Twin quintuplet surfaces in CVD diamond

Dan Shechtman

Abstract Chemical vapor deposition (CVD) of diamond films and wafers is a well established and flexible technology in which deposition parameters control the deposition rate as well as diamond properties, quality and shape. This article deals with surface morphology and crystallography of wafers, with emphasis on twin blocks and twin quintuples. In the study described here we have determined surface facet crystallography of two diamond wafers groups, one that contains $\Sigma 3$ twin blocks and the other that has a large population of twin quintuplets. The tool used for the study is a scanning electron microscope (SEM) and the technique to identify surface crystallography involves only accurate tilting and surface observation. A basic knowledge of the twin structure enables accurate determination of surface crystallography.

Introduction

Twin quintuplets have been observed in a large number of crystals and nanoparticles [1], but were rarely thoroughly studied. CVD diamond contains high density of twin quintuplets that form during the initial film growth process, and at the onset of nucleation some of the crystals have an icosahedral shape. These icosa-

D. Shechtman (✉)
Materials Engineering, Technion, Haifa, Israel
e-mail: danny.shechtman@gmail.com

D. Shechtman
ISU, Ames, IA, USA

hedral diamond particles have 12 twin quintuplets emerging from the center of the particle. Although prior to the creation of a continuous diamond film most of these free standing crystals are not icosahedral, the shape of many of them indicates at least one twin quintuplet formation (Fig. 1). Presented here is a crystallographic study of twin quintuplets that form in CVD diamond crystals. We have used an SEM to determine the surface crystallography of diamond films in wafers that are about 1 mm thick.

Twinned surfaces

Surfaces of commercial and experimental CVD diamond wafers and films are usually faceted and in many cases twinned. Each facet is either {001} or {111}, and there is a tendency to form {111} facets when the growth is from a lean solution (low carbon gas content). In this article we will use coincidence-site lattice (CSL) notations to define the different twin boundaries. CSL is the ratio of the crystal lattice sites to the coincident lattice sites, denoted by Σ. The occurrence of coincidence-site lattices was first identified by Kromberg and Wilson [2] in their study on secondary recrystallization of copper [2].

Diamond grains in the growing wafer that contain $\Sigma 3$ twin boundaries and have special orientation such that a <110> coincides closely with the growth direction that is contained in a {111} twin plane, can extend through the thickness of the wafer (Fig. 2). When this is not the case, the grain is not favorably oriented and will stop growing. This is the case along the thickness of the growing wafer, and true for grains that emerge with the favorable orientation from the bottom of the
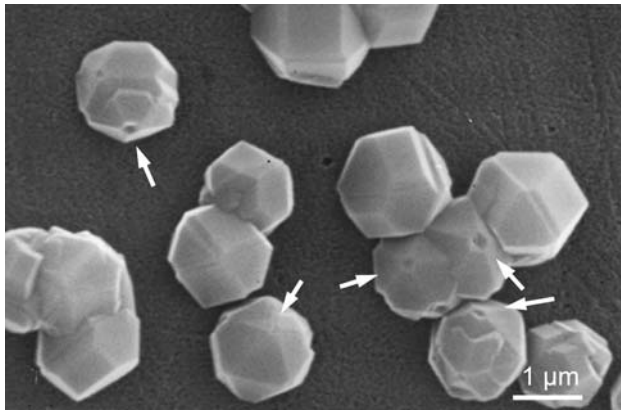
Fig. 1 A large proportion of the nucleating diamond crystals are twinned and many are twin quintuplets with 5-fold rotational axes

wafer, as well as for newly formed grains along the growth path. Shown in Fig. 2 is a polished and etched cross-section of diamond wafer and the straight lines of Σ3 twin boundaries aligned close to the growth direction, are clearly seen.

Several features can be observes on twin-containing surfaces of CVD diamond wafers:

(1) Each diamond crystal is subdivided by a series of parallel or non-parallel Σ3 twinned plates, separated by Σ3 coherent twin boundaries. These twin boundaries do not significantly harm properties of the wafer, but are rather conducive to fast film growth.

