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MOIRE-FRINGE IMAGES OF TWIN BOUNDARIES IN
CHEMICAL VAPOR DEPOSITED DIAMOND

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MOIRE-FRINGE IMAGES OF TWIN BOUNDARIES IN CHEMICAL VAPOR DEPOSITED DIAMOND^{a)}

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ABSTRACT

Features in lattice image micrographs of chemical vapor deposited diamond can be interpreted as Moire fringes that occur when viewing twin boundaries that are inclined to the electron beam. The periodicities in images of inclined twin boundaries with $\Sigma=3$ and $\Sigma=9$ misorientations have been modeled by computer graphic simulation.

Key words: chemical vapor deposition, CVD, diamond, twins, lattice images, Moire fringes

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MOIRE-FRINGE IMAGES OF TWIN BOUNDARIES IN CHEMICAL VAPOR DEPOSITED DIAMOND

Recent work strongly suggests that lattice defects such as twins and stacking faults play an important role in the growth of diamond films prepared by chemical vapor deposition (CVD)¹. CVD diamond usually grows as a polycrystalline material consisting of highly twinned grains. Typically, each grain is not a single crystal but consists of many twins, each twin within the grain having a well defined orientation with respect to every other twin within the grain. All of the twins observed in CVD diamond have a common $\langle 110 \rangle$ rotation axis.

High resolution transmission electron microscopy (HRTEM) of CVD diamond has revealed a variety of twin boundary types¹⁻⁸. Narayan³ has noted the presence of twin boundaries classified as $\Sigma=3$ (first order twins) and $\Sigma=9$ (second order twins) in the nomenclature of the coincident site lattice (CSL)⁹, where the order n of the twin boundary is such that $\Sigma=3^n$. Twin boundaries have been observed previously in other cubic materials having the diamond lattice structure, such as silicon¹⁰⁻¹² and germanium¹³. In addition to the twin boundaries observed by Narayan, boundaries of types $\Sigma=27$ and $\Sigma=81$ have also been observed in CVD diamond¹⁴ and examples are shown in this letter.

In this letter, we report on several Moire-fringe features observed in high resolution lattice images of CVD diamond. We interpret these features as images of twin boundaries of types $\Sigma=3$ and $\Sigma=9$ where the boundary surface is inclined to the electron beam; the beam passes through both of the twin-related crystals and double diffraction occurs. The periodicities in the resultant image depend on the relative orientations of the twins. By overlapping computer-generated $\langle 110 \rangle$ projections of the diamond lattice at the misorientation angles of the crystals, the principal features seen in these lattice images are reproduced.

We have examined the twinning structure of a fine-grained diamond film grown by microwave-assisted chemical vapor deposition on a single crystal silicon substrate. The film growth parameters were: microwave power - 1 kW; nominal graphite susceptor temperature - 650 °C; gas pressure - 6.6×10^3 Pa; gas flow rate - 260 standard cm³/min; gas composition - 99.5% H₂, 0.5% CH₄; deposition time - 45 min; growth rate - 0.4 $\mu\text{m}/\text{h}$; total thickness - 0.3 μm ; average grain size - $\sim 0.1 \mu\text{m}$. The details of the specimen preparation and the HRTEM technique are given in Ref.[1].

We classify the twin boundaries into two categories. The first category consists of planar tilt boundaries lying on crystallographic planes that mirror the bordering twins; these are called 'coherent' boundaries. The second category consists of boundaries that rarely lie on well-defined crystallographic planes and whose orientations may vary from place to place. In this paper, we call these 'noncoherent' boundaries.

Figure 1 shows both coherent and noncoherent twin boundaries in the CVD diamond

specimen. The coherent boundaries are all of type $\Sigma=3$. A noncoherent boundary can be observed meandering across the micrograph. Where the boundary is parallel to the electron beam (V), its image is lighter than the images of coherent boundaries because of preferential ion thinning; this suggests that the noncoherent boundary has greater energy than the coherent boundaries. From the relative orientations of the $\{111\}$ planes on opposite sides of a boundary, we have identified noncoherent boundaries of types $\Sigma=3$ and $\Sigma=9$. Noncoherent twin boundaries of types $\Sigma=27$ and $\Sigma=81$ can be seen in Fig. 2, which shows a region containing a twin quintuplet (discussed below).

