A SEARCH ON THE IDENTITY OF THE Ev+0.34 eV C-RELATED DEFECT IN p-Si

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ABSTRACT

DLTS measurements were used to study a hole trap with activation energy Ev+0.34 eV in electron irradiated, boron-doped, floating zone silicon. The corresponding DLTS peak arises in the spectra after the migration of the Cl’s around room temperature. A delay observed between the appearance and the growth of the former defect and the onset of the decay of the latter, it might be taken as an indication of the existence of electrically inactive precursor defects, prior to the formation of the final defect configuration. The relevance of the defect to the boron concentration found out by our experiments, is commented. Comparisons are also made between this peak and another one with energy Ev+0.37eV arising in the spectra of Czochralski-grown Si under similar circumstances.

1. INTRODUCTION

Impurity atoms is silicon participate in the formation of various defects and complexes when the material is irradiated with high-energy particles. Among the impurities carbon (Cs) which is inadvertently added substitutionally into the lattice during processing, forms a number of defects which have been the subject of a large number of investigations. At first carbon interstitial (Cl) is formed through the Watkins replacement mechanism (Cs±Si → Cl) giving a level Ev+0.28eV in p-type Si. At around room temperature Cl begins to migrate and another level positioned about 0.34 eV (herein to be refered as H (0.34)) above the top of the valence band in float zone silicon emerges in the spectra. This level has received much attention in the recent years. However, the results of various researchers are in some respects controversial and the final identity of the level remains a subject pending further investigation.

Initially, the H(0.34) level has been attributed (1) to a complex formed by two carbon atoms one at regular lattice site and the other at an interstice (Cl-Cs). Recently, Song et al (2) have raised serious doubts about this correlation. In p-type material, it was proposed that the Cl-Cs pair is a bistable trap possessing two levels at Ev+0.09 eV and Ev+0.05 eV, each of them corresponding to the two configurations of the defect. So far, only Ev+0.09 eV has been unambiguously verified as arising from the above center (3). It is worth noting that in some experiments, signals from the H(0.34) level were not observed (4,5). On the
other hand this level has been reported in float-zone Si submitted to electron, proton and helium irradiations by a number of authors (6,7,8).

Thus, the present understanding of the trap is not complete. In this work we have observed a delay between the emergence of the H(0.34) peak and the start of the migration of the Cl's. This delayed growth, not previously reported by DLTS measurements, if combined with recent results about the levels of the Cl-Cs pair (2,3), gives food for some new thoughts concerning the identity of the H(0.34) peak in float-zone Si. Experimental evidence linking boron with the defect is presented and discussed.

2. EXPERIMENTAL

Schottky diodes were created as a result of evaporation of Aluminum (Al) film through a metal mask onto the surfaces of the samples. Prepolished wafers purchased from Wacker with dopant concentrations in the range of (0.8-9)x10^{15} cm^{-3} were used. The samples were irradiated from the Al contact side with 1.5 MeV electrons to a dose of 1.7x10^{16} e/cm^2. The irradiations were performed at 80K (in situ) and at room temperature. DLTS measurements were performed in the temperature range of 80-320K using the boxcar integrator technique (9). The trap energy level positions were determined from Arrhenious plots (ln en/T^2 versus 1/T) without making allowance for the temperature dependence of the capture cross-sections. During annealing the temperatures were maintained withing less than +10°C. After each annealing DLTS measurements were performed to monitor changes in the DLTS spectra.

3. RESULTS AND DISCUSSION

Figure 1 depicts the DLTS spectra as received at the indicated annealing temperatures.

![DLTS Spectra](image_url)

**Fig.1.** DLTS spectra of float-zone, boron-doped Si material, electron irradiated at 80K and subsequently undergone 40min isochronal annealing at the indicating temperatures (e_p=5s^{-1}).
The observed peaks H(0.19), H(0.28), H(0.32), H(0.37) were previously reported (10) and associated respectively with the V₂, the Cl and the latter two levels with the one configuration of the Bs-V pair. H(0.34) peak is the main concern of this investigation. A careful look at the spectra reveals that the concentration of the Cl peak during annealing is not correlated exactly with the growth of the H(0.34) peak.

