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Graphitic carbon growth on crystalline and amorphous oxide substrates using molecular beam epitaxy

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Abstract

We report graphitic carbon growth on crystalline and amorphous oxide substrates by using carbon molecular beam epitaxy. The films are characterized by Raman spectroscopy and X-ray photoelectron spectroscopy. The formations of nanocrystalline graphite are observed on silicon dioxide and glass, while mainly sp^2 amorphous carbons are formed on strontium titanate and yttria-stabilized zirconia. Interestingly, flat carbon layers with high degree of graphitization are formed even on amorphous oxides. Our results provide a progress toward direct graphene growth on oxide materials.

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Keywords: graphite, molecular beam epitaxy, Raman, oxide

Introduction

Graphene growth on Ni or Cu by chemical vapor deposition [CVD] is now well established. However, the CVD graphene needs to be transferred onto insulating substrates for application, which may degrade the quality and bring complications to the manufacturing process. This is why direct graphene growth on insulator is still intensively being studied. Notably, the growth on oxide is of great interest because graphene is expected to face current metal-oxide semiconductor [MOS] technology through an oxide layer. Recent studies have shown some accomplishments toward this goal by using CVD [1-3].

Here, we attempt molecular beam epitaxy [MBE] of carbon onto several oxide substrates to figure out the potential of graphene growth. So far, carbon MBE has been applied mostly on group IV semiconductors [4-7], where graphitic carbon growth was observed. We have shown previously that nanocrystalline graphite [NCG] can be formed on sapphire (Al_2O_3) and observed a Dirac-like peak for the first time in MBE-grown NCGs [8]. In this study, we expand the subject to include

various crystalline and amorphous oxides. We observe that graphitic carbon or NCG can be grown by carbon MBE on amorphous SiO_2 , the most important oxide in the MOS technology. We also obtain similar results on glass (Eagle 2000™, Corning Inc., Corning, NY, USA). In contrast, carbons on amorphous TiO_2 or Ta_2O_5 do not seem to form graphitic structures. Among the crystalline oxides, mainly sp^2 amorphous carbons are observed on $SrTiO_3(100)$ and yttria-stabilized zirconia [YSZ] (100).

Methods

Materials and film fabrication

Samples were fabricated in a home-made ultra-high-vacuum MBE system. Carbons were sublimated from a heated pyrolytic graphite filament. The pressure of the chamber was kept below 1.0×10^{-7} Torr during the growth with the help of liquid nitrogen flowing in the shroud. Details about the growth procedure can be found elsewhere [8]. Both crystalline and amorphous oxide substrates were purchased from commercial vendors (AMS Korea, Inc., Sungnam, Gyeonggi-do, South Korea; INOSTEK Inc., Ansan-si, Gyeonggi-do, South Korea). The growth temperature (T_G) was in the range of 900°C to approximately 1,000°C, based on our previous study with sapphire. The typical thickness of

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carbon film, determined by measuring the step height after lithography, was 3 to approximately 5 nm.

Characterization

Raman-scattering measurements were performed by using a McPherson model 207 monochromator with a 488-nm (2.54 eV) laser excitation source. The spectra recorded with a nitrogen-cooled charge-coupled device array detector. X-ray photoelectron spectroscopy [XPS] measurements to analyze carbon bonding characteristics were done by using a Kratos X-ray photoelectron spectrometer with Mg K α X-ray source. C1s spectra were acquired at 150 W X-ray power with a pass energy of 20 eV and a resolution step of 0.1 eV. Atomic force microscopy [AFM] images were taken by a commercial system (NanoFocus Inc., Seoul, South Korea) in a non-contact mode.

