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## Dislocation dipole annihilation in diamond and silicon

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**Abstract.** The mechanism of dislocation dipole annihilation has been investigated in C and Si using atomistic calculations with the aim of studying their annihilation by-products. It is shown, in C as well as in Si, that dipole annihilation yields debris that can be depicted as a cluster of vacancies, or alternately by two internal free surfaces. These defects have no strain field and can hardly be seen using usual TEM techniques. This suggests that the brown colouration of diamond could be due to microstructures resulting from deformation mechanisms associated with dipole formation and their annihilation rather than to a climb mechanism and vacancy aggregation. In silicon where a number of dipoles have been evidenced by TEM when dislocation trails are found, such debris could be the missing link responsible for the observation of strong chemical reactivity and electrical activity in the wake of moving dislocations.

### 1. Introduction

Point defects or association of point defects have been assigned to some changes in physical properties in plastically deformed semiconductors. In diamond, it has been recognized that the brown colour of diamond is concomitant with the presence of dislocations but not directly related to dislocations. Rather this colour change has been attributed to point defect clusters [1, 2], the presence of which are related to some specific plastic deformation conditions. Those defects are usually thought to be associated with climb mechanisms leading to vacancy aggregation [3]. However, the relationship between deformation conditions and the actual formation mechanism of these vacancy clusters is not clearly understood yet. As far as silicon is concerned, a puzzling question remains about the presence of point defects in the wake of moving dislocation in the lower temperature range of plasticity evidenced through EPR measurements (see for example [4]). Chemical etching in the same range of deformation temperature has also evidenced trails lying in crystallographic directions behind dislocations in their glide plane [5]. Those trails also appear to have an electrical signature [6].

Some effort has been devoted to understand the relevant features in the deformation microstructure of diamond [7, 8]. In brown diamond many paired perfect dislocations and small dislocation loops are found building the microstructure suggesting a link to the current brown colour mechanism involving vacancy clusters or disks. However no significant change in the microstructure before and after high pressure high temperature (HPHT)-treatment was evidenced although this treatment alters the brown colouration. The authors suggest that changes should occur at dislocation core.

Very few observations were devoted to the characterisation of deformation microstructures of silicon in the regime where trails are evidenced. Recent observations [9] put forward the large density of dislocation dipoles found in deformation microstructures obtained in those conditions. Faint

contrasts were also observed in the neighbourhood of dislocation dipoles. The structural objects associated to these faint contrasts have not been determined. It is thought that they could correspond to dipole annihilation by-products in agreement with their geometrical features. However these TEM observations are difficult to relate unambiguously to the fingerprints of trails.

It comes out from these TEM studies that a common feature of these deformation microstructures in diamond and silicon is the presence of dislocation dipoles and small dislocation loops. Unidentified defects present in these microstructures should be associated to physical signatures. The question then arises as to whether specific defects such as clusters of point defects may be associated with such populations of dipoles.

Indeed, several computational works dealing with dipole annihilation in various materials have put forward that the classical dipole annihilation issues have to be revisited [10-12]. Dipole annihilation by-products, beside those relevant to screw orientations which restore the perfect crystal [13] have been found to consist of debris of almost atomistic dimensions which are difficult to evidence by TEM. For example in alkali halides it was shown that voids result from vacancy dipole “annihilation” which is consistent with the experimental results of plastic deformation tests and TEM observations [14] as well as with atomistic computations [10].

In this context the present paper investigates the possible transformation of small height vacancy dipoles in diamond and silicon into vacancy clusters using atomistic simulations.

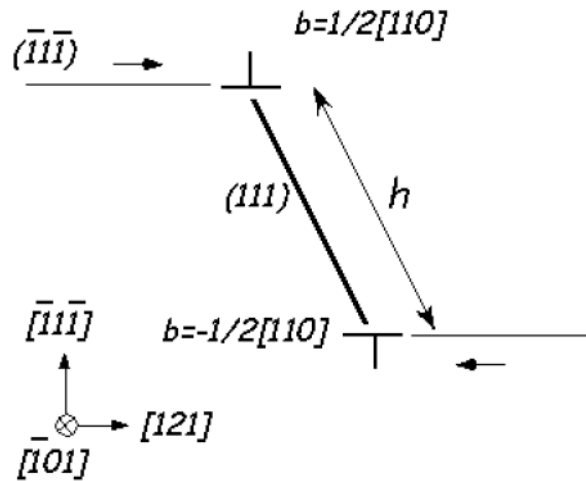
## 2. Simulation techniques

There are several issues which are of importance in the numerical simulations of small dislocation dipoles.

