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High speed mask-less laser controlled precision deposition of metals

Jyi Sheuan Ten[1], Martin Sparkes[1], William O'Neill[1]

[1]*Centre for Industrial Photonics, Institute for Manufacturing, Department of Engineering, University of Cambridge*

Email: Jst44@cam.ac.uk

Abstract
In this paper, laser chemical vapour deposition (LCVD) is explored as a method for the deposition of conductive metal tracks via thermal dissociation of metal organic precursor gases at locations defined by a laser spot on graphene. This allows for a rapid and mask-less deposition technique compared to electron and focused ion beam (EFIB) deposition and lithography methods commonly applied for the deposition of metal contacts to nano- and micro-electronic devices. Lithography involves the use of chemical masks that may contaminate the substrate and may be an issue for building contacts to sensitive materials like graphene and organic materials. EFIB deposition techniques do not require masks but the deposition rate is very slow. With LCVD, a range of metals can be deposited e.g. tungsten, copper and silver; in a freeform pattern, defined by the laser; on substrates such as oxide coated silicon wafers, fused silica and metal substrates. This paper reports on the laser processing conditions necessary for effective deposition and samples are characterised by deposition temperature, deposition profile, electrical conductivity, microstructure and elemental composition of the deposits

Keywords: Laser chemical vapour deposition, conductive metal tracks, graphene, nano- and micro-electronic devices.

1. Introduction

Advanced carbon-based materials such as graphene have promising application areas in electronics such as flexible electronics, high-frequency transistors and logic transistors [1]. The manufacturing route for graphene devices in a research and development environment follows the synthesis of graphene, followed by transfer to a suitable substrate, patterning and finally the deposition of other functional materials [2]. These additional materials include conductive metals that are used as electrical contacts to the graphene-based device. The deposition is typically done using EFIB deposition [3] or lithography. This paper explores the use of laser chemical vapour deposition (LCVD) as a rapid and mask-less deposition method for those conductive metal tracks. LCVD is based on the chemical vapour deposition (CVD) process, whereby materials are deposited on a substrate from a precursor vapour or gas. The precursor molecules contain the deposition material and other atoms to stabilize the gas or vapour. The chemical breakdown of this precursor is initiated at high temperatures. In the typical CVD process, the entire substrate is heated thus the deposition covers the whole substrate. In LCVD, a laser is used to locally heat the substrate limiting the deposition to the areas defined by the laser, eliminating the need for masks to create patterns. While the deposition mechanism of LCVD is similar to that of EFIB, the laser is typically a more energetic heat source resulting in higher deposition rates with less impurities.

2. Experiment methods

A deposition chamber has been set-up for the deposition of tungsten from a tungsten hexacarbonyl precursor on stainless steel (SS) and Si substrates typically used with graphene devices [1], system schematic Figure 1. The laser used is a SPI G3 1064 nm fibre laser in continuous wave mode with a maximum average power output of 20 W. The beam output is scanned using a Nutfield XLR8 galvo-scanner and focused using a Jenoptik JENar 125 mm focal length f-theta lens to achieve a $1/e^2$ beam diameter of around 40 µm. The precursor cylinder is heated to a temperature of 50 °C and the deposition chamber to 100 °C and left for one hour. The chamber is first evacuated to a pressure of 0.3 mBar, measured using an Edwards APG100-XLC Pirani vacuum gauge, then the precursor valve is opened to allow the precursor into the chamber to reach a pressure of 3 mBar. The laser is then used at focus to scan dots and lines on the substrate at a power of 2 W - 4 W and scan speed 0.01 mm/s - 0.2 mm/s.

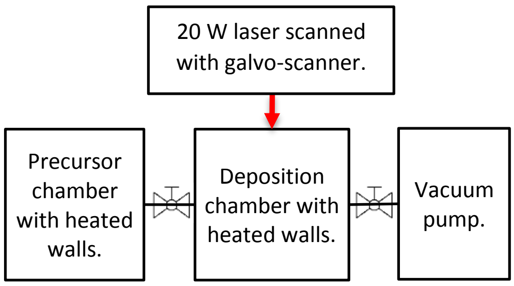

Figure 1. Schematic of deposition system used.

