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TWIN QUINTUPLETS IN CVD DIAMOND

D. Shechtman*, A. Feldman, J.L Hutchison**

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Twin quintuplets in CVD diamond

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ABSTRACT

The atomic structure of twin quintuplets in a chemical vapor deposited (CVD) diamond film was investigated by high resolution transmission electron microscopy (HRTEM). We conclude that the twin quintuplets have two main morphologies. The first consists of four $\Sigma=3$ twin boundaries and one $\Sigma=81$ twin boundary. The $\Sigma=81$ twin boundary contains the dislocations needed to accommodate a 7.35° misfit angle between a set of $\{111\}$ planes on opposite sides of the boundary. In the second case, the 7.35° misfit angle is accommodated by two or more grain boundaries that are tilted slightly more than the 70.53° tilt of a $\Sigma=3$ boundary. These grain boundaries and the conventional diamond lattice twin boundaries are the only types of boundaries that we have observed in CVD diamond.

1. INTRODUCTION

The defect structure of chemical vapor deposited (CVD) diamond has been studied in recent years as the technology to grow diamond has developed¹⁻⁷. Most of these defects were found to be twins of well defined orders, $\Sigma=3, 9, 27$ and 81 . Analyses by transmission electron microscopy (TEM) and by high resolution TEM (HRTEM) have revealed the fine structure of the twins and has shed light on their formation and their role in the growth of CVD diamond⁸⁻¹⁰. In addition to cataloging the types of twins observed, several authors have examined formations typical of twin interactions. Among these are twin quintuplets which have been found both near the center of grain cross-sections and at the periphery of grains. It is the purpose of this article to define some of the crystallographic parameters of these twin quintuplets and to describe how these defects influence the growth and morphology of CVD diamond.

2. EXPERIMENTAL

The film used in this study was prepared by microwave plasma CVD. Details of the deposition have been described previously and will not be discussed here⁸. The film was placed

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between TEM grids and thinned by ion milling for the HRTEM study. The high resolution transmission electron microscope used has a point resolution of 0.16 nm. All of the diamond grains studied were tilted so as to align a [110] direction parallel to the electron beam. Under this condition, each part of the diamond specimen contained two {111} planes and one (002) plane in an edge-on position relative to the electron beam axis. Atomic resolution images were recorded at 500K magnification close to the Scherzer defocus.

3. RESULTS AND DISCUSSION

3.1 Diffraction from twins

A diffraction pattern from a multiply-twinned diamond crystal is shown in Figure 1. The pattern is composed of five diffraction pattern sets, each with a [110] zone axis. The discrete patterns are rotated 70.53° relative to one another. This results from the rigid structural characteristic of the diamond lattice which allows only five sets of twins to exist in each [110] zone. There is, however, some slack in this rigidity which we discuss below. An analysis of the diffraction pattern from one pair of $\Sigma=3$ related twins in CVD diamond has been given elsewhere⁸.

3.2 Twin quintuplets

The twins, whose boundaries are observed in an edge-on position, are in most cases present throughout the specimen. The twinning frequency is small at the center of the grain and higher toward the periphery of the grain. The twins intersect one another to form $\Sigma=3$ boundaries and boundaries of higher order, namely $\Sigma=9$, $\Sigma=27$ and $\Sigma=81$ ^{9,10}. In some cases more than two twins intersect and an important case is that of five intersecting twins which we call a twin quintuplet. It has been suggested⁹ that a twin quintuplet is an important nucleation site for new planes in CVD diamond, but not all twin quintuplets serve such a central role. Our observations indicate that in addition to the main twin quintuplets near the center of a grain that may manifest themselves in the final morphology of the crystal, there are numerous secondary twin quintuplets. Several of these can be found in each [110] section of a diamond crystal.

