

## Selective Formation of Graphene on a Si Wafer

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### ABSTRACT

We report a technique that can, in principle, selectively convert SiC into graphene at any location and in any size or shape, limited only by the ability of the available lithographic techniques. This technique relies on our discovery that, at ambient condition, a laser beam can convert SiC into graphene layers at the illuminated site, and the conversion can be realized in two ways. One can pattern the SiC film, which is already grown on a Si wafer, with desirable features and then illuminate the SiC film with the laser, or simply “write” the graphene features directly onto the unpatterned SiC film with the laser. Alternatively, one can pre-pattern the Si substrate to achieve selective growth of SiC, then perform the laser conversion. We have demonstrated the feasibility of both approaches. Fullerene (C60) was used to grow a thin SiC film on a Si (111) substrate using molecular beam epitaxy (MBE) at 700-800 °C. The results are verified by various structural, chemical and optical characterization techniques. This work yields the possibility of fabricating graphene based (electronic) nanostructures or superlattices, photonic crystals, and integrated electronic and optoelectronic devices on a large Si wafer.

### INTRODUCTION

Much of the graphene growth effort has been devoted to the goal of obtaining uniform and large area material [1-6]. The large area graphene is useful for applications such as the electrode in a large device or substrate for growing another material. For applications where graphene is used either as an active material (FET for instance) or electrode in a 2-D device array, or to form a 2D (electronic) superlattice or photonic crystal, it is critically important to form graphene at selective locations, in desirable sizes and shapes on a large substrate, without relying on mechanical cutting and post-growth transfer. It would be even more advantageous if the substrate were a Si wafer in order to integrate with the mature microelectronic technology. Most reported device fabrication processes involve a graphene transfer process, which may incur contamination or damage to the sensitive graphene layer. Further patterning may also introduce impurities and damage during the ion etching process. In this work, we have developed an on-site graphene formation method without any transfer process. Specifically, a 3C-SiC layer was directly grown on a Si substrate under ultra-high vacuum (UHV), and then at ambient condition transformed into graphene in the desired size and shape, using a programmed local laser annealing process. We have demonstrated this technique in two ways: (1) First growing SiC on a Si substrate, then directing a focused laser beam from a confocal optical system onto the SiC film to convert the local SiC layer into graphene under ambient conditions. The feature size of the graphene is similar to that of the laser beam, currently sub-micron as determined by a confocal optical system with a regular lens. (2) First growing SiO<sub>2</sub> on a Si substrate, then using a lithographic

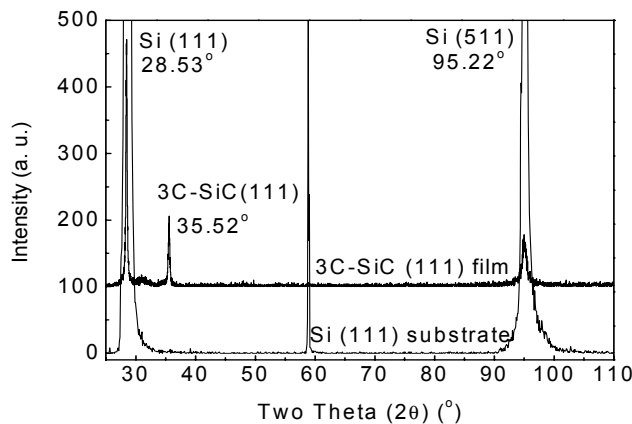
method to selectively expose the Si substrate with the desirable feature size, followed by selectively growing SiC at the exposed Si site and the above mentioned laser transformation.

