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J. Phys.: Condens. Matter **9** (1997) 2947–2954. Printed in the UK PII: S0953-8984(97)77047-4

Investigation of the transition region between SiO_2 layers wet grown at 700 °C and Si

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Received 9 August 1996, in final form 10 February 1997

Abstract. Silicon oxide layers wet grown at 700 °C on silicon substrates of integrated circuit quality have been investigated by slow-positron-implantation spectroscopy and Auger electron spectroscopy. The total thickness of pure SiO_2 on top of a SiO_2/Si transition zone is determined by ellipsometric measurements; the positron/Auger results indicate that the transition zone extends over 15–23 nm. Its thickness decreases as the SiO_2 layer is thinned by a wet-chemical process at room temperature. The results are consistent with earlier secondary-neutral mass spectroscopy measurements.

1. Introduction

It is desirable that modern semiconductor devices operate under conditions of minimum power consumption. Of great importance in this context is the quality of interfaces, for example between SiO_2 and a Si substrate. This paper describes new investigations into the interface region of SiO_2/Si after wet oxidation at 700 °C.

Even though thermal oxidation of silicon has been one of the basic processes in electronic device fabrication for about 30 years, there remain great uncertainties about the exact nature of the growth mechanisms. Of concern is the transport mechanism for dopants and oxidants as well as their interactions at various interfaces. The thickness of the transition region has generally been assumed to be several atomic layers; in earlier positron measurements it has been fixed at 1 nm [1–3]. Investigations using x-ray diffraction techniques have also pointed to thin transition regions of between 1 and 2 nm [4]. In contrast, depth profiling of oxygen and silicon (by secondary-neutral mass spectroscopy, SNMS) has indicated thicker transition regions [5]. For discussion of other techniques used to study transition regions the reader is referred to review papers [6, 7].

Using infrared spectroscopy (IRS), the vibrational frequency of the TD_3 stretching mode was measured for SiO_2 layers thermally grown on Si substrates at 700 °C in steam to a thickness of about 120 nm. Subsequent wet-chemical thinning at room temperature to about 30 nm markedly reduced the vibrational frequency from 1073 to 1065 cm^{-1}. This shift is due to changes in Si atom spacing and also in the oxidation conditions, which influence the

elasticity of the SiO_2 layer and the hydrogen distribution therein. The result is believed to indicate a densification of the SiO_2 layer remaining after the wet-chemical etching process is complete [8]. For a discussion of IRS studies of density variations of layers produced by dry oxidation at various temperatures see reference [5].

In general, there is no clear and uniform definition of the SiO_2/Si transition zone which is independent of experimental method. The present paper describes the performance of positron implantation spectroscopy in conjunction with oxygen and silicon depth profile determination by Auger electron spectroscopy (AES) in order to estimate thicknesses of this transition zone for different layers produced by wet oxidation on Si. This is regarded as a first but essential step towards a more precise determination of the nature of the transition, which has been discussed in structural, chemical, and electrical terms [5–7].

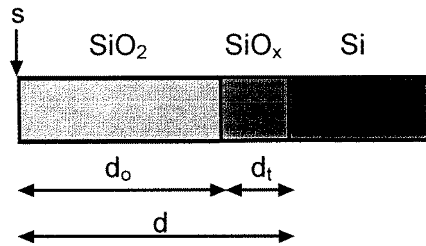

Figure 1. The layer structure of SiO_2/Si.

2. Experimental method

2.1. Sample preparation

A boron-doped Czochralski grown Si(100) wafer of 100 mm diameter and with a specific electrical resistivity between 15 and 25 Ω cm (integrated circuit (IC) quality) was cleaned by the standard RCA procedure. Thermal oxidation was performed in steam at 700 °C for 16 h. The oxidation process produced an oxide surface layer of about 90 nm thickness. Subsequently, the oxide layer on the back of the wafer was chemically removed and the wafer then divided into three parts. Using an aqueous Merck solution containing 6.5% HF and 34.8% NH_4F the oxide layers of two of them were thinned at room temperature to 63 nm and 29 nm. Finally, the three parts were further divided in order to produce identical specimens for positron and AES measurements. The layer structure of the samples is illustrated in figure 1; the total thickness of the pure SiO_2 layer plus the SiO_2/Si transition region was measured by ellipsometry.

