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Fingerprinting diamonds using ion implantation

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It is possible to ion implant patterns in diamond crystals at fluences below that which would impart visible damage and then to reveal those patterns by electrostatic charging and dusting. The charge distribution – and therefore the dust attachement – is related to the difference in electrical conductivity between the implanted region and the rest of the crystal. The technique may have applicability for "fingerprinting" or personalizing diamond gemstones.

1. Introduction

The technique of electrostatic charging and dusting to reveal internal structure of both natural and synthesized diamonds was described earlier [1]. It was suggested that diamond crystals had rather sharply defined regions of different electrical conductivity and some regions could be charged electrostatically to attract and hold fine particles to reveal the structure. This technique provides a simple, non-destructive way to reveal the growth history of the crystal and also to "fingerprint" it, because the growth pattern will be unique to each crystal. The success of the method obviously requires the presence of the growth structure; that it be intersected by a cut surface because it is not revealed on an external growth surface; and that the pattern can indeed be revealed by the electrostatic charging technique. Diamonds differ with respect to the last condition, i.e. their ability to be charged and to hold a charge. As with all electrostatic phenomena, there is also a great sensitivity to humidity, and the net result is that not all natural diamonds could readily be made to reveal a pattern even though there was reason to believe a pattern existed.

In an effort to make the technique more generally applicable with respect to fingerprinting of gemstones, we considered ion implantation as a way deliberately to introduce regions of differing electrical conductivity in the crystal in a predetermined pattern. Although it is relatively easy to put a visible mark on a diamond by high fluences of ions, it is preferable to place in the crystal an invisible pattern that could subsequently be revealed by some technique such as electrostatic charging and dusting. This would be a unique fingerprinting for a diamond gemstone and would be independent of the "grown-in" pattern. This has been achieved and a patent has been issued on the technique [2].

2. Experimental procedure

Both natural and synthesized diamonds were implanted; for former consisted of unpolished sawn flats and stones with one polished surface; the latter were colourless (Type IIa), yellow (Type Ib), and blue (Type IIb) crystals grown at the GE Corporate Research and Development Centre and later polished.

The ion implantation was done at various fluences and voltages with boron, phosphorus, and carbon ions (see Table I) in a Varian-Extrion 400-10 implanter in a vacuum of about 5×10^{7} torr at room temperature for about 30 sec. The samples were offset 7° to the beam to minimize channelling effects; however, it may be advantageous to allow channelling to occur to achieve deeper penetration into the crystal lattice to make it more difficult to remove the implanted region. The shape of the implanted region was determined by masking the crystal with aluminium foil in which the desired pattern was formed by simple cutting out or by photographic reduction of designs plus photoresist/etching procedures. The sophisticated and routine techniques of microelectronics should be applicable

TABLE I (a) Colourless (Type IIa) synthesized diamond, (1 0 0) surface

Fluence (carbon ions/cm^2)	(keV)	Visible surface damage	Dust pattern
1×10^{14}	350	yes	yes
1×10^{13}	350	no	yes
5×10^{12}	350	no	yes
1×10^{12}	350	no	doubtful

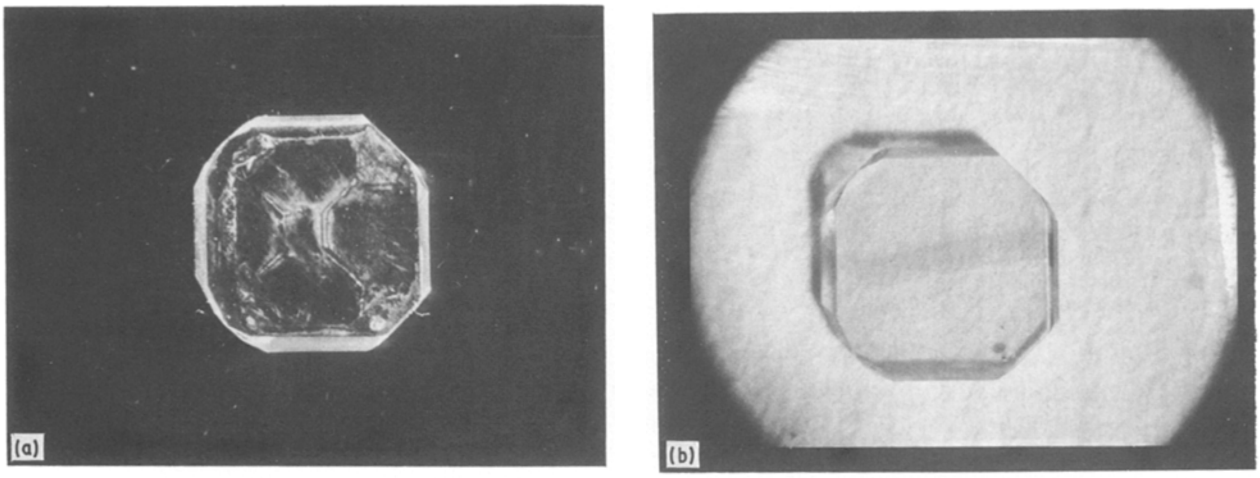
(b) Colourless (Type Ib) synthesized diamond, (1 0 0) surface

