JOURNAL OF MATERIALS SCIENCE 14 (1979) 2650–2658

An electrostatic technique for revealing internal structure in diamonds

R. C. DeVRIES, R. E. TUFT
Corporate Reseach and Development, General Electric Company, Schenectady, New York 12301, USA

Using a simple technique based on electrostatic charging (essentially xerography of crystals), it has been found possible to reveal internal structure which appears to be directly related to that seen by other methods. It is necessary to expose the interior of the crystal in order to see the internal growth structure – i.e. to intersect the external growth surfaces since the latter are essentially homogeneous with respect to the electrostatic technique. If there are heterogeneities or discontinuities in the growth history of a crystal, we have found that the table, crown and pavilion facets of a cut stone are adequate intersecting planes for revealing patterns by the electrostatic technique. This technique might be the basis for a simple fingerprinting method for some gemstones.

1. Introduction

There are several different ways of revealing internal structure related to the growth history of a diamond: etching, X-ray topography, interference or phase contrast microscopy, cathodoluminescence, relief polishing based on differential hardness, observation of bi-refringence between crossed polarizers, light scattering, and u.v. transmission [1–18]. The active interest in this field is motivated not only by the desire to understand the internal structure and how the crystal grew, but also as a means of characterization of gemstones – sometimes called “finger-printing” [19–24].

Using a simple technique based on electrostatic charging (essentially xerography of crystals), it has been found possible to reveal internal structure which appears to be directly related to that seen by some of the above methods. It is necessary to expose the interior of the crystal in order to see the internal growth structure – i.e. to intersect the external growth surfaces, since the latter are essentially homogeneous with respect to the electrostatic technique. If there are heterogeneities or discontinuities in the growth history of a crystal, we have found that the table, crown and pavilion facets of a cut stone are adequate intersecting planes for revealing patterns by the electrostatic technique. The pattern can also be seen on cleavage surfaces that intersect the discontinuities. This technique could be the basis for a simple fingerprinting method for some gemstones and also might be a useful additional tool for the diamond cutter during cleaving and facetting operations or to those selecting crystals for various applications.

2. Experimental details

2.1. Charging techniques

Electrostatic charging can be done by rubbing the crystal on a dielectric material (cloth, paper, leather, organic polymer), by stripping a piece of adhesive tape from the surface, by using corona discharge apparatus, by piezoelectric charging devices, etc. The last two methods permit application of dust during the charging operation; this is sometimes advantageous under conditions where the charge might leak away between the sequential operations of charging and dusting (e.g., under high humidity conditions). The corona discharge techniques which have been highly developed for xerographic copying [28] give the most consistent results for all stones and in addition permit choice of polarity of charging, but simply rubbing on a piece of cloth suffices for many crystals. A com-

0022–2461/79/112650–09 $02.90/0

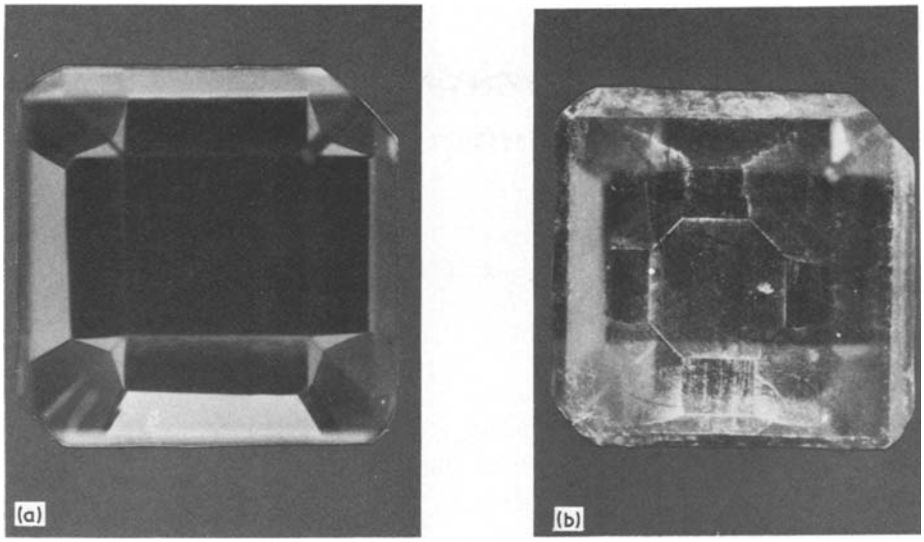

Figure 1 Electrostatic dust pattern on a yellow (Type IB) man-made diamond. (a) Original uncharged surface (0 0 1); crystal is about 0.2 g and about 5 mm × 5 mm on a side; direction to corners is ⟨1 0 0⟩. (b) Same surface as (a) after charging and dusting with Kyread [30]; the sides of the octagonal-shaped centre section are parallel to {1 1 1} and {1 0 0}.

mercially available piezoelectric antistatic device [29] has been found very useful, and it also enables one to charge the surface positively or negatively.

