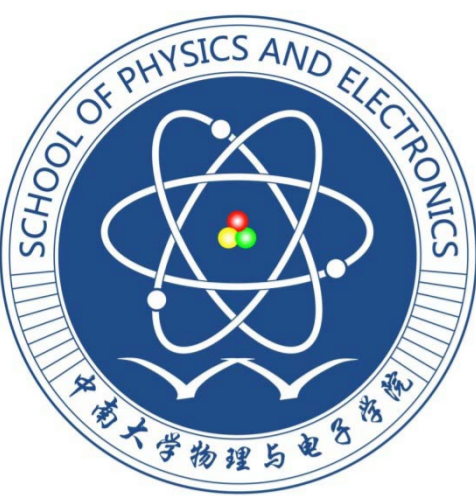


Incorporating Isolated Molybdenum (Mo) Atoms into Bilayer Epitaxial Graphene on 4H-SiC(0001)

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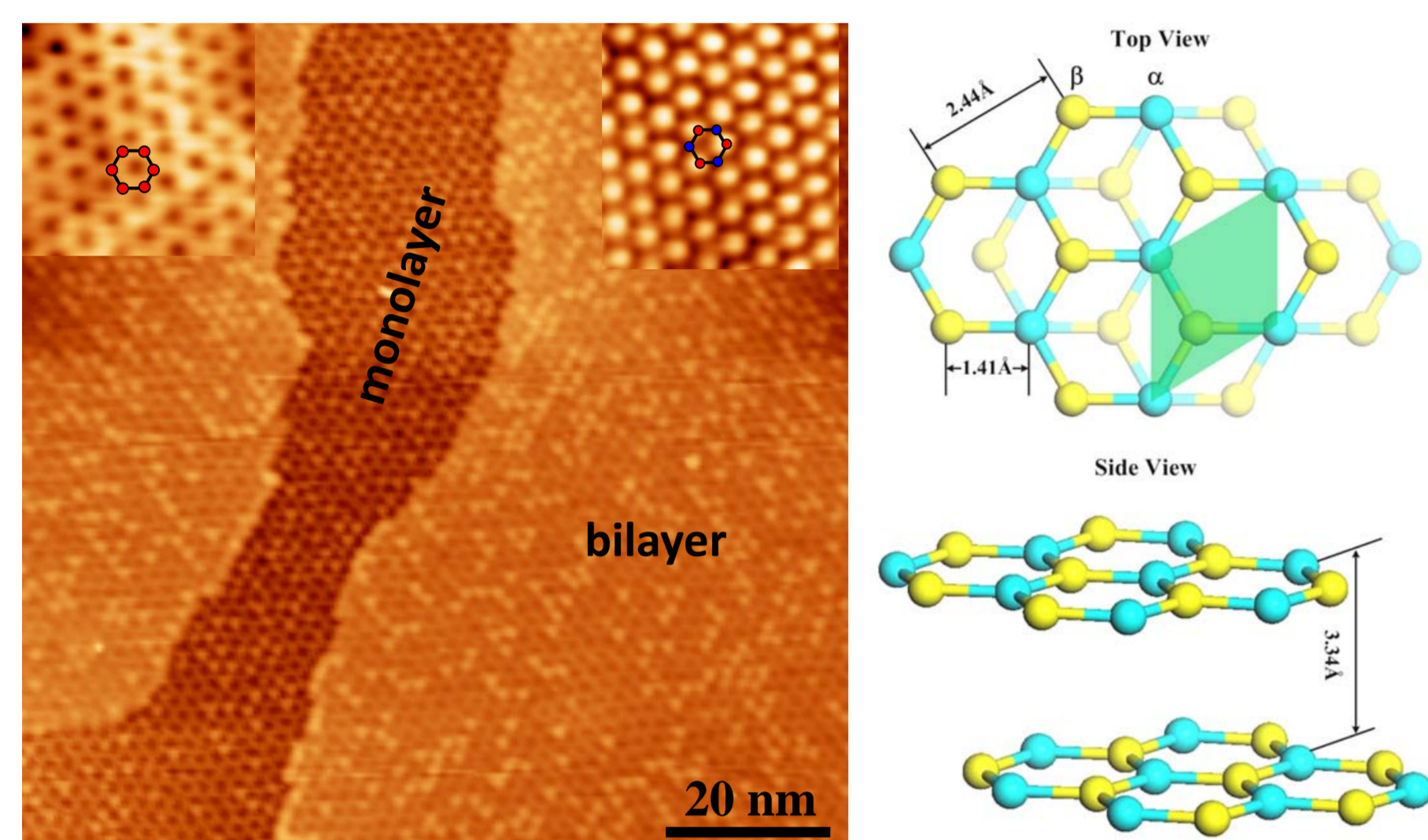
Introduction

