

Graphene and Other 2D Materials Focus Topic

Room: Hall B - Session GR-ThP

Graphene and Other 2D Materials Poster Session

GR-ThP4 Characterization of Coatings for Tribological and High Temperature Applications. S. Vijayalakshmi, V. Thippesamy, M.R. Sridhar, K.A. Harsha, R. Roshan, GE Global Research, India, B.A. Record, GE

Metal Matrix Composite Coatings as wear resistant coatings and thermal barrier coatings play a crucial role in the life of current tribological and high temperature applications. Understanding the surface of these coatings in terms of its material structure, porosity, composition, mechanical strength, and bond strength is crucial. These properties essentially govern the final tribological and thermal properties and thereby dictate the life of the coatings. Various characterization techniques have been employed in studying the properties of the coatings. Proper choice of the characterization techniques; tools and method of evaluation are critical for distinguishing coating with very similar properties. This article presents the use of selected characterization techniques like Micro hardness, Scanning electron microscopy coupled with EDS, Image analysis, XRD and Surface Profilometry to analyze the mechanical, material and surface properties and understand the structure property correlation of coatings of varied microstructures with different volume fraction of ceramic particles embedded in metallic matrix.

GR-ThP5 Plasma Treatment of Thin Film Coated with Graphene Flakes for Sheet Resistance Reduction. S.H. Kim, J.S. Oh, G.Y. Yeom, Sungkyunkwan University, Republic of Korea

Recently, study of transparent electrode using graphene flake has been attracted in this field. The advantage of graphene flake is the high productivity, scalability, and the flexibility on using various substrate materials. However, a thin film coated with graphene flakes generally showed a high sheet resistance due to the defects existed within graphene edges, domains, residual oxygen contents, etc. In this study, the effect of plasma treatment to thin film coated with graphene flake on the improvement of electrical properties was investigated. Graphene flake films were coated on the polyethylene terephthalate (PET) film by the spray coating system. By using a Cl₂ plasma treatment, the sheet resistance was decreased with the increase of treatment time. However, when the thin film was treated too long, the sheet resistance was again increased with the increase of the treatment time. The optimum treatment time was related to the thickness of the thin film. In this experiment, at an optimum condition, it was observed that the surface resistance of the graphene film could be decreased higher than 50 %. The detailed mechanism on the change of graphene sheet resistance & structure will be presented.

GR-ThP6 Characterisation of Mo Oxidation States in MoO₃ and MoS₂ Layer Materials Using X-ray Photoelectron Spectroscopy. A.J. Roberts, Kratos Analytical Limited, UK, N.A. Fairley, CasaXPS, UK, B. Mendoza-Sánchez, Trinity College Dublin, Ireland, C. Moffitt, Kratos Analytical Limited, UK

The characterisation of layered materials has been dominated by graphene in recent years. There are however other examples of layered materials which retain stability down to a single monolayer and whose properties are complementary to graphene. Of these materials both MoS₂ and α -phase MoO₃ are of interest due to electronic and optical properties which may lead to applications as diverse as optoelectronics and light emitting devices for the former material or energy storage and catalysis for the latter. The chemical state and therefore electronic structure of these materials is readily characterised using x-ray photoelectron spectroscopy. In the case of MoO₃, which may be reduced quite easily, there are a number of stable phases where the Mo becomes progressively reduced until reaching the stable dioxide with the formal oxidation state Mo(IV). Here we present a study of electrochemically reduced MoO₃ where a mixture of lower valence oxides have been generated with concentrations varying as Mo(V) > Mo(IV) > Mo(VI) with MoO₂ as the main component created below 0.185 V (vs Ag/AgCl). The stability of α -MoO₃ under x-ray irradiation has also been studied with particular focus on the possibility of x-ray / in-vacuo reduction of Mo(VI) causing misinterpretation of the valance of the samples generated electrochemically. To complement the work on the oxide material we also present a study of the oxidation state of MoS₂ where the Mo(IV) disulphide has been reduced in ultra-high vacuum by preferential sputtering of the sulfur. This relatively aggressive form of reduction leads to the creation of Mo(0) metallic-like molybdenum and demonstrates the extreme care required for in-vacuum sputter cleaning of layered materials.

