Graphene/Galinstan Contacts for Reliable Liquid Interconnects

Patrik Ahlberg, Seunghee Jeong, Zhigang Wu, Shi-Li Zhang and Zhi-Bin Zhang

Uppsala University, P.O. Box 534, SE-751 21 Uppsala, Sweden
patrik.ahlberg@angstrom.uu.se

Abstract
Shortly after its discovery graphene has been shown to possess extraordinary chemical stability and also the ability to work as a protective membrane for gases such as helium and hydrogen [1]. This has inspired us to investigate the inertness of graphenes towards galinstan as well as graphene as diffusion barrier to protect the ordinary metals used in interconnection from the attack of galinstan. The application concerns flexible and stretchable electronics where the galinstan is used as interconnects. Galinstan, a Ga-In-Sn alloy, is a relatively new material but has already found many applications. One example is that it can act as a non-toxic replacement for mercury. The alloy has a large liquid window of temperature ranging from -19 ^{o}C up to 1300 ^{o}C. It has a high conductivity of 3.46×10^{6} S/m at room teperature [2]. This makes galinstan ideal to be used in stretchable and bendable electronics. It unfortunately has the drawback of being highly reactive with some metals that are ordinarily used in interconnects. For instance, aluminum is fully reacted within days were as tungsten can survive up to a year [3][4]. Al and galinstan interdiffuse into each other. Redox reactions between Al and water occur when water is present at the galinstan surface, resulting in insulating aluminum oxides and hydroxides [4]. We show here that graphene can both act as diffusion barrier and survive in direct contact with the galinstan.

In this work the graphene was synthesized in our home-made chemical vapour deposition (CVD) system. The graphene is produced according to the today's ordinarily used procedure that argon, hydrogen and methane flow over a copper foil in a furnace at 1000 °C under medium vacuum. When the foil has cooled and removed from the furnace it is subsequently spin coated with poly(methyl methacrylate) (PMMA). Two different techniques of transfer were employed. The first transfer process constitutes etching the copper with $FeCl_3$, removing etchant residue from the PMMA/graphene stack in DI water and finally attaching the PMMA/graphene stack onto a substrate. It was however found that this transfer method carried a significant amount of chlorine with it, which etched the aluminum substrate. The second procedure starts from the first layer of any stacks of graphene. To the PMMA/graphene/Cu-foil a cut mask of a plastic foil was glued on and this stack was immersed in a NaOH solution. The graphene system was connected to a cathode and a platinum piece acted as anode, Hydrolysis was performed until the graphene is separated from the Cu foil [5]. The graphene-polymer structure was cleaned in DI water. At this point in both processes the samples were heated, followed by acetone wash to get clean graphene. The galinstan from Geratherm Medical was used as received. All aluminum films were deposited by means of sputtering on microscope slide glass.

After applying a drop of galinstan on Al, it shows quickly that the galinstan attacks the underlying Al (see figure 1a and b). The Al below the droplet was quickly dissolved and a black layer formed on the surface and around the edge of the droplet. The black layer was later confirmed to be aluminum oxide by energy-dispersive X-ray spectroscopy (EDS) and Raman spectroscopy (not shown here) [3]. Initial testing showed that a graphene film of three layers and beyond is required to act as a barrier for the drop casted galinstan (see figure 1c).

To electrically evaluate the effect of graphene as a diffusionbarrier, three samples were prepared. Two of them are covered 1 and 4 layers of graphene, respectively, in the middle region from side to side. A channel of galinstan was air brushed within the graphene area (see figure 2a). A sample without graphene is used as reference. The resistance of the samples were monitored as a function of time using the measurememt configuration as shown in Fig 2a.

It is found that for the spray-coated galinstan, the tiny galinstan droplets of high momentum impact the weak spots of the graphene layer which leads to the patchways for galinstan to reach the underlying Al. This can be evidenced by the reaction spots of galinstan/Al visualized from the rear side after 0.5 hour (see figure 2b). After around 2 hours, the reaction spots evolves to a line (figure 2c). The untouched graphene however blocks the supply of moisture and thus prevents the Al from the gallium facilitated oxidation. This results shows that graphene works as efficient diffusion barrier towards galinstan and holds promising application in liquid interconnects in stretchable electronics.

