takes place at two defects, A and B, characterized by  $(S_A, W_A)$  and  $(S_B, W_B)$  and with trapped fractions  $f_A$  and  $f_B$ ,  $f_B = 1 - f_A$ , then the measured parameters ( $S_M, W_M$ ) will be given by:

$$S_M = f_A \times S_A + f_B \times S_B \quad (1a)$$

and

$$W_M = f_A \times W_A + f_B \times W_B. \quad (1b)$$

The peak shape that is actually measured, not only depends on the microscopic structure of the defects, but also on the geometry of the detection system. This feature makes it difficult to directly compare  $S$  and  $W$  data from different laboratories. To circumvent this drawback, some well-defined reference systems are used to characterize the equipment. Bulk crystalline Si is such a reference, and therefore we could very conveniently use the  $S$  and  $W$  values measured for large implantation energies for the normalization.

Earlier PA studies on metals and semiconductors have taught that the positrons have a preference to occupy the so-called 'open-volume defects' such as vacancies, clusters of vacancies or voids [18,19]. In the relatively large open-volume defects, there is little overlap of the trapped positron with the high momentum core electrons. Annihilation mainly takes place with the low momentum valence electrons which results in a narrow  $\gamma$  peak with a large  $S$  and a small  $W$  value. With decreasing volume, the positron will become more enclosed which causes a stronger interaction with the core electrons of the confining atoms. The enhanced interaction with the high momentum core electrons broadens the  $\gamma$  peak. This results in a smaller  $S$  and a larger  $W$  value; i.e.,  $S$  increases and  $W$  decreases with the "volume" of the defect [20].

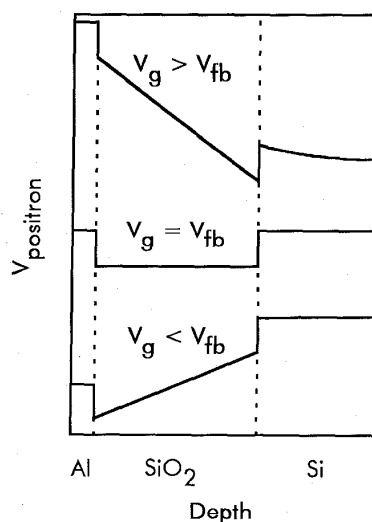


Figure 3. Electrochemical potential for positrons in MOS system at positive bias, flatband voltage or negative bias. Opposite to the case of electron affinities, the positron affinity of the oxide is larger than that of Si or Al.

The experience from PA studies of the past decade shows that defects can be characterized by means of an  $S$  parameter. The work of Liskay et al. [21] and the results presented in this paper show that the  $W$  parameter may contain independent information. Because of this it is favorable to use the  $S$ - $W$  pair as a fingerprint of a particular defect.

If positrons are implanted in an insulating layer such as an oxide, it is possible to control their transport after thermalization by applying an electric field. Figure 3 schematically shows the electrochemical potential for the positrons in a MOS system for different signs of the bias voltage. Opposite to the case of electron affinities, the positron affinity of the oxide is larger than that of the Si or the Al. In the case of a bias more positive than the flatband voltage, the positrons that are implanted into the oxide are driven towards the Si/SiO<sub>2</sub> interface. However, these positrons can not enter the Si because of the potential barrier; they are confined to the oxide region bordering the substrate.

Figure 4 shows the  $S$ -value normalized with respect to that of Si as a function of the implantation depth for a MOS system subjected to different positive bias voltages. In the case of implantation into the Al we obtained an  $S$ -value of about 1.075. Implantation into the oxide layer results in an  $S$ -value exhibiting a minimum. However, this minimum depends upon the field strength: for increasing fields it can be seen that it approaches an absolute minimum ( $S_{min}$ ) of about 0.973.