Fluence (carbon ions/cm^2)	(keV)	Visible surface damage	Dust pattern
1×10^{13}	350	no	yes
1×10^{13}	200	no	yes

(c) Colourless (Type Ia) natural octahedron, (1 1 1) surface

Fluence (carbon ions/cm^2)	(keV)	Visible surface damage	Dust pattern
1×10^{13}	350	no	yes
1×10^{12}	200	no	no
1×10^{13}	350	no	yes
1×10^{12}	400	no	no

* Retired.



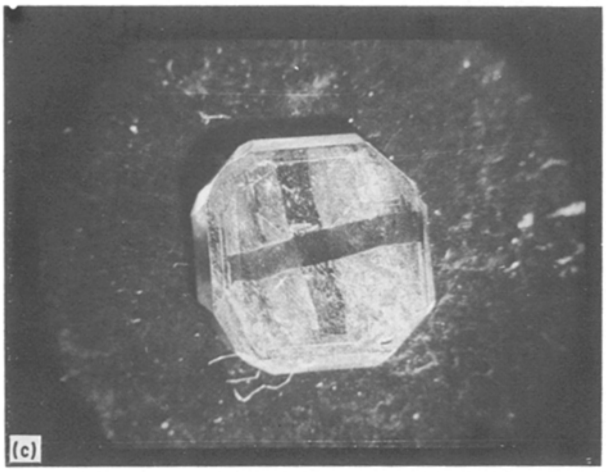


Figure 1 Ion-implanted pattern in synthesized colourless diamond crystal (Type IIa). (a) Dust pattern showing original growth structures revealed by electrostatically charging the (1 0 0) surface prior to ion implantation. The approximate dimensions of the crystal are 0.5 mm × 6 mm × 6 mm. (b) Crystal surface after carbon-ion implantation but prior to electrostatic charging and dusting. The horizontal band is visible because the ion fluence was too high (1×10^{14} ions/cm^2) and the crystal surface was visibly altered. A vertical band of ion implantation at lower fluence (1×10^{13}) is not visible, see (c). (c) Ion-implanted pattern revealed after electrostatically charging and dusting. The horizontal band is the same as seen in (b); the vertical band formed by ion implantation at lower fluence (1×10^{13}) is visible only after electrostatic charging and dusting. Part of the original growth structure of (a) can also be seen.

quite possibly directly on the diamond without an intermediate foil mask.

Because it is important not to put visible damage in the gemstone by ion implanation, the range of the ion fluences that could be used had to be determined. By shifting a mask to a different position on the same crystal and using different fluences, it was possible to determine a range in which it was safe to work, much as one would do in determining photographic exposures. A fluence of 1×10^{14} ions/cm^2 produced a visibly discoloured region; 1×10^{12} was inadequate, and 1×10^{13} ions/cm^2 was satisfactory (see Table I). This fluence was successfully used on the crystals implanted in this study, but there may be variations on the proper exposure because natural diamonds are notoriously inhomogeneous, and it is conceivable some regions of a crystal might react differently. Our results cover seven Type Ia natural stones plus several Type IIa, IIb and Ib synthesized crystals.