At first, the emergence of H(0.34) is not simultaneous with the onset of the migration of the Cl's, as indicated by the decay of the H(0.28) peak. Thus a small, nevertheless characteristic delay is observed between the beginning of the decay of H(0.28) peak and the appearance in the spectra of the H(0.34) peak. Secondly, after the emergence of the H(0.34) peak subsequent annealings show that its increase is smaller than the corresponding decrease of the H(0.28) peak.

In most DTLS studies of point defects we generally focus our attention on deriving activation energies and capture cross-sections, usually paying scant attention to the various details and characteristics of the defects. However, some manifestations of underlying realities which if suitably explained, may provide information or reveal the mechanisms of important phenomena. In this particular case, we shall attach considerable interest in the above two observations and we shall try to draw conclusions about the structure of the H(0.34) trap by considering the various available ways of the Cl complexing in the Si lattice.

At first, it seems worthwhile to speculate about the idea that H(0.34) may arises from a non C-related defect. In that case carbon might only play a catalytic role in the formation process of the H(0.34) trap without participating in the end product. Such an assumption does not have to account for the observed delayed growth. Cl should be trapped mainly by undispersed carbon atoms forming Cl-Cd pairs with levels H(0.09) and H(0.05) not seen by DTLS due to the limitations in scanning below 80K. However, since only Cl seems to decay in the spectra when H(0.34) grows we have to accept that some electrically neutral defects dissociate around room temperature and their products provide the suitable partners which combining give rise to the H(0.34) state. We believe that this idea has a farfetched possibility to occur in reality. In the following we shall consider C-related structures as sources of the H(0.34) state.

\[ \text{a)} \quad \text{As it is well-known Cs and OI are the main traps for the migrating Cl's. In a float-zone material where the concentrations of Cs and OI are of the same order (} \sim 10^{16} \text{ cm}^{-3} \text{) the final product will depend upon the capture cross-section } \sigma \text{ of the impurities for the Cl.} \]

According to Davies et al (11) \( \sigma_{\text{Cs}} = 3.25 \sigma_{\text{OI}} \). Thus, at first sight, Cl-Cs emerges as the main candidate for H(0.34) peak, a fact also consistent with recent photoluminescence data (12) reported a delay between the growth of the G-line attributed to the Cl-Cs pair and the onset of the Cl's migration. On the other hand the Cl-Cs center, as mentioned above, has been recently correlated with other levels within the gap (2,3).

In a previous experiment (13) performed in room-temperature, electron-irradiated float-zone Si, a level H(0.09), exhibiting metastable behaviour, was detected. Although no assignment of the level was attempted at that time, on the basis of the new available information (2,3) it possibly arises from the Cl-Cs pair. In figure 2 the whole spectrum of room-temperature irradiated float-zone Si is presented for the sake of completeness and for comparisons with the corresponding spectrum of liquid Nitrogen irradiated material. In the latter figure the concentrations of the H(0.09) and H(0.34) levels are not equal, an indication that they could not arise from the same center.

\[ \text{b)} \quad \text{On the other hand, it is not unreasonable to consider OI as a possible trap for the Cl in float-zone material. It is important to note here, that the results by Davies et al (11) have been seriously challenged (14) and the main trap for the Cl was found to be OI (} \sigma_{\text{OI}} = 3 \sigma_{\text{Cs}} \text{). Secondly, a level at Ev+0.35 eV has been unambiguously correlated with the Cl-OI pair in Cz-} \]
grown Si(15) In this respect, it is worth noticing that in a recent paper(16) reported defect studies in C-rich, electron-irradiated float-zone Si, levels at H(0.09) and H(0.36) were correlated with the Cl-Cs and Cl-Ol centers respectively. However, the correlation of the H(0.34) level to the Cl-Ol pair presents difficulties concerning the aforementioned delayed growth. One has to consider the question of precursor defects in the formation of the Cl-Ol pair, a fact never reported so far. Another alternative is that the Cl might change configuration prior to be captured by the O1(17). In addition, it should be noticed the previously postulated(18) possible existence of different configurations of C-O complexes.