GR-ThP7 Development of Field Effect Transistors Based on Graphene using Dielectrophoretic Deposition and Tantalum Nitride Electrodes. A.M. Pascon, J.A. Diniz, L.R.C. Fonseca, J.F. de Souza, University of Campinas, Brazil

For devices based on graphene, non-refractory metallic electrodes of Ti/Au or Ti/Pd are frequently used. However, to reduce the contact resistance between metal electrodes and graphene, an annealing step in vacuum at a temperature of 700° C is generally required, which is incompatible with non-refractory metals [1]. On the other hand, refractory metal electrodes, such as tantalum nitride (TaN), can tolerate the annealing step but are less studied. Furthermore, the many techniques established to obtain graphene and to build high quality devices based on graphene are severely limited for large scale integration (LSI). Here we attempt a new approach to reach LSI. In our approach, graphene was obtained in large quantity from dielectrophoretic (DEP) assembly [2] of a few layers of insulating graphene oxide followed by thermal reduction at 450°C. Next, for the metal contacts with graphene we used tantalum nitride (TaN) electrodes deposited by DC reactive sputtering in N₂/Ar environment. FET devices were obtained with the graphene sheets deposited between TaN electrodes, which are employed as source and drain, and laying on top of a TaO_x high-k gate dielectric deposited on an n+ silicon substrate used as the back electrode. To improve the contacts between graphene and TaN, ac signals were applied between electrodes, followed by annealing at 700° C in high vacuum to prevent electrode oxidation.

Scanning electronic microscopy and current-voltage (I-V) measurements were carried out to obtain the physical and electrical characteristics of our devices, respectively. The resistance values measured before and after annealing differ by five orders of magnitude, in agreement with [2], resulting in good contact characteristics.

In parallel, *ab initio* calculations were performed to investigate the nature of graphene/TaN interface employing two models for the interface. While this simulation effort is still ongoing, we have found that for the Ta/N-rich TaN surface and for the Ta-rich TaN surface the absence of the Dirac cone in the BL for each case is not due to the BL roughness caused by the strong interaction with the TaN surface, especially for the Ta/N-rich surface, but due to metal surface states induced in the BL. Because in graphene the inter-layer separation is large, the electronic properties of the second graphene sheet are graphene-like, displaying a clear linear dispersion near the Dirac point.

[1] Souza, J. F., Development of Materials and Methods of Fabrication of Chemical/Biochemical Sensors based on Silicon and Carbon Nanostructures (ISFET, CNTFET and GrafFET), PhD, University of Campinas, 2012;

[2] Burg B R et al, Appl. Phys. Lett. 94 053110 (2009);

GR-ThP8 An Infrared Sensor using a Multi-walled Carbon Nanotube Sheet. D. Jung, M. Han, G.S. Lee, The University of Texas at Dallas

Carbon nanotubes (CNTs) have a potential capacity to be efficient infrared (IR) sensing materials due to their outstanding electronic and optical properties. There are many reports on the IR photo-response in the conductivity/resistance of single-walled carbon nanotube (SWCNT). Although theoretical and experimental development toward individual SWCNT based IR sensor has been reported, several obstacles disturb the further progress of SWCNT based IR sensors. Firstly, SWCNTs still have some issues in their purification, separation, and dispersion in a liquid/polymer used to enhance their electrical and optical properties. It is difficult to modify the density and thickness of the SWCNTs causing reduction in their production efficiency. Secondly, there is no a reliable and efficient transfer way to reproducibly fabricate SWCNT based sensors up to now. Lastly, how to make large scale and uniformly aligned films for mass production by using SWCNT. In this paper, spin-capable multi-walled carbon nanotube (MWCNT) is proposed to fulfill the above three challenges. The IR detector fabricated by MWCNT sheet, which pulled out from spin-capable MWCNT forest has large surface area and well aligned individual MWCNT. By investigating theoretical analysis with experimental results, we focused on which factors can affect the sensitivity and response time of MWCNT IR detectors, which gives help for further design for practical applications. We've founded that the extremely low heat capacity per unit area of MWCNT in sheet enabled a fast IR response of the MWCNT IR detectors. Experiments by acid treatment and increasing the surface area of CNT films have been carried out to improve the sensitivity and response time of the CNT film detector. We've observed that the MWCNT IR sensor exhibits shows a 16 % resistance change with a fast response time of 10 ms under 10 mW/mm² of IR illumination at room temperature.

