Hafnia nanoparticles –
a model system for graphene growth
on a dielectric

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We study graphene growth on hafnia (HfO_2) nanoparticles by chemical vapour deposition using optical microscopy, high resolution transmission electron microscopy and Raman spectroscopy. We find that monoclinic HfO_2 nanoparticles neither reduce to a metal nor form a carbide while nucleating nanometer domain-sized few layer graphene. Hence we regard this as an interesting non-metallic catalyst model system with the potential to explore graphene growth directly on a (high-k) dielectric.
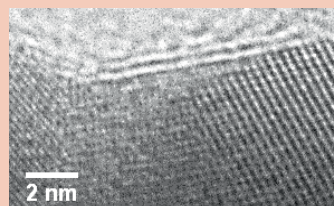
HfO_2 nanoparticles coated with few layer graphene by atmospheric pressure CVD with methane and hydrogen at 950 °C.

1 Introduction Catalytic chemical vapour deposition (CVD) is the most promising technique towards scalable device integration of graphene. Progress thereby requires a detailed understanding of the growth mechanisms and direct device process integration, which, for most electronic applications, means ideally direct growth on a dielectric, such as on SiO_2 or HfO_2. Most literature currently focuses on optimising graphene or few layer graphene (FLG) growth on sacrificial elemental metal catalyst foils which necessitates post-synthesis transfer processing [1–3]. Recent studies indicate that FLG nucleation may be possible on single-crystalline, non-metallic supports [4–6] and the nucleation of graphitic domains directly on MgO and ZrO_2 nanoparticles has also been reported recently [7, 8]. However, to evaluate the potential of oxide-catalysed CVD of carbon nanostructures a much more detailed understanding of the processes that trigger such self-organisation is required [9, 10].

Here, we report on FLG CVD directly on HfO_2, the current technologically most important high-k dielectric [11]. We find that monoclinic HfO_2 nanoparticles neither reduce to a metal nor form a carbide while nucleating graphitic domains, hence presenting an interesting oxide model system. We note that carbon coated metal oxide nanoparticles form an active area of research in their own right with applications ranging from photocatalysis, energy storage to functional filler materials [12–14].

2 Experimental methods
2.1 HfO_2 nanoparticle synthesis HfO_2 nanoparticles were deposited onto SiO_2 (200 nm) covered Si-wafers by the Karlsruhe Microwave Plasma Process which is described in detail elsewhere [15]. This method is a non-thermal, low-pressure process, and therefore highly applicable for the synthesis of nanoparticles of sub-10 nm dimensions and a narrow particle size distribution. A mixture

of 20% O_2 and 80% Ar was used as reaction gas (5 litres per minute (lpm)), and pure Ar (0.5 lpm) was used as carrier gas for the precursor. Hafnium (IV) t-butoxide, $Hf(OC(CH_3)_3)_4$, was used as the precursor, and evaporated at 150 °C with a feeding rate of 5 ml h^{-1}. The microwave power was 600 W at 2.45 GHz and a system pressure of 8–9 mbar, leading to a synthesis temperature of ~550–600 °C. After the formation of the nanoparticles, they were deposited for 5–7 min *in-situ* on pre-heated substrates. The nanoparticles formed loosely packed films of ~750 nm thickness with a columnar appearance on the wafers, as previously reported in detail [13, 16].

2.2 CVD growth A 2 inch diameter quartz tube furnace was used for CVD experiments at atmospheric pressure. A typical experiment consisted of heating the samples in pure Ar to 900–950 °C, pre-treatment for 10 min in pure H_2 followed by an exposure to a methane/hydrogen (CH_4/H_2) mixture for 20 min and subsequent cooling in pure Ar. The samples were analysed using optical microscopy, high resolution transmission electron microscopy (HRTEM, JEOL JEM 4000EX, 400 kV), and Raman spectroscopy (Renishaw 1000 Raman spectrometer, 514 nm excitation).

