Institution: University of Exeter

Unit of Assessment: 9, Physics

Title of case study:

Modelling defects in diamond to preserve consumer trust in the global diamond trade

1. Summary of the impact (indicative maximum 100 words)

An atomistic modelling program developed at Exeter University has been used to make a significant, recognised contribution to the strong business performance of the De Beers Group, the world's leading diamond company. It gave De Beers the confidence to fund the successful development of new methods to identify synthetic and treated diamonds, which the company says has minimised the impact of fraudulent behaviour on consumer confidence, supported jobs in the global diamond trade, contributed to sales of $7.4bn in one year alone and was a factor in its decision to invest £20m in new research facilities in the UK.

2. Underpinning research (indicative maximum 500 words)

Natural diamonds are among the world's most precious natural resources; diamond jewellery had a global retail value of $72 billion in 2012 according to management consulting firm Bain & Company [5.1]. However, the last two decades have seen a rapid development in the production of synthetic diamond and the artificial enhancement of colour of natural diamond. The increasing quality of counterfeit natural diamonds represents a serious threat to consumer confidence. Bain & Company reported that 2011 marked the appearance of a large batch of synthetic diamonds believed by their dealer to be natural, highlighting the need for better techniques to guarantee the authenticity of natural diamonds and preserve trust in the industry.

Research by Robert Jones, Emeritus Professor (at Exeter since 1971) in Physics has developed new methods to understand colour caused by defects in diamonds and to distinguish between natural and artificial or heat-treated diamonds. The new methods are based on prior studies by Jones into the defects that exist in a wide range of materials. A computer code – AIMPRO (Ab-initio Modelling Program) – that calculates, among other things, the optical properties of materials was first developed by Jones [3.1] and now has an international community of users. It analyses the structural, electrical, optical and mechanical properties of solids in order to identify material defects. It is unusual in that it uses Gaussian functions (similar to a normal distribution bell curve) to represent the quantum-mechanical wavefunctions, and hence the electron density within a solid, rather than the more commonly used plane waves. Fewer Gaussian functions than plane waves are needed per atom meaning that larger unit cells can be investigated.

Jones used AIMPRO to model complex defects in Gallium Nitride and Silicon [3.2, 3.3]. The code works by arranging atoms in a structure. If the atoms are aligned incorrectly, the code calculates the force between the atoms and rearranges the structure until equilibrium is reached. Then the optical properties and other properties such as the electron energy loss spectra (EELS) are calculated.

At the request of the Diamond Trading Company (DTC), the rough diamond distribution arm of De Beers, Jones used AIMPRO to determine the optical properties and EELS signature of various defects in the diamond. Three types of defect exist in natural diamond: vacancies and interstitials (where an atom is either missing from or added to an otherwise regular structure), impurities (which replace carbon atoms in the lattice), and dislocations (where neighbouring planes of atoms have slipped in relation to each other). Jones began by calculating the energy spectrum of the most stable dislocation that is found in all types of diamond. He showed that the dislocation itself is not responsible for the colour of brown diamonds – the most common colour variety of natural diamonds. Instead he proved that it is the vacancy clusters that can give rise to the brown colour and he argued that such clusters are introduced by movement of dislocations when a diamond is plastically deformed under heat and pressure [3.4]. The vacancy clusters and therefore the brown colour can be removed by exposure to 2000°C heat. Crucially, Jones discovered that this causes the vacancy clusters to decay into other types of defect, such as nitrogen-vacancy defects, the optical properties of which are well known. Counterfeiters are not yet able to remove these new defects, which show up through optical spectroscopy used by companies like De Beers to validate their natural diamonds.

Further studies considered the optical properties of a number of other defects such as silicon and nitrogen vacancies, all of which are present in treated diamond and cause colour changes. More recent work has dealt with the properties of graphene and related doping mechanisms [3.5], [3.6].

3. References to the research (indicative maximum of six references)

References in bold best indicate the quality of the underpinning research.

