

## Soft X-ray spectromicroscopic study on graphene toward device applications

Graphene, the honeycomb network of carbon atoms, is promising for electronics, photonics and even spintronics owing to its excellent electronic properties, such as linear band dispersion and giant carrier mobilities arising from the fact that the behaviors of charged carriers are governed by relativistic quantum mechanics. As shown in Fig. 1, we have developed epitaxy of graphene on 3C-SiC thin films on Si substrates (GOS) toward graphene-Si fusion devices with the aid of surface science techniques, such as X-ray photoelectron spectroscopy and spectroscopic photoelectron and low-energy electron microscopy, at beamlines **BL23SU** and **BL17SU** [1]. Note that GOS has the unique property of the face-specific-dependent electronic band structure, which can offer multifunctionality in GOS-based devices [1]. In combination with surface micromachining techniques [2], 3D nanoscale multifunctioned GOS (3D-GOS) will be realized in the near future.

However, there are practical issues toward the realization of graphene-based integrated devices. One of the practical issues is device isolation. Site-selective epitaxy of GOS (SSE-GOS) before device fabrication is efficient because this simplifies device fabrication processes and can prevent sample damage and contamination during processing. Consequently, we have developed SSE-GOS by spatially controlling the defect density of a 3C-SiC(111) thin film on a Si(111) substrate [3].

The SSE-GOS production method is schematically shown in Fig. 2. First SiO<sub>2</sub> micropatterns on the Si(111) substrate were formed as a mask for SiC patterning. Then 3C-SiC(111) thin films were grown

on both the bare Si and SiO<sub>2</sub>-covered surface regions by gas-source molecular beam epitaxy with monomethylsilane as a gas source, followed by lifting the 3C-SiC(111) thin films off the SiO<sub>2</sub>-covered regions using a dilute HF aqueous solution. Again, 3C-SiC(111) thin films were grown on the sample. Finally, the sample was annealed at 1523 K for 30 min in ultrahigh vacuum for graphitization.

To verify SSE-GOS, we have characterized the sample surface by microscopic low-energy electron diffraction ( $\mu$ -LEED) and microscopic X-ray absorption spectroscopy ( $\mu$ -XAS). The  $\mu$ -LEED observation was performed by low-energy electron microscopy (LEEM) at the NTT Basic Research Laboratories. In Fig. 3, graphene (1 $\times$ 1) spots are visible in region A but are absent in region B. However, the (1 $\times$ 1) spots of the base SiC(111) thin film are visible. These results suggest the site-selective formation of graphene in region A.

$\mu$ -XAS near the Si K-edge ( $\mu$ -Si-K XAS) was carried out by photoemission electron microscopy (PEEM) at **BL17SU** to elucidate the cause of the site-selectivity of GOS epitaxy. The  $\mu$ -Si-K XAS spectra obtained from regions A and B are shown in Fig. 3. These spectra were similar to the previously reported Si-K XAS spectra of SiC. Note that the peak D (~1847 eV), which is related to Si vacancies [3] can be observed. The reduced intensity of peak D in the spectrum from region B indicates a higher density of Si vacancies in the SiC thin film in region B. It is concluded from the  $\mu$ -LEED and  $\mu$ -Si-K XAS results that the formation of Si vacancies suppresses the graphitization since the intensity of peak D is reduced by increasing the

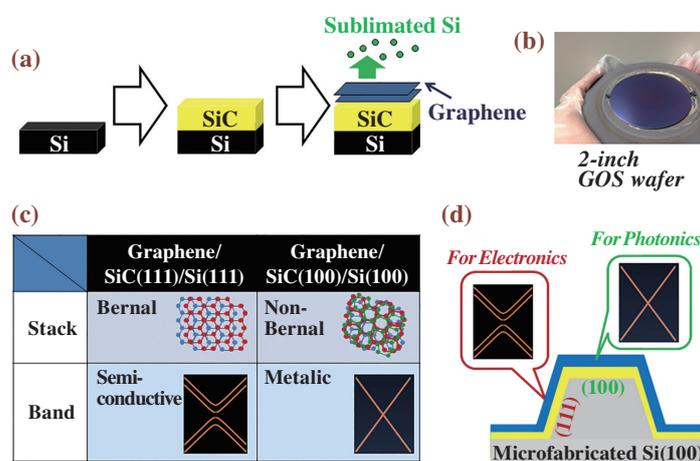


Fig. 1. (a) Schematics of GOS production process. (b) Optical micrograph of 2 inch GOS wafer. (c) Face-specific dependence of electronic structure of GOS. (d) Conceptual drawing of 3D-GOS.

density of Si vacancies, maybe because the increased Si vacancy density can increase the Si partial pressure near the surface that inhibits graphitization. The Si vacancy formation is ascribable to the increased surface roughness in region B during the removal of the SiC thin film before the second SiC growth. Intelligent microscopic control techniques for Si vacancies such as ion implantation shall be useful for precise device isolation for graphene-based integrated circuits.