Graphene, a one-atom-thick sheet of carbon atoms in honeycomb arrangement, has sparked much interest in both fundamental studies and technological applications in the past 10 years due to its outstanding physical, electronic, and optical properties. How to modify graphene to improve its properties has been one of the hottest issues nowadays. Density functional theory studies have predicted that atomic dopants (such as N, B, Fe, Mn, Bi, etc.) can deeply influence graphene properties. Here, we show a simple method to incorporate isolated Mo atoms into BLEG on SiC(0001). The incorporating structures and corresponding electronic properties of Mo-doped BLEG were investigated by means of LT-STM (77 K) and first principles calculations, revealing that substitutional Mo atoms prefer the α -sites of the upper graphene layer and between graphene bilayers. Furthermore, each Mo atom introduces a magnetic moment of $1.81 \mu_B$ into bilayer graphene.

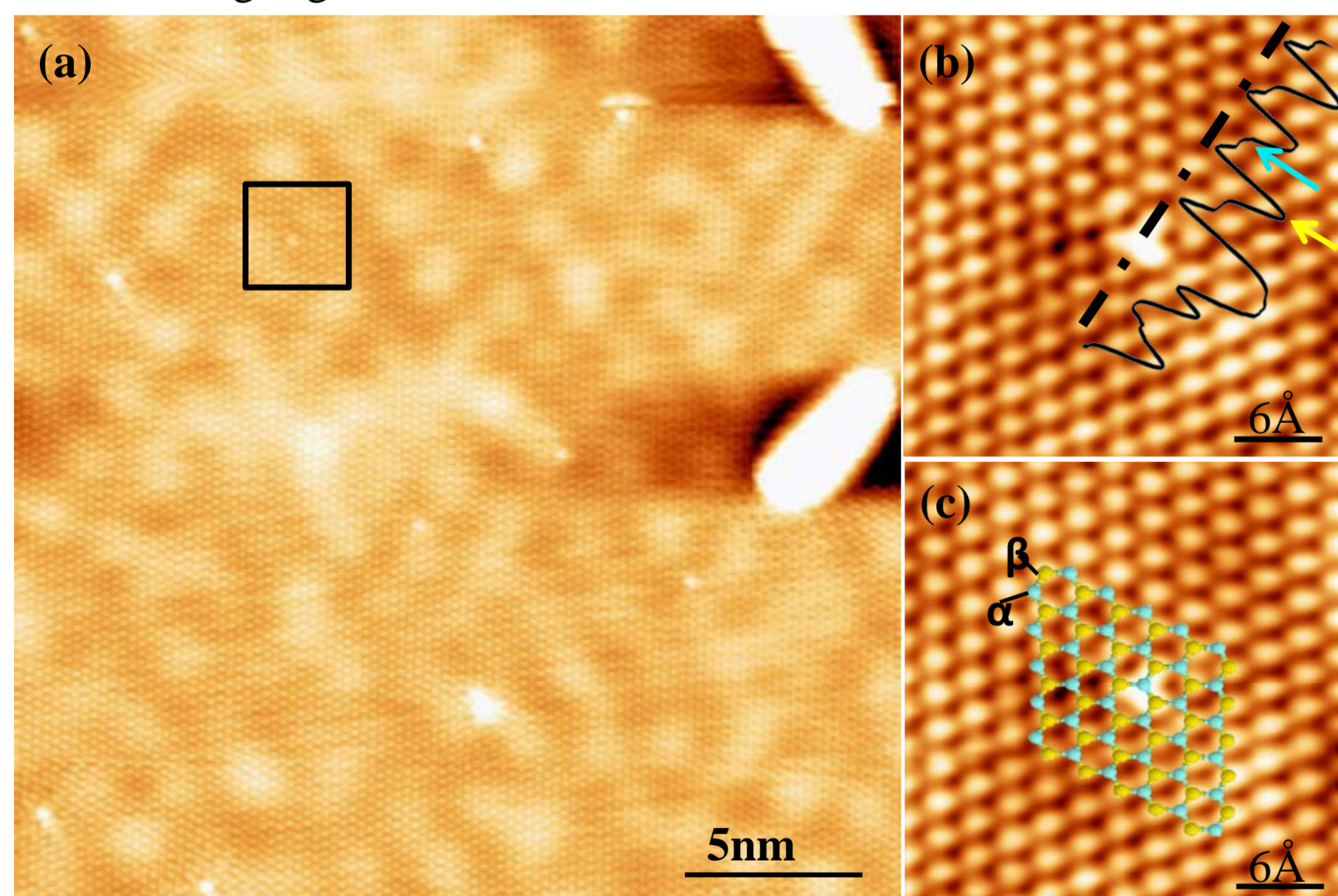
Methods

All the experiments were carried out in a custom-built multichamber ultrahigh vacuum (UHV) system housing an Omicron LT-STM with base pressure better than 6.0×10^{-11} mbar. The sample temperatures were measured by an optical pyrometer. All STM images were recorded in constant current mode using chemically etched tungsten (W) tips and were further analyzed using WSxM. All the calculations are performed by Vienna Ab Initio Simulation Package (VASP). A 5×5 supercell of BLG is used with the vacuum space of 20 Å. van der Waals corrected Becke88 functional (optB88-vdW) is employed to better describe the weak interlayer interaction of BLG.