3.1. **"LDA calculations using a basis of Gaussian orbitals", P. R. Briddon and R. Jones, Phys. Stat. Solidi B 217, 131-171 (2000), *cited 231 times* in WoS.**

3.2. **"Theory of threading edge and screw dislocations in GaN", J. Elsner, R. Jones, P. K. Sitch *et al.*, Phys. Rev. Lett. 79, 3672-3675 (1997), *cited 242 times* in WoS.**

3.3. **"Oxygen and dioxygen centers in Si and Ge: Density-functional calculations", J. Coutinho, R. Jones, P. R. Briddon *et al.*, Phys. Rev. B 62, 10824-10840 (2000), *cited 180 times* in WoS.**

3.4. "Dislocations, vacancies and the brown colour of CVD and natural diamond", R. Jones, Diamond and Related Materials **18**, 820-826 (2009), ***cited 14 times*** in WoS. This issue of the journal contains the proceedings of the 19th European Conference on Diamond, Diamond-Like Materials, Carbon Nanotubes, Nitrides and Silicon Carbide, held in Sitges, Spain 7-11th Sept 2008.

3.5. "Plasmon spectroscopy of free-standing graphene films", T. Eberlein, U. Bangert, R. R. Nair, R. Jones, M. Gass, A. L. Bleloch, K. S, Novoselov, A. Geim, and P. R. Briddon, Phys. Rev. B **77**, 233406 (2008) ***cited 125 times*** in WoS.

3.6. "p-type doping of graphene with F4-TCNQ", H. Pinto, R. Jones, J. P. Goss et al., J. Phys.: Condens. Matter 21, 364220 (2009), ***cited 33 times*** in WoS.

4. Details of the impact (indicative maximum 750 words)

Diamond modelling research at Exeter has made an impact in two principal areas. It has provided De Beers with the scientific understanding it needed to develop techniques to identify synthetic and treated diamonds, maintaining consumer confidence in De Beers' diamond trading and, by way of the company's long-established dominance, in the diamond industry as a whole. Secondly, it was a factor in a decision by De Beers to invest £20m in strengthening its research base in the UK, creating high-level employment for UK scientists [5.2].

The continued success of De Beers is crucial to the employment of thousands of people around the world. The De Beers Group employs approximately 20,000 people, of whom 17,000 are based in Africa. The company has mining operations in South Africa, Botswana, Namibia and Canada and is part of the Anglo-American Group that has 145,000 employees in 30 countries. De Beers sells approximately 40% of the world's rough diamonds, thus supporting a huge number of downstream jobs in the diamond trade, from polishing through grading to jewellery manufacture and retailing. In 2011, De Beers had sales of $7.4 billion with earnings before interest, taxes, depreciation and amortisation (EBITDA) of $1.7 billion. According to the Head of Physics [5.2] at the De Beers Research Centre in Maidenhead, a key factor in achieving such a strong performance was the high consumer demand that drove price increases for rough and polished diamonds. This, he says, "was underpinned by work supporting consumer confidence in diamonds in the face of rapid development over the last 20 years of processes for production of synthetic diamond and artificial treatment of natural diamond. It is vitally important for the diamond trade that consumers can buy diamonds without fear of product misrepresentation."

Referring specifically to Exeter's contribution, De Beers Head of Physics said: "Prof Jones's work since 1993 in modelling defects in diamond has played a major role in helping us build the foundation of knowledge on which our identification methodology is based and has been an important factor in enabling the detection and containment of recent attempts to sell synthetic or treated diamond fraudulently as natural untreated diamond."

Jones's research, supported by two collaborative awards in science and engineering (CASE) PhD studentships funded jointly by EPSRC and De Beers [5.3, 5.4], helped the company to develop and test the idea that vacancy clusters are responsible for brown colouration in natural diamonds with low nitrogen content. It enabled De Beers to understand the mechanism by which the brown colour is removed by relatively short high temperature heat treatments, and the identity and stability of by-products of this heat treatment. The work also helped unravel the link between nitrogen-vacancy-hydrogen defects and their optical signatures. These defects have not been detected in any natural diamond but tend to be present in synthetic diamond, changing its colour. Prof Jones' work helped De Beers understand these phenomena. De Beers Head of Physics concludes: "[Exeter's research] has therefore been of fundamental importance in the development of a robust identification methodology that has safeguarded consumer confidence and therefore many jobs in the diamond industry."