(2) When the Σ3 twin boundaries are parallel, a jagged block of twinned plates is formed and the facets on the free surface of the plates can be either {001} or {111}.
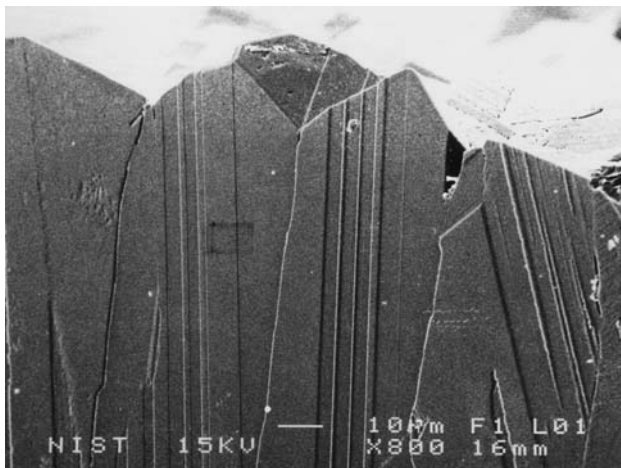

Fig. 2 Σ3 twins can grow through the thickness of the wafer if properly oriented, as seen in this polished and etched cross-section

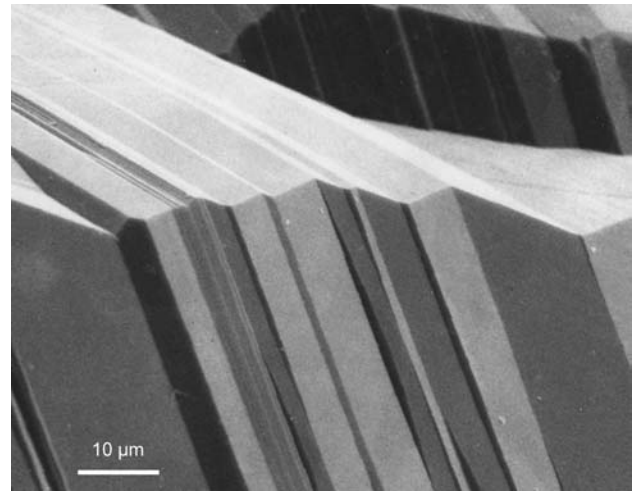**Fig. 3** Faceted surface of a diamond wafer. The lines between the facets are Σ3 twin boundaries

An example of such a block of twinned plates is shown in Fig. 3.

(3) When the Σ3 boundaries are not parallel, they usually belong to the same <110> zone axis and can form twin quintuplets, Fig. 4.

Crystallography of parallel twinned facets

The analysis of facet crystallography can be performed in the SEM by means of electron back-scattered diffraction (EBSD) from individual planes. However, in many cases of twinned surfaces the surface crystallography can be easily determined by a method developed by Shechtman et al. [3]. This analysis requires only a standard SEM and is based upon understanding of the
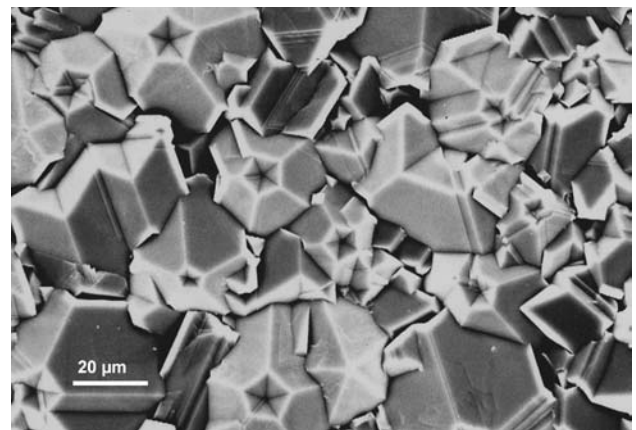

Fig. 4 Twin quintuplet at the surface

nature of diamond twins, usually coherent $\Sigma 3$ which form on {111} planes. A reentrant corner that forms at the intersection line of a twin boundary with the surface provides a preferred nucleation site for new planes on the growing diamond, thus accelerating the growth process. The line of intersection of $\Sigma 3$ twin boundary with the surface is along a <110> direction. This knowledge is all that is needed for crystallographic analysis of twinned CVD diamond surfaces. The convex angles that may form in untwined diamond crystals are given in Table 1 while the convex and reentrant angles possible in twinned diamond are shown in Table 2.