The deposition temperature on SS is measured using a FLIR A615 infrared thermal camera. The laser spot is defocussed to 0.5 mm in diameter so that it is larger than the 0.2 mm length per pixel of the thermal camera. The emissivity of SS304 was first determined using K-type thermocouples to calibrate the thermal camera. The deposition temperature for LCVD is not commonly measured directly in LCVD experiments [2], however, it is important because the deposition temperature needs to be below the damage threshold of graphene. The deposition profile was measured using a Veeco Wyko NT3300 white light interferometer (WLI). The electrical resistivity is measured using the two point probe measurement method with silver paste as contact pads. The microstructure of the deposit was observed using a Zeiss Gemini 1540 XB scanning electron microscopy (SEM) and the elemental composition of the deposit is analysed using an Oxford Instruments X-Max^N 80 energy dispersive X-ray spectroscope (EDX) using a beam energy of 20 kV.

3. Results and analysis

The deposition temperature was measured to be 210 °C, in-line with predictions of Turney et. al. 1992 [4] but lower than the 350 °C deposition temperature used in CVD with the same precursor [5]. This is likely due to the lower precursor pressure of 0.02 mBar used in the CVD experiment. The low temperature makes the deposition technique suitable for deposition on graphene, being below the thermal damage threshold of graphene on SiO_2, around 500 °C [6]. Figure 2 shows the deposition height profile of the deposit on a SS substrate. The deposited track is continuous, essential when forming conductive metal tracks. There is slight swelling of the substrate or possibly deposition outside the laser irradiated track. Based on the average cross-section profile and scanning speed, the deposition rate is 3641 μm^3/s.

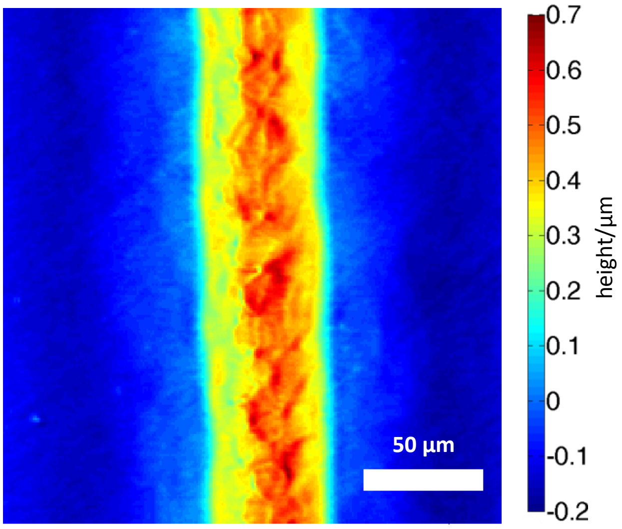

Figure 2. Deposition height profile measured using WLI and done by scanning the laser at 2.4 W in the presence of the precursor at a speed of 0.18 mm/s on SS.

The resistivity of the W track deposited on Si substrates was measured to be 31 µΩ cm which is around 5.5 times the bulk resistivity of tungsten. This is on the high side of the values reported by Y. Nambu et. al. 1990 [7] for LCVD of W but is still suitable as conductive tracks especially since W has a low contact resistance with carbon-based materials [8]. The microstructure of the deposit, seen in Figure 3, is quite similar to the β-W polycrystalline film grown in CVD using the same precursor [5]. The tungsten grains have a lateral dimension of 100 nm - 300 nm. EDX analysis of the deposit reveals that it consists of above 84 % of W on both SS and Si substrates, comparable to CVD [5] and higher than EFIB techniques at 60 % [3].

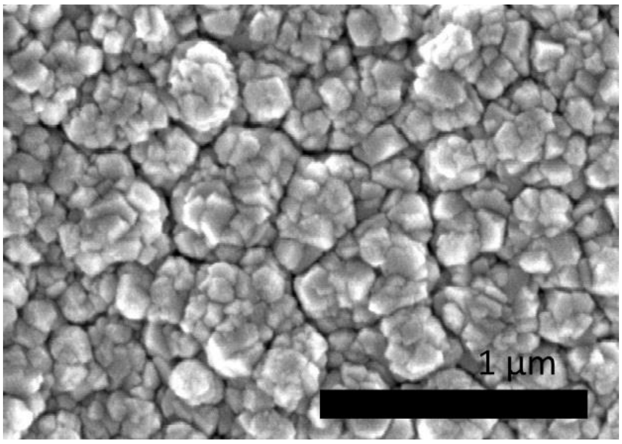

Figure 3. High resolution SEM images of W deposited on Si showing lateral grain dimension of 100-300 nm.

4. Conclusion

An apparatus has been made that is capable of depositing tungsten from a tungsten hexacarbonyl precursor on locations defined by a laser. This deposit has a resistivity of only 5.5 times bulk and is deposited at a temperature of 210 °C, lower than the thermal damage threshold of graphene. The deposition has been demonstrated on materials commonly used as graphene device substrates such as Si.

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