DEEP LEVELS ASSOCIATED WITH OXYGEN PRECIPITATION IN CZ SILICON AND CORRELATION WITH MINORITY CARRIER LIFETIMES+

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ABSTRACT

A dominant electron trap in boron-doped CZ silicon at E_c -0.41 $\pm$ 0.02 eV with a electron capture cross section $>10^{-14}$ cm^2 has been observed with DLTS in 2-step annealed (16 hrs at 800°C + 16 hrs at 1050°C) seed end wafers where oxygen precipitation is pronounced. A strong correlation between the generation lifetime τ_g (as calculated from junction reverse generation currents) and the density of this trap is also observed. Electron microscopy showed the dominant precipitates to be {100} plate type containing only Si and O, with dislocations and punched-out loops in close proximity. Wafers from the center- or tang-sections of the ingot or those given a 1-step anneal (conditions which result in much less oxygen precipitation) contain a low density ($<1.2 \times 10^{12}$ cm^{-3}) of a hole trap at E_v +0.25 eV not correlated with τ_g. These wafers contain precipitates with a different morphology with much lower or minimal dislocation densities. Possible origins of the lifetime controlling electron trap is discussed.

INTRODUCTION

The effects of oxygen precipitation on minority carrier lifetime degradation and secondary defect production have been studied [1]. However, relatively little has been reported on the deep levels which act as generation-recombination centers. A 0.767 eV photoluminescence emission peak has been associated with a lifetime killing deep level produced in conjunction with thermal donors after prolonged (64 hrs) annealing at 450°C [2]. A small concentration (a few times 10^{12} cm^{-3}) of a level at E_c - 0.59 eV has been detected by DLTS but no lifetime data was reported in conjunction with it [3].

In this paper we report the results of a DLTS study on the deep levels associated with oxygen precipitation in silicon and the identification of a level closely related to the degradation of minority carrier generation lifetime. TEM results are also presented to assist in tracing the physical origin of this level.

EXPERIMENTAL PROCEDURES

Wafers were selected from the seed, center and tang sections of a boron-doped <100> CZ ingot ($N_A \simeq 7 \times 10^{14}$ cm^{-3}) and heat treated to observe oxygen precipitation effects. Initial concentrations of interstitial oxygen $[O_i]$ and substitutional carbon [C] have been measured by FTIR (ASTM methods F121 and F123) and determined to be $1.3 \times 10^{18} \leq [O_i] \leq 2.1 \times 10^{18}$ cm^{-3} and [C] $< 5 \times 10^{15}$ cm^{-3}. Two heat treatment schemes have been used: a 2-step "lo-hi" anneal (16 hrs at 800°C in N_2 + 16 hrs at 1050°C in O_2) which maximizes precipitation up to the surface and a 1-step "hi" anneal (16 hrs at 1050°C in

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O_2) which tends to result in the dissolution of smaller precipitates and oxygen outdiffusion at the surface. The electrical effects of oxygen precipitation were characterized by fabricating phosphorus diffused n^+-p gated diode arrays on the heat-treated wafers and performing DLTS, recombination lifetime and reverse generation current measurements. The type and characteristics of the precipitates were examined by TEM to study possible physical origins of the electrical effects observed.

Two different DLTS techniques have been used: a computerized system using a PAR 410 1 MHz capacitance meter [4], and a more conventional double boxcar system using an rf bridge [5]. The computerized system is advantageous for majority carrier trap measurements and survey scans while the double boxcar system is used for minority carrier trap measurements where current injection is required.

Recombination lifetimes were measured by diode reverse recovery. Generation lifetimes were calculated from reverse generation currents, assuming that other sources of junction reverse currents are negligible. Excessive reverse biases were avoided to keep this assumption valid.

