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High quality wafer-scale CVD graphene on molybdenum thin film for sensing application

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Abstract

The superb physical properties of graphene make it a material with great potential for sensing applications, including chemical sensors, Hall sensors and pressure sensors. However, its availability on large area substrates and the development of a scalable manufacturing process need to be addressed. In this work we propose wafer-scale, chemical vapour deposition (CVD) of graphene on sputtered thin-films of molybdenum, as alternative to the more commonly used CVD graphene processes based on copper films. The high melting point of Mo, its low thermal expansion, along with its smooth surface, create potentially favourable conditions to produce large area, wrinkle free, high quality graphene. Furthermore, the advantage of Mo, being commonly used in IC and sensor manufacturing environment, makes it an attractive choice for large volume production of sensing devices.

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1. Introduction

Graphene is a material that consists of an atomic mono-layer of carbon atoms that form sp² bonds in a hexagonal lattice. It was first isolated from graphite in 2004 using mechanical exfoliation. This relatively new material offers an extraordinary potential for several research and engineering applications thanks to its unique physical and chemical properties. Due to the absence of the bulk and low noise characteristics it has been envisioned as the ideal sensing material [1].

Graphene has attracted significant attention of the research community particularly for gas-sensing, because of its large theoretical specific surface area (2630 m²/g) [2] and extreme sensitivity up to single molecules [3]. Moreover, the high electron mobility at room temperature (above 15000 cm²/Vs) can be exploited in ultra-fast and sensitive Hall effect sensors [4], its high sensitivity and low signal-to-noise ratio reported gain ~10 A/W is appealing for photo-sensing [5], and graphene membranes can be quite suitable for pressure sensors [6].

To take advantage of this remarkable material it is necessary to take its manufacturing to a commercial level, which for the semiconducting industry translates into the capability to provide wafer scale high-quality graphene. The most scalable and cost-effective deposition technique is catalytic chemical vapour deposition (CVD) on transition metals. Many metals such as Ru, Pd, Ir, Ni and Cu have been analyzed and tested for graphene growth [7]. Graphene CVD growth on Cu is currently the most commonly used deposition process for the fabrication of monolayers of graphene. However, its application in wafer-scale fabrication is difficult, as one of the major drawbacks of Cu is the difference in thermal expansion between the substrate and Cu itself, which causes strain, eventually leading to wrinkles in the graphene layer, thus lowering the graphene mobility [8]. Besides that, the graphene growth is performed close to the melting point of Cu resulting in evaporation of the Cu film and the formation of holes in thin Cu layer.

In this work we report CVD growth of wafer-scale graphene on Mo thin films as an alternative to Cu. The thermal expansion coefficient of Mo (4.8 μm·m⁻¹·K⁻¹) is very close to that of Si (2.6 μm·m⁻¹·K⁻¹), while that of Cu is 17 μm·m⁻¹·K⁻¹, resulting in less thermal stress and encouraging wrinkle-free graphene deposition. Mo-grown graphene has been previously reported [9], but only on 100 μm thick Mo foils. In this paper we demonstrate for the first time the feasibility of graphene growth on very thin (50 nm) films of Mo on 100 mm diameter Si wafers.

2. Experimental

The 50 nm Mo or 500 nm of Cu was deposited using magnetron sputtering at room temperature with pure Mo (99.95%) or Cu (99.995%) target, on 100 mm Si (100) wafers coated with 100 nm thermal oxide. The deposition of graphene was performed using an AIXTRON Black Magic Pro system at 25 mbar. The wafer with Mo is brought to the temperature of 1010°C in Ar (250sccm) and H₂ (100sccm) environment, and then annealed for 300s in order to
remove the native oxide. Subsequently, during the graphene deposition step, CH₄ is introduced in the chamber at 15 sccm for 90s. After this the process the chuck is cooled down from 1010°C to 650°C with a rate of 500 °C/min. A typical process sequence is illustrated in Fig. 1. For Cu a temperature of 900 °C and a more gradual cooling of 50 °C/min are employed to reduce stress in the film. Scanning electron microscopy (SEM, Philips XL50), Raman spectroscopy (Renishaw inVia, 633nm laser), and Atomic Force Microscope (AFM, NT-MDT NTEGRA) analyses were performed on the processed wafer to evaluate the quality of the graphene layer.

3. Results and discussion

Fig. 2 and Fig. 3 show AFM and SEM analysis results, respectively. Already in the SEM images it becomes clear that the morphology of the metal layers after graphene growth are completely different. The Cu layer has large grains, which increased during the growth process, while the Mo layer has small grains. There is also a noticeable difference in the surface roughness as determined by AFM (average 118 nm for Cu and 35 nm for Mo). The Mo surface is thus smoother than that of Cu, which can be advantageous for the deposition of wrinkle free layers of graphene and for subsequent transfer to target wafers.

The Raman spectra of graphene on Mo and Cu thin films are shown in Fig. 4. The characteristic bands of graphene at ~1340 cm⁻¹ (D-band), 1584 cm⁻¹ (G-band), and ~2680 cm⁻¹ (G'-band) are detected in both cases. The band intensity ratio between G’ and G peaks is inversely proportional to the number of graphene layers [10]. It is evident that on Cu a mono-layer is grown, while for the Mo-grown layer it is mostly a bi-layer, although we did observe isolated spots showing mono-layers. The D band is related to the number of defects, and can be used to estimate graphene layer quality [11]. The ratios are comparable for both layers, but can be further reduced by optimizing the growth conditions.

Another advantage of Mo is its thermal stability. We observed that Cu has a narrow process window (several tens of °C) for graphene growth, as at high temperatures the film starts to break-up. On the other hand, Mo is much more stable due to it higher melting point (2623 °C vs 1085 °C for Cu), resulting in a much larger process window (~100 °C), which is advantageous for large volume production.

Figure 2: AFM images of Cu (left) and Mo (right) after graphene growth. Insets: histograms displaying surface roughness in nm.
4. Conclusion

We demonstrated a graphene growth process on Mo thin-films of only 50 nm. Compared to Cu the Mo films are less rough (118 nm for Cu and 35 nm for Mo) and thermally more stable. Furthermore, Mo is a cleanroom compatible material, while Cu is often regarded as a contaminant. The Raman spectra of both materials were found to be comparable, although Cu resulted in mono-layer growth and Mo nucleates mostly bi-layers. We expect that further tuning of the growth process will result in uniform mono-layers grown on Mo on 100 mm diameter wafers, which can be used to fabricate high performance sensors in an IC-compatible manufacturing process.

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