References

[1] J. Scott Bunch , Scott S. Verbridge , Jonathan S. Alden , Arend M. van der Zande , Jeevak M. Parpia , Harold G. Craighead and Paul L. McEuen, *Nano Lett.*, 2008, 8 (8), pp 2458–2462

[2] N.B. Morley, J. Burris, L.C. Cadwallader and M.D. Nornberg, *Rev. of Sci. Instr*. **79**, 056107, (2008)

[3] J. Ziebarth, J. Woodall, R. Kramer and G Choi, , *Int. J. Hydrogen Energy*, **36**, 5271, (2011)

[4] S. H. Mannan and M. P. Clode, *IEEE Transaction on advanced packaging*, **27**, 508-514, (2004)

[5] César J. Lockhart de la Rosa, Jie Sun , Niclas Lindvall, Matthew T. Cole, Youngwoo Nam, Markus Löffler, Eva Olsson, Kenneth B. K. Teo and August Yurgens, Appl. Phys. Lett. 102, 022101 (2013)

Figures

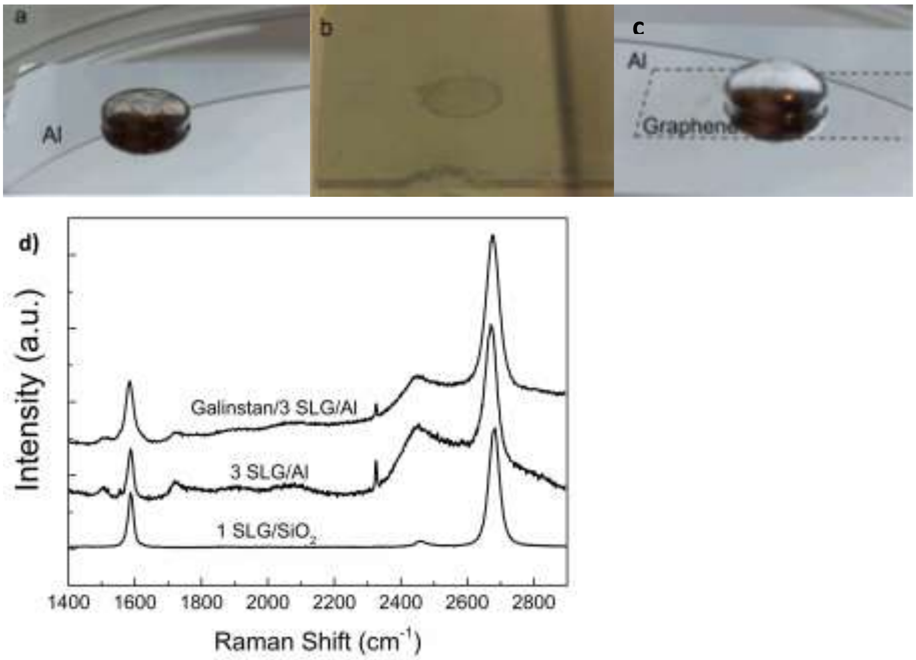

Figure 1: a) Galinstan on Al after it has reacted and precipitated aluminum oxide on the surface. **b)** Picture a seen from beneath the sample **c)** Galinstan on four layers of graphene 6 month after deposition. **d)** Raman curves of the graphene, lowest single layer graphene on SiO2, middle 3 layer graphene on Al, top 3 layer graphene that has been under galinstan for several months.

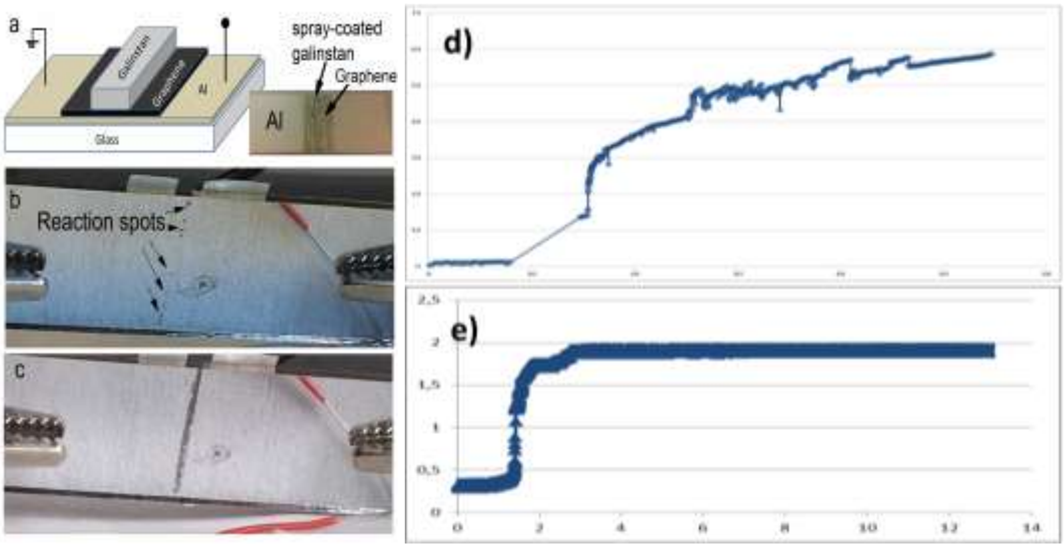

Figure 2: Spraycoated sample seen from beneath while the resistivity is being measured. **a)** Sketch of set up. **b)** 4 layer sample seen from beneath 30min after deposition. **c)** same sample as in b 2 hours after deposition. **d)** Resistivity over time of unprotected sample **e)** 4 layer graphene protected sample.