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Positron lifetime studies of defects in MBE-grown silicon

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Abstract. A timed positron beam has been used to study defects in MBE-grown silicon layers previously studied by conventional slow-positron techniques and electron microscopy. An expected void-related positron lifetime component has been observed, but at a much lower intensity than expected from the Doppler-broadening results. The implication is therefore that the momentum of the annihilation positron–electron pair at the void is considerably lower than previously assumed. In the lifetime spectra, there is evidence of a trapped positron state in the overlayers with a lifetime similar to that of a positron freely diffusing in silicon. The nature of this defect is, at present, unclear.

1. Introduction

Molecular beam epitaxy (MBE) has led to an impressive series of achievements in semiconductor physics and device construction because of the ability to engineer the electronic and structural properties of a heterostructure with almost atomic precision [1]. However, progress in silicon MBE has been somewhat slower than that in compound III–V semiconductors because of problems related to the low incorporation and segregation of the dopants. Apart from doping problems, lowering the growth temperature is potentially a simple way of preventing strain-enhanced intermixing at interfaces.

A large proportion of recent work has centred on the attempt to lower the temperature of MBE growth and the resultant breakdown of epitaxy. In simple terms: how hot must the substrate be to achieve a good single-crystalline layer, and how cold to suppress the redistribution of dopant atoms? In several papers [2–4] Jorke *et al* have studied the breakdown of epitaxial growth with respect to deposition rate for both constant and varying substrate temperatures. As the temperature is decreased, or the growth rate increased, the grown layer changes from single crystal through twinned polycrystalline to amorphous. They accurately predicted a limiting thickness for epitaxial growth at constant temperature [4] which has been observed by other researchers in both Si [5] and GaAs [6, 7]. However, in the Si study [5], the intermediate polycrystalline phase was not observed.

In a recent study, using positron annihilation [8, 9] and transmission electron microscopy [9, 10] all three phases in the same sample were observed but the

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breakdown of epitaxy occurred via chains of spherical defects originating from cusps at the growing surface. The defect chains were identified as voids and extended through all three regions. They have also been produced in otherwise epitaxial (100)-oriented single-crystal layers. These layers are the principal object of study in this work.

In the study of point defects, positrons are an ideal probe, being readily trapped at any open volume. The annihilation characteristics, photon momentum and annihilation rate, are extremely sensitive to the local electronic environment at the annihilation site. Among the commercial semiconductors, silicon [11–16], has been characterized extensively using positron techniques and the results are reasonably well understood. Recently slow-positron beams have been applied to the study of layered [17–20] and ion implanted semiconductors [21, 22]. With this method, monoenergetic positrons are implanted into the sample with an assumed energy-dependent depth profile [23]. By measuring at different implantation energies information can be obtained concerning the depth distribution of different defects. Implanted positrons can either diffuse back to the surface or be trapped before annihilating, allowing the fraction of positrons reaching the surface to give an indication of the near surface defect structure in addition to the more usual positron annihilation parameters. Trapped positrons annihilate predominantly with the lower-momentum valence electrons, resulting in a narrower energy spread, caused through Doppler-broadening, of the 511 keV annihilation radiation. As the local electron density is reduced at an open volume defect, trapped positrons tend to live longer than freely diffusing positrons. Additionally, as internal electric fields influence the diffusion of positrons [18, 24, 25], the electrical properties of a structure can, in principle, be examined microscopically.

Annihilation in homogeneous infinite samples leads to exponential decay components (discrete lifetimes) resulting from the different annihilation and trapping probabilities [26]. A rigorous treatment of a beam lifetime experiment requires the solution of the one-dimensional diffusion–annihilation equations [27, 28], but for most purposes discrete lifetimes can be applied, except very near the surface or other discontinuities [28]. However great care must be taken with the interpretation as the contribution from positrons annihilating in the bulk can deviate from the ideal exponential form.

Except for a recent paper on amorphous silicon films [29], all previous positron beam studies on silicon have used the Doppler-broadening of the annihilation line as a measurement signal, whereas bulk studies have tended to concentrate on the positron lifetime. The two measurements are complementary but not necessarily directly correlated. Doppler-broadening samples the local electron momentum density, but the lifetime is a measure of the local electron density. In some cases this complementary information may be essential for the identification of defect–impurity complexes [30]. In this paper we report positron beam lifetime studies, with comparison to Doppler-broadening methods, on different MBE-grown silicon layers as well as on substrate wafers.