3 Results and discussion Figure 1(a) and (c) show optical microscopy images of the HfO_2 nanoparticle film before and after CVD with CH_4 and H_2 at 950 °C. The as-deposited nanoparticle film is white in colour and turned black after CVD, suggesting carbon deposited on the particles. This was confirmed by HRTEM: Figure 1(b) shows HRTEM images of the nanoparticles before CVD. The mean particle size is ~4 nm. A fast Fourier transform (FFT) analysis [example shown in the inset of Fig. 1(b) with a projection along the (110) plane] shows that the nanoparticles are monoclinic HfO_2 (space group $P2_1/c$). The *d* spacing of ~0.32 nm and ~0.28 nm extrapolated from the FFT analysis is in agreement with tabulated X-ray diffraction pattern *d* spacing of 0.3145 nm and 0.2826 nm for the ($1\bar{1}1$) and (111) planes of monoclinic HfO_2, respectively [17]. The measured angles of $\alpha = 90°$, $\beta \sim 99–100°$, $\gamma = 90°$ also fit this assignment. The monoclinic phase is consistent with previous reports of HfO_2 synthesized by similar methods [15, 18].

The HRTEM images of the particles post CVD are shown in Fig. 1(d–f) at different magnifications. In Fig. 1(d) the HfO_2 nanoparticles appear encapsulated by 2–3 layers of graphitic carbon. We see no evidence of a phase transition in the HfO_2 particles following the CVD process. In particular, no metallic hafnium or hafnium carbide (as likely products from a carbo-thermal reduction) are seen in the post-CVD FFT analysis, indicating that the nanoparticles retain monoclinic HfO_2 phase [example shown as inset in Fig. 1(d) with a projection along the ($2\bar{1}1$) plane]. The observed structural stability is consistent with previous high temperature annealing studies on similarly prepared HfO_2 nanoparticles [18] as well as carburi-
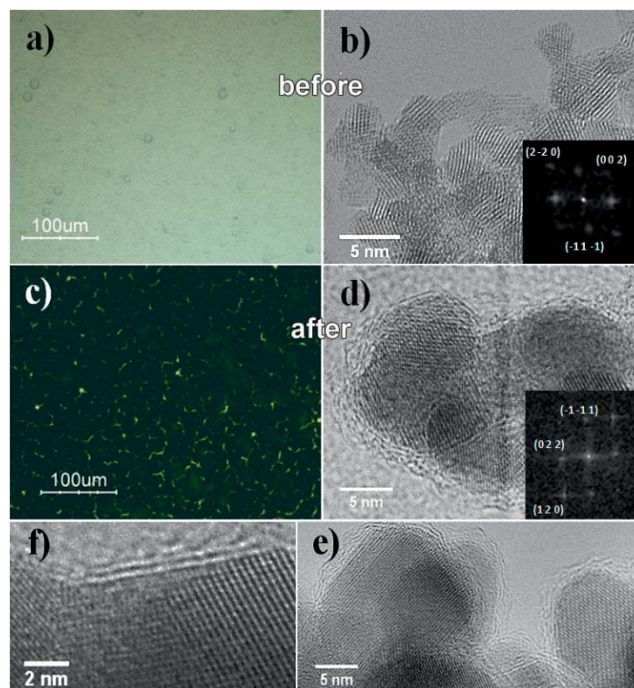

Figure 1 (online colour at: www.pss-rapid.com) Optical microscopy image of SiO_2/Si supported ~750 nm HfO_2 nano-particle film (a) before and (c) after CVD in CH_4/H_2 at 950 °C. HRTEM images of the HfO_2 nanoparticles scratched from the film (b) before and (d), (e), (f) after CVD. Insets in (b), (d) show the FFTs of the respective HfO_2 nanoparticles.

zation studies of HfO_2 nanoparticles, where the onset for carbothermal reduction was found to be at ~1200 °C [19]. In Fig. 1(e) the HfO_2 nanoparticles are covered with 3–5 layers of graphitic carbon. In Fig. 1(f), at higher magnification, we see 2 layers of graphitic carbon anchored along the ($1\bar{1}1$) plane of the HfO_2 nanoparticles for a projection along the (011) plane. The 1–5 layers of carbon have an interlayer spacing of ~0.35 nm, corresponding to FLG [20]. Additionally, the mean particle size of the HfO_2 has increased to ~12 nm most probably due to coarsening during the pre-treatment stage in agreement with previous reports [18]. Albeit present, we emphasise that the level of coarsening is significantly lower compared to metallic catalysts, which highlights a clear advantage of oxide systems here.