In CVD diamond, $\Sigma=9$, $\Sigma=27$ and $\Sigma=81$ boundaries are usually observed to be noncoherent. This is in marked contrast to observations made in silicon, where $\Sigma=9$ and $\Sigma=27$ boundaries are usually coherent^{10,15,16}. Noncoherent boundaries arise when the free surfaces of two twin-related crystals grow toward each other and meet at an arbitrary surface. Because of the relatively low homologous temperature of CVD diamond during the deposition process (650 °C), the atoms in the boundary region have insufficient energy to rearrange once the twins have met; therefore, the boundary plane cannot rotate into a more symmetrical and lower energy orientation. The boundary that is formed results from the detailed kinetics and energetics of the diamond growth specific to a particular specimen. Thus, a noncoherent boundary can even occur when two crystals of the same orientation grow together. There may be some slight displacement of the two crystals relative to each other and there is insufficient energy to allow the boundary to annihilate. Such a displacement is seen in Fig. 1 (W), where two crystals of identical orientation have formed an interface of relatively low density.

Noncoherent boundaries can arise during the early stages of the nucleation and growth of a diamond twin quintuplet, a structure frequently observed to be the origin of growth of a grain^{3,7,14}. An example is shown in Fig. 2 where the center of the twin quintuplet is marked $\star$. Figure 3(a) shows a computer simulation of the twin quintuplet in $\langle 110 \rangle$ projection; in three dimensions, the twin quintuplet consists of five successive tilt boundaries radiating from a common $\langle 110 \rangle$ rotation axis. Four of the boundaries are coherent twin boundaries of type $\Sigma=3$ with a tilt angle of 70.53°. The fifth boundary is of type $\Sigma=81$ with a tilt angle of 77.88°. The difference between the $\Sigma=81$ tilt and the $\Sigma=3$ tilt leaves a small mismatch angle of 7.35° between $\{111\}$ planes in the twins separated by the $\Sigma=81$ boundary as shown in Fig. 3. The $\Sigma=81$ boundary can be modeled as a $\Sigma=3$ twin boundary containing regularly spaced secondary dislocations to accommodate the mismatch angle¹⁰. However because of the low homologous temperature referred to above and because this boundary is the last to form during nucleation of a twin quintuplet, the boundary forms in a noncoherent manner inherent to the quintuplet structure.

Several regions in Fig. 1 do not exhibit the typical appearance of $\langle 110 \rangle$ oriented diamond evident throughout most the micrograph. In all cases, these anomalous regions are associated with the noncoherent boundary. The images in these regions can be interpreted as Moire-fringe patterns that result when the twin boundaries are inclined with respect to the electron beam so that the beam passes through two overlapping twins. In Fig. 1, overlapping

twins with boundaries of type $\Sigma=3$ are indicated by X and with boundaries of type $\Sigma=9$ are indicated by Y.

We have modeled the periodicities observed in the images of the inclined $\Sigma=3$ and $\Sigma=9$ noncoherent boundaries using a graphical projection of the diamond lattice viewed along the $\langle 110 \rangle$ direction. In the twin quintuplet modeled in Fig. 3(a), each twin is bounded by $\{111\}$ planes; no attempt has been made to model the $\Sigma=81$ boundary. We have divided the figure into 5 twin domains labeled A, B, C, D and E. Table 1 identifies the boundary type that would occur if one twin, oriented as defined in the twin quintuplet figure, were to border another. If we enlarge the twin in region A to overlap the entire twin quintuplet, we obtain overlap patterns with the periodicities of the CSLs having $\Sigma=3$, $\Sigma=9$, $\Sigma=27$ and $\Sigma=81$ misorientations (Fig. 3(b)). The overlap of region A with region B shows a striped pattern having the same periodicity as the $\Sigma=3$ overlap region labeled X in Fig. 1. The overlap of region A with region C shows a centered hexagonal pattern having the same periodicities as the $\Sigma=9$ overlap region labeled Y in Fig. 1. Furthermore, the relative orientations of the $\Sigma=3$ CSL, the $\Sigma=9$ CSL, and the non-overlapping regions seen in Fig. 3(b) are the same as the relative orientations of the stripes in region X, the hexagonal patterns in region Y and the non-overlapping crystals seen in Fig. 1.