Results and discussion

Raman-scattering measurements have become a powerful, non-destructive tool in the study of sp^2 carbons (carbon nanotube, graphene, and graphite). The well-known G peak is observed in all sp^2 systems near 1,600 cm^{-1} . With the advent of graphene, the so-called $2D$ peak, which occurs near 2,700 cm^{-1} , has become important. Single-layer graphene is characterized by the sharp and large $2D$ peak. This $2D$ peak is actually the second order of D peak. The typical position of D peak is 1,350 cm^{-1} , one half of the $2D$ peak position. The D peak is absent in a perfect graphene sheet or graphite because of symmetry and increases as defects or disorders in the honeycomb structure increases. However, it should be noted that the D peak also disappears in amorphous carbon. That is, Raman D peak does indicate the presence of sixfold aromatic rings as well as sp^2 bonds. It is from A_{1g} symmetry phonons in which the D peak becomes Raman active by structural disorders in the graphene structure.

Ferrari and Robertson studied the degree of sp^2 bonding and the relative strength of D and G peaks thoroughly [9-11], and recent experiments confirmed their theory [12,13]. Here, we follow their arguments and evaluate the degree of crystallinity based on the sharpness and the intensity of D , G , and $2D$ peaks. Let us start with carbon deposited on crystalline oxide substrates. Figure 1 shows the Raman spectra from the carbon films grown on SrTiO₃(100) and YSZ(100). The well-developed D and G peaks with similar intensities indicate that the film consists of sp^2 carbons with a number of defects. However, the $2D$ peak is hardly seen although a small bump is observed at the expected position in Figure 1a. According to recent criteria, the absence of a clear $2D$ peak implies the transition from NCG to mainly sp^2 amorphous carbon [11]. Based on

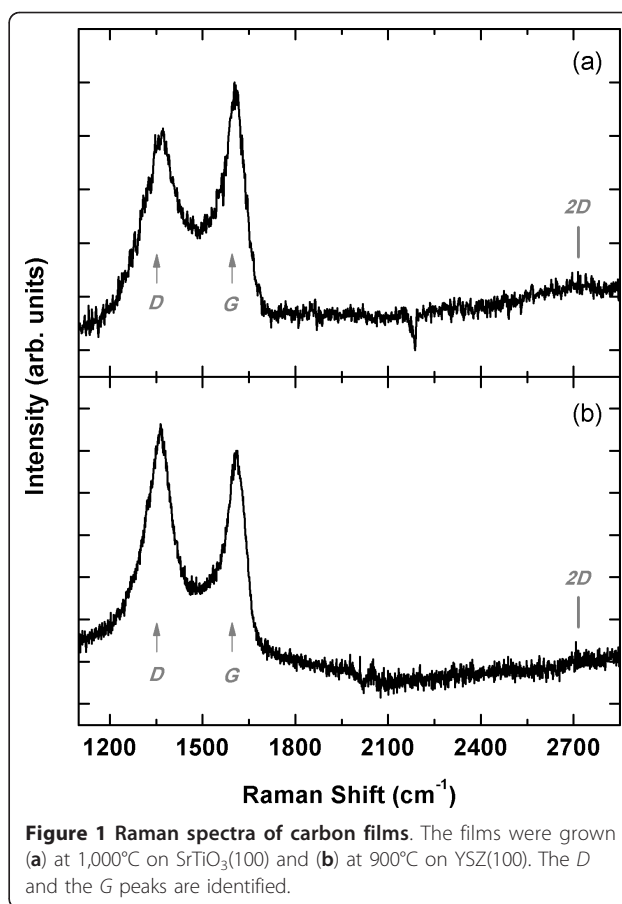


Figure 1 Raman spectra of carbon films. The films were grown (a) at 1,000°C on SrTiO₃(100) and (b) at 900°C on YSZ(100). The D and the G peaks are identified.

the intensity ratio, $I_D/I_G \sim 1$ (Table 1), we can conclude that the carbon films on SrTiO₃(100) and YSZ(100) are in the middle of 'stage 2' as defined by Ferrari and Robertson [9].