2.2. Printing by dusting

The powders used for revealing the electrostatically charged pattern should be fine grained ($\lesssim 5\,\mu$m) with a uniform particle size for maximum resolution of detail, but in some crystals the internal structure is sufficiently large for less stringent requirements. Obviously the powders should not damage the crystal in any way and should be easily removed by conventional cleaning. A variety of powders have been used without refinement: carbon black, graphite, flour, talc, alumina polishing powder, Cr_2O_3, CrO_2, Pb_3O_4, ZnO, $BaTiO_3$, Kyread* (a commercially available magnetic tape developer), and Xerox Blue Toner #125 [30]. This list is sufficiently broad to indicate the flexibility available in powder selection. For us the most useful have been the last two because they are specifically designed with a very narrow size range of fine powder for good definition of magnetic and electrostatic fields, respectively. Coloured powders like Cr_2O_3, Pb_3O_4 and the blue Xerox toner increase the visibility of the pattern especially against colourless crystals. The pattern can also be enhanced if a luminescent powder such as activated ZnS is viewed under ultra-violet radiation.

A dry powder can be blown on from an atomizer or bulb or simply dusted or shaken over the surface. The crystal can also be immersed in a pile of powder and then shaken or blown to remove the excess not held by the charged regions. The well-developed xerographic techniques using a development electrode [28] permit enhancement of the pattern and provides an extra degree of freedom with respect to the sign of the charged powder.

The Kyread developer is sprayed on as a suspension of metal powder in a liquid vehicle (chlorofluoroalkane) from a pressurized bottle. The evaporation of the last bit of liquid often leaves a ring of dust unrelated to the intrinsic electrostatic pattern. This is easily recognizable and generally does not interfere with the pattern on a large flat surface but can be a problem on the smaller crown facets of a cut stone.

2.3. Recording the patterns

The dust patterns can be recorded photographically or more simply by stripping them off the transparent or translucent adhesive tape just as done in lifting fingerprints. The pattern and its

---

*We thank D. Fink and A. Holik for this suggestion.

relationship to the crown facets and mount also can be precisely recorded in a casting rubber such as commercially available silicones and subsequently photographed. The tape record could be placed on a card or along with the usual sketches of the features of the crown and pavilion. If the tape is mounted on a glass slide, the pattern can be enlarged by projection. The adhesive tape technique has been used to combine cleaning, charging and recording in one operation on some crystals.

2.4. Description of the dust patterns

In Figs. 1 to 5 are shown examples of electrostatic dust patterns on both yellow (Type IB) and colourless (Type IIa) crystals grown at General Electric Corporate Research and Development by one of us (R.E.T.) and on the table and crown facets of a ½ carat brilliant-cut natural diamond mounted in an engagement ring. Patterns of varying degree of complexity have been found on all of the synthetic stones that we have studied; but of the approximately 50 natural cut stones examined, only a few have shown a useful pattern on the as-polished facets. The most spectacular one is shown in Fig. 3. The surfaces which expose the interior of all the synthetic crystals were examined first with the Nomarski interference contrast technique, and all were found free of structure with the exception of shallow polishing lines which bore no relationship to the dust patterns. However, if a crystal is relief-polished a differential hardness pattern can be seen, and it is essentially identical to the electrostatic dust pattern.

In Fig. 1 a comparison can be made of the polished surface of a yellow crystal (Fig. 1a) with the dust pattern revealed after electrostatic charging and spraying with the Kyread developer

