

HYDROGEN DIFFUSION IN DIAMONDS

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Hydrogen is an important impurity in natural and synthetic diamonds. Extensive studies using nuclear techniques have shown that hydrogen is present in concentrations up to 7000 at.ppm. Comparison of nuclear and spectroscopic studies shows that optically active hydrogen constitutes only a fraction of its total content in diamond. Optically inactive H possibly resides in microscopic inclusions of growth medium and/or its position in the lattice prevents optical activity. The diffusion of hydrogen in diamond is also not very well understood. The formation of the hydrogen-vacancy (H-V) complexes may lead to slower diffusion of nitrogen because its diffusion is vacancy-assisted.

Previous experimental studies of H diffusion in diamonds mostly used microwave plasma to introduce hydrogen. However, these results are not very relevant to investigation of hydrogen behaviour in natural and synthetic monocrystals in conditions of growth and postgrowth annealing. The emphasis of the current study is on the interaction of hydrogen with another important impurity – nitrogen. To address this interaction we have studied H infusion from gas phase at PT conditions similar to those during the growth and annealing of natural and synthetic diamonds. Nuclear methods, namely, Nuclear Reaction Analysis (NRA) and Elastic Recoil Detection Analysis (ERDA), are used for depth profiling of hydrogen and allow investigation of spatial distribution of this element with the use of microbeams (μ ERDA). The hydrogen thermal desorption spectroscopy is a powerful tool to measure the activation energy of hydrogen in different positions. A set of natural and synthetic diamonds with different concentration and type of nitrogen impurities was selected. The diamonds were cut into plates and heated in H-rich atmosphere for periods between 1.5 and 113 h at temperatures between 700 and 900 °C. Some of the samples were studied in as-received form.

Results

Hydrogen interaction with the diamond surface is rather strong. Many surface states with different bond energies could be formed. Configuration and diversity of these states depend on the crystallographic faces and degree of surface degradation. The diffusion of the hydrogen molecule into the diamond bulk is extremely slow. It is believed that the most stable hydrogen site in pure diamond is the bond-centred position. However, the creation of this defect from infusing molecules requires dissociation, which is energetically rather unlikely.

The N-defects influence H diffusion in diamonds. The strongest contribution is from the single substitutional nitrogen atom, the C-defect. It effectively blocks the diffusion, which presumably indicates strong H trapping. The radiation-induced loss from Ib diamonds is slow, suggesting high binding energy. The likely position of proton is on the elongated C-N bond. The nitrogen A-defect is less effective in diffusion blocking. The energy of hydrogen interaction with the A-defect is not very strong since ion beam induces heavy hydrogen loss. The B-defect is likely not very important. Deep penetration of hydrogen in diamonds heavily deformed under HPHT conditions show that dislocations may promote hydrogen diffusion.

One of the most remarkable observations made in this work is a marked sectorial dependency on the hydrogen concentration in one of the synthetic samples. In the octahedral growth sector of this sample both the bulk and the sub-surface H concentrations are higher than in the cubic one.

The desorption pattern from the natural untreated diamonds show a strong peak at high temperatures (1400-1600 K). It was previously shown that at temperatures exceeding 1350 K diamond surface is essentially H-free. Therefore, the observed band is related to hydrogen in the diamond bulk. The large FWHM (~150 K) of the band could be explained by the presence of many structural positions for hydrogen. These hydrogen traps should have similar activation energies being, for example, complexes of VH_n -type. Another plausible explanation, which does not contradict to the previous one, is that the hydrogen species escape via decrepitation of micro-inclusions [18]. These micro-inclusions may contain water and/or methane (origin of the hydrogen species) trapped during the diamond formation in the mantle. Therefore, fluid inclusions trapped during diamond growth and/or hydrogen-vacancies complexes are very important hydrogen reservoirs in diamond.

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