

Highly Efficient *n*-Type Doping and Band Renormalization in Ti-Adsorbed Graphene

Using the concept of orbital hybridization engineering, scientists have now succeeded to achieve highly efficient *n*-type doping in graphene.

Graphene consists of a single layer of carbon atoms arranged in a hexagonal two-dimensional structure. Graphene is, thus, a one-atom thick layer of the quasi-two-dimensional layered mineral graphite. High-quality graphene is strong, light, nearly transparent and an excellent conductor of heat and electricity.¹ These properties make graphene a favored material for making electronic devices, and hence, there is a lot of interest in making *n*-type and *p*-type doped graphene.

However, this is easier said than done. This is mainly because, to achieve doping, one needs to add specific atoms to graphene and this can lead to unintentional changes that degrade its physical and chemical properties. The goal is thus to find the best way to dope graphene, and to simultaneously ensure that the properties do not degrade, but rather improve, after doping.

In this article, we highlight the study done by Chia-Hao Chen (NSRRC), Chung-Lin Wu (National Cheng Kung University) *et al.*, in which the attempt was successful in achieving highly efficient *n*-type doping in epitaxial graphene.² The authors relied on the concept of orbital hybridization to achieve their goal of doping graphene. *Orbital hybridization* effectively means that an adsorbed atom is chosen and deposited in such a way that its electronic orbitals have the best chance to strongly hybridize with C $2p_z$ orbitals which determine the electronic structure of graphene. The authors chose to adsorb Ti atoms on graphene as Ti is known to have a large cohesive energy, and while this can lead to clustering and aggregation for high Ti coverages, the authors explored the novel idea of extremely low Ti coverages to obtain well isolated adatoms.