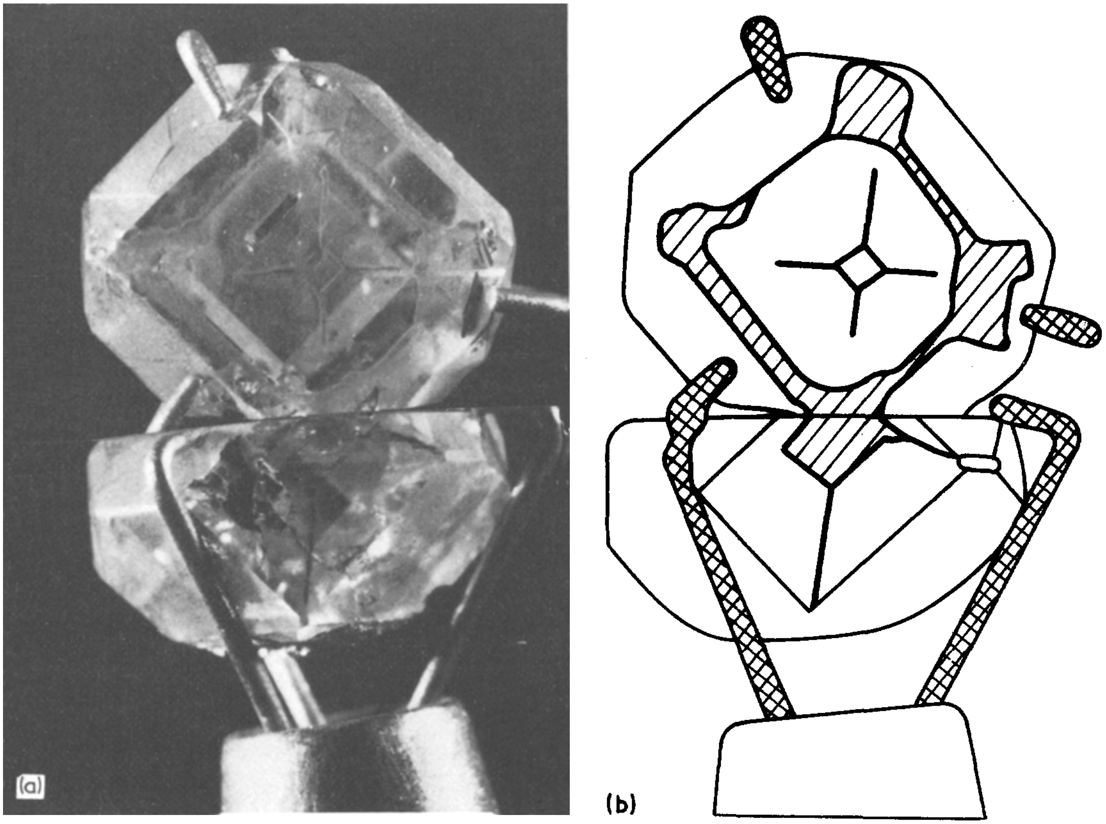

Figure 2 Dust pattern on a colourless (Type IIa) man-made diamond (composite photograph). (a) Top; polished (0 0 1) surface parallel to original largest surface of the crystal. Bottom; polished surface (approximately {1 0 0}) at right-angles to the surface shown in top of the photograph. (b) Tracing of dust pattern to show the relationship of the two surfaces shown in (a).

(Fig. 1b). The central part of the pattern as seen on the (1 0 0) face shows an octagon with edges parallel to both {1 0 0} and {1 1 1} growth surfaces. Some more or less crystallographically defined lines extend outward toward the sides of the crystals from the octagon.

In Fig. 2, the pattern was developed after charging by using the Blue Xerox Toner #125 on a (1 0 0) surface of a colourless crystal. This pattern is characterized by a small square at the centre of the face with the sides parallel to {1 1 1} growth faces and by limbs extending outward from the corners of the square in ⟨1 0 0⟩ directions. A less distinct but highly reproducible larger square pattern can be seen parallel to and near the crystal edges. A new surface (approximately {1 0 0}) was polished at right angles to the large face just described above, and the pattern was revealed at various depths of polishing into the crystal to establish the three-dimensional nature of the inhomogeneities in the crystal. A composite tracing of the dust pattern from both surfaces shows the relationship of these two patterns. This crystal also has a large black inclusion and a rectangular void, but the pattern bears no relationship to either defect. The three-dimensional nature of the patterns has also been seen on the crown and pavilion facets of the synthetic crystals which have been cut into round brilliants. Thin slabs (0.25 mm x 5 mm x 5 mm) also show different but related patterns on the opposite flat faces.

A rather complex pattern is shown in Fig. 3 on the table – with some lines extending into three of the crown facets – of the round brilliant cut natural gem stone. Tracings of the dust pattern at two different magnifications are shown to aid in recognition because the contrast is not too good in the photograph. The detail of the pattern is reproducible and is quite well resolved on the crystal and can be seen easily with a 10 x hand lens. This pattern is quite similar to those reported by others using different techniques [1–18], and by analogy we believe the lines to represent intersections of concentric {1 1 1} growth surfaces with the table facet. This pattern is a true one-of-a-kind "fingerprint" of this gemstone and would be useful added information in identification and characterization of this stone. However the number of natural stones which show this phenomenon appears to be rather small.

The technique using translucent adhesive tape and silicone rubber to record the pattern is illustrated in Figs. 4 and 5 for the crystal shown in Fig. 3, for another Type IIa, and for a large irregular yellow crystal. The latter is also used to show the effect of changing the polarity during charging the surface with the piezoelectric antistatic gun. The intrinsic charge on the powder also makes a difference in details of the dust pattern as shown by comparing the Kyread developer pattern with the Xerox Blue Toner #125 when the crystal has been charged with the same polarity (Fig. 5).

3. Discussion

3.1. Observations on charging behaviour

For those interested in bringing greater understanding to the xerography of diamond crystals, the following are additional observations on this fascinating phenomenon which appears to be related to marked conductivity differences in a material which is primarily an insulator.