The core of a twin quintuplet is a line defect called a quintuplet axis. In a main quintuplet, the quintuplet axis frequently propagates from the center of the diamond crystal to its surface. This axis is usually viewed in an end-on position in the HRTEM images. At the surface, the quintuplet axis emerges as the apex of a five sided pyramid. The sides of this pyramid are usually {111} planes. A maximum number of twelve main quintuplet axes can form at the center of a diamond crystal, thus, creating an icosahedrally shaped diamond crystal⁸. The icosahedron is not perfectly regular because of the 7.35° misfit angle. In some instances a quintuplet axis does not emerge from the surface of the grown crystal, thus remaining a local internal phenomenon.

A discussion of the crystallography of the twin quintuplets follows. Because the twinning angle of a $\Sigma=3$ boundary is 70.53° , there can be no more than four $\Sigma=3$ boundaries in a twin quintuplet. Thus, an angle of 7.35° would remain between {111} planes in a pair of the twins, and this angle we call a misfit angle because it results in a noncoherent twin boundary. Our observations indicate that the lattice deals with this misfit in one of two ways.

Twin Quintuplet Type I: In this case the misfit angle creates a $\Sigma=81$ twin boundary which is a fourth order twin boundary; the twinning angle is 77.88° . The $\Sigma=81$ twin boundary contains the dislocations needed to accommodate the 7.35° misfit angle between a set of $\{111\}$ planes on opposite sides of the boundary. This case has been documented previously^{9,10}, where it was shown that the boundary thus formed can transform into a $\Sigma=3$ boundary by emitting a series of dislocations⁹. An example of a Type I twin quintuplet is given in Figure 2. The inset illustrates the misfit angle that forms the $\Sigma=81$ boundary. In addition, the $\{111\}$ planes near the quintuplet axis are marked. An example of a similar twin quintuplet can be seen at the upper left corner of the micrograph (marked with a circle). The orientation and crystallographic character of both examples are identical.

Twin Quintuplet Type II: This case differs from Type I in that the 7.35° misfit angle does not result in a $\Sigma=81$ boundary. Instead, the misfit is accommodated by more than one of the quintuplet boundaries to form grain boundaries whose tilt angles are slightly more than the 70.53° tilt angle of a $\Sigma=3$ twin boundary. Because the misfit angle of one of these boundaries does not have a determined value, we consider the boundary to be non-crystallographic. In Figure 3, the 7.35° misfit angle is divided so as to create two non-crystallographic boundaries. These form between the crystallite pairs (B,C) and (A,E). The other boundaries, between the pairs (A,B), (D,E) and (C,D), are of the $\Sigma=3$ type. The inset in Figure 3 illustrates the twin quintuplet and the division of the misfit angle. Several $\{111\}$ plane traces are also marked on the micrograph. Near mirror symmetry is clearly observed on the two sides of the (A,B) $\Sigma=3$ boundary. This symmetry is probably caused by nearly identical strain patterns on both sides of the (A,B) twin boundary. The characteristic shape that emerges from this type of twin quintuplet is rather abundant in CVD diamond crystals. Thus, the (A,B) $\Sigma=3$ twin boundary is not only a crystallographic mirror plane for the neighboring twins, but also a morphological near mirror plane for the characteristic "Coat of Arms" shape outlined by the high order twins on both of its sides.

In addition to the situation discussed above, we have observed a misfit angle divided into three parts in other micrographs containing twin quintuplets.

4. CONCLUSION

Atomic resolution electron microscopy of a CVD diamond film was used to determine the crystallography and morphology of twin quintuplets. Two basic types of twin quintuplet centers were revealed and the twin boundaries around them studied. The first type consists of four $\Sigma=3$ twin boundaries and one $\Sigma=81$ twin boundary. The $\Sigma=81$ twin boundary contains the dislocations needed to accommodate a 7.35° misfit angle between a set of $\{111\}$ planes on opposite sides of the boundary. In the second type, the 7.35° misfit angle is accommodated by two or more grain boundaries that are tilted slightly more than the 70.53° tilt of a $\Sigma=3$ boundary.