RESULTS AND DISCUSSION

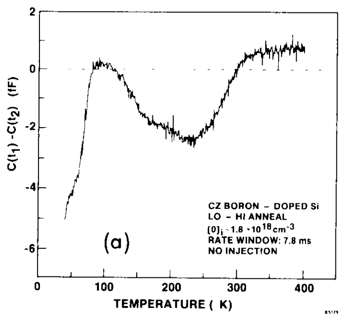
Lifetime

FTIR measurements before and after the heat treatments show that the interstitial oxygen concentration in wafers from the seed section of the ingot is driven to its solid solubility at 1050°C by precipitation after a 2-step "lo-hi" anneal. The resulting junction reverse currents (I_r) are the highest and the minority carrier recombination lifetimes (τ_r) the shortest (200-300 ns). In fact, τ_r is close to the limit of the measurement system (200 ns). The same "lo-hi" anneal results in much less or no precipitation in wafers from the center and tang sections. The 1-step "hi" anneal produces minimal precipitation in wafers from any part of the crystal. The I_r values associated with these latter two experimental conditions are an order of magnitude lower and the τ_r values an order of magnitude higher.

DLTS

Both majority carrier (hole) and minority carrier (electron) trap spectra have been obtained to investigate the deep levels responsible for the lifetime effects described in the previous section. A reverse bias of -20 V is used in conjunction with a 19 V bias pulse in the majority carrier trap scans, thus sampling a total depletion depth of $\sim$6.2 µm. Hole trap densities are quite small: $\leq 1.2 \times 10^{12}$ cm^{-3} in all cases. With a rate window of 7.8 ms, diodes from seed wafers with a lo-hi anneal show a broad spectrum consisting of at least 2 unresolved peaks extending from 120°K-300°K (Figure 1(a)). All other devices (i.e., those from center and tang wafers with a lo-hi anneal and those from any part of the ingot with a 1-step hi anneal) show a recurrent peak (hereafter called H1) at T = 214°K with the same rate window (Figure 1(b)). Generally, the magnitude of H1 decreases from the seed end of the ingot to the tang-end of the ingot, where it is essentially undetectable in some cases. The activation energy of H1 is $E_T - E_V = 0.25 \pm 0.015$ eV and the capture cross section as determined from the Arrhenius plot is $\sim 10^{-19}$ cm^2. Thus H1 is an unlikely origin of lifetime degradation effects. Indeed, no evident correlation of H1 with I_r or τ_r is observed.

Minority carrier (electron) traps have been examined by pulsing the diodes into forward bias using the double boxcar system. A reverse bias of -5 V is used and the forward current pulse (electrons) is 40 mA for 20 µs. The only samples in which electron traps are observed are from seed-section wafers with the lo-hi anneal, where oxygen precipitation is the most pronounced. The



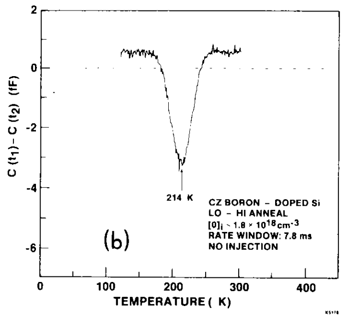


Figure 1. Majority carrier (hole) traps. (a) Seed wafer, lo-hi annealed, (b) all other conditions.

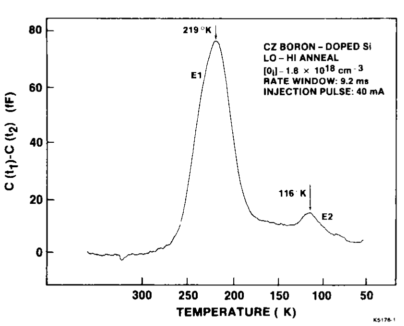


Figure 2. Minority carrier (electron traps) in seed wafers, lo-hi annealed.

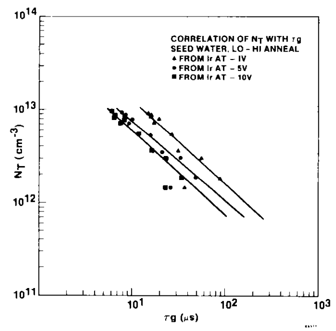


Figure 3. Correlation plot of N_T due to E1 and calculated τ_g.

trap spectra in these cases (Figure 2) are dominated by a level (hereafter called E1) with $E_C-E_T = 0.41 \pm 0.02$ eV. The electron cross section σ_n as obtained from the Arrhenius plot is $\sim 10^{-15}$ cm^2, but a direct measurement using very short trap filling pulses shows that it is at least 1×10^{-14} cm^2 and is too large to be measured by the available instrumentation. $\Delta C/C_0$ values indicate that the concentration of E1 can reach 8×10^{12} cm^{-3} in some samples. A second level (hereafter called E2) with $E_C - E_T = 0.23$ eV and $\sigma \sim 7 \times 10^{-15}$ cm^2 (as determined from the Arrhenius plot) is also observed simultaneously with E1, but its concentration is typically an order of magnitude smaller.

