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ELECTRONIC STRUCTURE OF A DISORDERED GRAIN BOUNDARY IN GRAPHENE

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Grain boundaries are constitutional elements of graphene grown on a solid metallic surface by CVD. The electronic properties of computer models of grain boundaries in graphene have been investigated by tight-binding calculations and compared with available *ab-initio* data and with recent experimental scanning tunneling spectroscopic measurements. It is shown that twofold coordinated atoms and non-hexagonal rings, both present in grain boundaries, give rise to specific features in the local density of states.

1. Introduction

The remarkable properties of graphene have triggered a race for the development of reliable and large-scale production techniques. Among them, the chemical vapor deposition (CVD) route is a promising technique. It consists in a thermal decomposition of light hydrocarbon molecules at the surface of a metallic substrate. Copper is a widely-used substrate for that purpose, because it has little interaction with the adsorbed graphene layer. The *d* bands of this noble metal are indeed located too far below the Fermi level to hybridize with the π orbitals of carbon [1]. As a consequence, the graphene layer is floating in a shallow potential well above the Cu surface. In usual CVD conditions, graphene flakes are growing simultaneously at many places of the surface, the smallest grains being able to diffuse and to merge with largest ones [2]. The graphene sheet so obtained is necessarily a polycrystal with many grain boundaries [3].

Like in all solids, the grain boundaries affect the mechanical, electronic, electromagnetic ... properties of the graphene layer and are, therefore, worth studying [4]. The present paper aims at making progress in the understanding of the electronic properties of grain boundaries in CVD graphene.

2. Methodology

The grain boundary (GB) investigated in this paper were relaxed by minimizing their

Tersoff-Brenner energy with the constraint that the atomic structure, supposed to be adsorbed on a solid surface, remains flat. This procedure avoids the σ and π orbitals of C to mix, even if sp^2 hybridization cannot be realized everywhere due to non-hexagonal rings and twofold coordinated atoms.

The electronic structure was explored with the π tight-binding Hamiltonian restricted to first-neighbor hopping interactions $V_{ij} = \gamma_0(d_{CC}/d_{ij})^2$ where d_{ij} is the distance between the atoms i and j , $\gamma_0 = -2.7$ eV and $d_{CC} = 0.142$ nm. The π orbitals were all supposed to lie at the same level, chosen as the zero of energy, irrespective of the atomic environment. Local densities of states (LDOS) were obtained by application of the recursion algorithm. For each LDOS, 155 pairs of recursion coefficients were computed on a cluster of about 63500 atoms.

3. Results and discussion

The grain boundary (GB) under consideration has been observed by STM on the surface of HOPG [5]: two graphene grains, mirror symmetric of each other, are tilted by an angle of $+20.8^\circ$ and -20.8° , respectively, from the GB line. The connection between the grains is periodic with length 0.65 nm. The tilt angle and the period correspond to the translation vector (2,1). An ideal structural model, shown in Fig. 1(a), consists in a periodic alternation along the GB line of a pentagon-heptagon (5-7) pair and a CC bond shared between two hexagons.

LDOS were computed on 50 atoms contained in the box marked by dashed lines in Fig. 1(a). The GB DOS represented by the dashed line curve in Fig. 1(d) is the sum of these 50 LDOS. It was found to be in reasonable agreement with *ab-initio* VASP calculations performed for the same type of structure [6]. It has been checked that neither a dislocation in graphene (isolated pentagon or heptagon) nor a dislocation core (isolated 5-7 pair) produces sharp low-energy peaks in the tight-binding density of states. The peaks at $+0.5$ and -0.8 eV in the DOS of the GB are therefore attributed to the repetition of 5-7 pairs and their concomitant interactions.

In the context of CVD, it is unlikely that two merging graphene grains can be connected exclusively with threefold coordinated atoms. For that reason, twofold coordinated atoms have been introduced in the GB of Fig. 1(c), whose structure derives from that of Fig. 1(a) by removal of these atoms located on the pentagonal sites that lie on the symmetry axis. The GB is now formed by a succession of 7- and 11-membered rings. The DOS of this GB (dashed line curve in Fig. 1(e)) has a Dirac delta peak located at zero energy. This peak results from states localized on the twofold coordinated atoms, which do not couple together along the periodic axis. Interestingly, the peak at $+0.5$ eV survives to the introduction of vacancies on the GB line, whereas the peak at -0.8 eV does not.