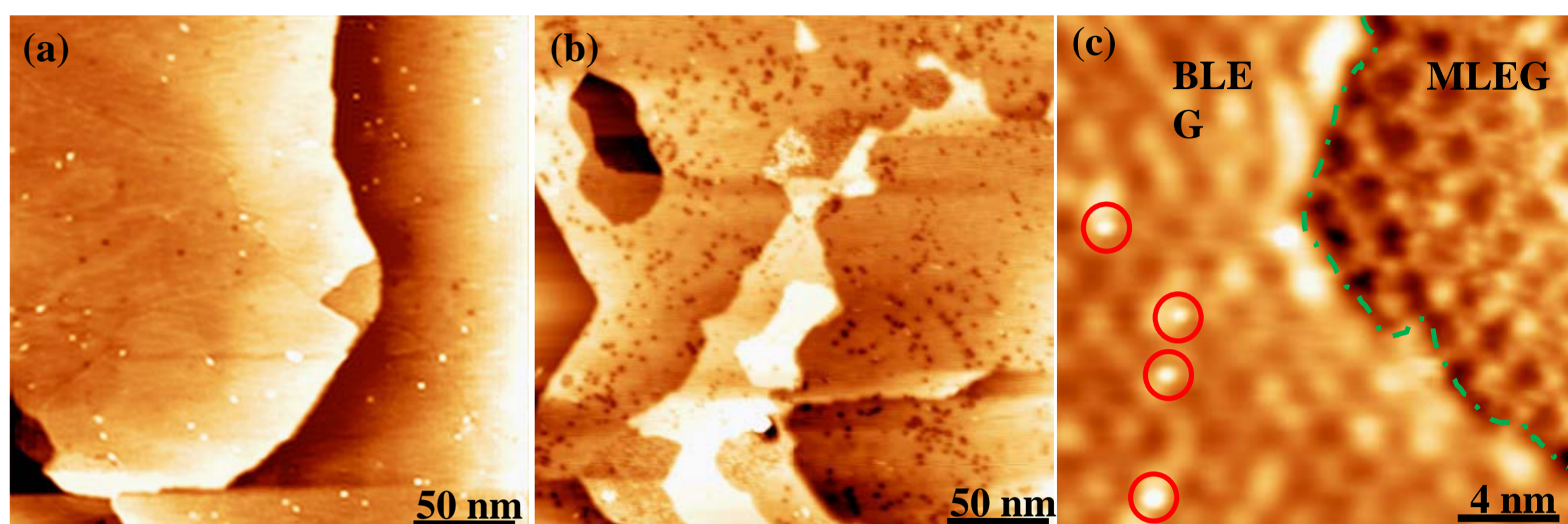
Results and discussion



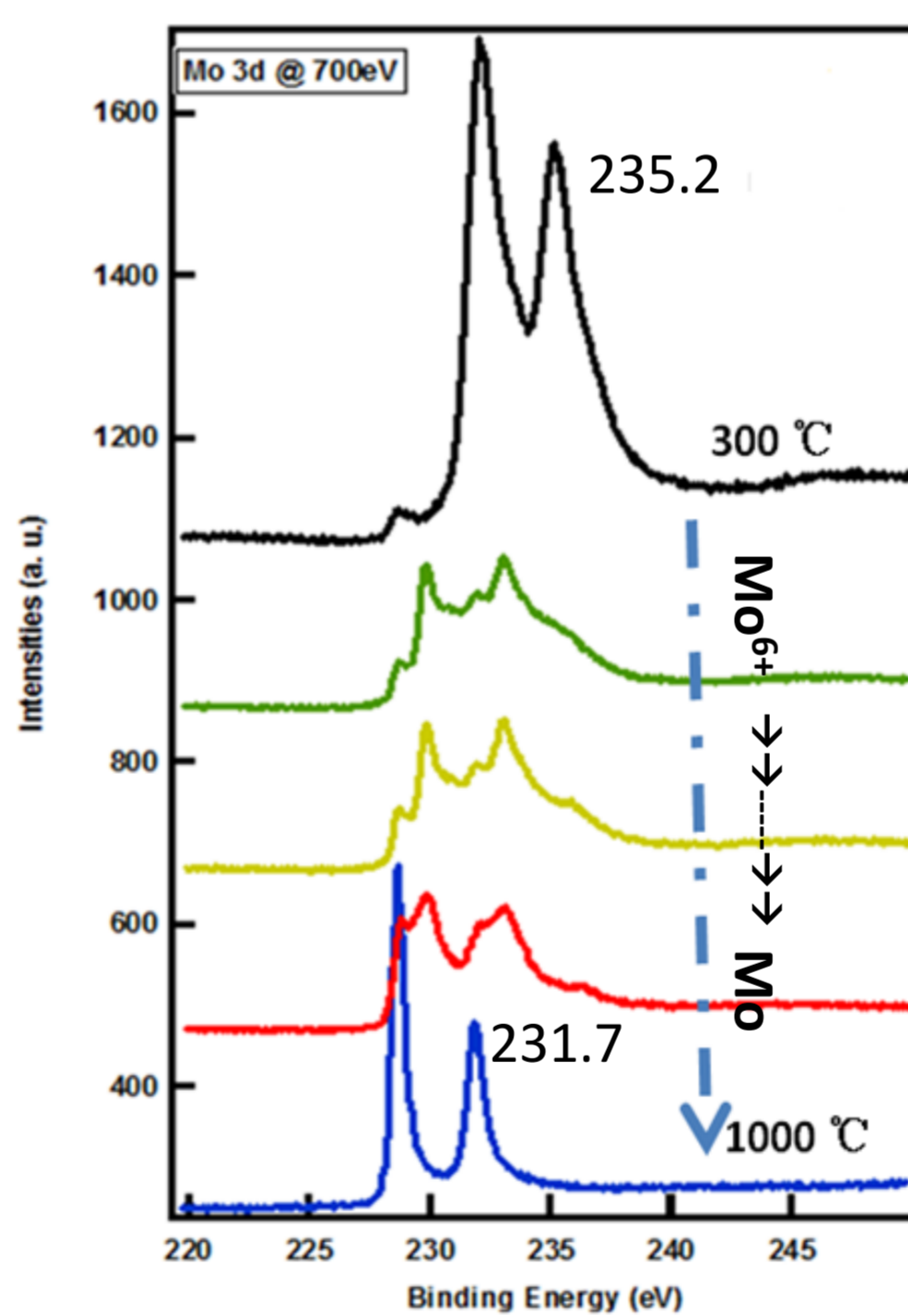
As prepared clean EG sample. Left: STM image taken from EG with monolayer and bilayer graphene. The inserts shows the atomic structure of monolayer and bilayer graphene respectively. Right: Ball-and-stick model of bilayer graphene showing the two inequivalent carbon atoms (α and β sites) per unit cell. The green diamond highlights its unit cell.