5. ACKNOWLEDGEMENT

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6. REFERENCES

1. B.E. Williams and J.T. Glass, *J. Mater. Res.* 4, 373 (1989)

2. J. Narayan, J. Mater. Res. 5, 2414 (1990)
3. B.E. Williams, J.T. Glass, R.F. Davis, K. Kobashi and K.L. More, Proc. 1st Int. Symp. Diamond and Diamond Like Films, J.P. Dismukes, editor 202 (1989).
4. G-H.M. Ma, Y.H. Lee and J.T. Glass, J.Mater. Res. 5, 2367 (1990).
5. J. Narayan, A.R. Srivatsa, M. Peters S. Yokota and K.V. Ravi, Appl. Phys. Lett. 53,1823(1988).
6. B.E. Williams, H.S. Kong and J.T. Glass, J. Mater. Res. 5, 801(1990).
7. K. Kobashi, K. Nishimura, K. Miyata, Y. Kawate, J.T. Glass and B.E. Williams, SPIE Diamond Optics, 969, 159(1988).
8. D. Shechtman, E.N Farabaugh, L.H. Robins, A. Feldman and J.L. Hutchison, SPIE Vol. 1534 Diamond optics IV (1991).
9. D. Shechtman, J.L Hutchison, L.H. Robins, E.N. Farabaugh, and A. Feldman, to be published.
10. D. Shechtman, A. Feldman, M.D. Vaudin, and J.L Hutchison, to be published.

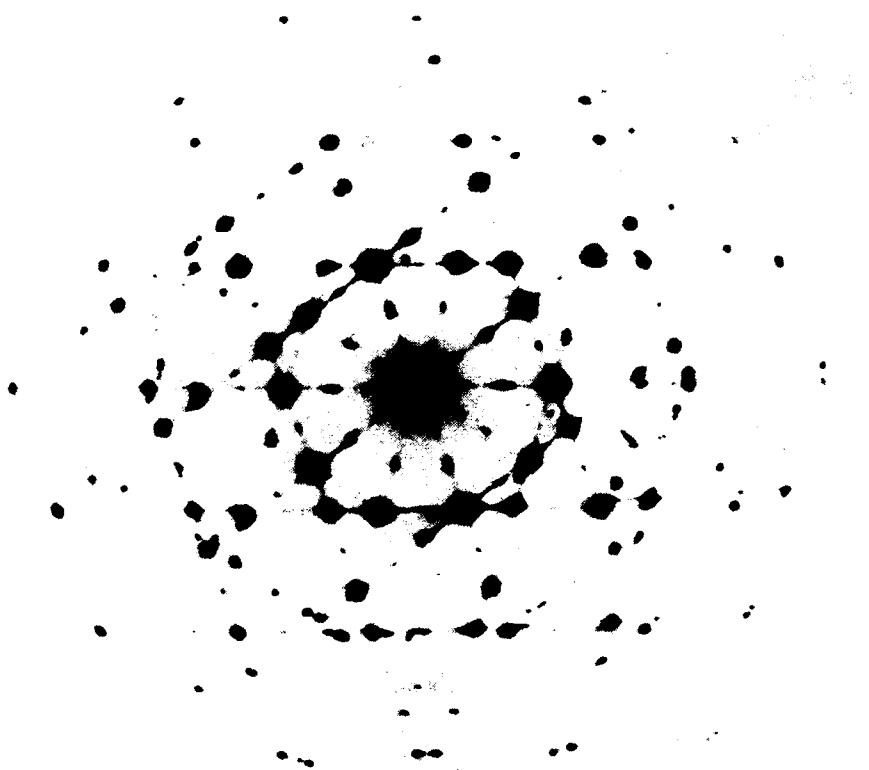


Fig. 1. A diffraction pattern taken from a whole diamond crystal is composed of five twin diffraction variations.