The electrostatic charging was done by rubbing on cloth or a piece of woven nylon rug or by using the Zerostat piezoelectric antistatic device, which permits charging of the surface either positively or negatively. The charged surface was dusted with Kyread fine particle powder from a pressurized can, although other powders can also be used. The charging and dusting technique was also further improved by doing the charging in the vicinity of the warm air from a hair dryer or laboratory heat gun. This low humidity environment significantly improves the ability to reveal

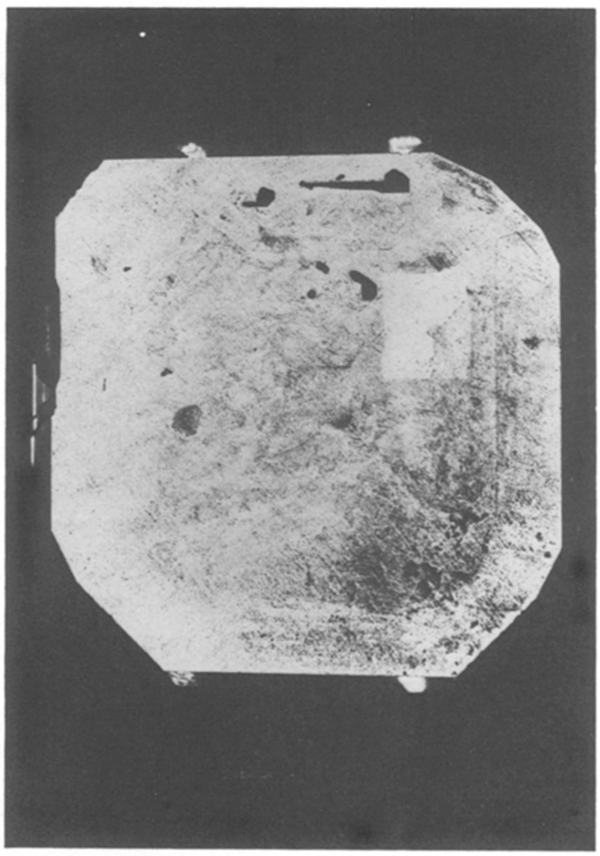


Figure 2 Dust pattern of rectangular boron-implanted region (upper right) in a colourless Type IIa synthesized diamond. Large black regions are flaws in the crystal.

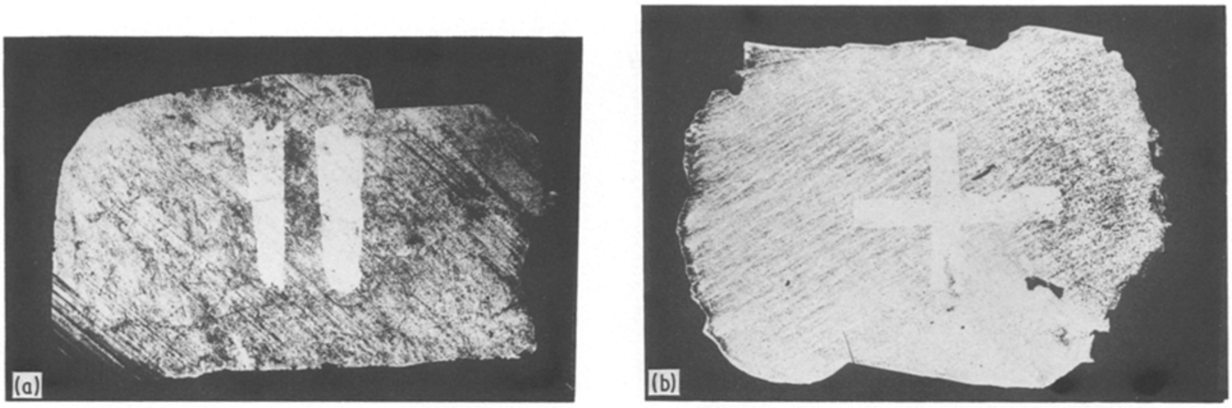


Figure 3 Dust patterns of boron-implanted region in colourless natural diamonds. (a) Two parallel bands on sawn surface. (b) Cross on polished surface.

internal structure of either natural or ion-implanted origin; in this way it has been possible to reveal patterns that eluded us earlier.

3. Ion-implanted patterns

The figures illustrate what can be done with rather simple marks on different kinds of diamonds.

