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Positron implantation studies of oxygen in p^+-silicon epilayers

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Abstract. The Doppler broadening of radiation from the annihilation of positrons in p^+-silicon epilayers 1 and 0.4 μm thick epitaxially grown at different temperatures has been measured. The signal from positrons decaying within the epilayers is enhanced at the expense of any significant contribution from surface annihilation, enabling direct measurement of the Doppler lineshape parameter S characteristic of the epilayers. The epilayer S-value is observed to decrease for samples grown at temperatures below 700 °C, for which the expected concentration of oxygen defects increases. The correlation between S and oxygen concentration is interpreted in terms of (a) transition-limited trapping by atomic oxygen defects and (b) diffusion-limited trapping by SiO_x precipitates. The former is consistent with secondary-ion mass spectrometry measurements if the specific trapping rate is reduced to at least half of the value quoted by earlier researchers; the latter implies that the results are consistent with the formation of $SiO_{1.75}$ precipitates of mean radius 3.2 ± 0.7 nm.

1. Introduction

Many techniques have been applied to the study of oxygen, the dominant impurity, in silicon. These include infrared spectrometry, electrical methods, x-ray diffraction, secondary-ion mass spectrometry (SIMS) and activation analysis. In this communication the sensitivity of response of low-energy positrons implanted into silicon epilayers to the presence of oxygen defects is examined.

The potential of the positron as a subsurface probe has been demonstrated on many occasions during the last decade (Schultz and Lynn 1988). The technique has been applied to probe the depth profile of near-surface defects in metals (Bentzon *et al* 1987) and, more recently, in semiconductors (Tandberg *et al* 1989). In the latter case, the charged positron is particularly suitable for probing the charge states of the defects present, although the interpretation of data is unavoidably more complex than in metals.

2. Experimental method

The basic features of the University of East Anglia (UEA) positron beam system were described by Hutchins *et al* (1985). A ^{22}Na source–annealed tungsten mesh moderator assembly provides approximately 10^5 slow positrons per second in a magnetically guided beam 10 mm in diameter with initially energies of up to 2.6 eV. These positrons are accelerated to the desired energy (from 0.5 to 30 keV) prior to implantation in the

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Table 1. Characteristics of the four samples used in the current measurements. See text for further details.

Sample number	p^+ epilayer thickness (μm)	Growth temperature (°C)	N_O (SIMS) (cm^{-3})
1	1.0	715	< Limit
2	1.0	645	8×10^{17}
3	1.0	590	2×10^{18}
4	0.4	550	5×10^{19}

sample target. The system is pumped by a turbomolecular pump to pressures below 10^{-6} Pa.

On implantation the positrons are rapidly thermalized; their depth profile can be approximated to a gaussian derivative (Valkealahti and Nieminen 1984). Further experimental and theoretical work is currently under way to UEA to test the validity of this assumption. The thermal positron can then diffuse through the sample—perhaps under the influence of internal electric fields—until, after times of the order of 10^2 ps, it is annihilated by an electron in the sample. The measured energy of the annihilation γ-ray is Doppler shifted by the momentum of the electron–positron pair, provided essentially by the electron. When a large number of decay γ-rays is detected by a high-resolution Ge detector, the observed annihilation line is broadened to an extent described by the shape parameter S, defined as the ratio of the area of the central section of the annihilation photopeak to the total area (the limits of the central region chosen so that S is approximately 0.5). Thus, the higher the value of S, the narrower the linewidth and the lower the average momentum of electrons involved in annihilation events.

In the measurements described below, the measured S parameter is a linear combination of contributions from all possible annihilation states in the sample (Baker and Coleman 1989):

$$S = \sum_i f_i S_i \qquad (1)$$

where f_i are the fractions of positrons annihilated in the given state i (and so $\Sigma_i f_i = 1$).

Samples of p^+-Si layers grown on Czochralski (Cz) substrates of n^+-Si(001) by a VG Semicon V80 MBE system were provided by British Telecom Research Laboratories (BTRL), Martlesham Heath, Ipswich, UK. Characterization of the samples had been performed using SIMS and electrical measurements.

The doping source used in the growth was boric oxide (B_2O_3) evaporated from a standard Knudsen cell. de Frésart *et al* (1986) reported a critical growth temperature for MBE-grown B_2O_3 doped layers, above which no oxygen remains in the sample after subsequent cooling and below which layers may be grown in which the oxygen content may be controlled by the growth temperature.