(1) The deep yellow (Type Ib) crystals (similar to the "fancy yellow" of the diamond trade) are the easiest to charge and print. Simply rubbing such a crystal with tissue to clean the surface will charge it. Even breathing on the crystal between charging and dusting does not remove the charge. We found it necessary to wash these crystals with water or alcohol or to use an antistatic device to provide an uncharged surface for study. The yellow crystals also have the highest electrical resistivity of any of the synthetic stones [15] and therefore charge leakage is less of a problem.

(2) On a small yellow crystal which was relief-polished to show a distinct pattern based on level differences [15] the dust pattern was identical to the differential hardness pattern. Additional work is planned on similar crystals of larger dimensions in the hope that a correlation between nitrogen content and electrical conductivity can be established.

(3) Colourless (Type IIa) and boron-doped (Type IIb) synthetic crystals are more conductive and more susceptible to humidity and therefore gave more difficulty in charging by friction. Dusting while charging with the corona discharge method proved reliable on synthetic crystals of these types even under humid conditions (Schenectady, New York in August).

(4) The small square area and one ⟨1 0 0⟩ limb of the pattern shown in Fig. 2a (left) were investigated for cathodoluminescence, and a pattern

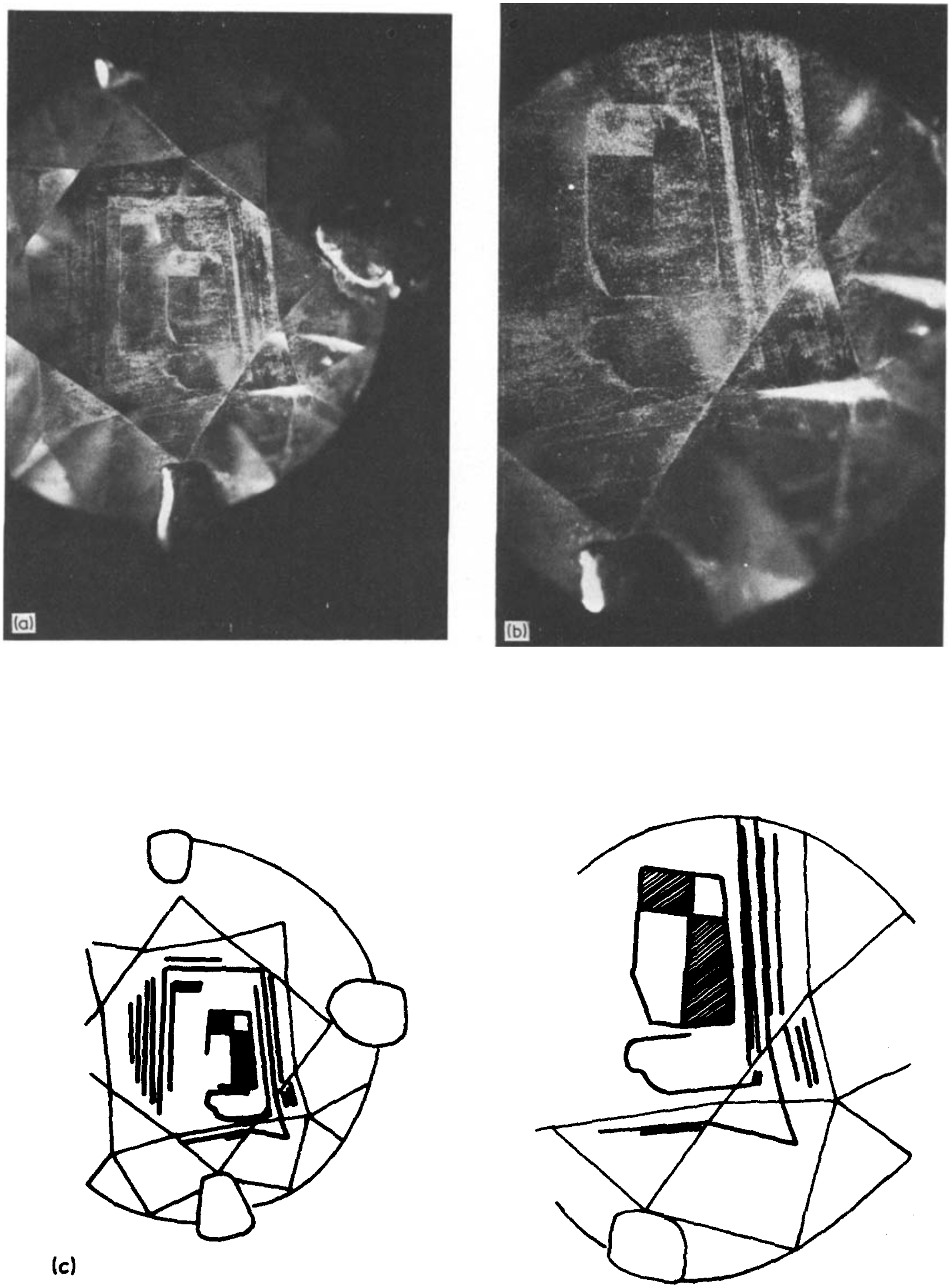

Figure 3 Dust pattern on a natural gem diamond mounted in a ring. (a) ~ 9 ×; stone is approximately $\frac{1}{2}$ carat and the diameter at the girdle is about 5 mm. (b) ~ 18 ×. (c) Tracing of dust patterns shown in (a) and (b).

identical to the dust pattern was found. Since cathodoluminescence is dependent upon excitation of defects or impurities, it seems reasonable that differences in electrical conductivity would exist along the same zones.