In conclusion, high resolution lattice images of CVD diamond have revealed a highly varied twinning structure. Moire-fringe patterns observed in the micrographs can be interpreted as overlapping twins with boundaries of types $\Sigma=3$ and $\Sigma=9$ that are inclined to the electron beam. A computer graphic simulation has been made to duplicate the periodicities and orientations of these boundary images. The patterns we have identified as being due to overlapping twins show the same periodicities and orientations as the corresponding coincidence site lattices.

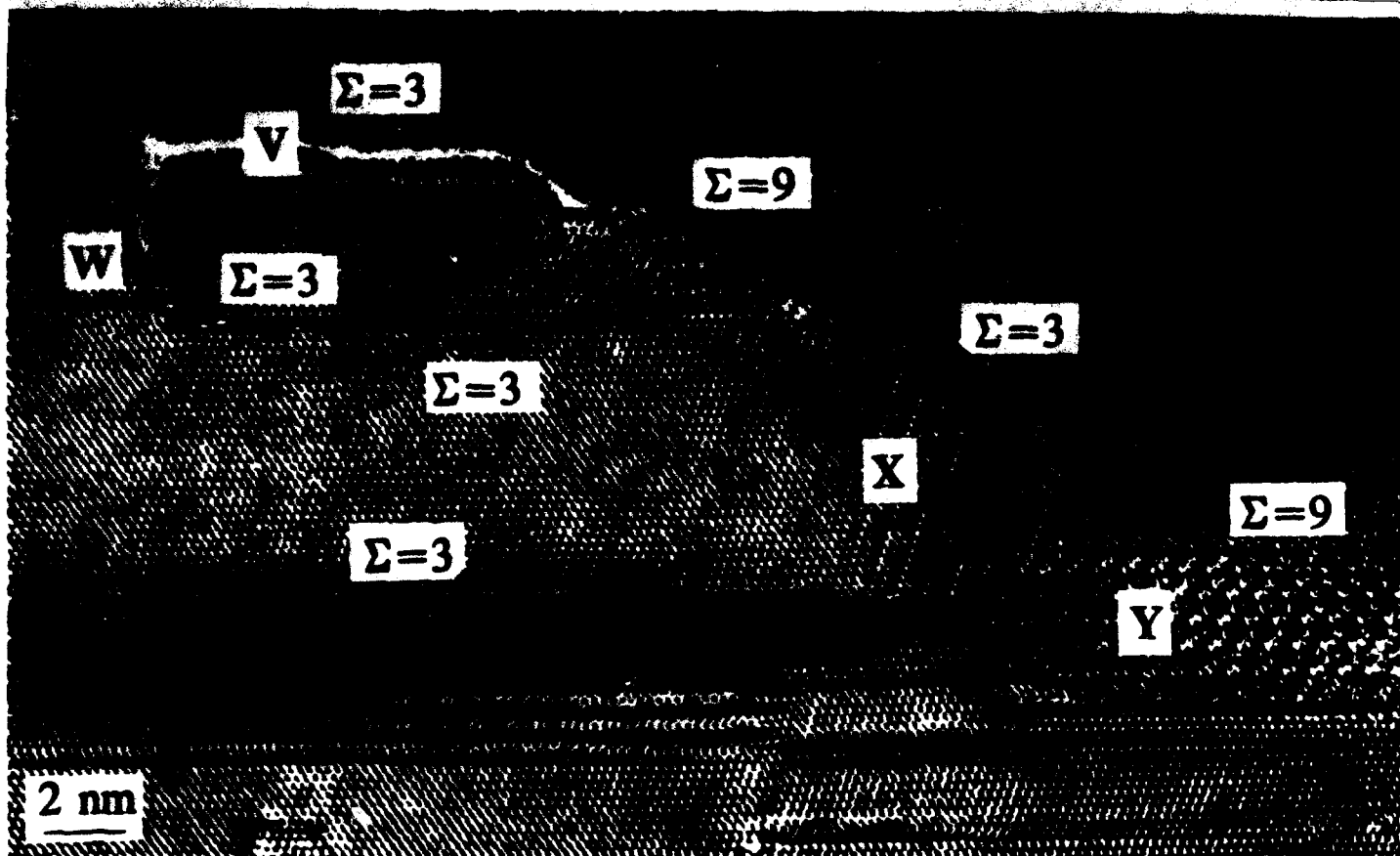
REFERENCES

1. D. Shechtman, E.N. Farabaugh, L.H. Robins, A. Feldman and J.L. Hutchison, in Diamond Optics IV, A. Feldman and S. Holly, Editors, SPIE Proc. 1534, 26-43 (1991).
2. B.E. Williams and J.T. Glass, J. Mater. Res. 4, 373 (1989).
3. J. Narayan, J. Mater. Res. 5, 2414 (1990).
4. 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).
5. G-H.M. Ma, Y.H. Lee and J.T. Glass, J. Mater. Res. 5, 2367 (1990).