2.2. Positron implantation measurements

Slow-positron-implantation spectroscopy was performed on the University of East Anglia computer-controlled positron beam system. Positrons of predetermined energies E are implanted at depths of up to a few μm in the sample under study [9]. The motion of positron–electron pairs prior to annihilation causes a Doppler broadening of the photopeak in the measured energy spectrum of the annihilation photons. This Doppler broadening is characterized by the lineshape parameter S, which is the ratio of the number of counts in the central region of the photopeak to the total number of counts in the peak ($\sim$0.5). The

measured value of S at each energy E is thus

$$S(E) = S_s F_s(E) + S_e F_e(E) + S_o F_o(E) + S_t F_t(E) + S_{Si} F_{Si}(E) \quad (1)$$

where S_s, S_o, S_t, and S_{Si} are the S-parameters associated with annihilation with electrons at the surface and in the oxide layer, transition zone, and bulk Si, respectively, and S_e is associated with the annihilation of epithermal positrons. The $F(E)$ are the fractions of the total number of positrons annihilated in each state; thus $\sum F_n = 1$ for each E.

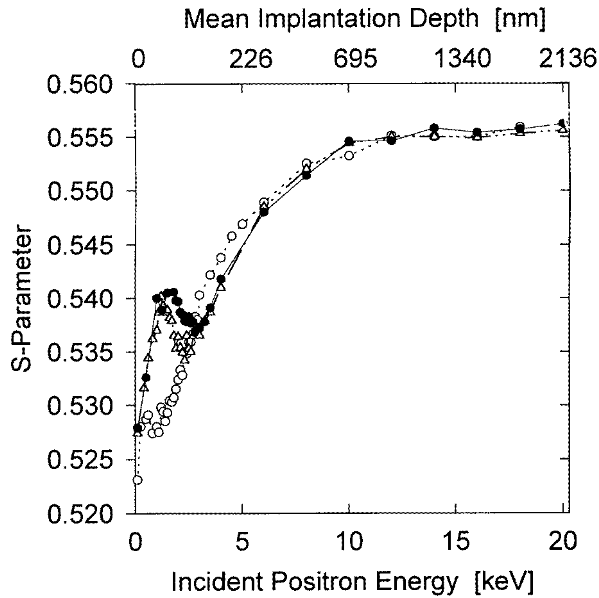

Figure 2. The annihilation lineshape parameter S versus incident positron energy E for samples with oxide layers of thicknesses 28 nm (○), 68 nm (△), and 89 nm (●).

Typical results for $S(E)$ measured for samples with different oxide layer thicknesses are shown in figure 2.

The data were analysed using the computer code 'VEPFIT' [10]. A reasonable fit could only be achieved when the transition zone thickness d_t was a free parameter—i.e., not fixed, as in references [2] and [3]. The magnitude of d_t is reflected in the value of F_t for each E.

The values of S_o, S_t, and S_{Si} were evaluated by fitting a three-layer model to $S(E)$ for sample 35, and fixed to these results in all further evaluations. The value of S_s was taken from the measured S-value at $E = 100$ eV. The positron diffusion lengths in the oxide layer and transition region were assumed to be 9.5 nm [3] and 0.01 nm (i.e., essentially zero) [11], respectively. A positron diffusion length L_+ of 100 ± 2 nm for bulk Si was obtained by fitting $S(E)$ for a sample covered with a very thin oxide layer (a few nm only). Furthermore, values of d(ell) were used to fix the total thickness of oxide + transition layers, in order to reduce the number of free fitting parameters. As an example, figure 3 shows the measured $S(E)$ for sample 35 and the fitted curve.