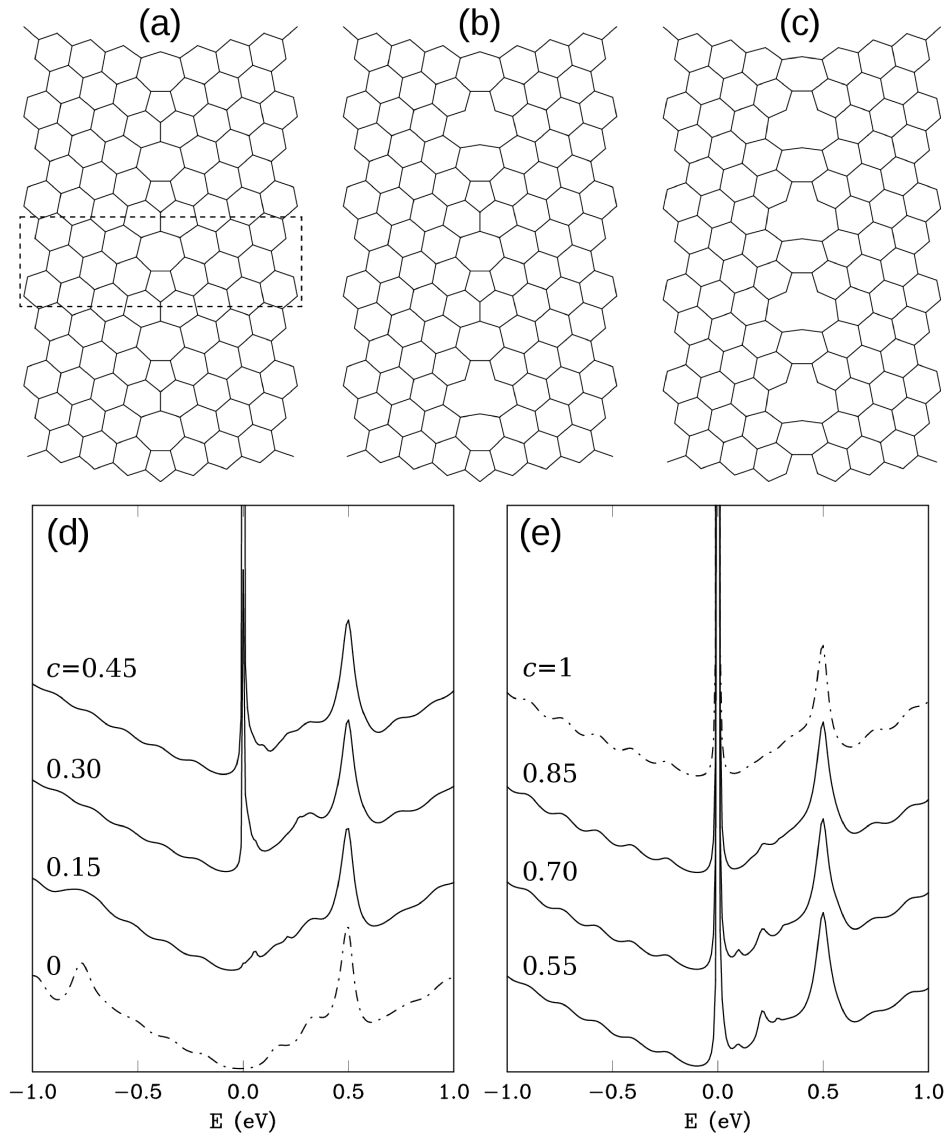


Figure 1. Structural model (top) and π DOS (bottom) of a disordered grain boundary in graphene. The disorder is generated by random removal of a fraction c of these atoms that sit on the lower pentagonal site in each period of the perfect GB: (a) $c = 0$, (b) $c = 0.4$, (d) $c = 1$. Configurational averages of the DOS computed by recursion for increasing values of c in a box centered on the GB (dashed rectangle in panel (a): width = 1.89 nm, height equal to the 0.65 nm period) are shown in panels (d) and (e). The dashed line curves correspond to the perfect GBs sketched in (a) and (c).

Interpolation between the two perfectly periodic GB models of Figs. 1(a,c) can

be realized by removing atoms on a fraction $0 < c < 1$ of the aforementioned pentagonal sites. Fig. 1(b) illustrates a configuration corresponding to $c = 0.4$. For a given value of c , atoms were removed randomly from the pentagonal sites with probability c and the GB DOS, computed in a box similar to that shown in Fig. 1(a), were averaged over 72 configurations of the vacant sites. The results obtained are displayed in Figs. 1(d,e) for six values of c . The peak at -0.8 eV rapidly washes out with increasing c , whereas the peak at $+0.5$ eV remains and broadens somewhat. In the interval $0.5 < c < 0.8$, additional well-resolved peaks show up between 0.1 and 0.3 eV (Fig. 1 (e)). The peak at zero energy, attributed to states localized around the vacant sites, emerges with an asymmetric shape in the DOS when c exceeds 0.2 (Fig. 1 (d)) and keeps growing with increasing c .

These results indicate that peaks observed at $0.1 - 0.2$ eV above the Fermi energy in experimental STS spectra recorded on and near disordered grain boundaries in CVD graphene [6,7] can be attributed to the presence of twofold coordinated atoms in the GB structure. In particular, the asymmetric peak observed at $E=0$ in Fig. 1(d) for, e.g., $c = 0.3$ might actually lie 0.1 eV above the Fermi level, in agreement with experiment, if the graphene sheet were slightly p doped.

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