De Beers cannot quantify the impact of Exeter's work in economic terms; to remain one step ahead of counterfeiters, the company discloses very little information about the methods they use to characterise diamonds. But further evidence that Jones's research has informed practice at De Beers comes in journal articles published by De Beers scientists [5.5, 5.6, 5.7], which reference the work. It is also highlighted by De Beers' decision, on the basis of Jones's results, to award two further CASE studentships in 2009 to academics at the University of Manchester, and to support further experiments at Helsinki University of Technology. The published paper from Helsinki [5.8] in 2009 cited Jones's work in their own calculations and acknowledged discussions with Jones during their own research. Jones's work is generally accepted as explaining the role of vacancy clusters in the colour of diamonds.

According to De Beers Head of Physics, De Beers has an increasingly strong research base within the UK, employing 56 highly trained people, including many PhD scientists, at its DTC research centre in Maidenhead. The DTC collaborates closely with Element Six (E6), part of the De Beers Group and the world's leading supplier of synthetic industrial diamonds. De Beers Head of Physics reports that in 2013 E6's global R&D will be consolidated into the E6 Global Innovation Centre (http://www.e6.com/gic) near Oxford, where "a pipeline of innovative products will be developed for customers in industries from oil and gas drilling to machining and electronics."

He said: "This £20m investment is consolidating E6's existing global innovation teams in the UK and the choice of location was strongly influenced by the excellence of UK research in diamond science as exemplified by Professor Jones at Exeter." He added: "De Beers organizes an annual conference to encourage presentation and discussion of new research relevant to the diamond industry at which Prof Jones has been an active and valued contributor." [5.9]

5. Sources to corroborate the impact (indicative maximum of 10 references)

5.1. Figure 1.1 in The Global Diamond Report 2013: http://www.bain.com/publications/articles/global-diamond-report-2013.aspx (accessed: 21/11/2013).

5.2. Letter from Head of Physics at De Beers Research Centre in Maidenhead, UK. The letter describes the nature and scale of De Beers business and the contribution made by Prof Jones to its development of methods to distinguish between naturally colourless, heat treated and CVD diamond. The depth of detail supplied reflects De Beers need to also protect their commercial interest. De Beers are obviously reluctant to put details of anti-counterfeiting measures in the public domain.

5.3. "Modelling of Point and Extended Defects in Group IV Semiconductors", PhD thesis, Naomi Fujita, University of Exeter (2009). CASE award funded by De Beers, supervised by Prof R. Jones.

5.4. "Defects and dopants in carbon related materials", PhD thesis, Hugo Pinto, University of Exeter (2009). CASE award funded by De Beers, supervised by Prof R. Jones.

5.5. "Brown diamonds and high pressure high temperature treatment", D. Fisher, Lithos **112S** 619–624 (2009). This journal article by a De Beers scientist describes methods for determining the history and origin of diamonds, making reference to the work of Prof Jones, and acknowledging his assistance.

5.6. "Charge transfer effects, thermo- and photochromism in single crystal CVD synthetic diamond", R. U. A. Khan, P. M. Martineau, B. L. Cann, M. E. Newton and D. J. Twitchen, J. Phys.: Condens. Matter **21**, 364214 (2009). This journal article by De Beers scientists describes the optical signature by which CVD synthetic diamond can be identified, and makes due reference to the work of Prof Jones.

5.7. "Brown colour in natural diamond and interaction between the brown related and other colour-inducing defects", D Fisher, S J Sibley and C J Kelly, J. Phys.: Condens. Matter **21**, 364213 (2009). This journal article by De Beers scientists describes optical absorption spectra of different types of diamond, and makes due reference to the work of Prof Jones.

5.8. "Properties of optically active vacancy clusters in type IIa diamond", J.-M. Mäki, F. Tuomisto, C. J. Kelly, D. Fisher and P. M. Martineau, J. Phys.: Condens. Matter **21**, 364216 (2009). The article makes reference to the work of Prof Jones and acknowledges his assistance.

5.9. Prof Jones received invitations to speak at conferences organised by scientists employed by De Beers, including the 19th European Conference on Diamond, Diamond-Like Materials, Carbon Nanotubes, Nitrides and Silicon Carbide, held in Sitges, Spain 7-11th Sept 2008.