The identification of planes which constitute the free surface is done by tilting the wafer in the SEM into a position where the <110> corner axes of the twinned block coincide with axis of the SEM. This ensures that the $\Sigma 3$ boundary is in an edge-on position and the crystallography of the surface can be determined in details by using a double stereographic projection [3] shown in Fig. 5. An example of surface crystallography determination is given in Fig. 6. Shown in the picture is a block of $\Sigma 3$ twins that has been tilted to an edge-on position so that the electron beam coincides with the [110] zone axis of all the facet planes. The reentrant and convex angles can be measured directly from the picture and by using Tables 1 and 2 the determination of plane identity is straight forward. In this example the first matrix (marked M) and twin (marked T) are chosen arbitrarily at one end of the micrograph. Note that all the reentrant angles are between a matrix and a twin. This is also true for the very thin and therefore hardly resolved matrix plate at point A. An atomic model of the different orientations is shown at the
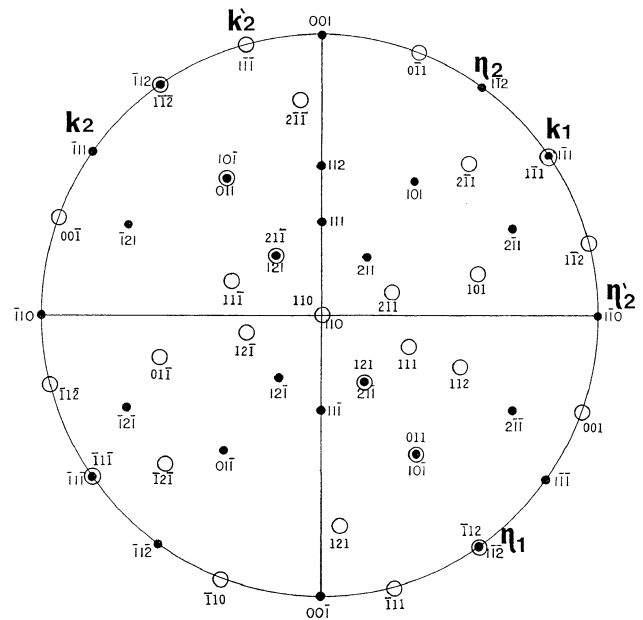

Fig. 5 Elements of a $\Sigma 3$ twin are marked on this double stereographic projection. Dark spots – matrix and open circles—twin
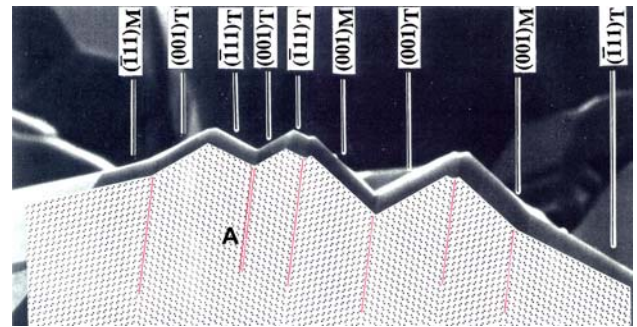

Fig. 6 Facet crystallography of $\Sigma 3$ twinned block

lower part of the micrograph. For detailed analysis of twinned facets see ref. [4]

Twin quintuplets

When a twin quintuplet is oriented so that the <110> 5-fold axis is approximately parallel to the growth direction of the film, it can reach the surface. Only a small fraction of the twin quintuplets that form in the nucleating film has the right orientation, but many more nucleate along the growth path under certain growth conditions as shown in Fig. 4.