The crystalline ordering is worse than that of graphitic carbon grown at the same T_G on a sapphire crystal, where a $2D$ peak is easily identified [8]. In the previous study, we observed that the crystal orientations of sapphire substrates did not affect the quality of NCG grown on them and speculated that the lattice constants and the substrate symmetry were not critical parameters in the NCG growth by MBE [8]. Then, we expect similar growth on cubic SrTiO₃ and YSZ, contrary to what we observe. One possible explanation is that the optimum T_G depends on the material. In fact, the Raman spectra in Figure 1 are similar to those of NCG on sapphire grown at 600°C, far lower than the optimum T_G of 1,100°C [8]. Because of the difference in the sticking coefficient of carbon to the substrate and/or the diffusion constant of carbon on the surface, the optimum growth temperature may depend on the substrate. Further experiments of carbon growth on SrTiO₃ or YSZ at different temperatures might prove this assumption.

Table 1 Fitting results of the Raman spectra for various samples

Substrate	Peak (D) (cm^{-1})	Peak (G) (cm^{-1})	I_D/I_G	I_{2D}/I_G	FWHM (G) (cm^{-1})	FWHM (2D) (cm^{-1})
SrTiO ₃	1,372	1,603	0.8	-	70	-
YSZ	1,364	1,609	1.1	-	63	-
SiO ₂	1,352	1,598	1.9	0.4	66	96
Glass	1,352	1,598	1.8	0.3	66	99

Mixed Gaussian and Lorentzian functions are used to fit D, G, and 2D peaks. FWHM, full width at half maximum.

Now, we turn to amorphous oxides, which are more relevant to the MOS technology. First, we tested 100-nm-thick TiO₂ and Ta₂O₅ grown on SiO₂(300 nm)/Si by sputtering. As shown in Figure 2, no sign of graphitic carbon is observed. The only peak near 1,000 cm^{-1} is the background Raman signal from Si wafer. Usually, this background is removed to highlight the carbon-related peaks, but we leave that in Figure 2 to show the absence of other peaks.

The situation changes drastically as the substrate is changed to SiO₂(300 nm) on Si wafer. Figure 3a shows that graphitic carbon of a relatively high degree of crystallinity is formed on SiO₂. The Raman spectra are similar to the best data from NCG on sapphire [8]: the sharp and large D peak and the clear 2D peak. Notably, the existence of 2D peak is an important evidence of successful NCG growth on amorphous SiO₂ [11]. This shows that the crystallinity of the substrate is not

essential and explains why the quality of NCG was independent of substrate orientation in the previous study [8]. This surprising result may find interesting applications because we also expect a Dirac-like conduction in NCG [8]. Further optimization along with transport measurement is under progress. Similar results are obtained from Eagle 2000™ glass, a widely used material in active matrix liquid crystal displays (Figure 3b). This glass is known to consist of SiO₂, B₂O₃, Al₂O₃, CaO, and Na₂O. It means that SiO₂ is not the only amorphous oxide on which graphitic carbon can be fabricated. Considering the variety of oxides, the quality of graphitic carbon can be improved much as the search for suitable substrates is continued.

Now that the carbon films grown on SiO₂ and glass by MBE are identified as NCGs, it is informative to calculate the crystallite size from Ferrari and Robertson's model applied to stage 2 [9]. According to the model,