The oxygen concentrations in each of the four samples studied in the current experiment are different, corresponding to their different growth temperatures. The important characteristics of the samples are shown in table 1. For sample 1, Gibbings and Tuppen (1988) found the oxygen concentration to be lower than their SIMS detection limit. Samples 1–3 are of identical morphology, with the p^+ epilayers being laid down

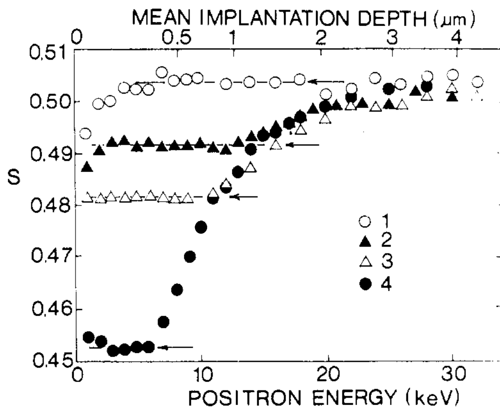

Figure 1. Doppler-broadened lineshape parameters S measured for samples 1–4 as a function of positron implantation energy. The mean implantation depths shown are calculated using $\bar{x} = 0.0172E^{1.6}$ μm, where E is in kiloelectronvolts; this assumes a gaussian derivative implantation profile.

on an undoped-Si buffer layer 0.1 μm thick above the Cz Si substrate; the only difference between them is their respective growth temperatures. In contrast, sample 4 has an epilayer of 0.4 μm thickness and higher doping levels; it also has an interfacial layer of p-type material 0.4 μm thick.

By electrical measurements on the samples, Tuppen *et al* (1988) established that boron was present in the epilayer in an electrically active form, thereby indicating that it was not present as B_2O_3. Samples 2–4 all have an oxygen content in excess of the solid solubility limit (Itoh and Nozaki 1985); so the precise form in which oxygen remains in the epilayers is a matter for discussion. While relatively high concentrations of interstitial atomic oxygen are known to exist in Si systems (e.g. melt-grown Cz Si), it has to be noted that, when the oxygen content is far in excess of the solid solubility limit, it has been observed (Jaussand *et al* 1985, Kim *et al* 1983) that microprecipitates of the form SiO_x (where x lies in the range 1.5–2) are produced. These microprecipitates have been found to be less than 10 nm diameter and, in heat-treated Cz silicon, polyhedral precipitates have been observed (Ponce *et al* 1983) with typical diameters of 15 nm.

Positron trapping at oxygen clusters will occur (Dannefaer and Kerr 1986) giving rise to a different S-parameter from that found in other (open-volume) defects such as vacancies or voids.

3. Results

Using the technique described above, the mean S-parameter was measured for each of the four samples as a function of positron implantation energy (refer to equation (1)). The resulting data are shown in figure 1. Mean implantation depths for positrons in silicon are also shown as a guide.

A value of 0.503 was deduced for the S-parameter S_B for bulk silicon, and this was used for all four samples; Coleman *et al* (1990) found the bulk S-parameter for Cz n^+-, n^-, p^+- and p^--Si(001) to be independent of the doping level. This is also the S-value for the epilayer of sample 1 (see figure 1), and in the discussions which follow it is assumed that, although there may be some oxygen present in the substrates and in the sample 1 epilayer, its concentration is not sufficient to cause appreciable trapping. Even if it were true that there was the same small trapping probability in the substrates and sample 1

epilayer, the interpretations below are still valid in terms of the *additional* trapping due to the *extra* oxygen sites left in epilayers 2, 3 and 4 at lower growth temperatures.

In order to account for the abrupt change in the gradient of $S(E)$ at the interface we must invoke a very low S-parameter there. This may result from positron trapping at boron sites; Kubiak *et al* (1986) have shown that the concentration of boron at an interface can be much higher than in bulk planes.

The most interesting feature of the results is the approximate constancy of S over the range of energies corresponding to the depth of the epilayer. This observation, only recorded for p^+-silicon (Coleman *et al* 1990), indicates that at energies above 3 keV a negligible fraction of the implanted positrons is diffusing to and annihilating at the surface of the samples. The explanation favoured by Coleman *et al* is that the electric field present at the surface—owing to the reduction in the occupation of surface electron states and the resultant band bending—prevents diffusing thermal energy positrons from reaching the surface, turning them back instead into the epilayer where they are eventually annihilated. The field strength, estimated to be about 5×10^6 V m^{-1} acting over 20 nm, is strong enough to act in this way, as demonstrated by the calculations of Tandberg *et al* (1989).

