Amorphised Quartz - evidence from cathodoluminescence microanalysis of silicon dioxide polymorphs

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Cathodoluminescence (CL) microanalysis techniques in a scanning electron microscope have been used to investigate and compare the defect structures of silicon dioxide (SiO_2) polymorphs. The CL emission from pure SiO_2 polymorphs is generally related to local point defects in the tetrahedrally coordinated SiO_2 host lattice. The structure of low pressure crystal and amorphous forms of silicon dioxide is characterised by similar corner sharing SiO_4 tetrahedra. The basic local defect-free tetrahedral SiO_2 bonding structure can be simply denoted as $O_3{\equiv}Si{-}O{-}Si{\equiv}O_3$ where (−) represents silicon-oxygen bonds. Thus in both crystal and amorphous forms of low pressure SiO_2, each silicon atom is surrounded by four approximately tetrahedrally coordinated oxygen atoms and adjacent silicon atoms are bridge bonded through a single oxygen atom. In α-SiO_2 (quartz), the bond angles and lengths are well defined, but in amorphous polymorphs of SiO_2 (a-SiO_2) there is a continuous range of possible bond angles and lengths. Crystal and amorphous silicon dioxide polymorphs form related analogous, but not identical defect structures. The neutral oxygen vacancy is the most similar of the native point defects in bulk low pressure crystal α-SiO_2 and amorphous a-SiO_2 polymorphs (Skuja 2000).

Quartz is an important and abundant mineral in the lithosphere. The physical and chemical properties of quartz are dependent on the defect microstructure. Defects in the SiO_2 microstructure may result from impurities (e.g. substitutional and interstitial impurities, inclusions, etc.) or imperfections (e.g. self-interstitials, vacancies, dislocations, etc.). Microscopic localised amorphisation of natural quartz may occur due to incorporation of impurities during growth or due to subsequent defect inducing processes (e.g. the effects of radiation, pressure, temperature, etc). Thus localised amorphous environments may occur within natural crystal quartz due to the presence of these defects. Valuable insights into the defect structure and possible identification of CL emissions observed in spectra from natural quartz can be provided by comparative investigations of crystalline and amorphous pure silicon dioxide. A range of pure synthetic amorphous SiO_2 polymorphs which have been synthesised under different conditions and pure synthetic electron-irradiation-amorphised crystal α-SiO_2 have been investigated. Their CL spectra have compared and their characteristic defects have been determined.

In Type I-IV amorphous SiO_2 these characteristic CL emissions are associated with oxygen deficient defects, (e.g. oxygen vacancies), non-bridging oxygen defects and self-trapped excitons, however the relative intensities, peak widths and/ or irradiation kinetics differ between each different type of a-SiO_2 polymorph (Stevens-Kalceff, 2013). The CL emissions from the amorphous SiO_2 polymorphs include the Non-Bridging Oxygen Hole Centre (NBOHC) at 1.9 eV (650 nm); the radiative recombination of the a-SiO_2 self-trapped exciton (STE) at 2.2 eV (565 nm); and Oxygen Deficient Centers (ODC) at 2.7 eV (460 nm) and ~4.5 eV (275 nm). A electron radiation sensitive CL emission at ~3.4 eV (365 nm) is observed from some types of a-SiO_2 and is attributed to be charged compensated substitutional Al^{3+}:M^+ defect (where M^+ is typically Li^+, Na^+, K^+ or H^+).

It is well known that CL emission from SiO_2 polymorphs may be modified during electron irradiation of sufficient power. The observation of changes in the CL spectra due to the generation and/ or transformation of electron irradiation sensitive defects can provide additional useful information. CL emission from synthetic and natural SiO_2 polymorphs are typically broad due to strong electron-phonon coupling, so irradiation induced modification of the CL spectra may be useful to help resolve broad overlapping components.

Under identical e-irradiation conditions, α-SiO_2 is more resistant to electron-irradiation induced damage than a-SiO_2. A single broad unresolved multi-component emission (FWHM 0.4 eV) at ~1.9 eV (650 nm) is initially observed from α-SiO_2 and is attributed to the Non-Bridging Oxygen Hole Centre (NBOHC) with contributions from at least two precursors. For higher electron beam irradiation doses, local defect concentration increases such that the irradiated quartz is damaged/ amorphised. The CL spectrum from α-SiO_2 is modified by the electron beam irradiation and resolved CL emissions are observed at 1.88 eV (~660 nm) associated with the NBOHC; at 1.93 eV (~640 nm) associated with the NBOHC with OH precursor; at 2.7 eV (~460 nm) associated with the radiative recombination of the α-SiO_2 self-trapped exciton (STE) and at ~4.5 eV (~275 nm) associated with Oxygen Deficient Centers (ODC). A electron radiation sensitive CL emission at ~3.2 eV (385 nm) is attributed to the analogous substitutional Aluminium impurity defect Al^{3+}:M^+ defect in α-SiO_2 where M^+ is typically Na^+ or H^+. (Ramseyer & Mullis, 1990) Following higher irradiation doses which induces amorphisation of α-SiO_2, (as evidenced by the swelling of the irradiated quartz surface) a broad ~2.3 eV (~540 nm) emission associated with the radiative recombination of the STE in amorphous-SiO_2 is observed.(Stevens-Kalceff 1995, 2013)

This analysis has also been extended to natural quartz by comparison of CL data from the synthetic pure irradiation-amorphised α-SiO_2 specimens with CL data collected from some examples of natural quartz specimens, including clear single crystal quartz and hydrothermal quartz. Tetrahedrally coordinated silicon dioxide is a relatively pure material in the natural state. In particular, impurities are not easily incorporated into the α-quartz tetrahedral structure in high concentrations (Götze et al, 2001). The substitution of impurity ions for silicon is limited by the high valency of silicon (Si^{4+}) and the relatively small atomic radius of silicon (0.42 Å). The natural quartz specimens are observed to be more sensitive to the effects of electron beam irradiation due to the higher concentration of pre-existing defect/ defect precursors. The intrinsic emissions (described above) which are associated with point imperfections in *both* crystalline and amorphous SiO_2 are also observed in CL spectra observed from the natural quartz specimens. Additional broad CL emissions which may possibly be associated with substitutional impurities including Al, Fe and Ge are also observed and are electron beam irradiation sensitive.

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