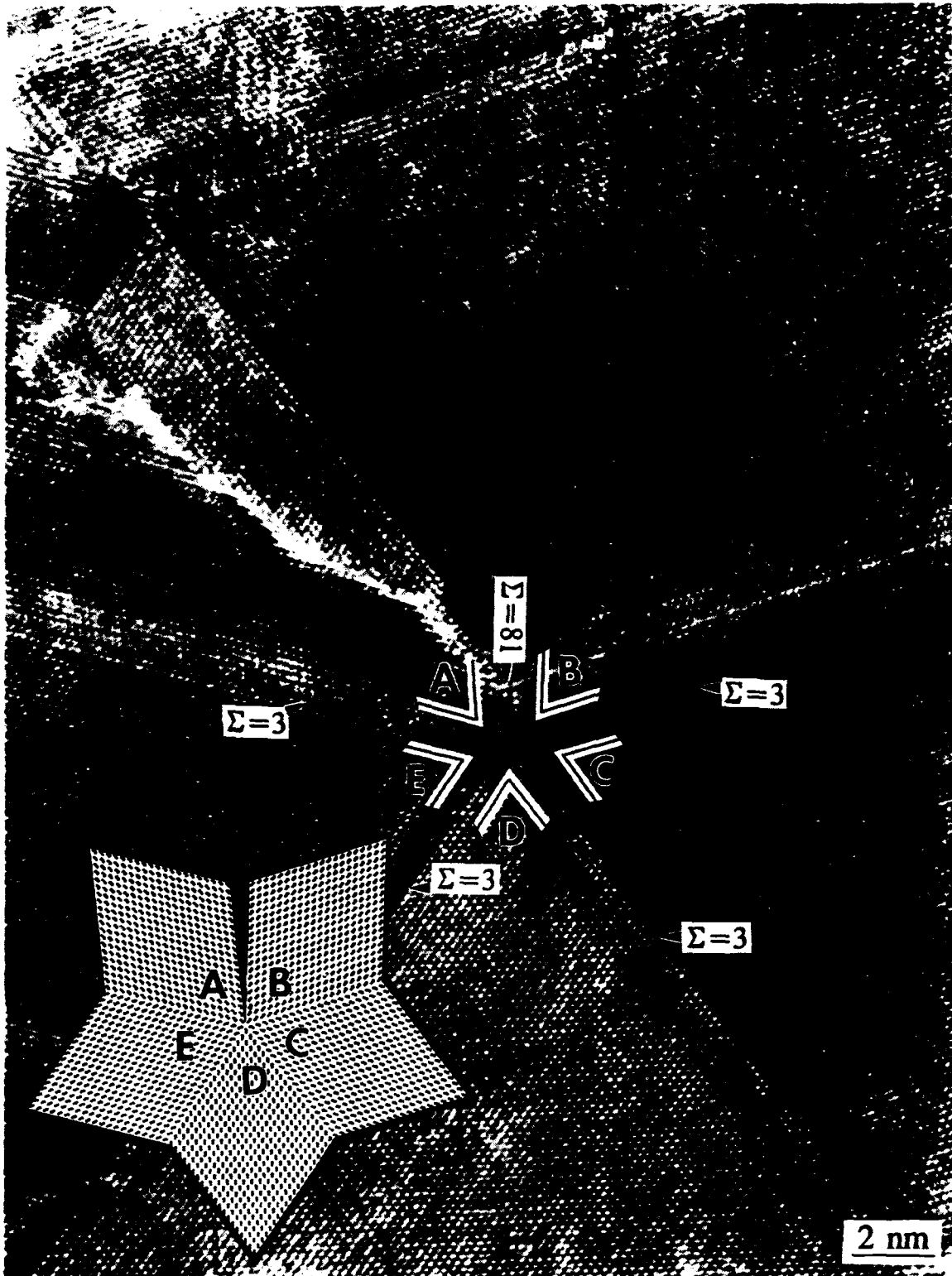


Fig. 2. A Type I twin quintuplet. The misfit angle creates a $\Sigma=81$ twin boundary.