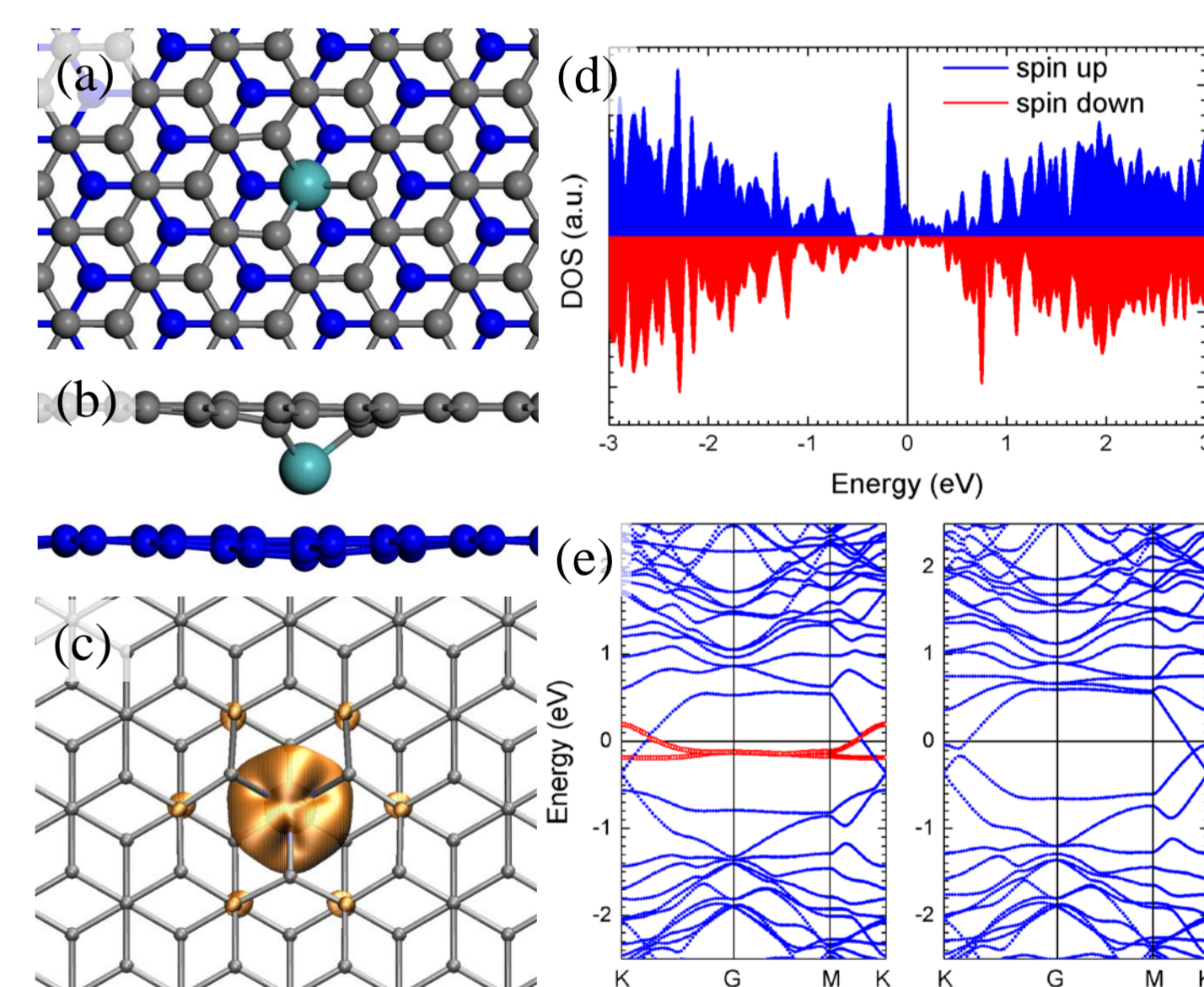
Atomic structure of Mo dopants into bilayer graphene (a) Atomically resolved STM image ($V_T = 0.5V$) (b,c) ($V_T = -0.3V$) The line-profile indicates α -site adsorption of Mo: yellow arrow for β site and cyan arrow for α site.