Scatter plots of N_T due to E1 vs the generation lifetime τ_g as calculated from I_r (using $\tau_g = qAWn_i/I_r$) show that they are correlated. The calculated values of τ_g are smaller if I_r values at larger reverse biases are used, suggesting the presence of current components which are electric field dependent or trap densities which increase with depth into the substrate. Using I_r values at reverse biases of -1 V, -5 V and -10 V, the calculated τ_g values can be fitted to a power law relationship (Figure 3) with the trap concentration N_T due to E1 of the form

$$N_T = A/\tau_g^{\,n} \qquad (1)$$

with the values of A and n given by the following table:

Reverse Bias	A	n	Coeff. of determination
-1 V	4.0×10^8	0.90	0.943
-5 V	4.5×10^8	0.84	0.979
-10 V	2.0×10^8	0.89	0.985

The notable point is that $n \simeq 1$, suggesting that E1 is the dominant lifetime controlling factor. The value of A also gives an estimate of the hole capture cross section σ_p of E1. Since $E_T - E_i = 0.16$ eV $\gg kT$, assuming σ_p is sufficiently close to σ_n such that $\sigma_n \exp[(E_T - E_i)/kT] \gg \sigma_p \exp[-(E_T - E_i)/kT]$, from ref [6],

$$\sigma_p \simeq (Av_{th})^{-1} \exp[(E_T - E_i)/kT] \qquad (2)$$

where v_{th} is the thermal velocity of holes and E_i is the intrinsic Fermi energy. Using an average value of $A \simeq 3.5 \times 10^8$, we obtain $\sigma_p \simeq 8 \times 10^{-13}$ cm^{-2} These values of σ_n, σ_p and the range of N_T are consistent with τ_r values of 200 ns or less.

The association of E1 with oxygen precipitation is further supported by results from oxygen implanted substrates [7]. A high concentration of oxygen ($>10^{19}$ cm^{-3}) is implanted into p-type CZ substrates and precipitated by a 30 min post implant anneal at 900°C. E1 and E2 have been identified in a DLTS spectrum very similar to Figure 2 after similar n^+-p test diodes were fabricated. The question remains, however, whether E1 is due to the oxygen precipitates themselves or lattice defects associated with certain conditions of precipitation. Kimerling and Patel [8] have observed an electron trap with the same energy as E1 by deforming n-type float zone (oxygen-free) silicon at 770°C and annealing for 1 hr at 800°C. It is possible, therefore, that E1 is related to dislocation and defect formation associated with the lattice deformation due to oxygen precipitation.

TEM

Transmission analytical electron microscopy has been used to provide additional information to identify the origins of the deep levels observed electrically. The "lo-hi" heat treatment produced the highest precipitate density in all cases, and the largest changes in electronic behavior. The single step "hi" anneals produced a lower precipitate density with a different morphology, but little change in electronic behavior, and will not be discussed further here.

Two-step annealed wafers from the seed section contain plate-type precipitates on {100} Si planes [9]. An example of a pair of intersecting plate precipitates is shown in Figure 4(a). These plate precipitates induce a large displacement field in the surrounding matrix, and often have dislocations associated with them. Microdiffraction has shown them to be amorphous, and electron energy loss spectroscopy has shown them to contain only oxygen and silicon, within detectability limits [9,10]. Wafers from the center-section of the ingot contain precipitates of the same morphology, but at a much lower density, for the same heat treatment.

Wafers from the tang-end of the ingot contain predominantly precipitates with octahedral morphology bounded by Si {111} planes (Figure 4(b)), with some {100} plate precipitates [11]. The octahedral precipitate is also amorphous and only silicon and oxygen was detected in it using energy loss spectroscopy. It is the same as the "equilibrium" morphology reported by Shimura after prolonged heat treatment at higher temperatures [12], but is of course much smaller in the present case. The precipitate density is higher in tang section wafers than in center-section wafers.

