



Diamond and its olivine inclusions: A strange relation revealed by ab initio simulations



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ABSTRACT

The study of diamond and its solid inclusions is of paramount importance to acquire direct information on the deepest regions of the Earth. However, although diamond is one of the most studied materials in geology, the diamond-inclusion relationships are not yet understood: do they form simultaneously (syngensis) or are inclusions pre-existing objects on which diamond nucleated (protogenesis)? Here we report, for the first time, adhesion energies between diamond (D) and forsterite (Fo) to provide a crucial contribution to the syngensis/protogenesis debate. The following interfaces were investigated at quantum-mechanical level: (i) (001)_D/(001)_{Fo}, (ii) (001)_D/(021)_{Fo}, and (iii) (111)_D/(001)_{Fo}. Our data, along with the ones recently obtained on the (110)_D/(101)_{Fo} interface, revealed an unexpected thermodynamic behaviour, all interfaces showing almost equal and low adhesion energies: accordingly, diamond and olivine have an extremely low chemical affinity and cannot develop preferential orientations, even during an eventual epitaxial growth. Combining these results with those of our previous work concerning the morphology constraints of diamond on its inclusions, we can state that the two main arguments used so far in favour of diamond/inclusions syngensis cannot be longer considered valid, at least for olivine.

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1. Introduction

The characterization of mineral inclusions in diamond (D) allowed to indirectly obtain information about the genesis and distribution of diamonds in the Earth's mantle (e.g., Pearson et al., 2014; Shirey et al., 2013; Stachel and Harris, 2008). Such inclusions have been classified, according to the timing of their formation with respect to the host diamond (Meyer, 1987; Harris, 1968a, 1968b), as: (i) *syngenetic*: when they form simultaneously with the diamond; then, syngensis implies either inclusion/host mutual growth through co-precipitation from the same medium or complete recrystallization of a pre-existing mineral occurring when diamond grows; (ii) *protogenetic*: when they represent pre-existing minerals passively incorporated into the growing diamond; (iii) *epigenetic*: when they are secondary minerals forming into a pre-existing diamond.

Determining whether an inclusion is syngenetic or protogenetic is of paramount importance in diamond studies. Indeed, any geological information concerning a syngenetic inclusion (i.e., pressure and temperature of formation, age, geochemistry of the mother-medium) is applicable to the host diamond: accordingly, a wrong

interpretation concerning the genesis of the diamond-inclusion couple could address a misleading idea about the geological processes involved in the diamond formation.

The most common proof invoked to establish if an inclusion is syngenetic lies in the imposition of the morphology of the diamond on the inclusion (e.g., Sobolev, 1977; Harris, 1968a). Such a traditional criterion is based on the belief that diamond can impose its cube-octahedral morphology upon the inclusion only during their mutual growth. However, this is not supported by any chemical-physical arguments, and even less by experimental evidences. Recently, the morphologic criterion has been strongly criticized (Bruno et al., 2014; Nestola et al., 2014; Taylor and Anand, 2004; Taylor et al., 2003). In particular, by analysing the diamond-imposed morphology (Bruno et al., 2014) and the orientations (Nestola et al., 2014) of 43 olivine inclusions in 20 diamonds from the world-famous Udachnaya kimberlite in Siberia (Russia), the authors found that many olivine inclusions in diamonds are protogenetic and the diamond-imposed morphology alone cannot be considered as a compelling proof of syngensis of mineral inclusions in diamonds.