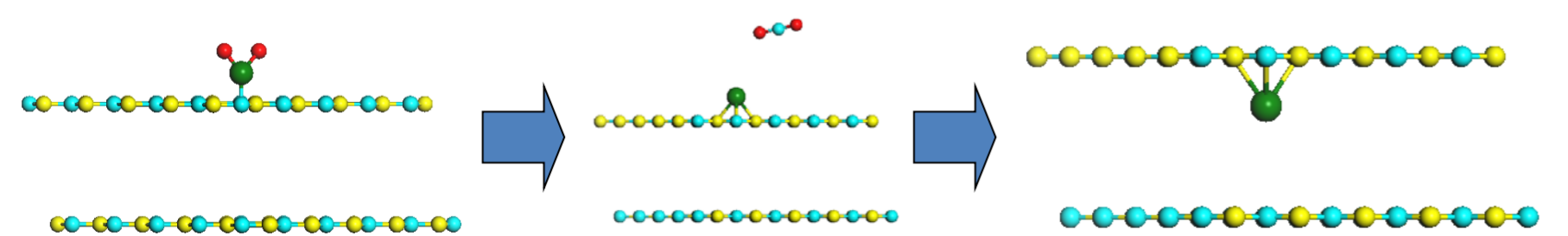
Graphene with randomly dispersed Mo dopants. (a) and (b): Typical large scale STM image ($250 \text{ nm} \times 250 \text{ nm}$) of EG with low Mo coverage ($V_T = -4 \text{ V}$) and higher Mo coverage ($V_T = -4 \text{ V}$). (c) Zoomed-in STM image ($20 \text{ nm} \times 20 \text{ nm}$, $V_T = 1 \text{ V}$) indicates isolated Mo dopants (protrusions) highlighted by red circles in BLEG only. The dash-dotted curve highlights the boundary between monolayer EG and bilayer EG.



ex situ Synchrotron-based high-resolution PES spectra of Mo 3d as a function of annealing temperature using photon energy of 700 eV.



DFT calculated results (a) Top and (b) side views of optimized structure of BLG with Mo-dopant at α -site and between the two freestanding BLG layers. (c) Spatial distribution of spin-polarized charge density (spin up minus spin down). (d) Density of states. (e) Band structures (left, spin up; right, spin down). Red lines highlight the localized spin state of the two flat bands around E_F .



Proposed mechanism of Mo incorporating into bilayer EG. Some MoO_2 was reduced into Mo and carbon vacancy was created at the same time. These Mo atoms stayed in the carbon vacancy and were tunneled in between two graphene layers at high temperature.

Conclusion

We have demonstrated the possibility of incorporating single transition metal (Mo) dopants into bilayer graphene in a stable configuration. Scanning tunneling microscopy results show that the substitutional Mo dopants prefer to embed inside bilayer graphene and the electronic structure of graphene is strongly modified only within a few lattice spacings of the Mo dopant site. DFT calculations show that each Mo atom introduces a local magnetic moment of $1.81 \mu_B$ into BLEG. This single Mo-doped bilayer graphene structure may be incorporated into the design of novel graphene spintronics devices.

Acknowledgements

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