Compound clusters in silicon dioxide obtained by N^+, C^+ and B^+ high-dose ion implantation: nature of the blue cathodoluminescence emission and relationship with the embedded phases

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Abstract: SiO_2 films on Si substrates have been implanted at 600°C by N^++C^+, N^++B^+ and $N^++C^++B^+$ ions at two different doses, and subsequently thermal annealed. Cathodoluminescence measurements of the samples have shown three bands at 3.45, 2.7 and 2.1 eV. The 2.7 eV band, observed in all the samples and more intensely in N+B annealed samples, is due to oxygen deficiency centers, while the 3.45 eV one, only present in N+B and N+C+B samples, seems to be related to BN or B associated centers. Infrared spectra of the implanted films showed Si-O-B and h-BN bands in samples containing B, as well as a contribution about 1200 cm^{-1} assigned to a ternary compound in the N+C+B implant. No modes different than those of Si-O bond have been found in samples without B.

Experimental:

Substrates: 1900A thick thermal silicon oxide grown on [100] n-type FZ silicon wafers at 1200°C in pure O_2 flow

Ion Implant.: N^++C^+, N^++B^+ and $N^++C^++B^+$

Energies: N^+, C^+ and B^+ 27, 23 and 19 KeV, respectively

Doses (any ion): 4.7×10^{16} at/cm² (low dose samples); 2.35×10^{17} at/cm² (high dose samples)

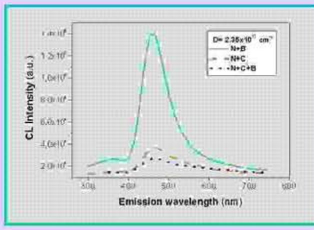
Process temp.: 600°C

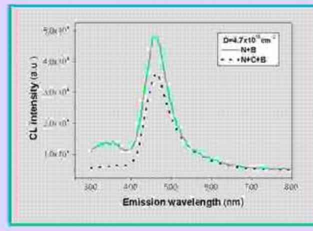
Annealing: 1200°C, three hours, in pure N_2 flow

Cathodoluminescence (CL):

Performed in a JEOL 820 SEM with a GATAN monoCL 2 system.

The excitation was carried out with acceleration voltages ranging from 5 to 10 KV and beam currents from 5 to 40 nA.





CL shows in all cases a **main band centered at 460 nm (2.7 eV)**, thus not related to the nature of the implants nor the phases formed during the implantation process. A similar band has been associated with transitions from the lowest triplet state to the singlet state in oxygen deficient centers (ODCs).

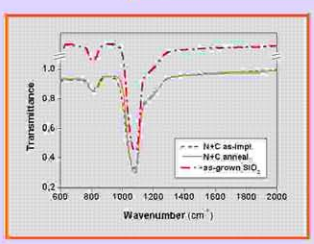
- Intensity of this band is higher for annealed N+B implanted samples.
- That probably means that around the BN clusters, ODCs density would increase during the annealing.
- In low dose implants the intensity of this band is similar for the different samples, as can be observed in N+B and N+C+B samples spectra.

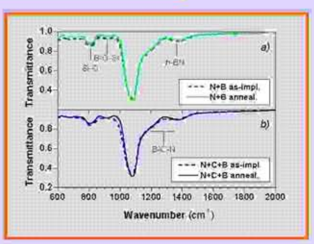
Two other contributions can be observed in the spectra:

- A **shoulder at 590 nm (2.1 eV)**, whose origin is not clear.
- A **band at 360 nm (3.45 eV)**, observed after thermal annealing.
  - It is especially intense in the N+B implanted samples, weaker in the N+C+B samples, and negligible in N+C implants.
  - A peak at 3.2 eV has been reported in Ge-implanted SiO_2 layers, related to ODCs created during annealing when Si atoms are replaced by Ge.
  - In our case, 3.45 eV band could be similarly assigned to centers created by the replacement of Si by B atoms, or to BN centers.
  - C atoms seem to inhibit this replacement.

Fourier Transform Infrared (FTIR):

A Bruker IFS-66v spectrometer was used for FTIR analysis using 6 cm^{-1} resolution.





- A common feature to all the sample spectra is the area decrease of the Si-O-Si main band, placed at 1080 cm^{-1}, as a consequence of the Si-O bond breaking during implantation.
- Samples implanted with N+C show no shape differences with regard to the reference sample.
- As the 2.7 eV peak has been observed also in N+C samples, the Si-O area decrease could be the result of the ODCs generation.
- For the N+B implanted ones, bands around 1375cm^{-1} (amorphous or hexagonal BN phase) and 920cm^{-1} (B-O-Si stretching mode) appear, more intensely for the highest implanted dose.
- N+C+B spectrum shows before annealing an additional contribution placed between that of BN and the shoulder of the Si-O band, that could be related to B-C bonds (1090-1200 cm^{-1}) and to a B-C-N ternary phase placed between the BN and BC modes. B-O-Si band also appears in this sample.
- We suggest that the B-O-Si band may be related to the 3.45 eV CL emission.

Conclusions:

N+B, N+C and N+C+B implanted SiO_2 layers show three main luminescence features:

- A main emission band at 460 nm associated to oxygen deficiency centers caused by the breaking of Si-O-Si bonds during the implant process.
- Increase of the density of this kind of centers is enhanced by thermal annealing of N+B high dose implanted samples.
- A second contribution at 360 nm that has been mostly observed in N+B annealed samples and has been related to B or BN associated emission centers.
- Presence of C atoms seems to inhibit this emission.
- Centers responsible of these two emissions have been identified by FTIR as Si-O-Si bond breaking and B replacing Si, respectively.
- Finally, a shoulder of the first peak at 590 nm, which origin is unknown.

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