The identification of an epitaxy, on the base of the orientation of the inclusion with respect to its host (Pearson and Shirey, 1999; Harris and Gurney, 1979; Orlov, 1977; Sobolev, 1977), has been considered as a further proof of syngensis. Unfortunately, the

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only two works reporting a statistically significant collection of data, have been recently published by Nestola et al. (2014) on the Udachnaya diamonds and Neuser et al. (2015) on the Yubileynaya diamonds (Yakutia). Only in the Nestola et al. (2014) paper the olivine inclusions were shown to be randomly oriented with respect to the hosting diamond: Nestola et al. (2014) performed X-ray diffraction measurements, whereas Neuser et al. (2015) carried out an EBSD analysis in order to determine the crystallographic orientations of the inclusions. Previous works only reported limited sets of samples that are not sufficient to identify, on a firm statistical ground, the mutual orientations between the crystallographic axes of the inclusion and those of the host diamond (Frank-Kamenetsky, 1964; Futergendler and Frank-Kamenetsky, 1961; Mitchell and Giardini, 1953). Moreover, the majority of these papers did not consider the crystallographic contact planes (CCPs) defining the epitaxial interface. The latter information is necessary to assess unambiguously a preferential epitaxial relationship since, on a purely geometrical point of view, no constraints can be required on the contact plane of two different phases with the same crystallographic orientation, the number of CCPs being potentially infinite (Fig. S1, Supplementary Material). Indeed, if the inclusions do not show a systematic preferential orientation with respect to diamond (random orientations), one is allowed to state that there cannot be preferential epitaxial relationships, yet undefined. Conversely, the absence of preferential orientation relationships is not sufficient to conclude that there is not an epitaxial growth, as we will show in this work. Accordingly, it is evident that the *epitaxial criterion* to define syngeneses can result rather ambiguous, if no information can be found on the thermodynamic properties of the epitaxial interface.

Here, we focus on the study of the epitaxial phenomena in olivine–diamond system by an *ab initio* quantum-mechanical computational approach, as such crystal features cannot be experimentally investigated. Olivine forms a complete isomorphous series, with composition ranging from forsterite (Mg_2SiO_4 , Fo) to fayalite (Fe_2SiO_4 , Fa). However, typical Earth's mantle olivines are Mg-richer ($\text{Fo}_{92}\text{Fa}_8$) (e.g., Nestola et al., 2011). For this and for sake of simplicity, the fayalite contribution in our model system was neglected. We investigated the $(001)_\text{D}/(001)_\text{Fo}$, $(001)_\text{D}/(021)_\text{Fo}$ and $(111)_\text{D}/(001)_\text{Fo}$ epitaxial interfaces determining their structures and thermodynamic properties. In detail, the specific adhesion energy $\beta_{(hkl)/(h'k'l')}^{\text{D}/\text{Fo}}$ (i.e., the energy gained, per unit area, once the interface is formed) and the specific interface energy $\gamma_{(hkl)/(h'k'l')}^{\text{D}/\text{Fo}}$ (i.e., the energy needed to create, per unit area, the interface), were calculated; (hkl) and $(h'k'l')$ define the crystallographic faces in epitaxy of D and Fo, respectively. We decided to study the $(001)_\text{D}/(001)_\text{Fo}$, $(001)_\text{D}/(021)_\text{Fo}$ and $(111)_\text{D}/(001)_\text{Fo}$ interfaces for two reasons: (i) the $(001)_\text{D}$, $(111)_\text{D}$, $(001)_\text{Fo}$ and $(021)_\text{Fo}$ are important faces in the crystal morphology of diamond and olivine (e.g., Bruno et al., 2014; De La Pierre et al., 2014); (ii) from a computational point of view, these systems are workable with the resources of calculus actually in our hand.

2. Calculation

The calculations were performed with the *ab initio* CRYSTAL09 code (Dovesi et al., 2009, 2005; Pisani et al., 1988) and at the DFT (Density Functional Theory) level with the B3LYP Hamiltonian (Stephens et al., 1994; Becke, 1993; Lee et al., 1988), which provided accurate results for the surface properties of the minerals considered in the present work (Bruno et al., 2014; De La Pierre et al., 2014; Demichelis et al., 2015). Further computational details (e.g., basis set, thresholds controlling the accuracy of the calculations) are given as Supplementary Material.