Fig. 1b shows the effect of too high a carbon ion fluence in one exposure leaving a visible dark band. On the same crystal another lower exposure transverse to the first is visible only after electrostatic charging and dusting (Fig. 1c). A boron-implanted square region in one corner of the polished surface of a flawed synthesized Type IIa diamond is seen in Fig. 2 after charging and dusting. Natural diamond (Type Ia) implanted with boron ions is seen in Figs 3 and 4. Two of the crystals in Fig. 3 are rough sawn flats of approximately cube face orientation. A polished flat on the colourless crystal of Fig. 4 shows two different implants plus a natural growth ring pattern. In all the crystals except that shown in Fig. 1b there is no visible pattern when the crystals are wiped free of dust. The ion-implanted regions and the natural growth rings are seen by virtue of the contrast associated with the way the dust settles and stays on the charged crystal surface. The attachment of dust is dependent on the difference in electrical conductivity between implanted regions or natural growth steps and the rest of the crystal.

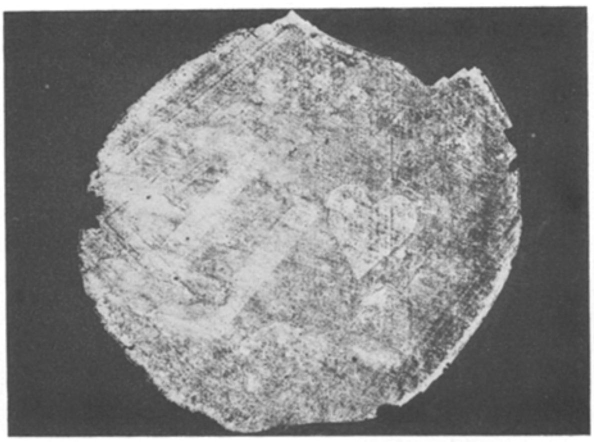


Figure 4 Dust patterns of ion-implanted regions and growth rings in a polished surface of a colourless natural diamond. The two side bands (left) are the result of the first implantation. Later the heart-shaped region was introduced. Sets of parallel lines near the outer edges are natural growth features also revealed by electrostatic charging and dusting.

In Fig. 5, an oval cut synthesized diamond has a heart-shaped ion-implanted region near one end of the table. Immediately above the heart is the sectorial growth pattern of the crystal – a tilted rectangular region with four radiating arms, one from each corner of the rectangle. Other "grown-in" patterns are visible also; the heavy line adjacent to the lower left side of the heart plus some lines in the upper right corner of the table. These lines are also unique identifying marks of this stone. The surface, after wiping off the dust, is shown in Fig. 5b. There is no visible evidence of the implanted region even when observed with Nomarski interference contrast at $\times 75$.

Some of these patterns were implanted over five years ago and are as readily and sharply revealed now as they were originally. However, because ion implantation is not a deep disturbance, and the pattern could be deliberately polished away, there was some concern about removal by normal wear. An ion-implanted region was abraded against very fine grain ($1\,\mu m$) Al_2O_3 polishing powder on a felt polishing cloth for about 1 h total cumulative time with no evidence of wear. This is considered a more severe treatment than most stones will ever experience in years of normal wear.

The crude cross pattern in Fig. 6 represents a possible variation combining two different ions; boron in the horizontal direction and phosphorus in the vertical direction. When the surface was charged positively with the Zerostat device and then dusted, the phosphorus band was seen; the boron band was revealed uniquely by the negative charge. Both were seen when the surface was rubbed on cloth or rug material. Other variations are probably possible with powders that characteristically have different charges. Although revealing a pattern on a more conducting crystal such as boron-doped blue stones it is more difficult than with Types Ia, Ib and IIa crystals, it was found possible to implant boron and phosphorus on IIb stones and change the local conductivity sufficiently to create a reproducible pattern.