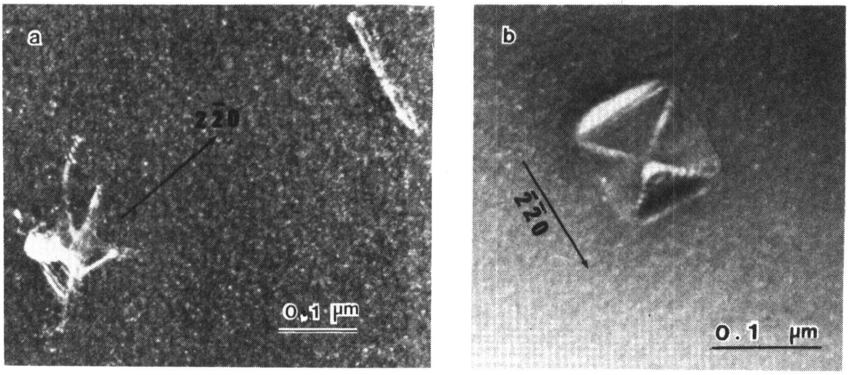


Figure 4. Oxygen precipitate morphologies in weak beam dark field, g/3g+ 100 kV, B $\simeq$ 001: (a) intersecting plate type precipitates, (b) octahedral precipitate.

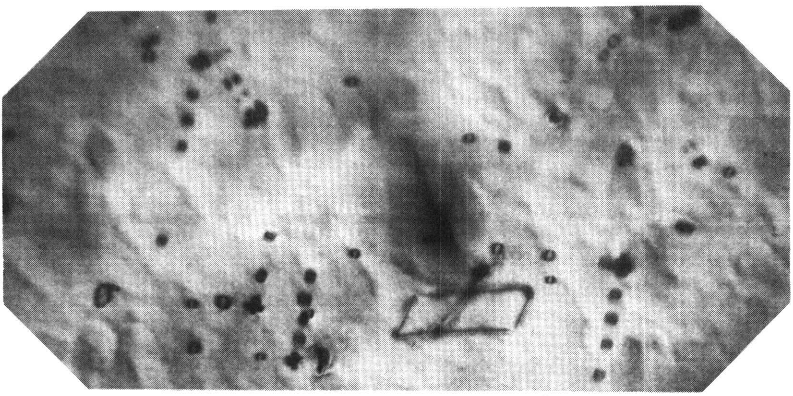


Figure 5. Thick section ($\sim$3 μm) high voltage (500 kV) micrograph of a seed wafer after the lo-hi anneal. The defect distribution is markedly heterogeneous.

The question of the coexistence of dislocations with these precipitates is of some importance, since dislocations are electrically active and produce a number of deep levels, one of which is at the same energy position as E1 [8]. The plate type precipitates almost always exhibited dislocations in close proximity, and also punched-out loops. In Figure 4(a) several of the closely associated dislocations are dissociated, and a punched-out loop is visible. Thick sections of the wafers examined by HVEM (Figure 5) showed that the punched-out loop array around plate precipitates is extensive. The remote loop density is $\sim 6 \times 10^{10}$, and the precipitate density is $\sim 10^{10}$ per cm^3. These defect densities are low enough that it is difficult to make statistically valid defect density measurements in thinner sections. The octahedral precipitates were seldom associated with dislocations, but did induce occasional loop arrays in the surrounding matrix.

CONCLUSIONS

A dominant electron trap E1 (E_c-E_T = 0.41 $\pm$ 0.02 eV, $\sigma_n > 10^{-14}$ cm^2) has been identified in boron-doped CZ silicon where a lo-hi anneal has been used to produce severe oxygen precipitation and minority carrier lifetime degradation. The values of τ_g as calculated from junction reverse generation currents are approximately inversely proportional to the densities of E1, suggesting that this is the principal lifetime controlling center. E1 is absent under conditions where oxygen precipitation and lifetime changes are more moderate (center and tang wafers with the lo-hi anneal, or any wafer with a 1-step hi anneal). The precipitates associated with the presence of E1 are {100} plates containing only oxygen and silicon with dislocations and punched-out loops in close proximity. From previous work on deformed float zone silicon [8], it is possible that E1 is associated with dislocation and defect production due to lattice deformation during severe oxygen precipitation.

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