(5) In a mineralogy text diamond is described as "Triboelectric. Not sensibly pyroelectric or piezoelectric" [32]. The charge is said to be positive on diamond whether polished or not [33]. The ease with which most diamond grains acquire a static charge is well known and generally is a nuisance in the handling of abrasive grain [34] but can be useful in separation processes [35]. It would be interesting to know if there is a significant difference in electrostatic behaviour of synthetic abrasive grain (all Type Ib) compared to natural grain where Type Ia tends to predominate.

(6) We took a brief look at the generality of the phenomenon in many crystals – both natural and man-made – available in our laboratory: tourmaline, emerald, quartz, sapphire and ruby, NaCl, CaF_2, LiF, MgO, ZnO, BeO, TiO_2, $BaTiO_3$, sulphur, AlN, cubic BN, CdS, ZnS and SiC. Growth patterns were seen only on cubic BN, AlN, and on a natural ZnS crystal. Reproducible dust patterns were observed also at the intersection of internal cleavage planes with surfaces in an NaCl and a CaF_2 crystal. In all these crystals, charging was a necessary step to reveal a pattern. However one has to be careful with conclusions based on non-centrosymmetric crystals (cubic BN, AlN, ZnS) since they can be pyroelectric and/or piezoelectric. However we could not produce dust patterns by electrostatic charging on either quartz or tourmaline, both of which are reported to collect dust in patterns by virtue of the pyroelectric effect. Unless one wants to revive the old argument of the non-centrosymmetric character of diamond, the only common ground for cubic BN, AlN, ZnS and diamond is their covalent character and the ability to sustain marked local differences in conductivity. The conductivity differences appear to be related to small concentrations of impurities (especially nitrogen) in diamond and probably also to non-stoichiometry in BN, AlN and ZnS.

(7) The technique of Pearson [36] for revealing p–n juctions in semiconductors such as Si uses a suspension of dielectric powder in an insulating liquid while a voltage is applied across the junction. Because of the difficulty of applying a uniform electrical field across a diamond, it was not possible to get reproducible patterns using this technique on laboratory made diamonds. However, when a crystal with such a suspension was placed in an electrostatic field, a reproducible pattern was developed.

3.2. Relationship to growth history

The structures revealed by the dust patterns in the synthetic diamonds are sufficiently similar to those seen in natural stones by other techniques [1–18] to be reasonably sure they are caused by the same phenomenon. When a crystal grows, it records in some way the events of its growth history. A change in the pressure, temperature or composition (*P–T–X*) will result in changes in

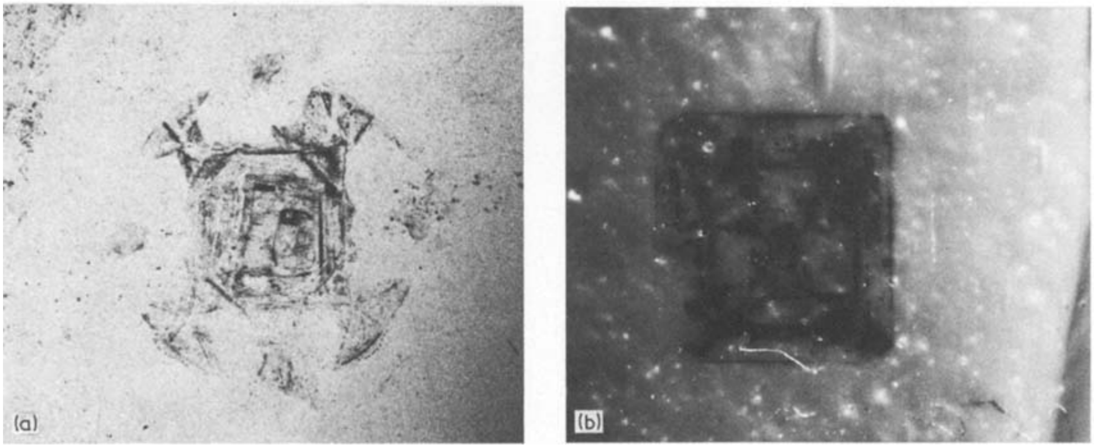

Figure 4 Recording of dust patterns with other techniques. (a) Pattern of Fig. 3 on translucent adhesive tape (12 ×). (b) Pattern from another Type IIa crystal as preserved in silcone rubber (12 ×).

growth rate, in the chemistry of the absorbed or rejected species, in the nature of defects, etc. Such changes make differences at the growing (or dissolving) surfaces, and the record in diamond often appears to be in the form of concentric inhomogeneities or discontinuities on the principal growth surfaces $\{1\,1\,1\}$ and $\{1\,0\,0\}$. The intersection of these discontinuities with an interior surface is what can be revealed by the electrostatic technique as well as by relief polishing or by etching.