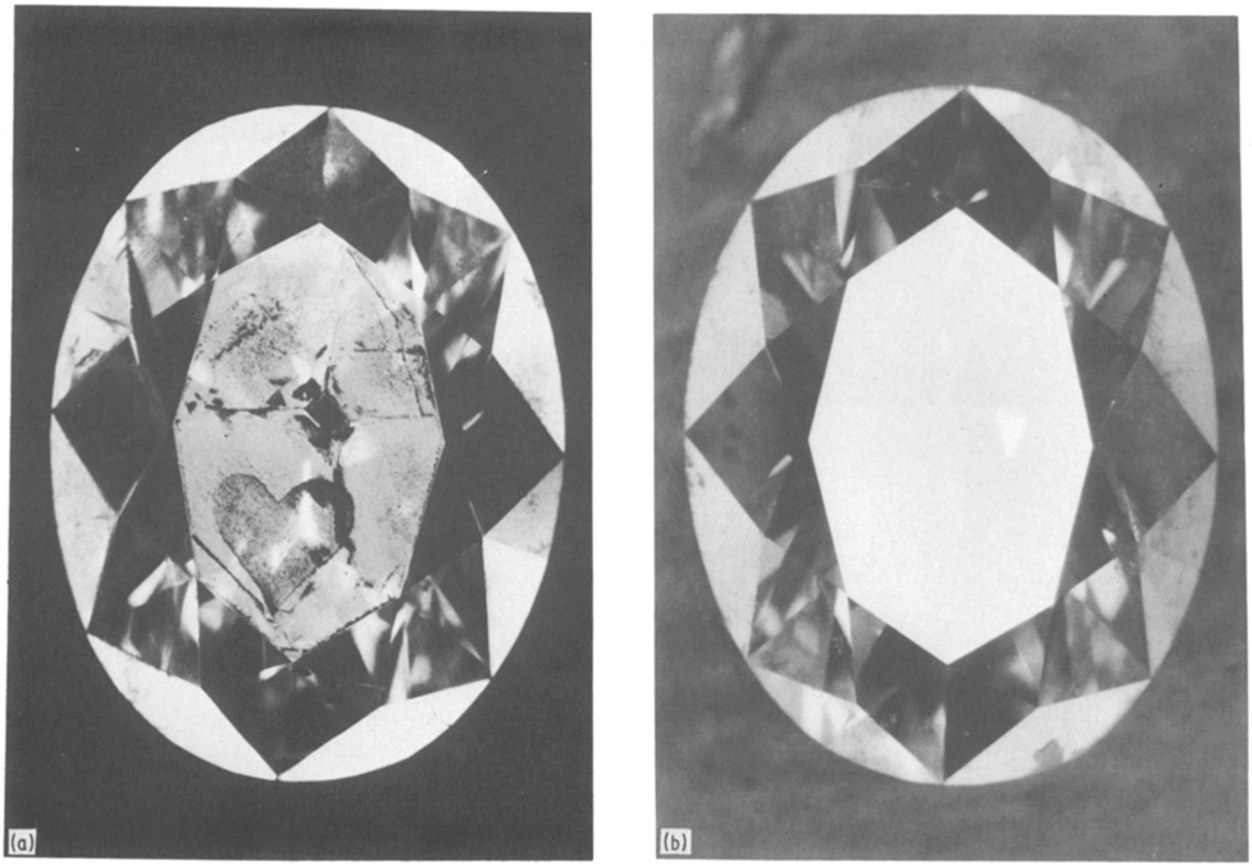


Figure 5 Heart-shaped ion-implanted region in the surface of a colourless, synthesized, oval cut diamond. (a) Dusted; see text for explanation of other features. (b) Wiped clean.

4. Conclusion

It has been demonstrated that ion implantation can be used to place a variety of patterns invisible to the eye in diamond surfaces, and these patterns can be revealed by electrostatic charging and dusting. In both natural diamonds and those synthesized in the laboratory the predominant conductivity change is based on chemical variations as the growth environment fluctuated. With ion implantation there is probably also some structural change such as formation of disordered or graphite-like regions. The technique may have applicability for both security and personalized functions in gemstones. For invisible patterns it is necessary to control the fluence of ions, and the inhomogenities of natural stones suggest more data than presented here are needed on the effect of different implantation conditions. Some currently available techniques for marking diamond gemstones are not concerned with invisibility (laser marking) so there might be an application for "burned" patterns if