Alternative models are less successful in explaining the constancy of S. For example, that in which the boron dopant acts as a shallow trap (as B^-) was discounted experimentally by Coleman *et al* (1990). A second possibility is presented by the suggestion of Mascher *et al* (1989) that oxygen–vacancy complexes can act as shallow traps. However, one would not expect that these would be present at room temperature in sufficient numbers to trap all the positrons. Thirdly, it may be that positrons are being trapped and annihilated in boron–vacancy complexes (Dannefaer *et al* 1989); in sample 1, for example, although the oxygen concentration is below the SIMS detection limit, there are 2×10^{18} B atoms cm^{-3}. However, it is very unlikely that the S-parameter characteristic of a boron–vacancy complex is identical with that of the n^+-Si(001) substrate; for example, one would expect a difference of between 1 and 2% based on the observations of Dannefaer *et al* 1989). Finally, an explanation in which saturation trapping occurs in samples 2–4, but at different types of defect site and hence with different characteristic S-parameters in each sample, is too unrealistic to warrant serious consideration.

4. Discussion

The only major difference between the samples studied is expected to be the oxygen concentration N in the epilayers, with which it is tempting to correlate the different S-values which we deduce directly from figure 1. Schultz *et al* (1988) stress the importance of the ratio of an S-parameter value to S_B, where S_B is characteristic of annihilation in the 'defect-free' bulk material. S/S_B ratios are essentially absolute quantities, as long as S is approximately 0.5, whereas individual S-values are not. For example, a typical S/S_B ratio quoted for oxygen-related defects is approximately 0.93; sample 4 has an epilayer S-value of 0.4525, for which $S/S_B = 0.90$. While the S_B value used herein is valid for the purposes of the analyses described below, it must be remembered that it represents the bulk value for Cz Si and not strictly for defect-free Si (as illustrated by Dannefaer *et al* (1989)). Caution, therefore, is required when quoting and interpreting S/S_B ratios.

In order to try to estimate the concentration of defects in the epilayers we invoke the simple two-state trapping model. We shall consider

(*a*) transition-limited trapping in atomic oxygen defects and
(*b*) diffusion-limited trapping by SiO_x precipitates.

4.1. *Transition-limited trapping*

The measured S-parameter is given by

$$S = f_D S_D + (1 - f_D) S_B \tag{2}$$

where f_D is the fraction of positrons annihilating from defect states in the epilayer, and S_B and S_D are the bulk and defect S-parameters, respectively. The two-state trapping model gives simply

$$f_D = n\nu/(n\nu + \lambda_B) \tag{3}$$

where n is the defect density per Si atom, λ_B is the positron annihilation rate in the bulk and ν is the specific trapping rate. Combining (2) and (3) then yields

$$n = [(S_B - S)/(S - S_D)]\delta(\lambda_B/\nu). \tag{4}$$

If we now take the epilayer S-parameter for sample 4 to be that for 100% trapping in oxygen defects (i.e. 0.4525), and using earlier values for ν (approximately $3 \times 10^{14}\ s^{-1}$ (Schultz *et al* 1988)) and λ_B ($4.55 \times 10^9\ s^{-1}$ (Motoko-Kwete *et al* 1989)), we find from (4) that the concentration of atomic O defects, obtained by multiplying n by the atomic density of Si ($5.0 \times 10^{22}\ cm^{-3}$), is $2.4 \times 10^{17}\ cm^{-3}$ for sample 2 and $5.5 \times 10^{17}\ cm^{-3}$ for sample 3. Both these values are some 3.5 times lower than those quoted from SIMS analysis. However, it must be remembered that SIMS measures only the concentration of *atomic* oxygen. The simple calculation outlined above, for example, would be consistent with the SIMS measurements if the trapping sites contained on average 3.5 oxygen atoms. Alternatively, consistency is achieved if the true atomic oxygen concentration is close to the bottom of the quoted tolerance range and the specific trapping rate is a factor of 2 or 3 lower than the value of $3 \times 10^{14}\ s^{-1}$ chosen above.

The transition-limited trapping model applied above assumes atomic-oxygen-trapping sites. However, in these relatively highly doped samples it is quite possible that large SiO_x precipitates are formed, such as those studied by Tuppen *et al* (1988). Therefore, we turn to a model in which the trapping of positrons by precipitates (with a consequently lower number density) is limited by diffusion.

4.2. *Diffusion-limited trapping*

It has been shown (Eldrup and Jensen 1987) that, when voids and helium bubbles are introduced into bulk aluminium, then diffusion-limited trapping becomes important for voids of diameter 5 nm and greater. In this model a positron which diffuses to a defect site is trapped with 100% probability.