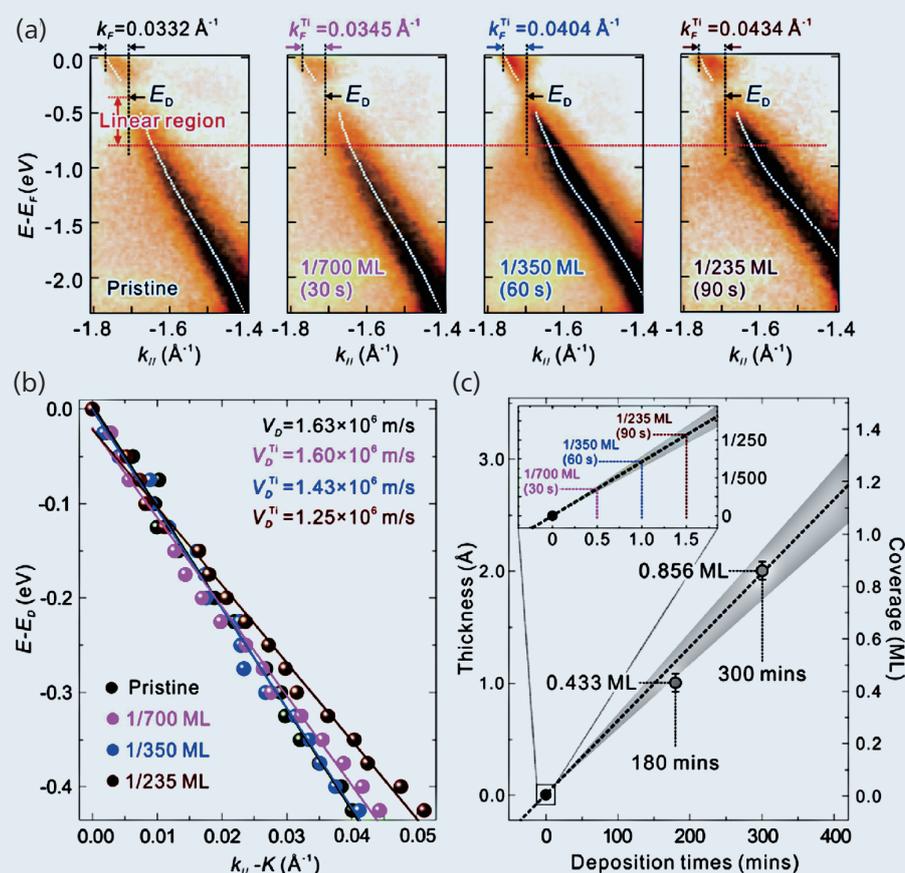


Fig. 1: Room temperature ARPES measurements on graphene with Ti adatoms, using synchrotron radiation of photon energy $h\nu = 52 \text{ eV}$. (a) Band structure of Ti-doped graphene for 0, 1/700, 1/350 and 1/235 ML coverages, measured along the $K \rightarrow \Gamma$ direction and in the vicinity of the K-point. The energy dispersion was obtained from fits to momentum distribution curves (MDCs; white dashed lines). The black arrow marks the binding energy position E_D of the Dirac point. The obtained Fermi momentum k_F values are also stated. (b) The Dirac velocity V_D in the low-lying valence band depends on Ti coverage. (c) The Ti coverage was calibrated with a quartz-crystal microbalance. Deposition conditions and corresponding Ti coverages are listed. The black dashed line shows a least-squares fit to the data. [Reproduced from Ref. 2]

They carried out very accurate low coverage studies of 1/700 monolayer (ML), 1/350 ML and 1/235 ML of Ti adsorbed on graphene, after a careful calibration of the rate of deposition as shown in **Fig 1(c)**. The authors then carried out angle-resolved photoemission spectroscopy (ARPES) of the pristine and Ti-adsorbed graphene samples. ARPES is a versatile technique which provides the electronic band dispersions of a material and is well suited for studying the electronic structure of two-dimensional materials. **Figure 1(a)** shows the results of ARPES measurements carried out on pristine and Ti-adsorbed graphene for different coverages. The main results that can be understood from the data are :

- (i) The so-called Dirac point (labeled E_D in **Fig. 1(a)**, and which is well known for the band dispersions of graphene) could be observed and confirms the high quality of the samples. The Dirac point does not shift upon Ti deposition: its energy is 360 meV for pristine graphene (0 s); it stays constant at 360 meV for 30 s and 60 s of Ti deposition, corresponding to 1/700 ML and 1/350 ML coverage, respectively. It shows a very small shift to 350 meV after 90 s of Ti deposition, which corresponds to 1/235 ML of Ti coverage. This result indicates that the Fermi level does not shift with Ti coverage.
- (ii) The authors could estimate that the density of charge carriers increases from $3.5 \times 10^{12} \text{ cm}^{-2}$ to $6.0 \times 10^{12} \text{ cm}^{-2}$ for Ti coverages from 0 to 1/235 ML.
- (iii) Most interestingly, the band dispersions get renormalized and the Dirac velocity V_D of the valence-band electrons changes systematically, as shown in **Fig 1(b)**.

From further analysis of the data, the authors obtained an experimental estimate of the effective charge transfer, $\Delta\rho_{\text{Ti,exp}} = (0.45 \pm 0.05)$ electrons per Ti adatom. The charge transfer $\Delta\rho_{\text{Ti,exp}}$ is the amount of charge transferred from Ti to graphene, and its value is significantly larger than previously reported values for transition-metal adatoms (Ti: 0.08-0.17 electrons per adatom, Fe: 0.017-0.040 electrons per adatom, Pt: 0.014-0.021 electrons per adatom).³ In order to un-

derstand the changes observed in the ARPES results, the authors performed first-principles calculations based on density functional theory for a Ti adatom on graphene and a 4×4 supercell. From the results, the authors confirmed that the Ti $3d_z^2$ orbital was strongly hybridized with the C $2p_z$ orbital of graphene, leading to a large transfer of electrons from Ti adatoms to graphene. While the calculated charge transfer was found to be $\Delta\rho_{\text{Ti,cal}} = 1.1-1.2$ electrons per Ti adatom at low coverages, and is larger than the experimental value ($\Delta\rho_{\text{Ti,exp}} = 0.45$ electrons per Ti adatom), it was attributed to the large cohesive energy of Ti on graphene that can lead to formation of three-dimensional Ti islands.² The authors also found that Ti $3d_{xy}$ and $3d_{x^2-y^2}$ orbitals contributed with a minor transfer of electronic charge. These results indicate the importance of orbital-hybridization engineering for tuning the carrier concentration and band renormalization using very low adsorption coverages of transition-metal atoms on graphene. (Reported by Ashish Chainani).

This report features the work of Chia-Hao Chen, Chung-Lin Wu and their co-workers published in Carbon 109, 300 (2016).

TLS 24A1 BM-(WR-SGM) XPS, UPS

- ARPES
- Condensed-matter Physics, Materials Science

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