Graphene Chemical Sensor Array for *in situ* Chemical Analysis

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Introduction: We are developing highly sensitive, selective and low resource graphene chemical sensor arrays for *in situ* detection of trace gases and volatile organics. The versatile nature makes graphene sensor arrays suitable for both orbiters and landed missions in Planetary Science. They can be used to detect gases that can help fingerprint various biological and abiotic processes on outer planets, moons, and asteroids. More specifically, it can be used to detect methane, ammonia, and other gases difficult to detect using mass spectrometry due to mass interference issues. In addition, these small, light and low power sensors can be employed to quickly pre-screen samples for sample return missions. The planetary Science Decadal Survey names Titan/Saturn System Mission, Neptune Orbiter and Probe, and Mars Sample Return as high priority missions, all of which may benefit from graphene sensor arrays.

Sensor Development: Graphene is a two-dimensional crystalline material comprised of sp^2-hybridized carbon atoms packed in a honeycomb lattice[1,2]. The unique structure offers many advantages as a chemical sensor. For example, it has the highest surface-to-volume raio, with all the atoms exposed to the target species. In addition, it has very low Johnson noise due to superior lattice structure. Furthermore, the superior mechanical and thermal stability, and radiation hardness due to its minute cross-sectional area make it ideal for space applications.

The operational principle of the graphene sensor is similar to that of solid state sensors. As gas molecules adsorb onto graphene's surface, they act as either electron donors or acceptors, inducing a local change in graphene's electrical conductivity[3-6]. This effect is very pronounced in graphene due to unique properties mentioned earlier, making it possible to detect the smallest of changes in resistance. The selectivity can be induced for a target gas by adding a proper functional group to graphene.The functional groups interact with different target gases in a way analogous to a lock and a key.

Large area monolayer graphene synthesized in-house with low pressure chemical vapor deposition was used to fabricate the sensor arrays. Graphene was characterized using microscopy and spectroscopy techniques. A device fabrication process compatible with single atomic layer materials was developed using the traditional microelectronics processing techniques[7]. Moreover, a funcationalization chemistry was developed for additing various functional groups to graphene. Table 1 lists the functional groups are are looking at for some of the test gases of interest.

Target Gas	Functional Group
Ammonia	Zinc Oxide
Hydrogen	Platinum, Palladium
Methane	Tin Oxide

Furthermore, a compatible packaging method was also developed using a daughter-board fabricated in house, a customized printed cirbuit board and wire bonding. A fully packaged chip is presented in Fig 1. Each chip consists of ten graphene sensors, on-chip heaters and temperature sensors. The sensor dimensions range from 20 μm to 200 μm.

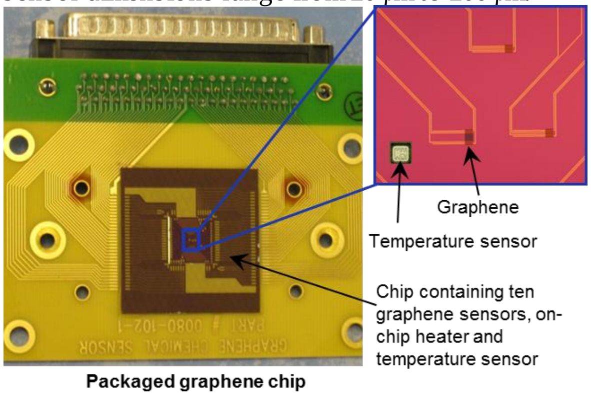

Fig 1- Completely packaged graphene chip consisting of ten sensor elements, on-chip heaters and temperature sensors

A sophisticated sensor test setup was designed and build in house (Fig 2). The setup includes a vacuum chamber connected to a turbo pump, a computerized multi-component gas mixing and dilution system from Environics Inc. that can dilute commercial gases down to parts per billion (ppb) concentration, a Keithley Source Measure Unit

(2400) for data collection, and a Keithley Multiplexing Unit for simultaneous testing of multiple graphene sensors, and a Lakeshore temperature controller that used the on-chip temperature sensor to control the temperature of the devices. Flexible heaters and on-chip heaters were used to desorb contaminants from the chamber walls and the chips, respectively, before performing any tests.

Fig 2- Characterization setup designed and built in house to test graphene sensor arrays

Hydrogen was used as one of the test gases, diluted with an inert. Argon, nitrogen and helium were explored as the carrier gas. Experiments were performed at various temperatures, ranging from room temperature to 200°C, as well as both under vacuum and at atmospheric pressure. The concentration was varied from 100 ppb, which was the instrument limit, to 30,000 parts per million (ppm). The graphene sensors were able to detect the lowest concentration of Hydrogen permitted by the system, namely 100 ppb, demonstrating the extremely high sensitivity of the sensors. The measurement data will be published in a full journal article.

Possible Mission Architectures: The versatility of graphene sensors with respect to operating conditions and ability to customize and select gases of interest makes them competitive for a broad range of missions. Mass Spectropetry is one of the state-of-the-art technologies used for orbiters and landed missions for *in situ* trace gas detection. However, it uses a specific mass to charge (m/z) ratio to identify gas species, and many trace gases of interest have overlapping m/z ratios, making it difficult to distinguish from one another. For example, water, which is often present in instrument background, has strong ion fragments at m/z 16, 17, 18, 19, and 20, complicating the detection of species such as ammonia (m/z 16) and hydroxyl groups (m/z 17). The other characteristic ion fragment for detection of ammonia is m/z 15, which is also characteristic of methane. Graphene sensors can be deployed in parallel with Mass Spectrometers for complementary measurements for these species without adding substantial weight to the payload.

Moreover, low budget missions that are unable to use Mass Spectrometers due to size, weight and power requirements will be able to utilize the low resource graphene sensors. In fact, the tiny size, light weight and low power of these sensors can enable new missions based on CubeSats or even FemtoSats. Furthermore, these sensors can also be useful for performing quick pre-screening of the samples for sample return missions such as Mars Sample Return.

Finally, a network of graphene chemical sensors can potentially enable new science by providing spatially resolved measurements of chemical species. For example, hundreds of these cheap, tiny sensors can be deployed to the surface of a planetary body, performing simultaneous measurements in many locations. The data then can be used to construct a spatio-temporal map of surface composition. This is in contrast to the current scenario where measurements are performed at one location at a time, and hence only a limited number of measurements can made over the lifetime of the mission.

References:

[1] Geim A.K. and Novoselov K.S. (2007) *Nature Materials, 6*, 183-191.

[2] Novoselov K.S. et al. (2012) *Nature, 490*, 192-200.

[3] Schedin F. et al. (2007) *Nature Materials, 6*, 652–655.

[4] Dan Y. P. et al. (2009) *Nano Letters, 9*, 1472-1475.

[5] Yavari F. et al. (2011) *Scientific Reports, 1*.

[6] Yuan W.J. et al. (2013) *Advanced Materials, 25*, 766-771.

[7] Sultana M. et al. (2013) *Radiation Effects and Defect in Solids, 168*, 805-811.