The fine structure of twin quintuplets was studied in details [3] and will not be repeated here. Figure 7 is an example of a twin quintuplet viewed along its [110] zone axis. In this case, and under many other deposition
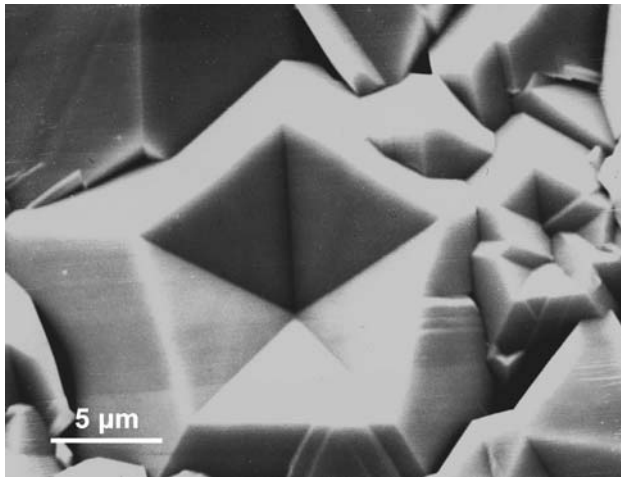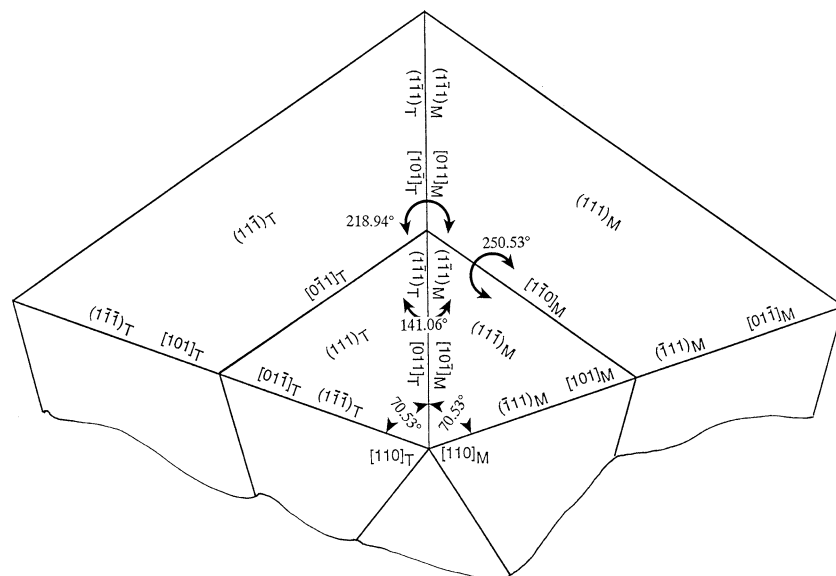
Table 1 Convex facet planes and convex angles θ in untwined CVD diamond

Facet planes	Corner axis	Convex angle $\theta°$
{111}–{111}	<110>	250.53
{111}–{100}	<110>	234.74
{100}–{100}	<100>	90.00

Table 2 Convex and reentrant angles possible in twinned diamond

Planes	Corner axis	Reentrant angle $\phi°$	Convex angle $\theta°$
{100}$_M$–{111}$_T$	<110>	164.21	195.79
{111}$_M$–{010}$_T$	<110>	164.21	195.79
{111}$_M$–{111}$_T$	<110>	141.06	218.94
{100}$_M$–{010}$_T$	{110}	109.48	250.52

Fig. 7 Twin quintuplet

conditions this direction is also the growth direction of the diamond film. In most cases [3, 4] four of the boundaries are coherent Σ3 with a tilt angle of 70.53° and one is Σ81 with a tilt angle of 77.88. The Σ81 forms because of the 7.35° misfit angle between 360° and five times 70.53°—the tilt angle between each two neighboring Σ3 boundaries. The Σ81 boundary can be modeled as a Σ3 twin boundary containing regularly spaced secondary dislocations to accommodate the mismatch angle [5]. Σ81 boundary associated with the quintuplet is short lived and in our observations does not extend more than several nanometers [3].