A similar procedure can be used to fit $W(E)$, where W is a second lineshape parameter, defined as the ratio of the number of counts in the wing regions of the annihilation gamma photopeak to the total number of counts in the peak. In principle $W(E)$ should yield the same information as $S(E)$. Although $W(E)$ does not show such sharp structure at low

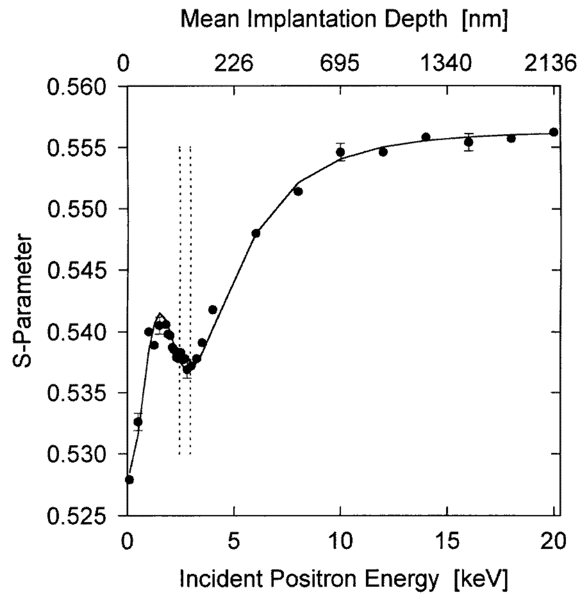

Figure 3. The annihilation shape parameter S versus positron energy E for sample 35. The solid line represents the fit obtained using VEPFIT. The dotted lines mark the values of E which correspond to mean positron implantation depths equal to the boundaries of the SiO_2/Si transition region.

energies as does $S(E)$, the percentage change in W as a function of E is about two times larger than that for S. A typical W-parameter curve is shown in figure 4.

2.3. AES measurements

The AES was carried out using a Fisons field-emission scanning Auger microprobe MICROLAB 310-F. The primary electrons have an energy of 10 keV and a sample current of about 10 nA. The Si(LVV), Si(KLL), and O(KLL) Auger peaks were detected in the direct mode by a hemispherical sector analyser. Sputter depth profiling was performed with a 3 keV Ar^+-ion gun and a current density of about 1 μA mm^{-2}, leading to a sputtering rate of about 0.33 nm s^{-1}. The sputtering rate itself was estimated by mechanical measurement of the sputtering crater after the profiling measurement using a DEKTAK profilometer. During sputtering the sample was rotated to minimize surface roughening and to maximize the depth resolution [12, 13].

It is well known that both Si Auger peaks are very sensitive to oxide bonding. The shapes and energies of the peaks are different for atomic and oxidized Si [14, 15], and this can be used to identify the Si bonding states. For this reason the Si(LVV) Auger peak at 92 eV was detected with an energy resolution of 0.2% while the Si(KLL) Auger peak at 1616.6 eV was measured with an energy resolution of 0.05%. The latter peak moves to 1608 eV while the first one changes its shape completely if the Si is oxidized. For depth profiling purposes the O(KLL) Auger peak was used and the Si(KLL) Auger peak was separated into two regions, the first at around 1608 eV to be ascribed to oxidized Si and the second at around 1616 eV to be ascribed to the atomic Si.

In figure 5 the Si(KLL) Auger peak of sample 24 is displayed for every sputtering step

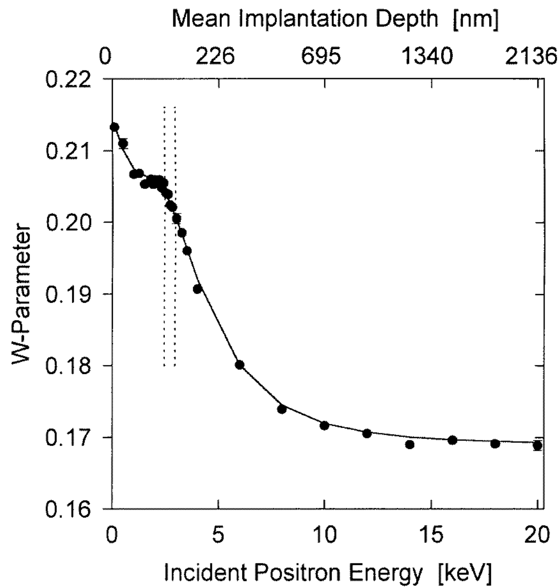

Figure 4. The annihilation lineshape parameter W versus positron energy E for sample 35. The solid line represents the fit obtained using VEPFIT. The dotted lines mark the boundary of the SiO_2/Si transition region, as in figure 3.