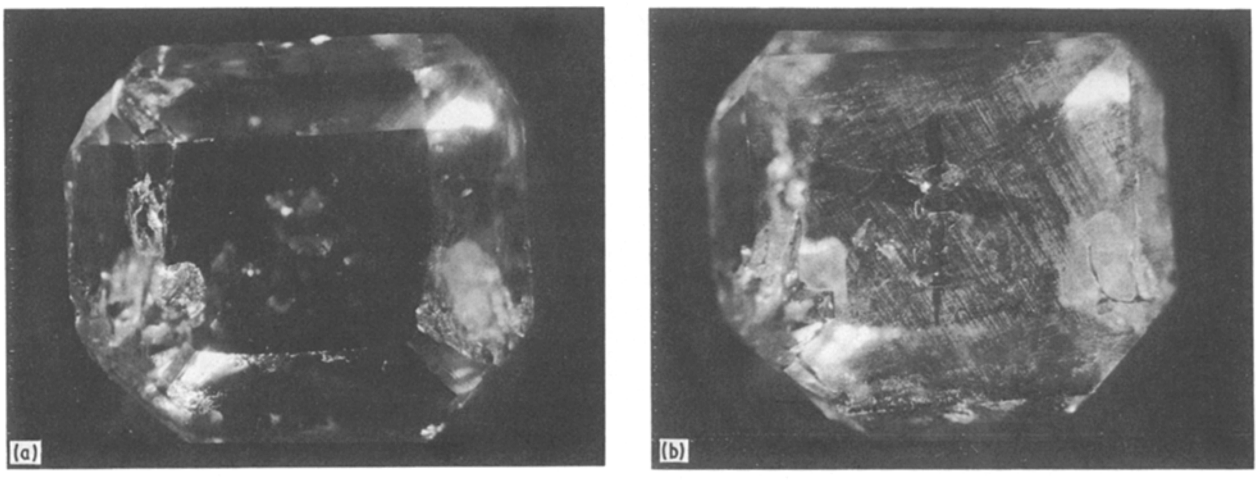
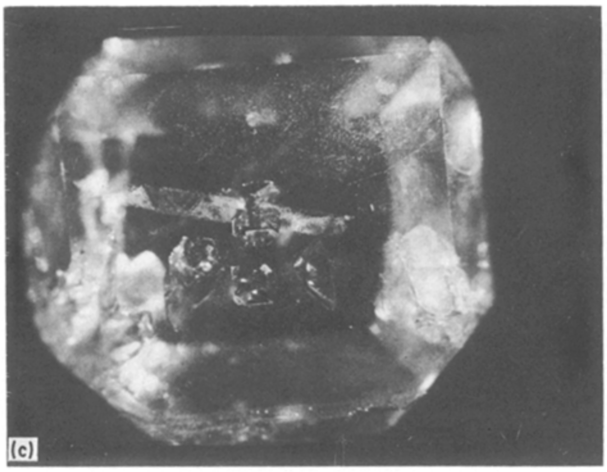


Figure 6 Ion-implantation pattern in a man-made colourless crystal. (a) Clean (1 0 0) surface (about 5 mm × 4 mm) which has been implanted sucessively with phosphorus and boron ions through a mask at fluences of 1×10^{13} ions/cm^2. (b) Dust pattern after electrostatically charging the crystal by rubbing on cloth. The X-pattern is composed of two separate ion-implanted regions which do not collect dust with this type of charging. (c) Dust pattern after charging the crystal negatively, revealing the horizontal band due to boron-ion implantation. (d) Dust pattern after charging the crystal positively, revealing the vertical band due to phosphorus-ion implantation. Other "grown-in" structures of the crystal are also revealed by this charging mode.



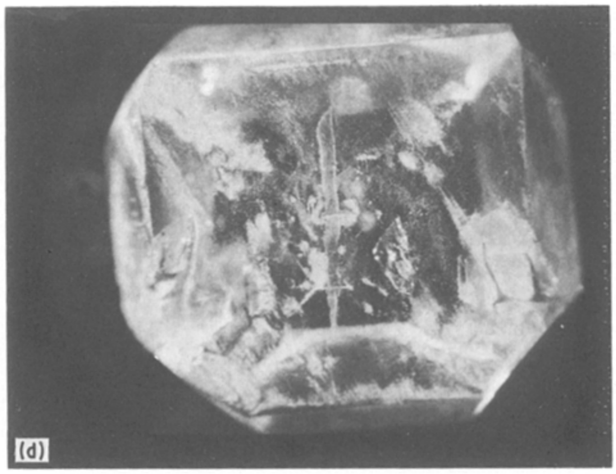


Figure 6 Continued.

placed in less obvious parts of the stone. These patterns conceivably could be read like the common price codes on groceries. It might also be interesting to explore other ions that could be read by other techniques free of such fluorescence dependency on electrostatic charges. It is expected that if there is sufficient interest in the technique described here, new developments will come from the microelectronics industry where expensive ion implanting devices are already available and photolithography techniques are highly developed.

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References

1. R. C. DEVRIES and R. E. TUFT, *J. Mater. Sci.* **14** (1979) 2650.
2. *Idem*, US Pat. no. 4 316 385, "Fingerprinting Crystals" (1982) assigned to General Electric Company.

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Note added in proof

We have found that cathodoluminescence can be used to reveal the implanted region.