A composed slab (D/Fo/D), made by diamond (D) and forsterite (Fo) (slab D and slab Fo hereinafter), was generated in the follow-

ing way: (i) the two-dimensional (2D) coincidence lattices between the two phases in epitaxial relationship were identified (Bruno et al., 2015); (ii) the slabs D and Fo of a selected thickness were made by cutting their respective bulk structures parallel to the hkl planes of interest and using the same 2D cell parameters describing the epitaxy; (iii) the slab Fo was placed in between two slabs D; (iv) finally, the composed slab structure (atomic coordinates and 2D cell parameters) was optimized by considering all the atoms free to move. The slab D/Fo/D was generated preserving the symmetry centre, to ensure the vanishing of the dipole component perpendicular to the slab. The CRYSTAL09 output files, listing the optimized fractional coordinates and optimized 2D cell parameters of the composed slabs, are freely available at <http://mabruno.weebly.com/download>. The calculations were performed by considering composed slabs with a thickness sufficient to obtain an accurate description of the interfaces. The slab thickness is considered appropriate when the bulk-like properties are reproduced at the centre of the slabs D and Fo. Further details are given as Supplementary Material.

The specific adhesion energy, $\beta_{(hkl)/(h'k'l')}^{\text{D}/\text{Fo}}$ (J/m^2), is calculated by means of the relation:

$$\beta_{(hkl)/(h'k'l')}^{\text{D}/\text{Fo}} = \frac{E(2\text{D}) + E(\text{Fo}) - E(2\text{D} + \text{Fo})}{2S} \quad (1)$$

where $E(2\text{D} + \text{Fo})$, $E(2\text{D})$ and $E(\text{Fo})$ are the static energies at 0 K of the optimized slab D/Fo/D, slab D/vacuum/D and slab Fo, respectively, and S is the area of the surface unit cell. Accordingly, the surface energy is calculated:

$$\gamma_{(hkl)}^i = \frac{E(i) - E_b(i)}{2S}; \quad i = \text{D}, \text{Fo} \quad (2)$$

where $E_b(i)$ is the bulk energy of the i -th phase and the factor of 2 in the denominator accounts for the upper and lower surfaces of the slab model.

3. Results and discussion

In Fig. 1, the optimized structure of the $(001)_\text{D}/(001)_\text{Fo}$ interface is reported; the $(111)_\text{D}/(001)_\text{Fo}$ and $(001)_\text{D}/(021)_\text{Fo}$ interfaces are given in Figs. S2 and S3 (Supplementary Material). A detailed structural analysis of the interfaces is out of the scope of this work, therefore only a qualitative and short description is given in the following. People interested to an in-depth structural analysis can carry out it by using the CRYSTAL09 output file reporting the optimized atomic coordinates.

The significant structural modifications we observe at the three interfaces are not due to a strong *chemical* interaction between the two phases, as it ensues from the comparison of the relaxed structures of the surfaces in contact both with vacuum and the other mineral (Fig. 1 and Figs. S2–S4). Indeed, the relaxation of the $(001)_\text{D}$ and $(111)_\text{D}$ surfaces in vacuum (De La Pierre et al., 2014) only slightly differs from that observed when they are in contact with the (001) and (021) faces of forsterite. To describe this geometry modification, we define the roughness of the carbon layer at the interface with the parameter Δz (i.e., the difference between the z coordinates of the carbon atoms within the same layer). Δz is 0.0206 Å for the carbon layer of the $(001)_\text{D}$ surface in vacuum, whereas Δz is 0.2144 Å and 0.1712 Å for the carbon layer in contact with $(001)_\text{Fo}$ and $(021)_\text{Fo}$, respectively. An analogous relaxation was reported by Bruno et al. (2015) for the $(110)_\text{D}$ surface: $\Delta z = 0.0038$ Å for the carbon layer in vacuum and $\Delta z = 0.1966$ Å for the one in contact with $(101)_\text{Fo}$. For the $(111)_\text{D}$ surface, the relaxation is smaller: $\Delta z = 0.0028$ and $\Delta z = 0.0298$ Å for that in vacuum and in contact with $(001)_\text{Fo}$, respectively.

Similarly, the $(001)_\text{Fo}$ and $(021)_\text{Fo}$ surfaces are slightly affected by the presence of the diamond. The strong distortion of the SiO_4

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