Figure 2 shows the Raman spectra for the HfO_2 nanoparticles before and after CVD. The HfO_2 nanoparticles before CVD show no carbon Raman signatures. In contrast, after CVD the samples show carbon-related G (~1600 cm^{-1}, FWHM = 86 cm^{-1}), D (~1360 cm^{-1}, FWHM = 83 cm^{-1}) and 2D (~2700 cm^{-1}, FWHM = 88 cm^{-1}) peaks [21]. This is consistent with Raman signatures from MgO and ZrO_2 catalysed graphitic domains [7, 8]. The high D/G ratio (compared to exfoliated graphene) may be a result of the higher contribution of edges in our FLG coatings, whilst a 2D to G intensity ratio of <1 is commonly observed for FLG.

We observe graphitic carbon signatures not only for HfO_2 nanoparticles but also for sputter-deposited poly-
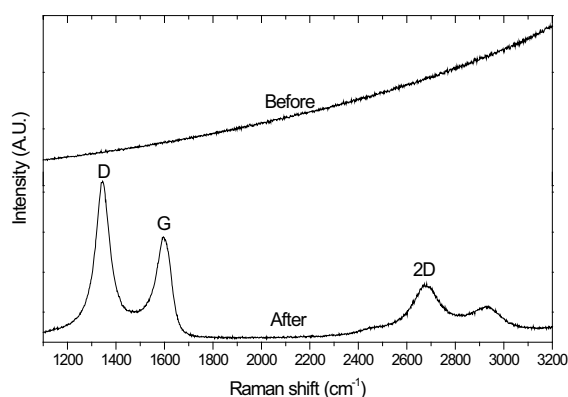
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Figure 2 Raman spectra for the HfO_2 nanoparticles before and after CVD with CH_4 and H_2 at 950 °C.

crystalline HfO_2 films processed at the same CVD conditions. Figure 3 compares post-CVD Raman spectra for such a HfO_2 film to post-CVD spectra of a SiO_2 film (grown by thermal oxidation). The HfO_2 film shows similar Raman features to the HfO_2 nanoparticles shown in Fig. 2, implying a similar FLG coating. In contrast, the SiO_2 film does not show any carbon-related Raman signal after being exposed to the same CVD conditions, confirming the absence of pyrolytic carbon deposition. This suggests catalytic capabilities of HfO_2 towards graphene growth, but further work is needed to study influences of film crystallinity, surface roughness, film stoichiometry and other film properties.

While nano-sized graphitic domains on nanoparticles of a high-*k* dielectric have very limited direct application potential for integration into electronics, they are interesting as a model system for catalytic chemical vapour deposition of graphene on oxides. From a fundamental growth mechanism point of view, the observed FLG growth on a high-*k* dielectric like HfO_2 with an inherently low bulk C solubility indicates either a purely surface-reaction based growth mechanism [10] or alternatively a significant change of C solubility for nanoparticulate HfO_2. We plan further *in-situ* studies to elucidate the details of this process.

4 Conclusions Monoclinic HfO_2 nanoparticles retain their structure following a FLG coating by CVD. While currently only nano-crystalline FLG domains are obtained,
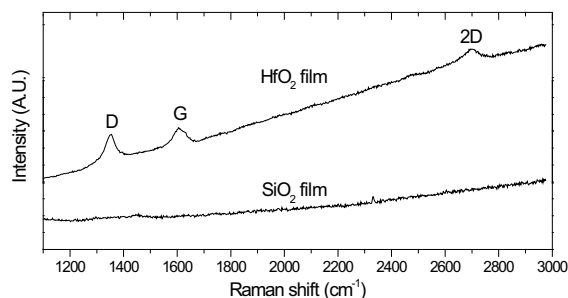

Figure 3 Raman spectra for the polycrystalline HfO_2 film and SiO_2 film after CVD with CH_4 and H_2 at 950 °C.

our results suggest that HfO_2 is an interesting model system for fundamental growth studies as well as for future device integration of graphene.

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