The fact that both synthetic and natural crystals show very similar structures is of considerable interest in itself in possibly leading to greater understanding of the growth of natural diamonds. It seems very likely that by varying nucleation techniques and the *P–T–X* conditions, the structural features seen in natural crystals can be simulated and possibly related to growth conditions of the source. For the complexity of the patterns in synthetic crystals, particularly near the nucleation site, it appears that in the early stages of growth the synthetic environment may be less stable than the natural one. This is probably due

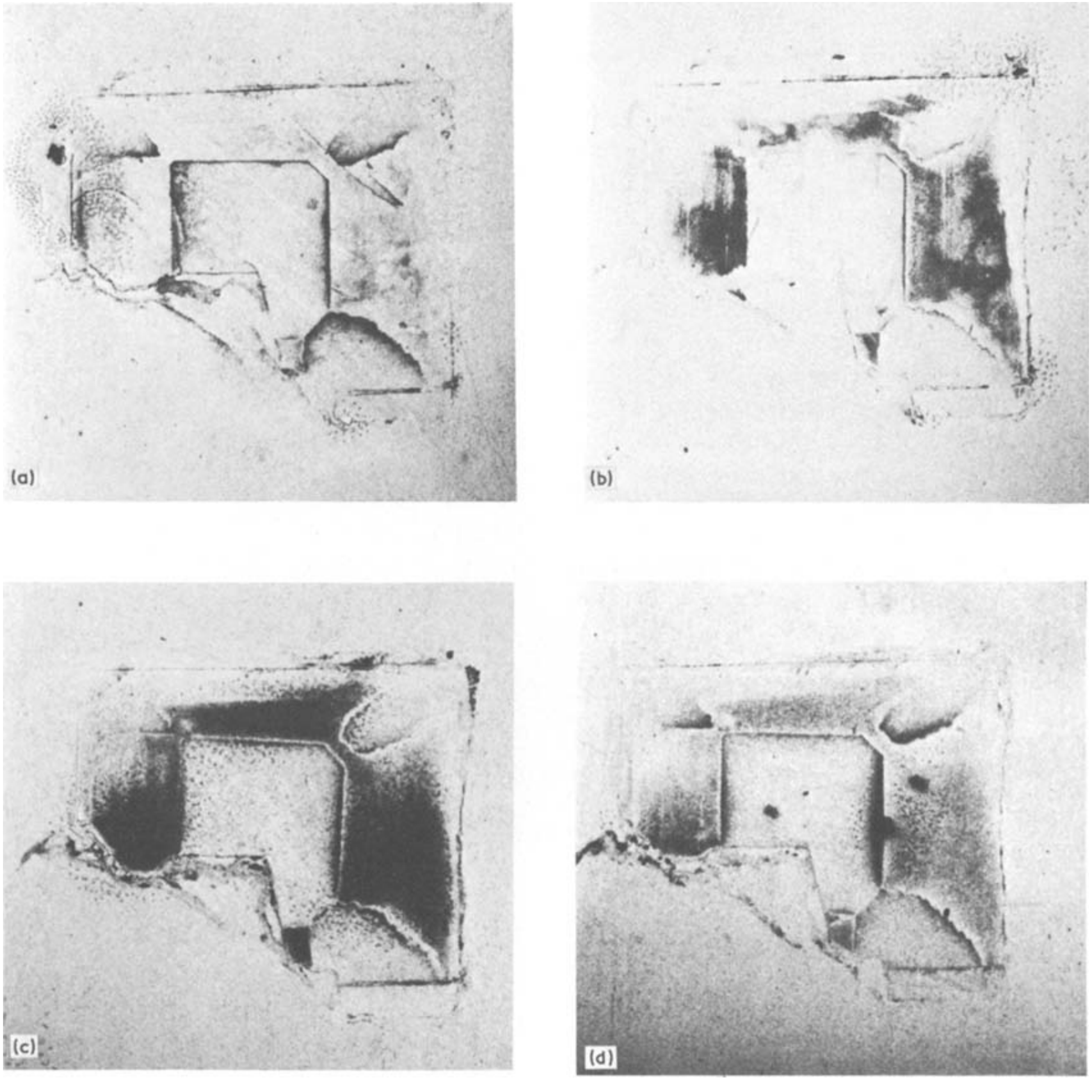

Figure 5 Effect of polarity of charging and of the charge on the powder as seen in stripped tape patterns of a large yellow imperfect crystal (a) (+) charge dusted with Kyread (15 ×). (b) (–) charge dusted with Kyread (15 ×). (c) (+) charge dusted with Xerox Blue Toner (15 ×). (d) (–) charge dusted with Xerox Blue Toner (15 ×).

to the more severe, P, T and X gradients in the comparatively small pressure vessels of the laboratory.