c) In this section we shall discuss possible complexing of the Cl with other point defects or impurities than those of Cs and O1. In our opinion, a potential candidate is the Bi. It is well-known that Si created by irradiation are selectively trapped by Bs to create Bi. Moreover, Bi can exist both in the positive Bi⁺ and the negative Bi⁻ state(19) and in a p-type material Bi is mobile below room temperature(20). Thus, in principle, reactions of the type Bi⁺+Cl⁻→ BiCl are possible.

In the further experiments reported here the role of boron in the defect formation was examined by recording the DLTS spectra of Si samples with different impurity content and measuring the concentrations of the corresponding H(0.34) peaks created after room temperature irradiation. The results are indicated in table I. A correlation of the level with the boron concentration is apparent, yet unclear, to us.

**Table 1.** H(0.34) Concentrations of float-zone material with different boron content immediately after room temperature electron irradiation.

<table>
<thead>
<tr>
<th>Ω cm</th>
<th>Boron content cm⁻³</th>
<th>Nₜ(0.34) cm⁻³</th>
</tr>
</thead>
<tbody>
<tr>
<td>9</td>
<td>1.8x10¹⁵</td>
<td>traces</td>
</tr>
<tr>
<td>6.4-7.4</td>
<td>3.5x10¹⁵</td>
<td>4.8x10¹²</td>
</tr>
<tr>
<td>1.45</td>
<td>1.5x10¹⁶</td>
<td>1.9x10¹³</td>
</tr>
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In a recent experiment (21) a level labelled H(0.34) both in float-zone and Cz-grown material has been attributed to the boron-carbon pair. Our results are, at first sight, not inconsistent with such a correlation for the O-lean material. However, this is not the case for the O-rich material where data previously cited in the literature lead to different conclusions.

At first, the level in Cz-Si arises from two energetically close defects (7) one of which is surely Cl-OI(15) and the other presumably the C-O-V complex(16). Secondly, the emergence of the H(0.34) level and its growth in the spectra (in comparison with the decay of the Cl) shows some characteristic differences between the two materials (Figure 3).

![Graph](image)

Fig. 3. DLTS spectra of Cz-Si, boron doped, electron irradiated at 80K and subsequently undergone 40min isochronal annealing at the indicated temperatures (eₚ=500 s⁻¹).

It is important to note that H(0.34) appears also in Al(22) and Ga(23) doped Si, a fact that tends to militate strongly against the level being a C-B pair. Clearly more work needs to be performed in Si doped with various acceptors (e.g. B, Al, Ga, In...) in order to verify or dismiss the above possibility.

In the context of this discussion it will be an omission not to refer to other C-related complexes as C-V(24) which have also been discussed in the literature. (B₅-V) is known(10) to decay below room temperature. If the defect anneals out by dissociation, it is a potential source for vacancies available for a possible association with the Cl. Other reaction processes could also provide vacancies at this temperature range.

4. CONCLUSIONS

This paper examines the various possible structures for C-related defects which could produce the H(0.34) state in boron-doped, float-zone silicon. Besides assignments previously cited in the literature correlating the defect with the Cl-Cs or the Cl-OI pair which are commented and discussed, the role of boron is also discussed in two respects. At first, boron may directly participate in the defect since the formation of Cl-B₁ pairs cannot be excluded. The fact that H(0.34) also appears in p-type Si doped with other acceptors pose serious doubts at such a correlation. On the other hand boron may indirectly contribute in the defect by facilitating the formation of C-V pairs. However, conclusive evidence for both cases are not provided. Evidently, DLTS alone could not probe the identity of a defect. A combination of techniques and experiments are required.
ACKNOWLEDGEMENTS

The author wishes to thank Dr. P.C. Banbury, of the Physics Department of Reading University for providing the research facilities to carry out the above experiments.

REFERENCES