INVESTIGATION OF BAND GAP ENERGY STATES AT DISLOCATIONS IN NATURAL DIAMOND

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This research examines natural brown diamonds in trying to ascertain if, as is generally thought, lattice dislocations in the bulk of diamond are responsible for the brown colouration. Brown diamonds essentially without impurities are studied here; therefore, to account for the brown colour, there must be some mechanism in the bulk of the diamonds that causes the absorption of photons with energies in the visible range. The optical absorption spectra of a type IIa (those without appreciable amounts of nitrogen) brown and colourless diamond appear in Figure 1. This graph shows absorption for brown diamond not only in the visible range (1.7-3.1 eV), which would account for the brown colour, but also at greater energies. The hypothesis that dislocations are responsible for brown colour is complicated by the fact that colourless diamonds also have dislocations, as do brown diamonds that have been annealed at high temperatures and high pressure and have turned colourless.

At a dislocation, the translational symmetry of the lattice is broken. This may be expected to give rise to localised states in the band gap. The possibility would then exist that an electron in a localised energy state in the band gap could be excited into the conduction band by the absorption of photons with energies in the visible range, causing the brown colour. Electron energy loss spectroscopy (EELS) in a dedicated scanning transmission electron microscope (STEM) is utilized in this project to search for these additional local energy states.

The characteristics of dislocations in diamond and other semiconductors are essentially governed by the structure and electronic properties of the dislocation core. In diamond there are two dislocation types, the glide set and the shuffle set, each having different core structures and, hence, distinguishing properties and behaviour. Figure 2 is the (011) projection of the diamond lattice, showing the stacking sequence of the (111) planes. The glide type of dislocation involves the breaking of bonds between planes of atoms with different indices, *i.e.*, those not lying directly above each other, such as layers *a* and *B* in Figure 2. The shuffle type has bonds broken between layers of atoms with the same index, such as planes B and b.[1]

Each of the dislocation types produces dangling bonds, with associated energy states in the band gap.[1] Structures with dangling bonds have either a wide, half-filled band or one filled and one empty band in the band gap. Those with reconstructed bonds are virtually free of states in the energy band gap.[2] At present, it is not yet known conclusively which type of dislocation predominates in diamond, although reconstruction of dangling bonds is thought to be energetically easier in the glide type.[3] The data from this experiment may not only offer answers to the question of the brown colour in some diamonds, it has and will continue to provide information of use to theoreticians in their attempt to substantiate the existence of the glide or shuffle type of dislocations in diamond and the form of the core reconstruction in this important semiconductor.

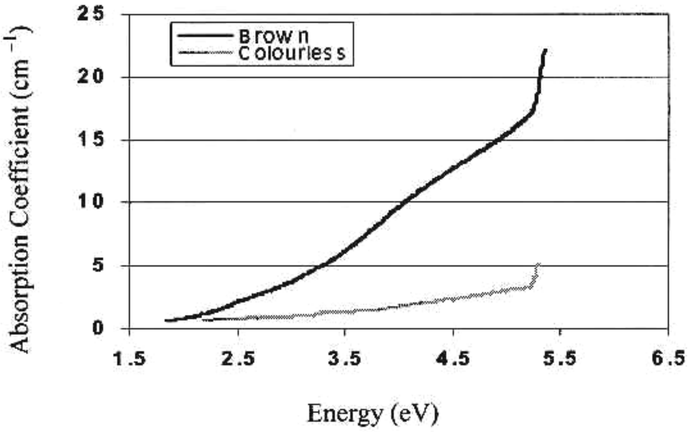

Fig. I Optical absorption spectra of type IIa brown and colourless diamonds (data courtesy of DeBeers Industrial Diamonds (Ireland))

As an overview of the experimental procedure, energy loss spectra were taken on and then off dislocations in the three types of diamond. The 'off' dislocation spectra were subtracted from the 'on' spectra to determine if additional localised energy states were associated with the dislocations. Evidence for such additional localised energy states in brown diamond was found in the form of a broad peak in the brown diamond 'difference spectra' from 6 - 7 eV, which was not present in the colourless diamond spectra. This peak can be interpreted as a pi star peak, consistent with sp^2 bonded material, at the dislocation cores.

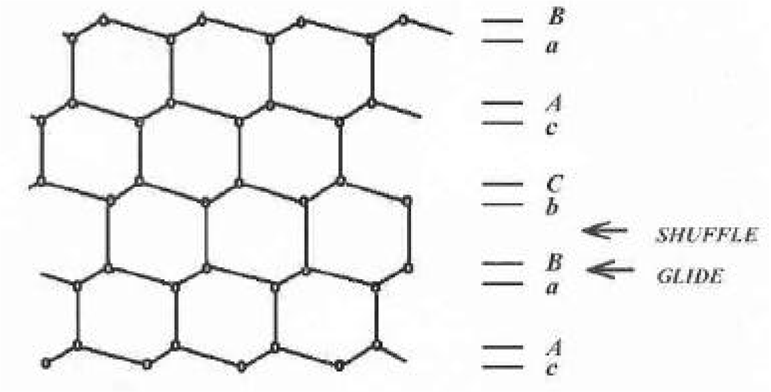

Fig. 2 (0 -1 1) projection of the diamond lattice, showing the stacking sequence of the (111) planes.

References

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