Growth of nanocrystalline graphene layers on various dielectric surfaces by CVD

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Abstract
The discovery of graphene, a two dimensional carbon sheet with unique structure and therefore electronic quality, has triggered the investigations of its potential applications in microelectronic as well as in photonic devices [1,2]. At this point, for the successful integration of graphene into various devices, an appropriate deposition technique is required in order to grow uniform, large area and high quality layers. Up to date, two common graphene synthesis methods, like decomposition of SiC and chemical vapor deposition (CVD) on Cu have been established [3,4]. However, these methods have some severe limitations due to the high temperatures or large area SiC wafers that are required for the SiC approach, or the necessity to transfer graphene from Cu to the target substrates, which causes wrinkles, holes or etching residuals to name a few. These drawbacks strongly limit the integration of graphene into the Si microelectronics. Therefore, the biggest challenge here is to grow continuous, defect-free graphene layers directly on the target substrates at low temperatures (<1000°C). Particularly, a direct growth of graphene on dielectric substrates is of a great interest for high frequency applications, where graphene has to be embedded between dielectrics [5]. A number of considerable efforts have been made to grow graphene directly on substrates like SiO_2, Si_3N_4 or Al_2O_3 [6-8]. However, continuous and high quality conductive graphene films are hard to obtain since the growth mechanism and therefore the graphitization process of the graphene on dielectrics is still not well understood. We have recently obtained high quality micrometer scale graphene layers on dielectric mica substrates below 1000 °C by Molecular beam epitaxy (MBE) using solid carbon source [9]. Raman spectra of graphene grown directly on mica show a negligible D mode suggesting a very high crystal quality as indicated in Fig.1. In the present work, we examined the possibility to grow graphene films on several dielectric substrates at various temperatures by employing low pressure CVD technique. Oxides, such as PrO_x or CeO_x (which are known to possess some catalytic activity to hydrocarbons) and CMOS compatible dielectrics such as HfO_2, SiO_2 and Si_3N_4 have been investigated in this study. The depositions were performed at 800 – 1000 °C using C_2H_4 as reactive gas at the pressures of 0.1 mbar. 4 inch Si wafers, covered with mentioned oxides were used as substrate materials. PrO_x and CeO_X films were grown at room temperature by MBE and then transferred to the CVD chamber without breaking the vacuum. On the other hand, HfO_2, Si_3N_4 or SiO_2 were externally deposited by the CVD technique. A typical deposition time was 30 minutes. Carbon content was determined by X-ray Photoelectron spectroscopy (XPS), whereas the quality of the deposited carbon was then evaluated by Raman spectroscopy.

In order to check the initial amount of carbon, all investigated dielectrics were examined by XPS before the CVD depositions. The carbon 1s signals of selected oxides are presented in Fig.2 and Fig. 3. As black line in Fig. 2 indicates, as grown amorphous CeO_x films had no carbon contamination, since they were deposited by the MBE and then directly transferred to the XPS chamber without breaking the vacuum. The exact same result was observed for as grown PrO_x films (not shown). On the contrary, the as grown HfO_2 films have already contained carbon, as can be seen in Fig.3. This effect was also expected, since HfO_2 as well as Si_3N_4 were grown externally by CVD. The evolution of carbon content on CeO_x was further analyzed after exposing the films to C_2H_4 at 800-1000 °C. As can be seen in Fig. 3, the highest C 1s signal was observed for the samples grown at 1000 °C, although some carbon was catalytically grown on CeO_x (as well as on PrO_x) even at the temperatures as low as 700 °C (not shown). In the case of the depositions on HfO_2, the reduction of the C 1s signal was observed as indicated in the Fig.3 (red line). This can be explained by the fact that carbon, which had been absorbed on the surface, was removed at 1000 °C and then the graphitic carbon was grown from the C_2H_4 precursor. In addition, after the deposition, the position of the C 1s signal moves the lower binding energies towards elemental carbon. Raman measurements of the grown carbon on PrO_x, HfO_2 and Si_3N_4, are summarized in Fig. 4 and Fig. 5. As can be seen, nanocrystalline graphene can be grown at the deposition temperature of 1000 °C on PrO_x (CeO_x not shown here) and HfO_2 dielectric substrates, whereas no crystalline features where detected on SiO_2 and Si_3N_4. These observations might lead to the suggestion that oxygen vacancies could affect the catalytic growth of the graphene on some dielectrics. A short possible graphitization mechanism is sketched in Fig. 6.