For the interpretation of the PA measurements it is often helpful to plot the data as trajectories in the  $S$ - $W$  plane, using the implantation energy as a running parameter. Such a plot is shown in figure 5. The direction of increasing implantation energy is indicated by the arrows in the figure. The annihilation at different sites can now be represented by trap coordinates in this plane. For example, annihilation in the Si

substrate is represented by the S-W coordinate ( $S_{Si} = 1, W_{Si} = 1$ ) and annihilation in the Al by ( $S_{Al} = \approx 1.08, W_{Al} = \approx 0.84$ ). In most cases we will have to deal with the involvement of three or more centers, located at different depth. The coordinates of the defects then define a polygon in the S-W plane. From the linearity property of the S and W parameters (Eqs. 1a and 1b) it immediately follows that in this situation the trajectory is confined to this polygon. If annihilation is determined by two distinguishable sites only, the trajectory is given by a straight line connecting the two defect coordinates; changing the implantation energy only changes the distribution of the positrons over the two traps. Such an effect is seen twice in figure 5; the trajectory can be quite satisfactorily approximated by two straight lines. Moreover, within the experimental error, the trajectories always run at the 'inner' side. This shows that at this particular positive bias condition at least three sites are involved but that there are no indications for the presence of a fourth. The trap coordinate of the third center is given by the point where the two straight lines cross.

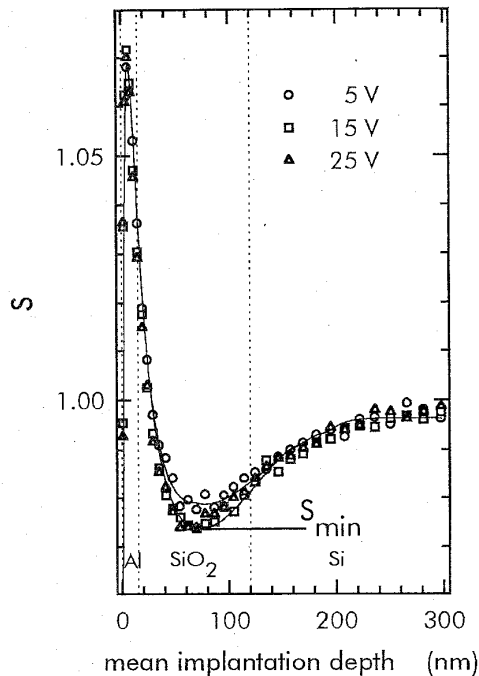


Figure 4. S parameter versus mean implantation depth of positrons in a Al/SiO<sub>2</sub>/Si system for various positive gate bias voltages. All data have been normalized to  $S_{Si}$ .

The trajectory of figure 5 closely approaches the crossing of the two lines, but does not reach this point completely. This feature shows that although a large fraction of the positrons is trapped at the third trap, there is always a small fraction that annihilates in the Al or the Si. This agrees with numerical simulations of the implantation made with the variable energy positron fitting program (VEPFIT) [11] which show that the implantation profile is stretched-out, with tails extending into Si and Al.

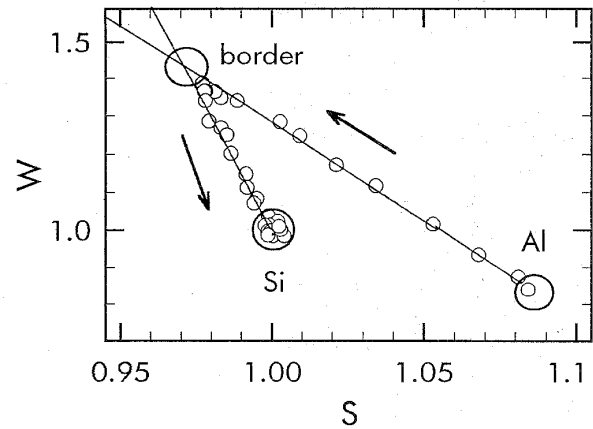


Figure 5. S-W trajectory for positrons implanted in a Al/SiO<sub>2</sub>/Si system for 15V positive gate bias. The arrows indicate the direction of increasing implantation energy.

Above we have argued that, if a positive bias of 15V is applied during the PA depth scan, effectively only three sites play a role in the trapping of the positrons. Considering this feature, we may also understand the approach of the absolute minimum S value ( $S_{min}$ ) for an implantation in the middle of the oxide for increasing positive bias (figure 4). Due to the electric field, the positrons implanted in the oxide will be transported towards the Si/SiO<sub>2</sub> interface. When this field has moderate values, the positrons will reside sufficiently long in the oxide to have an appreciable fraction trapped at sites in the bulk of this layer; those not trapped in the oxide will be first driven into the triangular potential well at the Si/SiO<sub>2</sub> interface and next captured at sites in this well. Changing the magnitude of the electric field thus changes the ratio between positrons trapped at sites in the bulk of the oxide layer and those captured by centers in the potential well. For the +15V bias, trapping at centers in the bulk of the oxide layer becomes negligible and all positrons are collected in the potential well. Thus, applying such a gate bias allows us to exclusively probe the sites in the oxide close to the substrate. For convenience, we will in the following refer to this region as the 'oxide border region'; the corresponding S-W coordinate will be denoted as ( $S_{border}, W_{border}$ ).