3.3. "Fingerprinting"

The uniqueness of a growth pattern in crystals is comparable to that of a human fingerprint and is the basis for considering the technique for characterizing and identifying gemstones just as similar claims are made for other methods [19–24]. To a certain degree even the absence of a pattern conveys some information now, and may become even more useful after more correlations with colour and conductivity are established. From the fingerprinting point of view it is unfortunate that so few natural gems show electrostatic dust patterns. Possible explanations for failing to see a pattern are: (1) the crystal was too conducting to be able to develop and hold an electrostatic pattern; (2) growth conditions for the crystal were so uniform that there were no discontinuities during the entire growth history (this would be expected to more likely in smaller crystals); (3) the polished or cleaved surface intersects only a homogeneous portion of a crystal with no local discontinuities (Fig. 6); (4) most natural crystals do not have the marked electrical conductivity changes which appear to be characteristic of synthetic Type Ib and IIa crystals; this may be related to the distribution and physical state of nitrogen.

In the modern brilliant cut diamond, the table is an ideal intersecting plane on which to reveal internal structure since it cuts just above the girdle of an octahedron, and therefore reveals a good proportion of the interior of the crystal. The crown and pavilion facets may also show structure but less conveniently because of the smaller area. Also in a mounted stone, the pavilion may be essentially inaccessible. If a large crystal is cleaved, the matching surfaces would be ideal for the technique and might provide useful information for subsequent cutting.

It is obvious that those who handle many cut stones, loose or mounted, could easily apply this convenient and nondestructive technique and accumulate some useful correlations with conductivity, bi-refringence, source, etc. Whenever a pattern is seen it can easily be recorded as a unique characterization of the stone. We expect the technique to be more useful for larger stones than for smaller ones if for no other reason than the former had more opportunity to experience environmental changes. Gemstones should be looked at immediately when removed from the scaife in the late stages of polishing.

It has been somewhat surprising that we have been unable to find any information on electrostatic patterns on polished diamonds from either the literature or from people who handle gemstones daily. The phenomenon may be rare but it is possible also that the emphasis on colourless crystals may have limited the probability of discovery while the availability of the Type Ib (dispersed nitrogen) synthetic, yellow crystals of high electrical resistivity (and the consequent ease of triboelectric charging) greatly improved the chances of seeing the dust patterns.

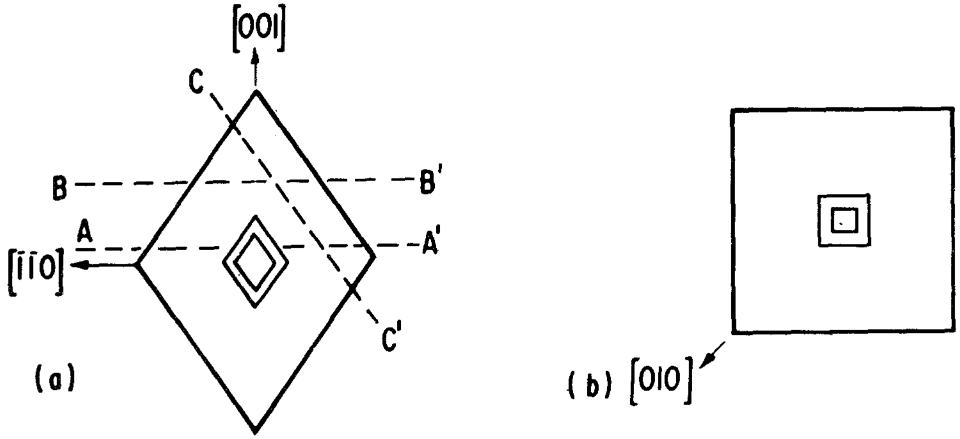

Figure 6 Schematic representation of concentric growth lines in an octahedron (a) Cross-section of octahedron with two growth discontinuities paralled to $\{1\,1\,1\}$ faces; (b) $\{0\,0\,1\}$ surface at A–A′. Sections at B–B′ and C–C′ will not show dust pattern.

4. Summary

A simple electrostatic technique for revealing structural discontinuities in synthetic and natural diamonds has been developed. The dust patterns seen are considered to record the growth history of the crystal, and because of their uniqueness are potentially useful for fingerprinting gemstones. The phenomenon appears to be related to the electrical conductivity of different zones in the crystal.