Rather than use the specific trapping rate of $3 \times 10^{14}\ s^{-1}$ referred to above, we now require the total diffusion-limited trapping rate κ, determined by the equation

$$\kappa = 4\pi R D_+ N \tag{5}$$

(Eldrup and Jensen 1987). Here D_+ is the diffusion constant for positrons in bulk silicon, and N the concentration of trapping sites (i.e. precipitates) in cm^{-3}. For this analysis we shall use $D_+ = 2.6\ cm^2\ s^{-1}$, measured by the present authors and others by observing

the diffusion of thermalized positrons to a silicon surface. N is estimated by calculating the number of oxygen atoms in a sphere of radius R containing $SiO_{1.75}$ of density 2.3 g cm^{-3}, and dividing into the total number density N_O of oxygen atoms measured by SIMS (in cm^{-3}). The value of x in SiO_x was taken as 1.75 ± 0.25. Thus

$$N = (5.5 \times 10^{-24})N_O/R^3 \text{ cm}^{-3} \tag{6}$$

and

$$\kappa = (1.8 \times 10^{-22})N_O/R^2 \text{ s}^{-1}. \tag{7}$$

By substituting this expression for κ into equation (4) in place of $n\nu$, and rearranging, one arrives at the following expression linking the precipitate radius R with the atomic oxygen concentration N_O:

$$R = 2.0 \times 10^{-9}[N_O(S - S_D)/(S_B - S)]^{1/2} \text{ nm}. \tag{8}$$

Substituting $N_O = 8 \times 10^{17}$ and 2×10^{18} cm^{-3}, with $S_D = 0.4525$, yields $R = 3.2$ nm for both sample 2 and sample 3. The uncertainty of ± 0.7 nm in these results for R is dominated by the $\pm 40\%$ tolerance in the SIMS measurements of N_O quoted by Tuppen *et al*; the other factors—the statistical uncertainties in the S-values, ± 0.1 cm^2 s^{-1} in D_+ and ± 0.25 in x (SiO_x precipitates)—together contribute only ± 0.1 nm to the overall uncertainty.

There is clearly remarkable agreement between the measured values of R for the two samples. It should be noted that, whereas the uncertainties in the absolute values of R are about $\pm 20\%$, the *relative* uncertainties are probably considerably smaller as, for example, any percentage systematic errors in the SIMS estimates of N_O are likely to be the same for both samples. The results imply that there are, on average, approximately 6000 oxygen atoms in each precipitate. The concentration N of precipitates calculated using equation (6) is 1.3×10^{14} cm^{-3} for sample 2 and 3.4×10^{14} cm^{-3} for sample 3; that is, as N_O increases, the precipitates do not grow larger than about 3 nm radius but instead increase in number density. Note that a positron is, on average, within 100 nm of a precipitate; this is approximately half the positron diffusion length in silicon, and the application of the diffusion-limited trapping model is justified. A final check on self-consistency is made by finding that the trapping rate κ for example 4 is given by equation (7) to be about 10^{11} s^{-1} (using $R = 3.2$ nm), so that the fraction $(\kappa/(\kappa + \lambda_B))$ trapped in precipitates for this sample is 96%. Therefore, the assumptions that there is essentially saturation trapping in sample 4 and that the measured S is equal to that characteristic of a trapped positron (S_D) are upheld.

5. Conclusions

Precise direct measurements of the Doppler broadening parameter S for positrons in MBE-grown silicon epilayers a micron thick doped with B_2O_3 have been possible because of the combination of circumstances which maximize the numbers of diffusing positrons annihilated in the epilayers in the p^+ samples. Of the two trapping models considered—transition and diffusion limited—the former is consistent with SIMS measurements only if small clusters form containing on average about three oxygen atoms, or the specific trapping rate used in the analysis is reduced to $(1–1.5) \times 10^{14}$ s^{-1}.

In contrast, the diffusion-limited model leads to the conclusion that the mean radius of $SiO_{1.75}$ precipitates in epilayers grown at temperatures below 700 °C is limited to

3.2 ± 0.7 nm. This value is consistent with TEM and other studies of precipitates in high-dose oxygen-implanted silicon (Tuppen *et al* 1988).

Although both models appear to work reasonably well in interpreting the data in figure 1—and indeed the true situation may involve both atomic and precipitate trapping sites—the present authors are led to favour the diffusion-limited trapping interpretation because of its self-consistency as well as its consistency with observations of near-surface precipitates by other methods.

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