## EXPERIMENTAL DETAILS

An MBE system is used to grow SiC on Si [7, 8]. A Si (111) wafer was cleaned with standard semiconductor cleaning processes to remove the contamination and thin oxide layer on the wafer. Then, the cleaned substrate was immediately transferred into the growth chamber, pending for the base pressure reaching UHV level ( $\sim 10^{-10}$  torr). The typical substrate temperature was 700-800 °C. Fullerene (C60) powders were used as the C source and the flux was controlled by the temperature of the Knudsen cell. The typical source temperature was 500-600 °C. During the growth, the substrate was rotated to improve the uniformity of epitaxial growth. Reflection High Energy Electron Diffraction (RHEED) was employed to inspect the surface quality and control the source temperature and thus flux. After the deposition, the sample was held at the growth temperature for 5-10 minutes to homogenize the epitaxial film. To ensure the uniformity and stability of the epitaxial layer, the film was allowed to cool slowly. To locally convert the SiC layer into graphene, the epilayer was illuminated with a CW visible laser focused by a confocal optical system. Appropriate power density and illumination time have been identified to realize the SiC to graphene transformation. The threshold power density is estimated to be  $1 \times 10^6$  W/cm<sup>2</sup>. Raman spectroscopy is used to monitor the process. The structure and morphology of the graphene layers were further studied by TEM, and SEM/EDS.

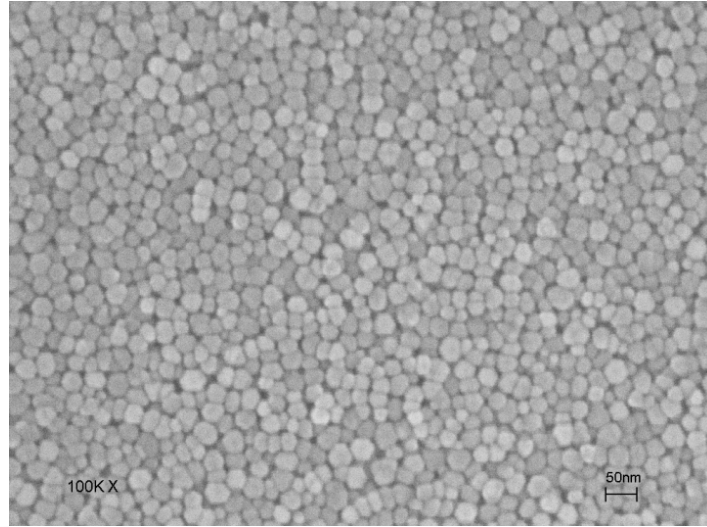
## RESULTS AND DISCUSSION

The crystalline structure of the epitaxial film was characterized by XRD. The Cu K $\alpha$ 1 X-ray with a wavelength of 1.5406 Å was used. XRD results of the Si(111) substrate before and after growth are shown in Figure 1. A new peak at 35.52° corresponding to the {111} planes of 3C-SiC appears. This value is slightly smaller than  $2\theta_{(111)}=35.60^\circ$  of single crystal 3C-SiC, indicating the d-spacing of {111} planes of the deposited film is larger than that of the single crystal.



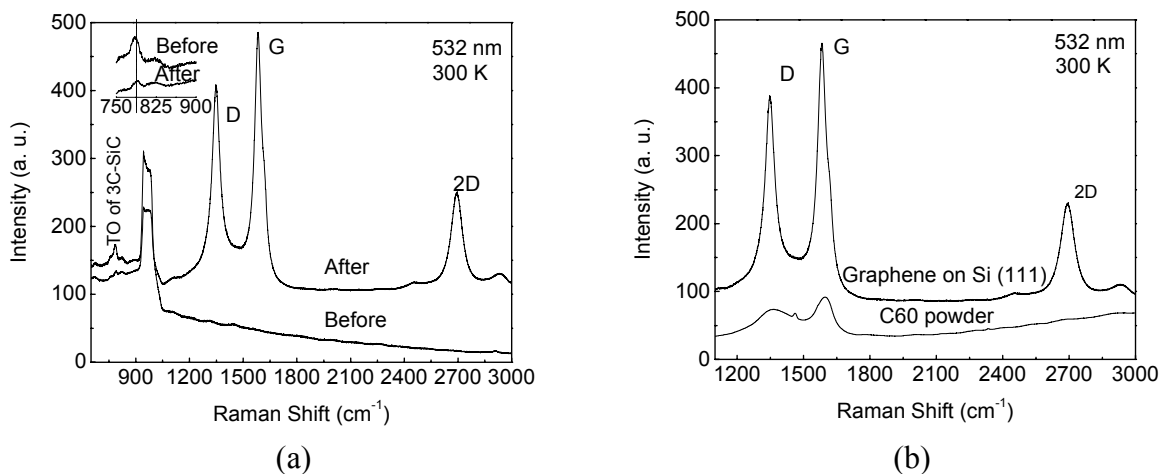
**Figure 1.** X-ray diffraction patterns of 3C-SiC/Si(111) epilayer grown on Si(111) substrate and Si (111).