References

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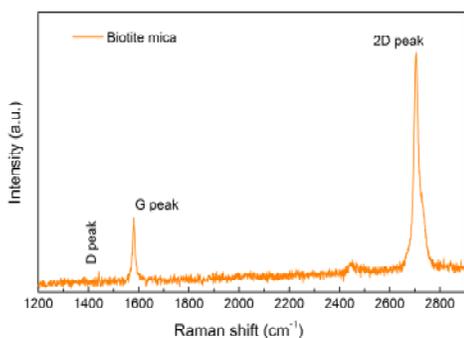
Figures

Fig.1. Raman spectra of high quality micrometer range graphene on biotite mica substrate.
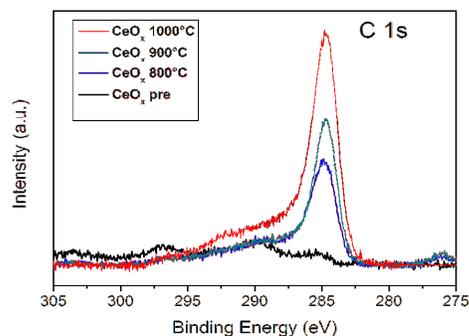

Fig.2. The evolution of carbon 1s signal on CeO_x for as grown film (black line) and after exposure to C_2H_4 gas at 800 °C (blue line), 900 °C (cyan line) and 1000 °C (red line).
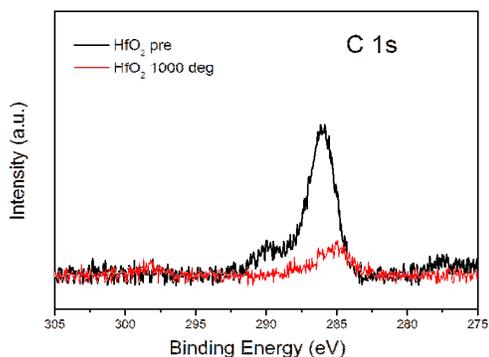

Fig.3. XPS spectra of carbon 1s line in HfO_2 for as grown layers (black line) and after Carbon deposition at 1000 °C (red) line.
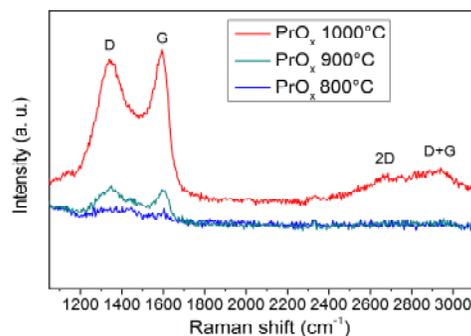

Fig.4. Raman spectra of nanocrystalline graphene grown at different temperatures on PrOx substrates.
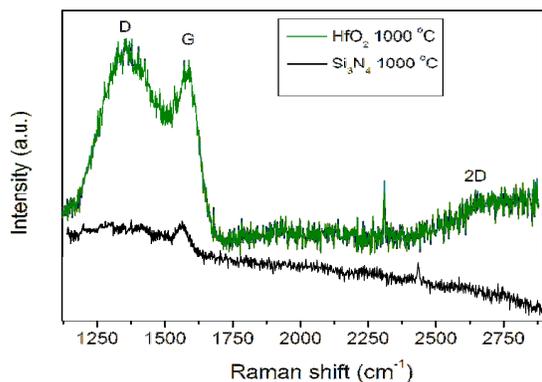

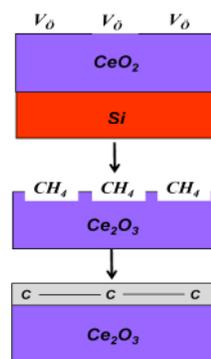Fig.5. Raman spectra after carbon growth on HfO_2 (green line) and Si_3N_4 (black line).

Fig.6. A possible mechanism for catalytic graphitization.