- (i) The choice of the interatomic potential. It has to describe correctly the initial configuration i.e. dislocation core structure and any defect resulting from dislocation dipole annihilation. Since no potential has proved to be superior to all others, several ones were employed.
- (ii) The nature of the core of the dislocation building the dipole. For the sake of simplicity and also since the microstructure associated to dipoles contains perfect dislocations (diamond) or were found in the low temperature deformation range (silicon), we chose to study the dipole annihilation of two perfect dislocations. Since the most common core issued from calculations is the  $60^\circ S_1$  core (see [15]), this core configuration has been chosen.
- (iii) The size and the limit conditions for the computational cells. Perpendicular to the dislocation line, computations were performed using either periodic boundary conditions, or fixed surfaces conditions; the computation cell is periodic along the dislocation line so that energies are computed per unit line of dislocation.

Calculations have been performed using systems of size  $96 \times 192 \times 3$ , i.e. 55296 atoms. Initial configurations have been built by inserting a vacancy dipole of  $60^\circ$  dislocations with the  $S_1$  core, with opposite Burgers vectors, with a variable distance,  $h$ . Since stable vacancy clusters were already found lying on (111) planes in diamond, the dipole plane was chosen as to be a (111) plane. The geometry of the system is depicted figure 1. After relaxation of the dipole, a second calculation is done, with a manual procedure as to open a vacancy cluster.

Different potentials were used for each material: Tersoff [16], EDIPA and EDIPB [17] potentials for diamond, Tersoff [16], EDIP [17], Stillinger-Weber [18] potentials for silicon.

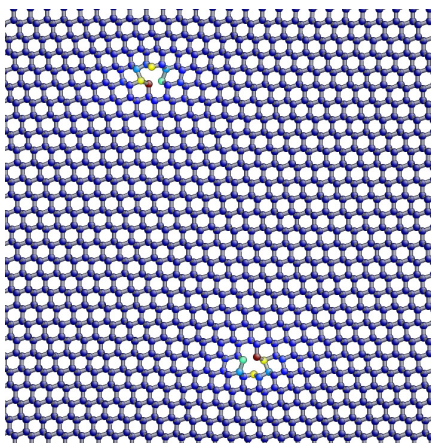


**Figure 1.** Geometrical features of a vacancy dislocation dipole.

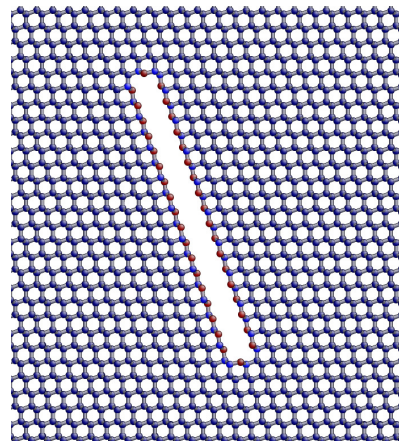
### 3. Results

Owing to the close agreement between calculations performed using periodic boundary conditions, and fixed surfaces conditions, only results using periodic boundary conditions are reported in this paper.

For various dipole heights, the energy of a vacancy dipole first modelled by elasticity and then relaxed atomistically was computed. Allowing these vacancy dipole configurations to open on part of the dipole height yields a relaxed configuration which is open all along the dipole height. The resulting defect can be described as a vacancy cluster aligned along (111) or as two (111) internal free surfaces. No strain field is found associated to such configuration: the parent dislocations building the dipole do not exit anymore so that this defect can be considered as the result of dipole annihilation i.e. “debris”. These two types of configurations are shown in figure 2 for the same dipole height.



**Figure 2a.** Vacancy dislocation dipole,  $h=3.9\text{nm}$ , diamond, Tersoff potential [16].



**Figure 2b.** Vacancy cluster resulting from dislocation annihilation, is as figure 2a.

The energy of the relaxed configuration after opening the dipole and the energy of the starting dipole configuration were compared for different dipole height,  $h$ . Depending on  $h$ , it is found that the stable configuration is either a vacancy dipole or debris. The dipole critical heights  $h_c$  for which a

vacancy dipole converts into debris have been calculated with the different potentials. The results are given in tables 1 and 2 respectively for diamond and silicon. It is found that  $h_c$  depends quite strongly on the interatomic potential, however it is shown that debris are stable at low dipole heights for any potential both for diamond and silicon.

From an elastic point of view this calculation compares the elastic energy of a dislocation dipole and that of two internal free surfaces. To achieve reliable results, the interatomic potentials have to describe correctly the dislocation core energetics as well as the surface energy. The surface energy we can extract from our computations is in good agreement with the (111) surface energy computed with the same potential taking the energy of the debris as  $E=2\gamma h$ . However the present calculations do not take into account (111) surface reconstructions; such reconstructions contribute to lower the surface energy so that the critical heights in this paper are under estimated.