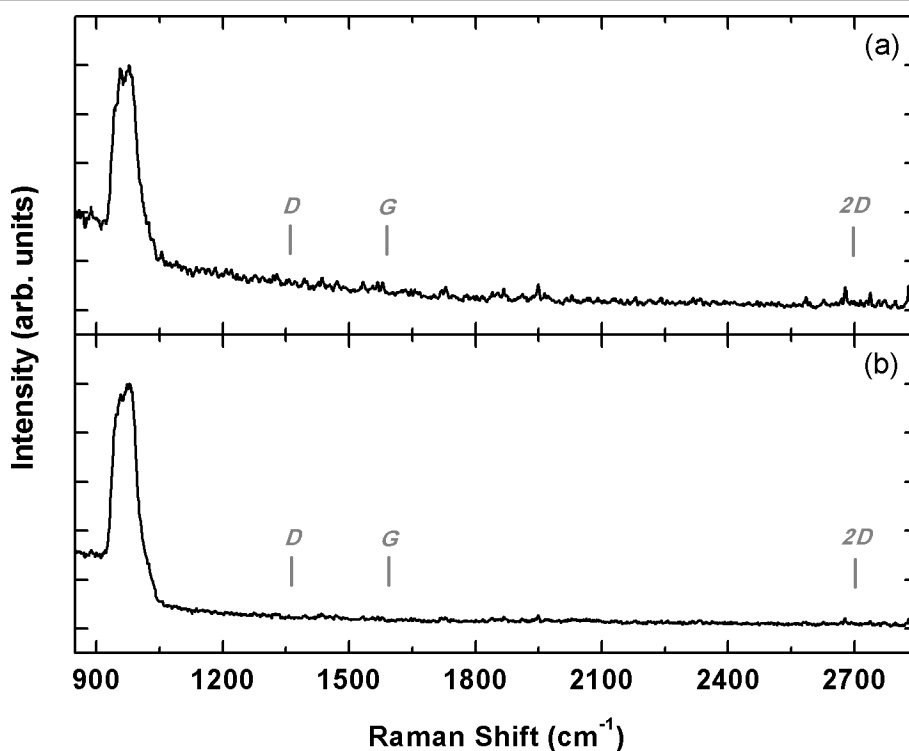
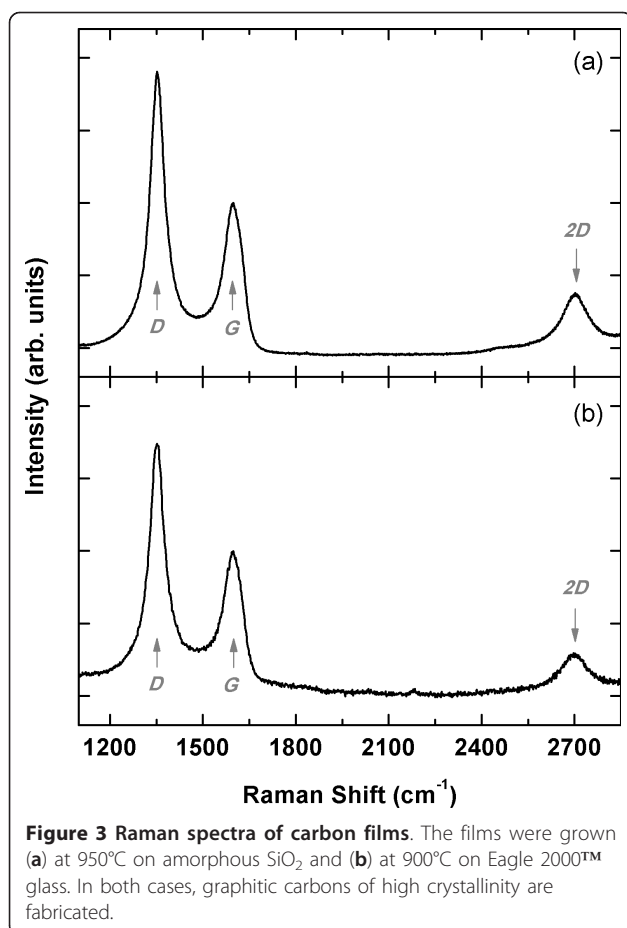