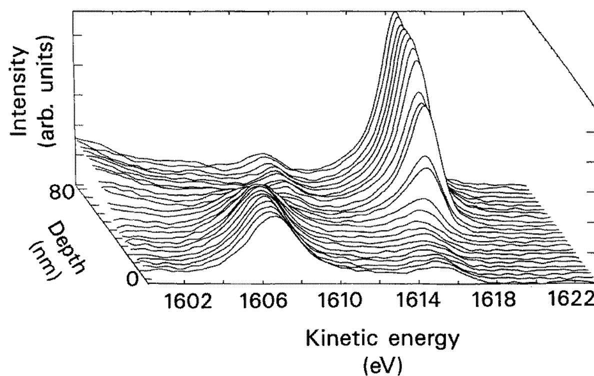

Figure 5. A 3D plot of the Si(KLL) Auger peak measured for every sputtering step for sample 24. The time axis points into the plane of the figure. At the beginning of the measurement the peak associated with oxidized Si is dominant ($E_{kin} = 1608$ eV). At the end of the measurement, at depths below the transition region, the peak is at 1616 eV, indicating atomic Si.

as a 3D plot, with the time axis pointing into the plane of the figure. The resulting depth profile is shown in figure 6. In the transition region between SiO_2 and Si several steps were detected. The thickness of the transition range was estimated to be 23 ± 5 nm using the procedure described in reference [16]; the same value was obtained if the Si(LVV) Auger peak was used. This value is somewhat larger than that determined by other methods. A possible explanation is that no deconvolution of the experimental data was performed to allow for the physical resolution ($\sim$2 nm here) or smearing due to the time duration of

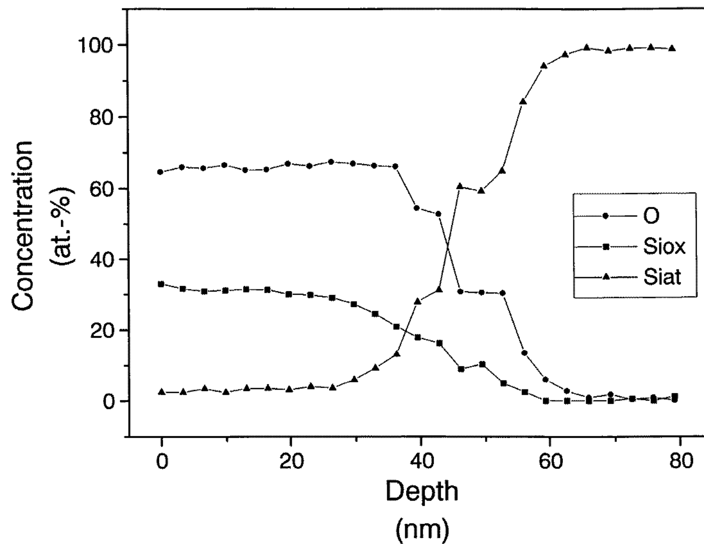

Figure 6. AES depth profiles of sample 24. ●: oxygen; ■: oxidized Si (Siox); and △: atomic Si (Siat).

the sputtering steps (10 s corresponds to 3.3 nm). Deconvolution would lead to profile sharpening [17].

Applying the same procedure to samples 12, 13, and 35, transition layer thicknesses of 10, 9, and 21 nm (all ±5 nm) were measured, respectively. Steps were detected in the depth profiles of samples 25 and 35, and possibly for sample 32, but no steps were seen in the results for samples 12 and 13, where the layer thicknesses were probably too small for us to resolve them.

3. Results

The measurement of simple parameters such as S and W yields important information about open-volume-type defects. The absolute values of the two parameters have little physical relevance, but it is possible to normalize the parameters in order to allow comparisons between different samples and different experimental arrangements to be made. Furthermore, S- and W-values reflect the average momentum of the electrons which the positrons annihilate. The annihilation peak is narrow (S is high, W is low) if the positrons annihilate predominantly slow-moving electrons, as in case of valence electrons or electrons from the bound-positron–electron state (positronium, Ps). The latter has been suggested as an explanation for the shape of $S(E)$ for SiO_2 on Si [3]; the relatively high S-values at low E are caused by Ps formation in the dioxide layer, and the subsequent decrease by the inhibition of Ps formation in the SiO_2/Si transition region. These effects are reflected in distinct changes in $S(E)$, in contrast to the relatively flat $W(E)$ (figures 3 and 4). For this reason the VEPFIT fitting was performed using the S-parameter data only; fits to $W(E)$ simply confirmed the results obtained using $S(E)$.