Unlike ordinal device materials, such as Si, charged carriers in graphene follow relativistic quantum mechanics. This can make the graphene device operation mechanism reasonably specific. Definite clarification of the device operation mechanism requires direct nanoscopic observation techniques for electronic states under operating conditions, such as gate bias control, in addition to (macroscopic) electrical measurement.

For this purpose we have carried out operando observation of a graphene transistor using  $\mu$ -XAS with PEEM at BL17SU [4]. In the graphene transistor, many-body effects, such as excitonic effects and Anderson orthogonality catastrophe, are remarkable and depend on the molecular orbital ( $\pi^*$  vs  $\sigma^*$ ). The magnitudes of many-body effects are controllable by gate bias and contact with source/drain electrodes, which vary the position of the Fermi level in graphene, because of the disappearance of density of states near the Dirac point. This PEEM study is interesting. However, the exact Fermi level position cannot be inferred, which makes it difficult to unambiguously relate information on electronic states with device characteristics. For this reason, 3D Nano ESCA at

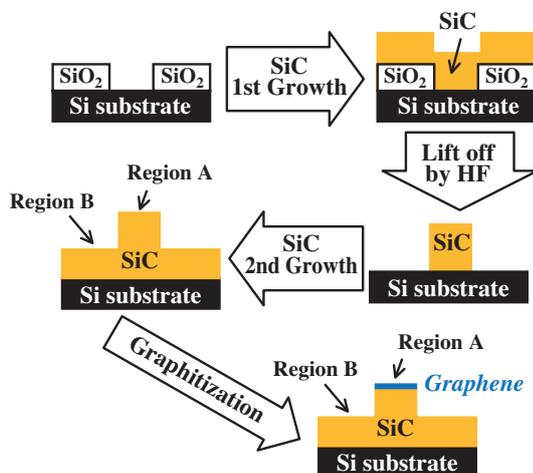


Fig. 2. Schematic drawing of production method of SSE-GOS.

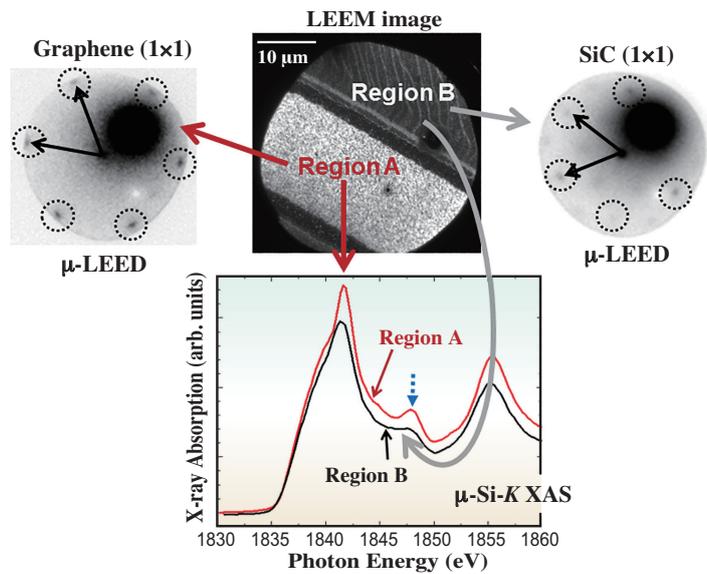


Fig. 3. Analyses of SSE-GOS using a LEEM image,  $\mu$ -LEED, and  $\mu$ -Si-K XAS.

BL07SU has been developed. The 3D Nano ESCA observation of the graphene transistor in fact made it possible to elucidate the charge transfer region between graphene and source/drain electrodes [5]. Furthermore, the 3D Nano ESCA operando observation, involving the addition of the gate-biasing function, is also now in progress [6]. The combination of PEEM and 3D Nano ESCA must be a novel way to fully understand device physics.

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References

[1] H. Fukidome *et al.*: J. Mater. Chem. **21** (2011) 17248.  
 [2] H. Fukidome *et al.*: Appl. Phys. Lett. **101** (2012) 041605.  
 [3] H. Fukidome, Y. Kawai, H. Handa, H. Hibino, H. Miyashita, M. Kotsugi, T. Ohkochi, M.-H. Jung, T. Suemitsu, T. Kinoshita, T. Otsuji and M. Suemitsu: Proc. IEEE **101** (2013) 1557.  
 [4] H. Fukidome *et al.*: Scientific Reports **4** (2014) 3713.  
 [5] N. Nagamura *et al.*: Appl. Phys. Lett. **102** (2013) 246104.  
 [6] H. Fukidome *et al.*: Scientific Reports **4** (2014) 5173.