In many cases that we have studied, a number of Σ3 boundaries form in the vicinity if the Σ81 termination site, and lower index Σ boundaries are formed, first a Σ27, then Σ9 and so on [3, 6, 7]. Facet crystallography of twin quintuplets were studied by tilting experiments

as described before and details of all the facet planes, directions and angles were determined and are given in Fig. 8. Also seen in Fig. 8 are the indexes of the edge-on Σ3 twin boundaries. Note that all the facets are {111} and all the ridge and reentrant directions are <110>.

## Spiraling twin quintuplets

In some cases, twin quintuplets spiral as seen in Fig. 9. This is because the high energy Σ81 boundary is very short and replaced by a Σ3 boundary which is 70.53 + 7.35 = 77.88° away from one of the nearest Σ3 boundaries, rather than 70.53° the angular spacing from the other near Σ3 neighbor. A spiral growth requires only Σ3 boundaries and every turn the outer twin quintuplet rotates open 7.35° relative to the inner quintuplet. In our studies we have observed spiraling twins with no more than two spiraling quintuplets and an example is shown in Fig. 9c.

Conclusions

Surfaces of diamond wafers made by Norton Diamond and Raytheon were studied and their crystallography analyzed. Special attention was given to twin quintuplets found in abundance among the nucleating individual crystals prior to continuous film formation, and in some cases also on the surface of growing wafers. In addition to almost regular twin quintuplets that are made of four Σ3 and one Σ81 boundaries some quintuplets have only Σ3 boundaries, in which case they

Fig. 8 The surface crystallography of a twin quintuplet

Fig. 9 Examples of spiraling twin quintuplets
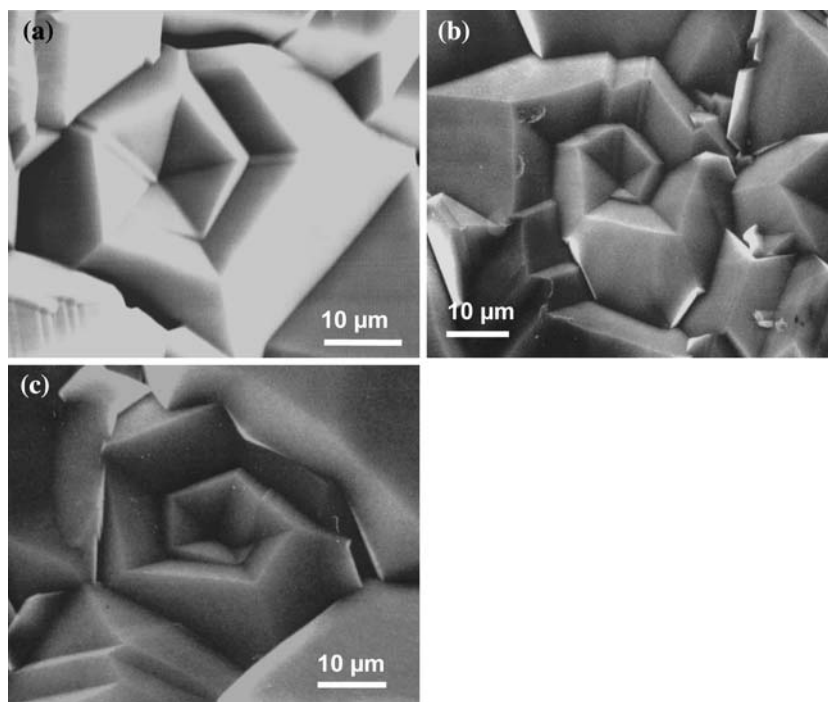
must spiral to compensate for the missing 7.35°, the angular difference between Σ3 and Σ81.

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