It is remarkable that for all of the specimens the mean positron implantation depths corresponding to the values of E at the local minima in $S(E)$ correspond well to the depths obtained by summing the thicknesses of the SiO_2 layers and the transition regions.

Table 1. Row 1: the total thickness d(ell) of the oxide + transition layers on Si, determined by ellipsometry. Row 2: the SiO_2 thickness d_o(pos) determined by positron spectroscopy. Row 3: the transition region thickness d_t(pos) determined as $d(\text{ell}) - d_o(\text{pos})$. Row 4: the transition zone thickness d_t(AES) determined by AES. Uncertainties are shown in parentheses.

	Group 1			Group 2			Group 3	
Sample	12	13	15	22	23	24	32	35
d(ell) (nm)	26.97 (0.68)	29.70 (0.71)	29.42 (0.67)	63.15 (0.32)	62.86 (0.39)	63.71 (0.16)	88.41 (0.16)	89.06 (0.23)
d_o(pos) (nm)	12(1)	—	12(1)	47(1)	46(1)	—	68(2)	66(1)
d_t(pos) (nm)	15(2)	—	17(2)	16(2)	17(2)	—	20(3)	23(2)
d_t(AES) (nm)	10(5)	9(5)	—	—	—	23(5)	—	21(5)

The results of the VEPFIT fits and AES measurements of layer thicknesses are shown in table 1, along with the total oxide layer thicknesses (i.e., SiO_2 + transition layer), determined by ellipsometry at five different positions on each sample. The results obtained both by positron implantation and by AES indicate the existence of an extensive transition region between the SiO_2 and the bulk Si substrate. It is characterized by a decrease in the oxygen concentration as a function of depth, so several Si suboxides exist in the region. The thicknesses of the transition regions obtained by the two methods are much higher than those reported in earlier papers describing positron studies of similar systems [1–3].

The thickness of the transition region depends on the thickness of the SiO_2 layer remaining after wet-chemical thinning at room temperature. However, to establish a clear dependence further comprehensive investigations are required.

An unexpected effect was observed by remeasurement of a sample covered with an 88 nm oxide layer. The repeated measurement, performed one year later, showed that the SiO_2/Si transition zone widened from 23 nm to 42 ± 4 nm in the direction towards the oxide layer. Additional investigations are required in order to understand this ageing behaviour, which could have important consequences for the physical properties of the SiO_2/Si system.

4. Conclusions and summary

SiO_2 layers thermally grown on boron-doped Si substrates of IC quality were investigated by slow-positron-beam implantation and AES. The results obtained by positron and AES measurements are in a good agreement. It could be shown that the transition region between SiO_2 and Si extends beyond a few atomic monolayers. The thickness of the zone seems to increase with increasing SiO_2 layer thickness, as already discussed in reference [5]. Further investigations are necessary to quantify this result.

The difference between the positron diffusion lengths of the different layers reflects the defect structure. The very short diffusion length in the transition region points to the presence of a large number of defects which are able to trap positrons, or of an electrical field. Only measurements done at elevated temperatures could rule out the influence of built-in electrical fields. Such studies need to be done in the future.

Furthermore, ageing effects on the nature and extent of the transition zone may influence the physical properties of SiO_2-coated Si; these should also be investigated further.

In the first measurements presented here only broad conclusions can be drawn about wet-grown SiO_2 on Si substrates and about the distinct zones within the structure. Further

investigations are needed, especially to elucidate the structure of the transition region. Whereas positron annihilation spectroscopy is sensitive to the defect structure in the material, AES can be used to detect modifications of the chemical bonding of the atoms as a function of depth. The results of the positron and AES measurements agree qualitatively with those from SNMS measurements [5]. Together, the two methods can obtain more information about the SiO_2/Si system and its transition region.

Acknowledgments

The careful sample preparation and the planning and coordination of measurements by colleagues at the Technology Laboratory of the Institute of Microelectronics and Solid State Electronics of the Technical University of Berlin are gratefully acknowledged.

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