

Growth of Tailored Graphene Structures on Titanium Oxide by Plasma Assisted Chemical Vapor Deposition

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Synopsis

In this contribution, we report the direct growth of graphene structures by plasma-assisted CVD, namely atomically thin films, nanodots and nanorods that present a clean and optimal chemical junction with TiO₂ (110) face [1].

Introduction

Since the discovery of the photocatalytic activity [2] and photosensitivity of TiO₂, significant effort has been made for the development of its practical applications. Under UV light irradiation, electrons and holes are created nearby the surface of the semiconductor that can be extracted or used to promote redox reaction. However, the photonic efficiency of TiO₂ is still low for practical uses, the main reason being charge recombination (>90%) inside the material. One promising strategy to minimize recombination is the combination of TiO₂ with graphene [3] due to the facile transfer and efficient separation of the yielded carriers across the interface between both materials. A high-quality interface between graphene and TiO₂ without recombination centers such as adsorbates or contamination is critical for this task that strongly depends on the synthetic route. Here, we report on a new approach for the direct synthesis of graphene-based structures on rutile TiO₂ (110) single-crystal surfaces as a model system to investigate the interface between both materials. Electron cyclotron resonance chemical vapor deposition (ECR-CVD) is used with acetylene (C₂H₂) as precursor and Ar/O₂ as diluents.

Results and Discussion

The developed synthesis protocol is a two-step process, consisting on nucleation at 650°C followed by growth at 735°C. The gas diluents influence the interface and the structure of the as grown graphene material. The inclusion of O₂ promotes vertical growth of graphene oxide nanodots/rods with controllable height and density (Fig 1(a-c)). The deposition with Ar results in continuous few layer graphene films with low resistivity ($\rho=6.8 \cdot 10^{-6} \Omega \cdot m$) (see fig.1(b-c)). It can be conjectured that the low nucleation density in the first case (Fig 1(a)) is due the critical role that O₂ gas plays in replacing the vast majority of the desorbed terminal O atoms which would promote the generation of vacancies on the surface due to the high temperature growth. In the case of Ar, this balance does not happen resulting in a highly activated surface that promotes a large amount of nucleation centers resulting in continuous films. The chemistry of the contact between both materials and the graphene structure are assessed by means of Raman Fig. 1(c) and XPS (Fig. 1(d)). The C 1s peak associated to the Ar sample mainly present a contribution of sp², thus compatible with graphene formation. Considering all the components present in the O₂-rich sample, we can affirm that great amount of C atoms are covalently bound to O, thus confirming the deposition of (reduced) graphene oxide and the formation of Ti-O-C bonds in the interface. Charge transfer through the interface under illumination is assessed (Fig.1(e)). The

response to the UV light is dependent on the wavelength and increases at shorter wavelengths. The detected photocurrent is in the order of μA , confirming the established contact.

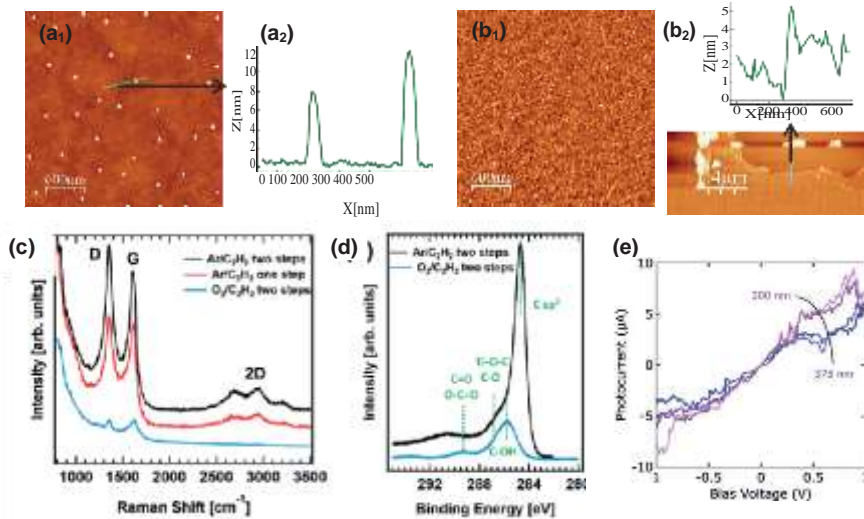


Figure 1. Graphene synthesis results. (a₁) AFM image of graphene dots-rods with O₂ diluent and line profile (a₂). (b₁) Structure of continuous films with Ar diluent and line profile (b₂). T.: 675°C (nucleation), 735°C (growth), t₁=4 min, t₂=12 min. O₂= 15 sccm, Ar = 30 sccm, C₂H₂=2 sccm. Plasma power 200W. (c) Confocal Raman spectra of samples deposited with O₂(blue line) and Ar (black line). The spectrum from one step deposition with Ar is included for comparison (red line). (d) High resolution XPS C(1s) core level spectra of the samples deposited in two steps with O₂ diluent (blue line) and Ar diluent (black line). The contribution of the Ti-O-C bonds to the spectrum confirms the intimate contact between graphene and TiO₂. (e) Photocurrent generated after exposure to UV light (from 300 nm to 375 nm) through the graphene-TiO₂ junction at low bias voltage.

Conclusions

The structure of the deposited materials can be tailored by modifying the synthesis atmosphere. Efficient photocurrent generation measured through graphene-TiO₂ interface indicates an intimate contact between both materials. The chemical state established between graphene and TiO₂ is carefully investigated and the chemical Ti-O-C bond formation is proposed. In conclusion, the present study demonstrates an efficient methodology to growth of graphenic structures on TiO₂ with a clean interface and chemical contact.

References

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