6. J. Narayan, A.R. Srivatsa, M. Peters S. Yokota and K.V. Ravi, Appl. Phys. Lett. 53, 1823 (1988).

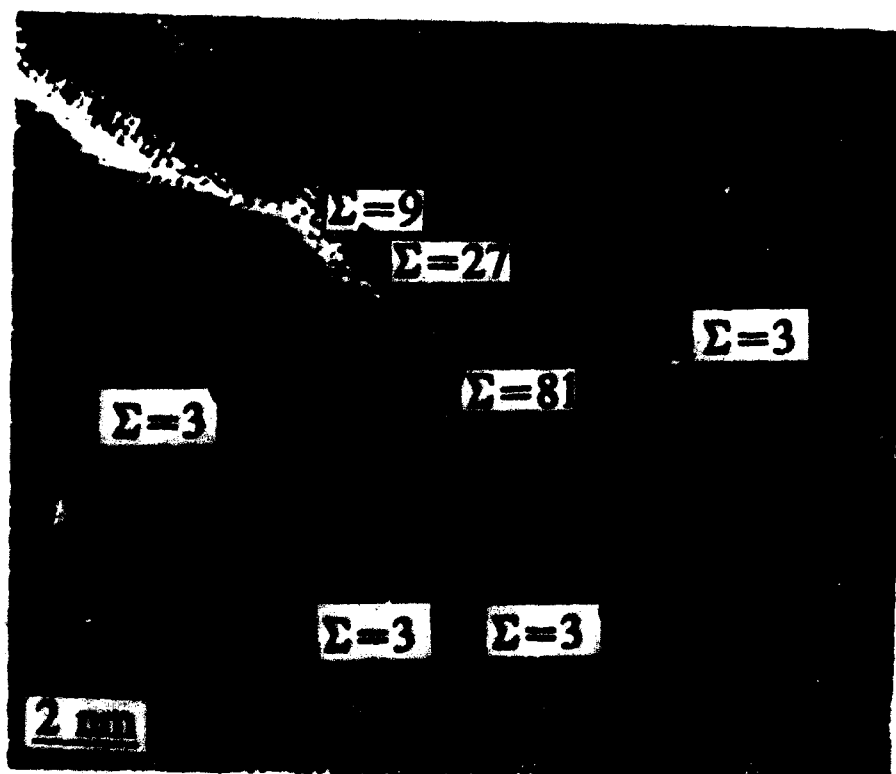
7. B.E. Williams, H.S. Kong and J.T. Glass, J. Mater. Res. 5, 801 (1990).
8. K. Kobashi, K. Nishimura, K. Miyata, Y. Kawate, J.T. Glass and B.E. Williams, SPIE Diamond Optics, 969, 159 (1988).
9. W. Bollman, Crystal Defects and Crystalline Interfaces (Springer-Verlag, New York, 1970).
10. M.D Vaudin, B. Cunningham and D.G. Ast, Scripta Met. 17, 191 (1983).
11. S. Iijima, Jpn. J. Appl. Phys. 26, 357 (1987).
12. S. Iijima, Jpn. J. Appl. Phys. 26, 365 (1987).
13. Z. Elgat, "Structure of Twin Boundaries in Ge and Spinel", Doctoral Thesis, Cornell University, August 1985.
14. D. Shechtman, E.N. Farabaugh, L.H. Robins, A. Feldman and J.L. Hutchison, in preparation.
15. B. Cunningham, H.P. Strunk and D.G. Ast, Scripta Met. 16, 349 (1982).
16. B. Cunningham, H.P. Strunk and D.G. Ast, Appl. Phys. Lett. 40(3), (1982).

Table I. Type of twin boundary occurring if one twin in Fig. 3(a), were to border another.