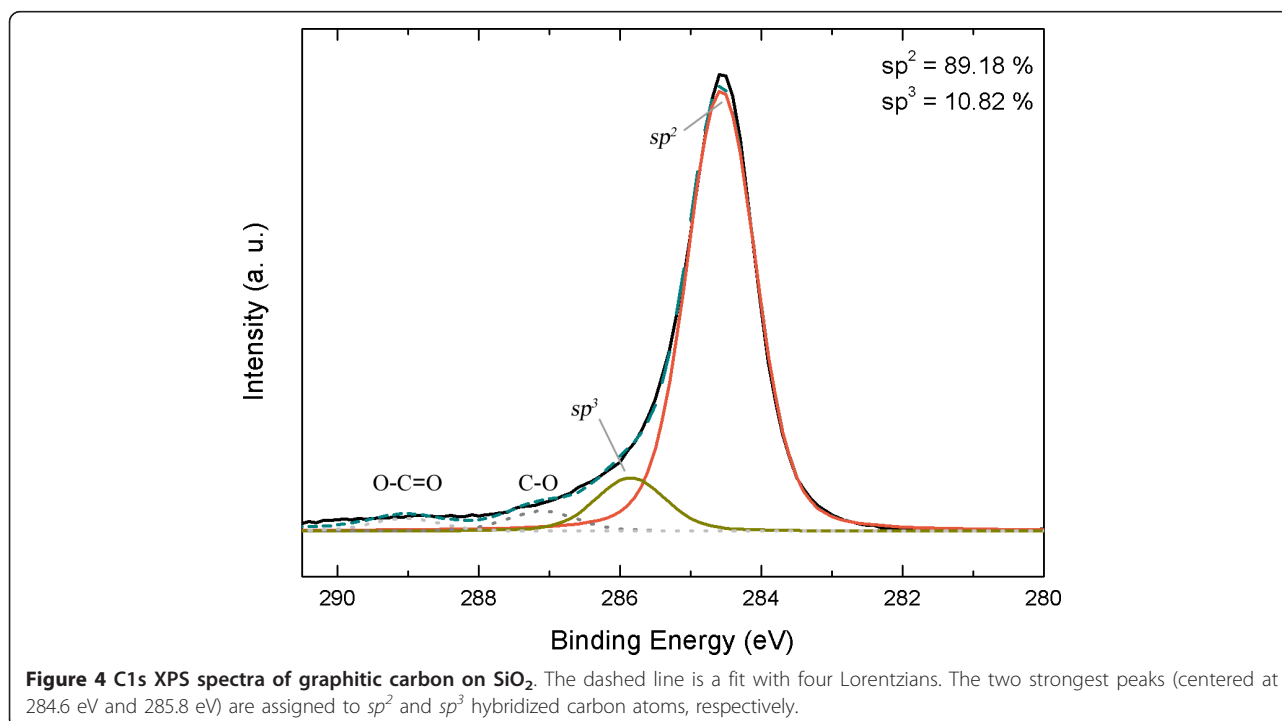
Figure 2 Raman spectra of carbon films. The films were grown (a) at 900°C on amorphous TiO₂ and (b) at 900°C on amorphous Ta₂O₅. No carbon-related peaks are observed. The peak near 1,000 cm^{-1} is from Si substrate.