The surface morphology of the epilayer was measured with SEM, as shown in Figure 2. The grain-like feature size in the uniform film was measured to be 20-30nm.

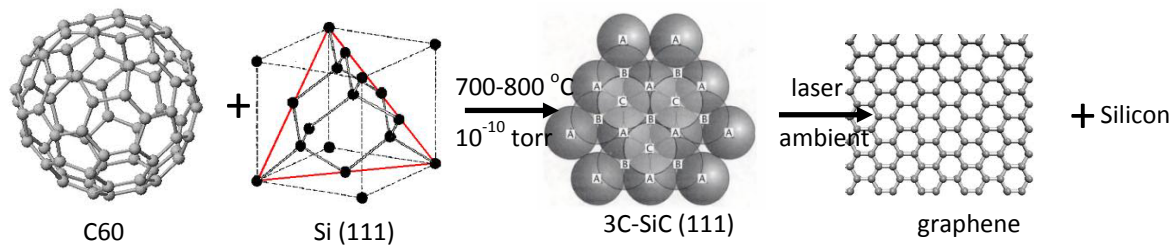


**Figure 2.** SEM morphology of the 3C-SiC epitaxial film grown on the Si(111).

Typical epitaxial growth of graphene is achieved by high temperature ( $> 1200$  °C) thermal annealing [6, 9]. In contrast, our approach requires only a low power CW laser focused by a confocal optical system to locally transform the 3C-SiC epilayer into graphene layers. The laser illuminated area was inspected in-situ with Raman spectroscopy, and subsequently with HRTEM. Figure 3a shows the Raman spectra of the sample before and after laser illumination. The spectrum acquired before illumination does not show any of the signature modes from graphene or C60 (Fig.3b), but only a TO mode of 3C-SiC at  $790\text{ cm}^{-1}$ , indicating that the C60 has been completely converted into 3C-SiC film. However, after illumination, the spectrum shows strong signature bands of graphene, i.e., the intrinsic G and 2D bands, though the defect-induced D peak is relatively strong. Concurrently, the 3C-SiC TO peak disappears or becomes much weaker, depending on the thickness of the SiC film. The G and 2D modes, which are the signatures of  $sp^2$  bonding of the hexagonal C ring, provide convincing evidence for the formation of the graphene layers. It can be inferred from the Raman spectra that the formation of the graphene layers resulted from the decomposition of SiC under laser illumination. Based on the intensity ratio of the G to 2D peaks and the shape of 2D peak, it can be inferred that the number of graphene layers exceeds 2 in turbostratic stack [10]. Because C60 is also known to exhibit Raman peaks similar to the G and D peaks in graphene, but does not have the 2D peak, we also compare the Raman spectrum of the converted sample to that of C60 powders, as shown in Figure 3b. The graphene formation process is schematically illustrated in Figure 4. The process likely bears some similarity to the high temperature Si sublimation process with local heating provided by the tightly focused laser beam, although the exact nature of the process is not clear at this stage.