**Table 1.** Vacancy dipole critical heights in diamond depending on the interatomic potential.

C	Critical height $h_c$ (nm)	Potential
	4.9	Tersoff [16]
	13.4	EDIP A [17]
	11.3	EDIP B [18]

**Table 2.** Vacancy dipole critical heights in silicon depending on the interatomic potential.

Si	Critical height $h_c$ (nm)	Potential
	2.4	Tersoff [16]
	3.1	EDIP [18]
	1.2	SW [19]

#### 4. Discussion

The geometry of the defect resulting from vacancy dipole annihilation is similar to that conjectured by Jones et al [1, 2]. Previous interpretation of vacancy cluster formation in diamond relies upon some climb mechanism associated to trails of high concentration of vacancies which aggregates to form cluster and aggregation of vacancies [2, 3]. Such circular disks of vacancies were found to be unstable as compared to the energy of a perfect vacancy loop, calculated according to elastic theory, for a loop radius of 1.2 nm containing 200 vacancies.

Discrepancy in the critical size of the cluster between the results of Jones et al [2] and this paper can come not only from the different geometry of the problem but also from the way the calculation was handled: ab initio methods in Jones et al [2], interatomic potentials in this work. Furthermore infinite dipoles are used in the present simulations; this does not take into account the energy of dislocation segments which necessarily close a defect of finite dimensions.

It is shown here that similar defects can result from the annihilation of a vacancy dipole in both diamond and silicon, although the critical height for the stability of this debris is quite different in the two materials. The possible occurrence of such defects in these two materials suggests that the analysis of deformation microstructures has to be revisited focusing upon dipoles and dipole annihilation by-products. However the formation mechanism of vacancy defect cluster related to dipole annihilation fits quite well the observations that clusters are likely to be located in the wake of moving dislocations. Such processes obviously hold for jogged dislocations and dipoles: extension clearly relates to dislocation movement.

Associated with dipole annihilation, several stages can lead to the formation of debris:

- (i) large vacancy dipoles can decompose into vacancy loops that, when shrinking can transform into debris,
- (ii) small dipoles can “annihilate” directly leaving debris.

The two pictures are somehow different as far as the deformation temperature is concerned. The first process requires point defect diffusion although the second one is an athermal process. In this second case it means that brown diamonds could be associated with a relatively low deformation temperature.

The formation of the debris has been found in this work using perfect dislocations as parent dislocations. However dislocations in semiconductors have been found to occur under several core structures, particularly they are found dissociated in quite a wide range of temperature. Is the formation of the debris liable to occur only if the deformation is controlled by perfect dislocations? Dipoles of dissociated dislocations in diamond or zinc blende crystals give rise to dissociated dipole S, or Z dipoles as in usual FCC materials. Is the final product of the annihilation of such extended dipoles in silicon and diamond debris like those depicted in this paper? Such calculations about the annihilation of extended dipoles have been done for FCC metals [11, 12] but the comparison with semiconductors cannot be followed up. Indeed different from what was found here, vacancy clusters were found to lie along (110) joining the two parent dislocations in FCC metals. It is clear that the structure and properties of the by-products resulting from the annihilation of extended dipoles should be investigated for semiconductors.

Another point that has to be addressed about dipole formation in silicon and diamond is the following. Do the deformation microstructures of semiconductors generate dislocation dipoles in the usual way as other materials do, or are dipoles the signature of a specific mechanism relevant to materials with diamond structure? Indeed those materials have been found to possess dislocations with multiple core structures associated to very different mobility [15]. Perfect dislocations and dissociated dislocation have been evidenced in these two materials which are likely to be relevant to the shuffle and glide set respectively. In silicon a perfect “shuffle core” was evidenced at high stress and low temperature and a dissociated “glide core” at medium temperature and low stress [20, 21]. Those two kinds of dislocation cores have been found to behave quite differently: perfect “shuffle core” dislocations are impossible to move at temperatures below the BDT [22] once they have been stopped. This seems to be corroborated by recent computations [23] showing that their lower energy configurations are sessile.

In that context one has to consider the possible occurrence of sessile core structures during plastic deformation at moderate temperatures. Then the nucleation of glissile dislocations can be facilitated in the stress field of pre-existing sessile dislocations in a {111} glide plane a few atomic distances from that of the parent dislocation. Interaction of these new dislocations, located in a different atomic glide plane, with the parent ones will give rise to the formation of dislocation dipoles. Annihilation mechanisms will result in by-products such as vacancy loops and debris. These by-products can provide nucleation sites of jog formation on mobile dislocations, interacting with them, feeding the formation of new dipoles and in fine the possible formation of debris in the wake of moving dislocations.

## 5. Conclusion

Calculations performed in this paper show that dipole annihilation can be considered as a possible mechanism of formation of vacancy clusters involved the brown coloration of diamond. Such defects could also exist in silicon under smaller dimension and could be related to the formation of dislocation trails. This has to be proved experimentally. However, due to the lack of strain fields associated with these defects, by-products of dipole annihilation will be difficult to image using TEM techniques. Besides looking at experimental evidence of such mechanisms, several points need to be addressed: the mechanism associated to the transformation between a vacancy dipole and debris and the relevance of this annihilation by-products for extended dipoles.

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