GR-ThP9 The Robustness of the Electronic Structures of the Quasi-Free Standing Graphene Layers Upon Deposition of the Strong Hole-Doping Materials. *W. Kim*, Korea Research Institute of Standards and Science, Republic of Korea, *G.-E. Yang, J. Kim, Y. Park*, Kyung Hee University, Republic of Korea, *B.-G. Park*, Pohang Accelerator Laboratory, Republic of Korea

We investigated the change in the electronic structure of the quasi-free standing epitaxial graphene(QFEG) layers upon deposition of strong hole doping materials by using angle-resolved photoemission spectroscopy(ARPES). To produce the QFEG layers, we tried hydrogen intercalation into a zero-layer graphene grown on the 4H-SiC(0001) surface, and confirmed the successful formation of the QFEG layers, judging from the coincidence of the Dirac point and Fermi levels in the ARPES spectra of the hydrogen-intercalated graphene layers. Then we monitored carefully the change of the position of Dirac point in ARPES spectra during the deposition of strong hole-doping materials such as Bi atoms and tetrafluoro-tetracyanoquinodimethane (4F-TCNQ) molecules, both of which are known to induce the significant shifts of the Dirac point to the Fermi level in the conventional epitaxial graphene layers. However, for the QFEG layers, we could not find any measurable shifts of Dirac point upon the deposition of Bi atoms or 4F-TCNQ up to the 1 ML thickness. The overall shape of graphene π -bands also remained almost same, unlikely the results for the conventional epitaxial graphene layers which show significant blurring of band width near 1 ML thickness. This robustness of the electronic structure of QFEG layer upon deposition of Bi atoms and 4F-TCNQ molecules implies that more sophisticated approach is required to understand the hole-doping effect in the conventional epitaxial graphene and QFEG layers grown on the SiC(0001) surface.

GR-ThP12 Structural Stability and Electronic Structure of Boron- or Nitrogen-Doped Graphene. *T. Umeki, J. Nakamura*, The University of Electro-Communications (UEC-Tokyo), Japan

Graphene, a two-dimensional form of carbon with atoms arranged in a honeycomb lattice, has attracted enormous attention because of its unique electronic structures. To realize graphene-based electronics, modulation techniques of its electronic properties are indispensable. The most fundamental approach to tailor the electronic properties of graphene is doping. Nitrogen atoms can be doped into graphene using chemical vapor deposition or NH_3 plasma exposure [1,2]. It has been confirmed that the nitrogen-doped graphene exhibits an n-type behavior [1,2]. However, there exists little knowledge about the well-defined atomic arrangements of nitrogen-doped graphene. In this work, we have investigated the energetic stability of boron- or nitrogen-doped graphene using first-principle calculations within the local density functional theory.

We have calculated the interaction energy between two substitutional N atoms. A (4×4) supercell for graphene is employed, in which two C atoms are replaced by N atoms. The interaction energy has been found to decrease with increasing distance between N atoms. It should be noted that N atoms prefer to locate at the third nearest neighbors with each other, as shown in the previous report [3].

Next, we have investigated the interaction energy for the homogeneously-arranged N-doped graphene using $(n \times n)$ and $(n\sqrt{3} \times n\sqrt{3})$ -R30 unit cells (n : integer), where substitutional N atoms form triangle or honeycomb grids on the graphene basal plane. It has been found that the interaction energy decreases with decreasing density of N atoms. However, anomalous stabilization is confirmed for the honeycomb-arranged N-doped graphene with N:C=1:3. We will also report on the band structures of N-doped and B-doped graphene.

[1] D. Wei et al., Nano Lett. **9**, 1752 (2009)

[2] Y.-C. Lin et al., Appl. Phys. Lett. **96**, 133110 (2010)

[3] Z. Hou et al., Phys. Rev. B **85**, 165439 (2012)

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