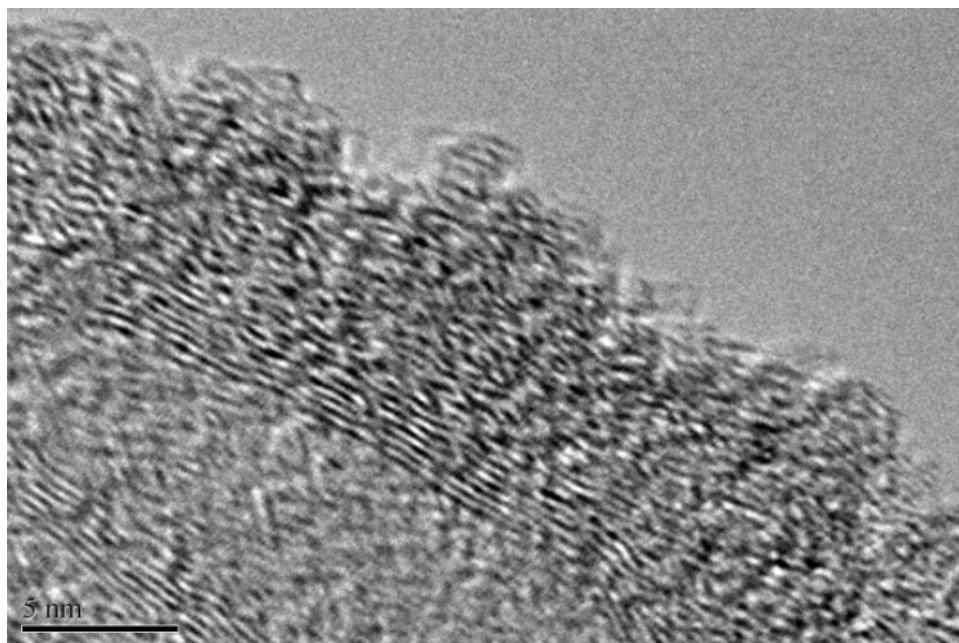
**Figure 3.** (a) Raman spectra of 3C-SiC/Si (111) before and after laser illumination (The inset shows the spectral range near the TO of SiC). (b) Raman spectra of graphene on Si (111) and C60.



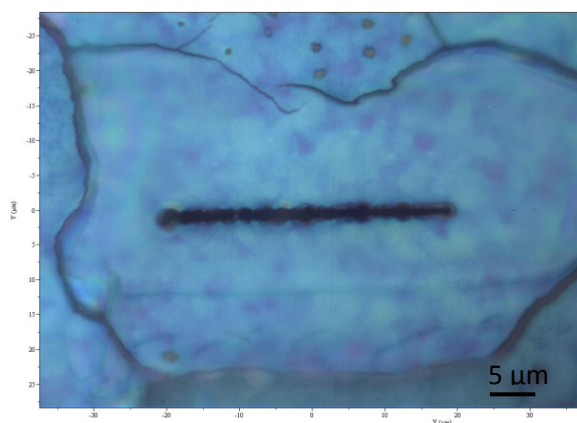
**Figure 4.** Schematic illustration of the fabrication process of graphene

The cross-section of the graphene layer was inspected with high resolution TEM (HRTEM) (JEOL 2100). The d-spacing between graphene layers shown in Figure 5 was measured to be about 3.70 Å, which is larger than that of crystalline graphite ( $c/2=3.35$  Å) by about 10%. The larger interlayer spacing indicates that the stacking order is probably turbostratic stacking rather than Bernal stacking [10]. This is also consistent with the symmetric shape of 2D peak, which should be asymmetric for the multi-layer graphene in Bernal stacking [11].

Since the laser spot size is approximately 1 μm, the size of the graphene area should be comparable to the laser spot size. However, the graphene feature size can, in principle, be substantially reduced by patterning the SiC film to expose only the area to be converted. Figure 6 shows a Raman mapping over a laser illuminated area for a typical sample. It clearly demonstrates the ability to selectively convert SiC into graphene. Note that the graphene layers produced in this way are interfaced with another material, SiC in this case, which could have rather different edge properties in comparison to the graphene nanostructure generated by other means.



**Figure 5.** TEM cross-section image of laminar multi-layer graphene (scale bar: 5 nm).



(a)



(b)

**Figure 6.** (a) Optical image of the laser induced graphene (laser scan area: 2 μm x 40 μm; scale bar: 5 μm). (b) Raman image of the 2D peak (2650-2750 cm<sup>-1</sup>) (scale bar: 5 μm).

## CONCLUSIONS

A new graphene formation process has been demonstrated with great potential for producing 2-D microscopic graphene features on a large area Si wafer. It offers major advantages for directed and controlled deposition of graphene in a dielectric medium (e.g., SiO<sub>2</sub>) or high bandgap semiconductor (e.g., SiC), without involving film transfer or mechanical cutting. Future effort is required to achieve precise control over the number of graphene layers and improve the quality of the graphene layer, which in principle can be accomplished through the control of the growth time, laser power, illumination time, and other growth parameters. We are currently doing point-by-point spatial scans, but the throughput can be greatly enhanced by adopting more advanced optical techniques, including line-scans and the use of a diffractive optical beam splitter to simultaneously illuminate a few hundred points.

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