## IV. RESULTS

Using the insights discussed in the foregoing section, we have first verified whether or not PA at a positive gate bias is suited to monitor the structural changes induced by POA of various times in N<sub>2</sub>. The result revealed a clear distinction between the samples with POA shorter than 4 min. ('short POA') and those with POA of 4 min. or longer ('long POA'). Within experimental error, identical trajectories were obtained for all specimens with a short POA. The systems subjected to

a long POA also produced approximately equal trajectories; however, these latter were quite different from the trajectories of the specimens with a short POA, without any indication of a gradual transition between the short and long POA. In figure 6 we present typical trajectories for each case. The data clearly show a distinct shift of the trap coordinate from ( $S_{\text{border}}=0.973$ ,  $W_{\text{border}}=1.45$ ) to ( $S_{\text{border}}=0.960$ ,  $W_{\text{border}}=1.50$ ).

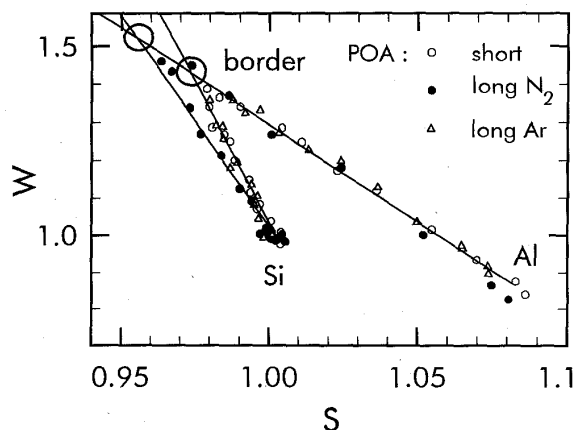


Figure 6. S-W trajectories of a specimen with a long (20 min.) POA in  $N_2$ , of one with a short (0 min.) POA in  $N_2$  and of one with a long (20 min.) POA in Ar. The trajectories are recorded at 15V positive gate bias.

To further explore the capabilities of PA we also studied a sample subjected to POA in Ar. Figure 6 shows the trajectory of a specimen with a 20 min. Ar anneal. The data do not exhibit a shift as observed for the  $N_2$  anneal; this shows that the Ar anneal does not affect the positron trapping centers in the oxide border region. Apparently, the annealing effect is element specific.

Next we investigated whether or not POA in  $N_2$  also affects the generation of interface traps. For this purpose we irradiated a set of capacitors at negative bias voltage. Figure 7 shows the number of radiation-induced interface traps above midgap versus the VUV doses. The data again reveal two clearly distinguished groups of data points: all specimens that had received a long POA in  $N_2$  of four minutes or more show a generation rate about a factor ten larger than those samples that had received a short POA. Again, no transition regime was found.

For the sample with a 20 min. POA in Ar we also studied the generation of interface traps. The result is shown in figure 7. For this specimen the data reveal a low generation rate. The Ar anneal did not notably change the susceptibility of the system towards interface state generation, in contrast to an equally long POA in  $N_2$ .

In figure 8 we have made a comparison of the PA and the VUV data. One should note that we have used here  $S_{\text{min}}$  instead of  $S_{\text{border}}$  for representing the PA data, however, this

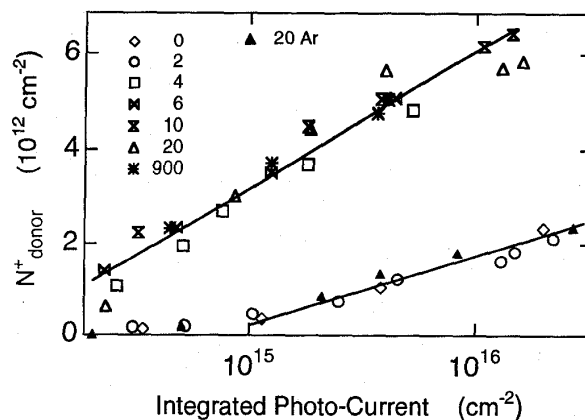


Figure 7. Density of VUV-induced interface traps above midgap versus the exposure. The oxides had received POA in  $N_2$  or in Ar. The POA times are indicated in the figure in minutes.

does not affect the observations. The number of interface traps generated by VUV exposure of  $5 \times 10^{15}$  photons  $\text{cm}^{-2}$  is plotted as function of POA time in  $N_2$  together with the  $S_{\text{min}}$ . As can be seen, interface state generation and  $S_{\text{min}}$  are correlated. Recalling the experiments on specimens with a 20 min. POA in Ar, large  $S_{\text{min}}$  and small generation rate, one should note that this result perfectly fits the correlation.