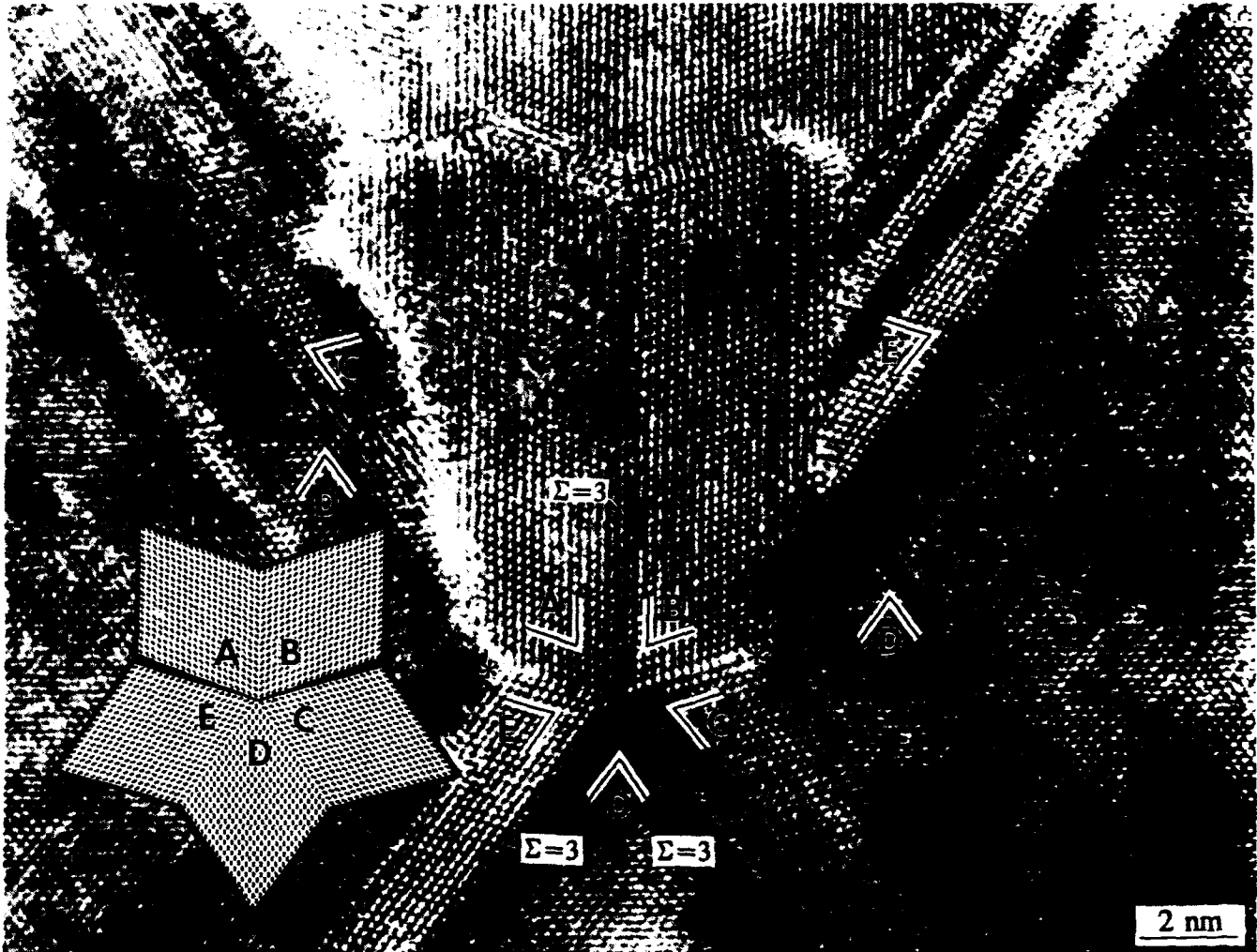


Fig. 3. A Type II twin quintuplet. In this example the misfit angle is divided into two grain boundaries. Between the points marked * a series of high order twin boundaries form a "Coat of Arms" shape, characteristic of Type II.

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