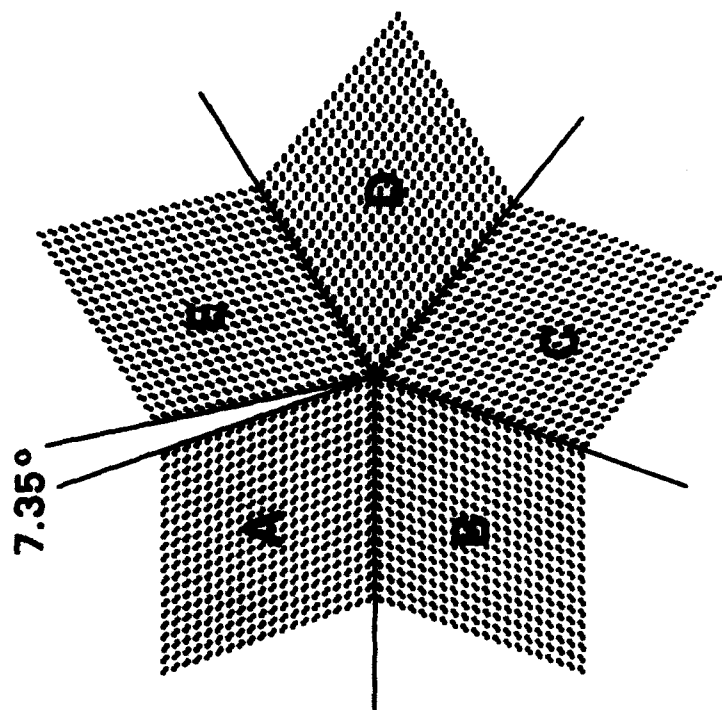
Boundary Type (coincidence site lattice notation)	Adjacent Regions
$\Sigma=3$	A-B, B-C, C-D, D-E
$\Sigma=9$	A-C, B-D, C-E
$\Sigma=27$	A-D, B-E
$\Sigma=81$	A-E



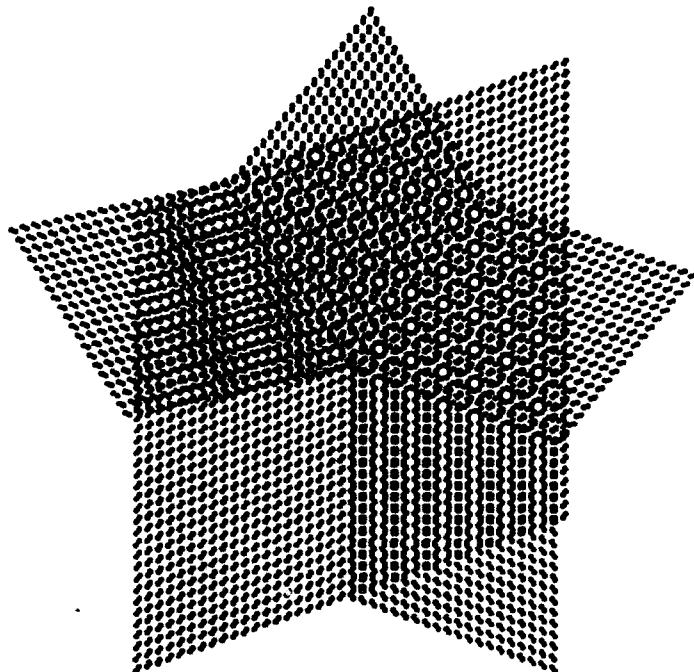
1. Lattice image of a CVD diamond specimen observed in a $\langle 110 \rangle$ direction. The figure shows coherent twin boundaries of type $\Sigma=3$, noncoherent boundaries of types $\Sigma=3$ and $\Sigma=9$, and Moiré fringes. See text for a discussion of the labeled features.



2. Lattice image of CVD diamond containing a twin quintuplet observed in a $\langle 110 \rangle$ direction. $\Sigma=3$, $\Sigma=9$, $\Sigma=27$, and $\Sigma=81$ boundaries can be observed.



(a)



(b)

3. (a) Computer model of a twin quintuplet where the $\{111\}$ planes bounding in each of the twins are indicated by the lines. (b) Overlapping twins having coincidence site lattices of types $\Sigma=3$, $\Sigma=9$, $\Sigma=27$ and $\Sigma=81$. The simulations are observed along a $\langle 110 \rangle$ direction.

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