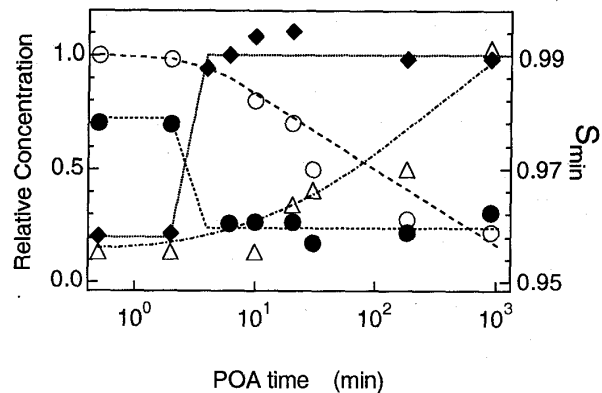


Figure 8. Evolution with POA time of  $S_{\text{min}}$  ( $\bullet$ ), interface traps produced upon VUV irradiation ( $\blacklozenge$ ), O vacancy-related hole traps ( $\Delta$ ), interface traps in the as-grown oxide ( $P_b$ ,  $\circ$ ). The right-hand axis applies to  $S_{\text{min}}$  whereas the opposite scale denotes the relative concentrations of defects. The maximum values are:  $5 \times 10^{12} \text{cm}^{-2}$  for interface traps generated upon a VUV dose of  $\approx 4 \times 10^{15}$  photons  $\text{cm}^{-2}$ ;  $9 \times 10^{12} \text{cm}^{-2}$  for the O vacancies; and  $5 \times 10^{11} \text{cm}^{-2}$  for interface traps in as-grown capacitors.

Although the data reveal a clear correlation between  $S_{\min}$  and interface trap generation, it is important to verify whether the sites measured with PA could not also be associated with point defects in the as-fabricated Si/SiO<sub>2</sub> system. The results of these measurements are shown in figure 8. The effect of POA in N<sub>2</sub> can be summarized as follows: Bulk oxide electron trapping centers show no dependence at all. For this reason these data are not shown in figure 8. The number of the as-grown interface traps associated with trivalent Si or P<sub>b</sub> centers [22], established on capacitors without PMA, decreases continuously with POA time. The density of hole traps with large cross section ( $\approx 3 \times 10^{-14} \text{ cm}^2$ ) increases gradually with the anneal time. This latter large cross section hole trap has been attributed to near-interfacial O vacancies, which after hole capture produce the well-known E' $\gamma$  signal [5]. Apparently, none of these defects shows a correlation with  $S_{\min}$ .

Comparing the results of figure 8 with the data from the electrical measurements presented by Warren et al. for metal gate systems with and without POA in N<sub>2</sub> at 1000°C, it appears that our results are qualitatively the same: they too found a strong enhancement of the susceptibility for the generation of interface traps and positive charging of the bulk oxide when applying POA [3,4].

Also for the sample subjected to the 20 min POA in Ar we have measured the trap densities; the specimen contained  $\approx 3.5 \times 10^{12} \text{ cm}^{-2}$  hole traps with  $\sigma \approx 3 \times 10^{-14} \text{ cm}^2$  and  $\approx 2 \times 10^{11} \text{ cm}^{-2}$  interface states. Within experimental error these data agree with the numbers obtained for a sample subjected to a 20 min POA in N<sub>2</sub>. Apparently the evolution with POA time of the O vacancies and that of the as-grown interface states does not depend on the annealing ambient, in contrast to the susceptibility for the generation of interface traps and the positron trapping centers.

## V. DISCUSSION

As shown in section III, at the positive bias condition, the positrons implanted into the middle of the oxide layer provide information on the oxide border region close to the Si substrate. From the PA measurements it follows that POA in N<sub>2</sub> removes certain positron traps located in this region and that their removal only correlates with an enhancement of the susceptibility of the system for the generation of interface traps.