Acknowledgements

The help of may people is gratefully acknowledged. Particulary we thank J. DeLuca, for his enthusiastic interest and for showing us corona discharge techniques; R. M. Chrenko, for many discussions, crystal characterization, and for being a storehouse of information about diamond properties; M. McConnell, for the cathodoluminescence experiments; L. Remus, for the repeated lending of her engagement ring; H. Graubart of Maurice B. Graubart and Sons, Jewellers, Schenectady, NY, and M. D. Beals of Lazare Kaplan and Sons, Inc., for kindly providing several natural stones for study; I. Mella, S. Banchard, A. Holik and D. Fink for excellent photographic work; H. Sharbaugh, W. Johnston, H. Bovenkerk, J. Binkowski and G. Slack and K. Yang, for critical listening and discussions; A. Urquhart and M. Aven for being interested and for supporting this study.

References

1. A. F. WILLIAMS, "The Genesis of the Diamond", Vol. II (Ernest Benn Limited, London, 1932) pp. 481–511 (Review of early work, especially Fersmann and Goldschmidt plus Williams' own observations).
2. S. TOLANSKY, "The Microstructure of Diamond Surfaces" (N.A.G. Press Ltd., London, 1954).
3. *Idem,* in "Physical Properties of Diamond", edited by R. Berman (Clarendon Press, Oxford, 1965) pp. 135–73.
4. F. C. FRANK and A. R. LANG, in "Physical Properties of Diamond", edited by R. Berman (Clarendon Press, Oxford, 1965) pp. 69–115.
5. M. SEAL, *Amer. Min.* **50** (1965) 105.
6. F. C. FRANK, in "Science and Technology of Industrial Diamonds", Vol. 1, edited by J. Burls (Industrial Diamond Information Bureau, London, 1967) pp. 119–35.
7. A. R. LANG, *Nature* (1967) 248–51.
8. S. TOLANSKY and H. KOMATSU, *Science* **157** (1967) 1173.
9. H. KOMATSU and A. R. LANG, *Min. Soc. Japan, Spec. Paper* **1** (1971) 35.
10. A. R. LANG, *J. Cryst. Growth* **24/25** (1974) 108.
11. I. KIFLAWI and A. R. LANG, *Phil. Mag.* **30** (1974) 219.
12. A. R. LANG, *Proc. Roy. Soc. London* **A340** (1974) 233.
13. G. S. WOODS and A. R. LANG, *J. Cryst. Growth* **28** (1975) 215.
14. A. S. VISHNEVSKY, *J. Cryst. Growth* **29** (1975) 296.
15. R. M. CHRENKO and H. M. STRONG, "Physical Properties of Diamond", GEC R & D Report No. 75CRD089, October 1975.
16. E. M. WILKES, *Nature* **262** (1976) 570.
17. R. A. P. GAAL, *Gems and Gemology,* 238244 (1976–7).
18. P. L. HANLEY, I. KIFLAWI and A. R. LANG, *Phil. Trans. Roy. Soc. London* **A284** (1977) 329.
19. A. R. LANG and G. S. WOODS, *Ind. Diamond Rev.* (1976) 96.
20. Anonymous, *Lapidary J.* (1976).
21. Anonymous, *Functional Photography* (1977) 18, 40.
22. E. BURTON, *Retail Jeweller* **15** (1977) 23.
23. N. McINNES, *Barron's* 21 June (1976) p. 9 ff.
24. K. OKUDA, U.S. Patent 4 056 952 (1977).
25. R. H. WENTORF Jr, *J. Phys. Chem.* **75** (1971) 1833.
26. H. M. STRONG and R. M. CHRENKO, *ibid.* **75** (1971) 1838.
27. H. M. STRONG and R. H. WENTORF Jr, *Die Naturwiss.* **59** (1972) 1.
28. R. M. SCHAFFERT, "Electrophotography" (The Focal Press, London and New York, 1965).
29. Zerostat, a piezoelectric antistatic device, purchased from Discwasher Inc., 1407 N Providence Road, Columbia, Missouri 65201, USA.
30. Kyread, DIP-C, magnetic tape developer from Kyros Corp., P.O. Box 406, Madison, Wisconsin 53701, USA.
31. Xerox Blue Toner #125, from Xeroradiography, 125 Vinedo Avenue, Pasadena, CA 91107, USA.
32. C. PALACHE, H. BERMAN and C, FRONDEL, "Dana's System of Mineralogy", 7th edn, Vol. 1 (John Wiley and Sons, New York, 1944) p. 148.
33. "Dana's Textbook of Mineralogy", 4th edn, revised by W. E. Ford (John Wiley and Sons, New York, 1932) p. 335.
34. R. H. WENTORF Jr, U.S. Patents 2 996 673 (1961); 3 125 418 (1974); 3 181 933(1965).
35. L. COES Jr, "Abrasives" (Springer-Verlag, New York, 1971) p. 91.
36. G. L. PEARSON, U.S. Patent 2 669 692 (1954).

Received 21 February and accepted 23 March 1979.