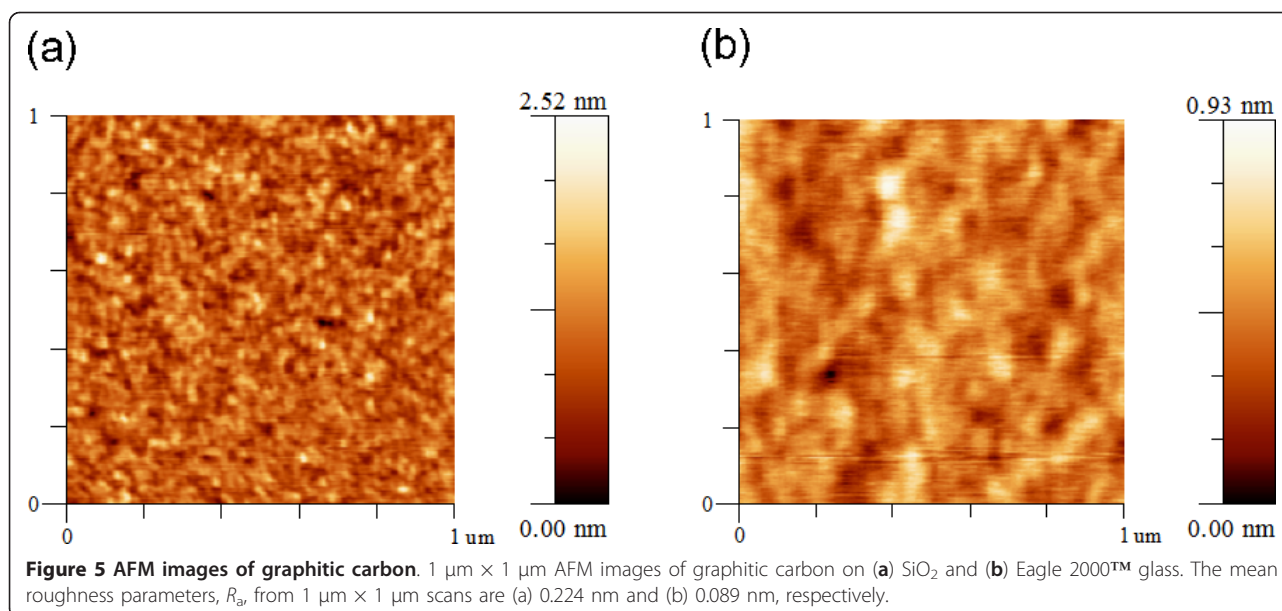


the average size L_a is related to I_D/I_G as $I_D/I_G = C L_a^2$, where $C = 0.0055$ and L_a in Å. From $I_D/I_G = 1.8 \sim 1.9$ (Table 1), we get $L_a = 18.1 \sim 18.6$ Å. In addition, the position of G peak at $1,598 \text{ cm}^{-1}$ is in accordance with the identification of NCG of insignificant doping [9].

In order to clarify the carbon bonding nature, we performed XPS measurements on the graphitic carbon layer on SiO₂. Figure 4 shows the C1s spectra, which are decomposed into several Lorentzian peaks. Here, we focus on the two strongest peaks centered at 284.6 eV and 285.8 eV. The relative intensity ratios are 89.18% (the peak at 284.6 eV) and 10.82% (the peak at 285.8 eV). In the literature, 284.7 ± 0.2 and 285.6 ± 0.2 eV components are attributed to sp^2 and sp^3 hybridization of C-C or C-H bonds, respectively [14]. In combination with the Raman spectra, the XPS results demonstrate that the sp^2 bonds are dominant in the carbon layer on SiO₂.

Another important result of this work is that the graphitic carbon on amorphous oxide is very flat, which is an important virtue for the integration with other materials. Figure 5 shows the AFM images of graphitic carbon on SiO₂ and Eagle 2000™ glass. Like the NCG on sapphire, no sign of island growth is observed. The mean roughness parameters, R_a , from $1 \mu\text{m} \times 1 \mu\text{m}$ scans are 0.224 nm (on SiO₂) and 0.089 nm (on Eagle 2000™ glass). Notably, the R_a of NCG on Eagle 2000™ glass is almost the same as that of the substrate itself which is famous for surface flatness.





Conclusions

In summary, we have grown graphitic carbon on crystalline and amorphous oxides by using carbon MBE. Notably, the graphitic carbons on amorphous SiO₂ and on glass show a relatively high degree of graphitization, evidenced by well-developed *D*, *G*, and 2*D* Raman peaks. The C1s spectra from XPS measurements confirm the dominance of *sp*² carbon bonding. In addition, the surfaces are almost as flat as the substrates, which may play an important role in the integration with the existing technology.

Abbreviations

AFM: atomic force microscopy; CVD: chemical vapor deposition; MOS: metal-oxide semiconductor; MBE: molecular beam epitaxy; NCG: nanocrystalline graphite; XPS: X-ray photoelectron spectroscopy; YSZ: yttria-stabilized zirconia.

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Authors' contributions

SKJ carried out the carbon molecular beam epitaxy experiments and X-ray photoelectron spectroscopy. DSY participated in the carbon molecular beam epitaxy experiments. JHL carried out the atomic force microscopy measurements. CK and SY characterized the thin films by Raman

spectroscopy. SHC designed the experiments and wrote the manuscript. All authors read and approved the final manuscript.

Competing interests

The authors declare that they have no competing interests.

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