2. Experimental details

The layers studied were produced using a VG Semicon V80 MBE system, on (100)-orientated Czochralski-grown silicon substrates rotated at 30 rpm [9, 10]. The

substrate is cleaned in situ prior to growth by heating to in excess of 850 °C under a 0.01 nm s^{-1} Si flux. The two principal samples (Nos 586 and 587) consist of a 5 μm layer of n-type Si (1×10^{17} As cm^{-3}) grown on p-type Cz silicon substrates with a 0.6 μm n-type (2×10^{18} As cm^{-3}) buffer layer. A p-type capping layer (4×10^{18} B cm^{-3}) was etched away before the positron lifetime measurements. The arsenic was introduced during growth by implantation of 1 keV ions using a VG IBD100 ion implanter. Sample 587 was grown at 400 °C, a much lower temperature than 586 (700 °C) and contains the spherical defects aligned along the growth direction. These samples have been extensively studied both by transmission electron microscopy [9] and with slow positrons [8]. Preliminary results with a timed positron beam were also presented at a recent conference [31].

Two other samples, 361 and 394, with good quality 0.35 μm n-type layers grown on n-type Cz Si, but with different substrate–epilayer interface qualities, were also studied to investigate the role of oxygen-associated defects and to allow easier comparison of epilayer and substrate in the same sample. These two layers had also been studied previously using the Doppler-broadening technique [17, 18]. Finally, substrate wafers of different doping type and concentration were also measured for comparison.

Positron lifetime spectra were measured as a function of depth using the pulsed positron beam at Munich [32]. The time resolution of the system was 180 ps, measured by deconvoluting the higher-implantation-energy lifetime spectra from bulk Si wafers. A similar resolution function was also obtained for measurements of a metal glass which has a shorter lifetime and effectively no positron diffusion [33], thus reducing complications due to any surface effects. The count rate during all the measurements was about 40 cps and the spectra contained typically one million counts. The substrate wafers were also checked with bulk lifetime measurements using a fast–slow system with BaF_2 scintillators. The resolution of this system, as extracted from the lifetime spectra, was typically 160 ps. Both bulk and slow positron lifetime spectra were analysed in terms of exponential lifetime components using a conventional program [34].

3. Results

Doppler-broadening results from sample 587 [8, 9] show an extremely narrow annihilation lineshape in the overlayer which led to the conclusion that the spherical defects observed by TEM are clean voids. In addition, the lineshape parameter was constant throughout the overlayer. This was, as is usually the case, interpreted as saturation trapping at the voids.

The lifetime spectra, obtained for this sample and shown in figure 1, also have a long lived component typical of clean voids [12, 14], but at a much lower intensity than expected for saturation trapping. In the two-component fits shown, the value of this lifetime has been fixed at an average value of 500 ps to allow consistent determination of its relative intensity throughout the energy range. At lower energies a two-component fit is clearly incorrect due to mixing with additional components due to annihilations in the surface region. These contribute a poorly defined 'surface' lifetime in the range 300–400 ps, the exact value of which is strongly dependent on the surface conditions. As expected from the TEM and Doppler-broadening results [8, 9] sample 586, grown at the higher temperature and without visible defects, shows no long-lived component deep inside the sample. In this case the second lifetime

was fixed at 325 ps which was the mean lifetime at 1 keV implantation energy. The intensity of the surface component falls smoothly to zero within the first 8 keV, consistent with the analysis of sample 587.