For metals and semiconductors it has been well established that the positrons are trapped by defects such as vacancies or clusters of vacancies [18,19]. However, for the less studied SiO<sub>2</sub> layers the nature of the positron traps is still an open question. Work of Uedono et al. [23] has convincingly shown that positron annihilation at the SiO<sub>2</sub> border region is not preceded by the formation of positronium, that is, a bound electron-positron pair, which shows that the positron traps have a diameter of less than 1nm [20]. Our PA data agree with theirs and therefore we can safely assume that also in our

samples the positrons are captured at sites smaller than 1nm. Furthermore, the data presented in figure 8 exclude the possibility that the positrons are captured by the O vacancies, hydroxyl groups or Si dangling bonds; these centers constitute the most important point defects in the Si/SiO<sub>2</sub> system as identified thus far. In our opinion, it is unlikely that there are other structural and compositional defects in the Si/SiO<sub>2</sub> system. However, thermally grown vitreous SiO<sub>2</sub> has a chemically saturated but very open network structure. Conceivably, the positrons are easily accommodated by the regular open spaces between the network atoms, the interstices. These interstices are interconnected by narrower openings (bottlenecks), thereby forming channels. Thus, most likely the thermalized positrons would not be really trapped in the interstices because they would be able to move from the one interstice to the other through the bottlenecks. When applying a positive bias, the positrons are driven towards the Si substrate. At the interface they are confined in one dimension by the triangular potential well but they will be still able to laterally move around, in search of a trapping site. Because of the flexible nature of the oxide network, the interstices will have a certain size-distribution. The Si substrate, to which the network is tied-up, could broaden this size distribution. Unable to escape from the triangular potential well, the positrons would become ultimately trapped by the larger near-interfacial network interstices.

In section III, it was argued that at the proper positive bias conditions, most of the positrons are collected in the oxide border region. This, however, does not exclude the possible presence of two or more positron traps, say A and B, in this region. The positron trapping probability for the A and B type centers ( $p_A$  and  $p_B$ ) is given by the product of their respective concentrations ( $C_A$  and  $C_B$ ) and capture cross sections ( $\sigma_A$  and  $\sigma_B$ ) [24]:

$$p_A = \frac{\sigma_A C_A}{\sigma_A C_A + \sigma_B C_B} \quad (2a)$$

and

$$p_B = \frac{\sigma_B C_B}{\sigma_A C_A + \sigma_B C_B} \quad (2b)$$

The shape of the  $\gamma$ -peak is determined by the contributions of each of the positron trapping centers. The shift observed in figure 6, thus has to be explained in terms of a change of the concentration of the dominant sites. The decrease in  $S_{\text{border}}$  and the increase in  $W_{\text{border}}$  after POA in N<sub>2</sub>, suggests that after annealing the mean size of the interstices at the interface has decreased. Subsequently, trapping is governed by those interstices with smaller volume.

The decrease of  $S_{\text{border}}$ , shown in figure 6, indicates that positron trapping sites with a larger volume are removed when applying POA of four minutes in N<sub>2</sub>. This 4 minutes period roughly corresponds to the typical time constant for the refreshment of the ambient of the furnace. Because of this we believe that this 4 minute limit only shows that already a (very) short exposure of the grown oxide at a temperature of 1000°C to N<sub>2</sub> substantially alters the structural properties of oxide network bordering the Si substrate.

POA in Ar did not remove the larger interstices in the oxide border region. This illustrates that the structural change is element specific. A straightforward explanation would be that nitrogen is chemically incorporated. However, in the case of such a chemical incorporation, which is easily accomplished by an anneal in ammonia or  $N_2O$ , we would expect a suppression of the generation of interface traps, and not an enhancement as presently observed [25]. Another explanation would be that larger interstices near the Si/SiO<sub>2</sub> interface are filled with  $N_2$  molecules which would reduce the trapping probability for the positrons. However, this does not immediately explain our main observation regarding the correlation between  $S_{min}$  and interface trap generation.

As stated before, Warren et al. observed for the metal gate MOS system a strong enhancement of the susceptibility for the generation of interface traps and positive charging of the bulk oxide when applying POA [3,4]. Both effects were attributed to the creation of O vacancies due to the out-diffusion of O atoms from the oxide network into the Si substrate. Our data also reveal an enhancement of both effects when applying POA, in agreement with the data of the aforementioned authors; however, the abrupt increase of the interface trap generation rate does not correlate with the more gradual development of the areal density of O vacancies. Moreover, in the case of the Ar annealed samples, the results indicate that O vacancies are still created but without affecting the generation rate of interface traps. Apparently we can not ascribe the enhanced interface trap generation rate to the formation of O vacancies, as proposed by Warren et al [3,4].