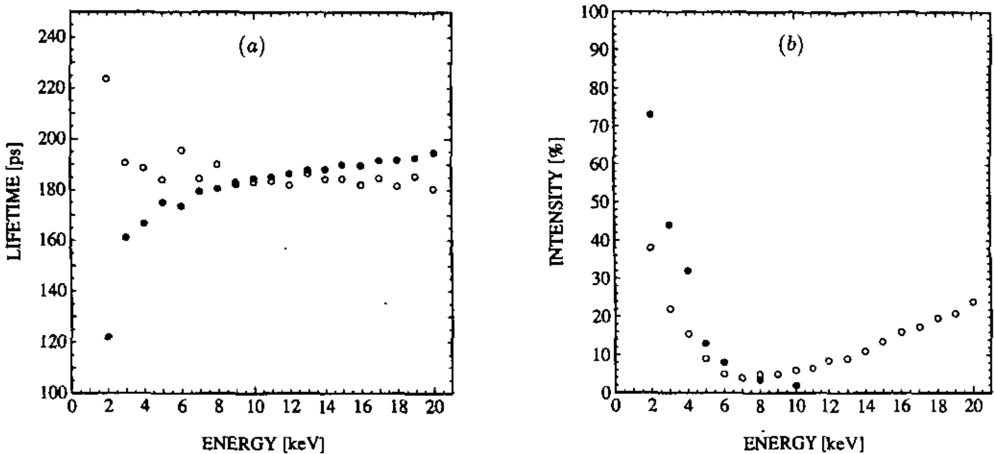

Figure 1. First lifetime (*a*) and intensity of the second component (*b*), as a function of incident positron energy, for 5 μm MBE-grown n-type silicon with (sample 587, ○) and without (sample 586, ●) grown-in void structures. For sample 587 the void lifetime has been fixed at 500 ps. For sample 586 the second lifetime has been fixed at the characteristic surface lifetime of 325 ps.

Of somewhat more interest, however, is that both samples exhibit a component with a lifetime around 185 ps, compared to around 220 ps normally reported for bulk Si [11–13]. Also, although the intensity of the 500 ps component in sample 587 increases with incident positron energy, this has no effect on the shorter component as would be expected from a simple trapping model [26] if the value of 185 ps corresponded to the free positron lifetime modified by trapping at the voids.

Figure 2 shows measurements on bulk silicon under the same conditions. The mean lifetime is presented here for clarity as the two-component fits contain no additional information. These data show a steady decrease in the lifetime from the surface value and approaching the bulk value btween 12–14 keV indicating that the positron diffuses more easily back to the surface than in the MBE-grown layers. This could be due to reduced diffusion in the overlayers or electric-field-induced drift away from the surface. More importantly, the lifetime deeper in the sample is around 200 ps for both p- and n-type at different doping levels, in agreement with conventional bulk measurements. The value of 185 ps for n-type reported in [31] came from a rogue sample and has proved not to be reproducible.

In the thinner epilayers (figure 3) the mean positron lifetime is again considerably shorter than in bulk silicon. Although the spectra are not well described by a single exponential function, we cannot resolve more components consistently. Sample 394, which has a clean interface, shows good mixing of substrate and overlayer lifetimes. However, sample 361 with a dirty interface, exhibits a broad minimum in the mean lifetime, indicating trapping at the interface.

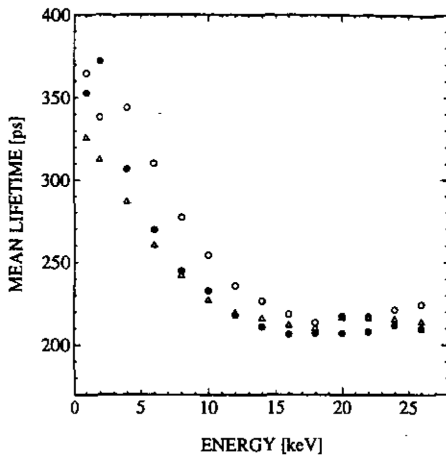

Figure 2. Mean lifetime as a function of incident positron energy for different silicon substrate wafers; 1–2 Ω cm n-type (○), P-doped n+ (●) and 15–25 Ω cm n-type (Δ).

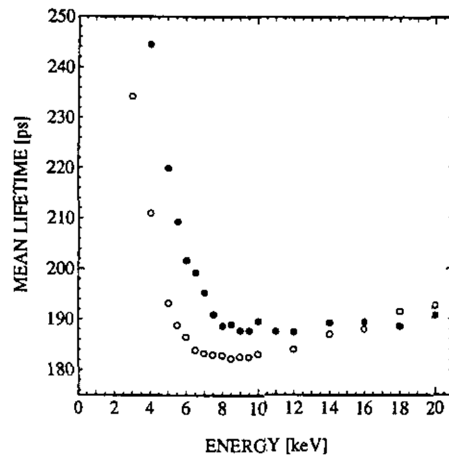

Figure 3. Mean lifetime as a function of incident positron energy for 3500 Å n-type layers with clean (sample 394, ●) and dirty (sample 361, ○) interfaces.

4. Discussion

The spherical defects observed in low-temperature MBE-grown silicon (sample 587) exhibit a long lifetime, characteristic of clean voids, confirming the interpretation given to both Doppler-broadening [8] and electron microscopy measurements [9]. However, the lifetime results do not indicate saturation trapping in these defects, although the Doppler-broadening parameter is constant in the overlayer and the calculated defect concentration is high enough. Coupled with the observation that all the overlayers in this study show less diffusion to the surface, this suggests that another type of trapping centre is present in the MBE-grown layers, independent of the formation of voids. The increase in the intensity of the longer component with depth in sample 587 would then indicate a relative change in the defect concentrations with depth. However, this explanation requires that the component in the annihilation lineshape resulting from positrons trapped at these voids is extremely narrow so that, even at relatively low intensities, the Doppler-broadening signal is saturated.

The dirty interface (sample 361) exhibits trapping of the positron at the interface but no additional longer-lifetime component corresponding to trapping in the overlayer. It is therefore likely that similar structures act as positron traps bo'h at the interface and in the overlayer. However, to explain the data we require a trapped positron lifetime that is no longer than the lifetime of a freely diffusing positron. The exact value depends on the trapping rate to the defect and cannot be determined, as the effective lifetime cannot be meaningfully resolved into several similar components. For all simple open volume defects, the trapped positron lifetime is increased relative to that of a free positron, and it would appear that a more exotic defect structure such as a vacancy–impurity complex is required to produce such a lifetime.

The main impurities at this interface are carbon, oxygen and boron, with other impurities such as germanium being distributed uniformly throughout the overlayer. In the other samples, oxygen is uniformly distributed at similar concentrations to the

Czochralski-grown substrates. Boron is present at all interfaces, including sample 394 which does not show preferential trapping at the interface, but is not present in the thicker overlayers.

Known values for oxygen associated vacancy-type defects are all longer than that in bulk silicon: the SiO_2/Si surface typically yields a lifetime in the range 300–400 ps, bulk SiO_2 ranges from 285 ps for α-quartz to 460 ps for amorphous [35] and the oxygen decorated divacancy complex V_2O lifetime has been measured at 270 ps [14, 15]. This last value represents a 30% increase in annihilation rate compared to the clean divacancy lifetime of 320–350 ps. A similar decrease in lifetime relative to that for an undecorated vacancy occurs for an oxygen–vacancy pair (A centre) to 225 ps (comparable to the bulk lifetime) but thermally activated detrapping prevents this from being observed at room temperature [14, 16]. There exists, however, a whole series of higher V–O complexes [36–38], that may well have fractional vacancy character, and could therefore act as positron traps with lifetimes close to the bulk value. Recent calculations of oxygen associated defects in silicon [39] suggest that interstitial oxygen helps the formation of a metastable vacancy–interstitial complex with a silicon dangling bond. The authors suggest that other, unspecified, impurities could also produce similar complexes.

Boron–vacancy complexes are also known to exist in p-type silicon [30] but the lifetime is expected to be similar to that of a monovacancy. Such a defect is also unlikely to be responsible for the strong trapping at the dirty interface as boron is also present at the interface in the other samples. A further possibility is a B–V–O complex, but the lifetime of this defect is 270 ps [30], the same as that of a vacancy.

5. Conclusions

For the first time positron lifetime and Doppler-broadening spectroscopy have both been utilized in positron beam experiments to study defects in MBE-grown silicon. While an expected void-related lifetime component was found in samples investigated earlier by Doppler-broadening and electron microscopy, there are substantial differences in the results from both methods. In particular, the intensity of the void-related component is too low to account for the saturation of the Doppler-broadening parameters in the same MBE layer. This suggests that the annihilation lineshape of positrons trapped in the voids is extremely narrow, and the momentum of the annihilating pair is negligible.

In the lifetime spectra there is evidence of a bulk-like trapped positron state in all the MBE layers studied, but the origin of this component and its exact lifetime are unclear. Oxygen is known, in some cases, to form vacancy complexes with relatively short lifetimes. However without a detailed *a priori* knowledge of the defect structures in the MBE layers it is difficult to imagine how, at similar oxygen concentrations to Cz–Si, near-saturation trapping can be achieved.

This study raises more questions than it answers, demonstrating the relative youth of the fields and the obvious need for more theoretical and experimental work in the areas of defects in MBE-grown structures and positron beam lifetime spectroscopy. Without knowing the lifetime and intensity of this proposed defect it is mathematically impossible, using the current analysis techniques, to separate it from the bulk component. In the case of the thinner layers, a decomposition of the lifetime spectrum into discrete exponential components could not be achieved. This could be

due to a rather complicated distribution of defect types, but is more likely to arise from a distortion of the spectra due to spatial diffusion of the positron. The thickness of these layers is about twice the positron diffusion length in silicon. It is, however, extremely improbable that spatial effects could account for the intriguing results in the thicker layers, which have an apparently homogeneous defect structure.

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