It has been well established that in the case of Al gated systems atomic hydrogen plays a major role in the generation of interface traps. One mechanism for their production is the depassivation of substrate trivalent Si centers [16]. However, recent studies have also revealed the existence of another type of defect, the so-called donor interface trap which has been associated with the presence of hydrogen atoms in the proximity of the Si/SiO<sub>2</sub> interface [12,14-16]. It has been proposed that the H atoms are weakly bonded at bridging O atoms in a strained situation close to this interface. The whole configuration would constitute a localized electronic state with an energy level within the forbidden bandgap of Si. Earlier work of our group has clearly shown that VUV irradiation produces predominantly large numbers of such donor traps [12].

In the present case we used 105 nm thick oxides for our experiments. The penetration depth of 10 eV photons is approximately 10 nm [13], thus excluding the possibility that the H-induced interface traps are produced by a direct action of photons, for example by direct cracking of  $H_2$ . Instead, a mobile intermediate is needed to bridge the distance between the point where the photon is absorbed and the Si/SiO<sub>2</sub> interface. The absorption of the photon takes place by the generation of an electron-hole pair, most likely bonded as an exciton. During the irradiation an electric field of  $-1MV\ cm^{-1}$  was applied. Thus, it appears that only a mobile neutral species could take care of the transport. Atomic H itself will play such a role; it is well established that such H is released

from the SiO<sub>2</sub>/Al interface by the interaction of the radiation-induced charge carriers and that such H can migrate through the oxide. However, excitons are also a possible candidate for this role. Upon arrival at the Si/SiO<sub>2</sub> interface such excitons could crack  $H_2$ .

Both the H atoms and excitons are rather unstable species; in both cases their numbers may be strongly reduced during transport through the oxide layer: excitons may recombine and atomic H may dimerize when meeting another H. Because of their metastable nature, the transport of both species and the probability of arriving at the Si/SiO<sub>2</sub> interface will be strongly affected by the presence of sites in the oxide layer that could trap such species.

If we ascribe the positron traps with large  $S_{min}$  to relatively large interstices in the oxide network in the vicinity of the Si substrate that can be filled with  $N_2$  but not with Ar, this would offer also a straightforward explanation for the reduced build-up of interface traps for samples with a short POA in  $N_2$  or an anneal in Ar: The open network spaces would also efficiently trap the metastable intermediate involved in the generation mechanism.

Warren et al. also presented data on the generation rate of border traps, which again is enhanced when applying POA in  $N_2$  [3,4]. According to their opinion, this enhancement is also caused by the creation of O vacancies; however, for the metal gated capacitors in which release of atomic H plays a prominent role, this observation can be alternatively interpreted within our framework of H-induced donor traps. As argued elsewhere, some of the H atoms would be weakly bonded at bridging O atoms in a strained situation further away from the interface; the whole configuration would be observed as a slow state or a border trap [26,27]. Thus the density of such H-related border traps would always track that of the donor-type interface traps. Their enhanced generation when applying POA in  $N_2$  could then be explained by the same mechanism as proposed for the H-induced interface traps.

## VI. CONCLUSION

The results of our study show that PA is a promising technique for the investigation of thermally induced changes of the Si/SiO<sub>2</sub> system, providing information that is not obtained by other experimental methods. Moreover, when implanting the positrons in the middle of the oxide layer and applying a positive bias, it is possible to drive the positrons to the oxide region close to the Si substrate, thus allowing one to focus on positron trapping sites in this region.

For the present case of POA in  $N_2$  at a temperature of 1000°C, the PA data show that such an anneal removes sites with a large  $S_{min}$  located in the oxide close to the substrate. Their removal is correlated with an enhanced generation of interface traps upon VUV irradiation. Apparently, the positron trapping sites are actively involved in the suppression of the generation of interface traps by trapping and removing mobile intermediates such as atomic H or excitons. The association of

the positron trapping sites with relatively large network interstices would fit with this explanation.

Although we have no direct evidence, we believe that the observed correlation between  $S_{\min}$  and interface state generation, which requires the transport of a metastable intermediate, supports the association of the positron traps with regular but relatively large oxide network interstices.

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