Supporting Information

Centimeter–scale epitaxial graphene with controlled number of layers on 4H-SiC by pulsed electron deposition

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1. Preparation of the substrate surface by hydrogen etching

Commercially on-axis 4H-SiC wafers (TankeBlue Semicon. Co. Ltd. Beijing) with thickness of ~400 μm were chosen. The Si-terminated samples (10mm×10mm) were first dipped into concentrated HF (49%) for 30 min, in order to remove surface oxide,[1] then rinsed in acetone, ethanol and high-purity deionized water for 20min respectively in turn. As shown in Fig. S1a, a mechanically polished substrate 4H-SiC(0001) full of scratches was annealed in subsequent hydrogen etching at 1550℃[2] for half an hour under hydrogen (5vol%)+Argon (95vol%) flow (500 standard cubic centimeters per minute) at atmospheric pressure, until an aligned series of steps was obtained (Fig.S1b). After 30 min H_2-etching (20 μm×20 μm), the terraces are about 35000 Å wide and the steps are 20 Å high. These steps are formed due to the agglomeration of atomic terraces caused by the miscut of the wafer surface from the (0001) plane.

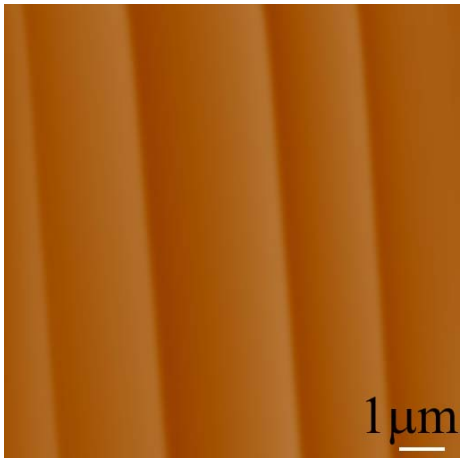


Figure.S1 The AFM image of substrate surface for epitaxial graphene.

2. Characterization of graphene sheets

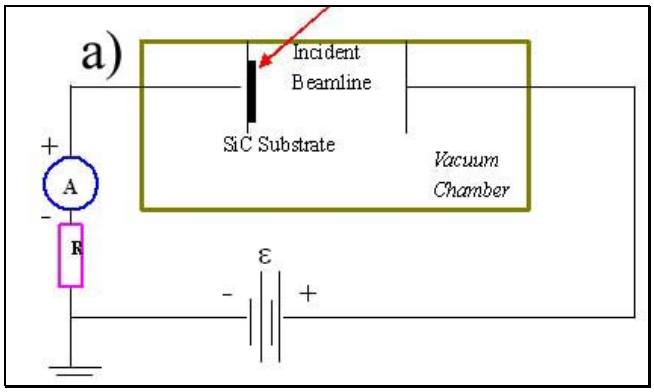
We first present qualitative characterization of the graphene structure using Raman spectrum. The Raman spectra were recorded by JYT64000 high-resolution Raman spectrometer using a He-Ne laser. The excitation source was a 632.8nm laser (1.96 eV) with power below 0.1 mw to avoid normal incident destroy. Then quantitative characterization of the number of layers by core level X-ray photoelectron spectroscopy (XPS) was performed using a VG Mark-□ instrument, which utilizes monochromatic Aluminum K-alpha X-rays (1486.6 eV) to strike the sample surface, and beam spot was a 5mm×3mm ellipse. In addition the optical image and scanning tunneling microscopy (STM) can provide supplementary information in characterization of formation of graphite too, the atomic force microscopy (AFM) can show the thickness of graphene overlayer and the uniformity of the substrate surface.

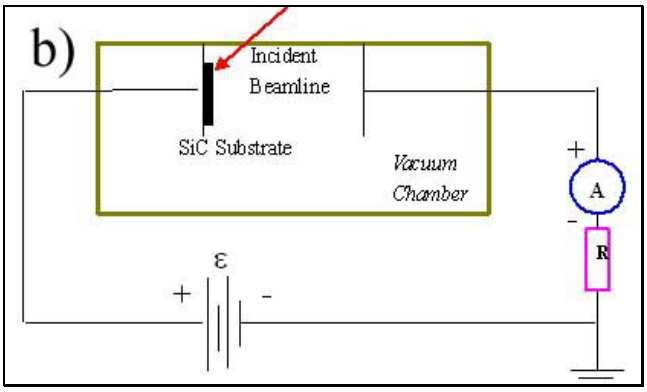
3. Sublimation of the silicon during the PED process

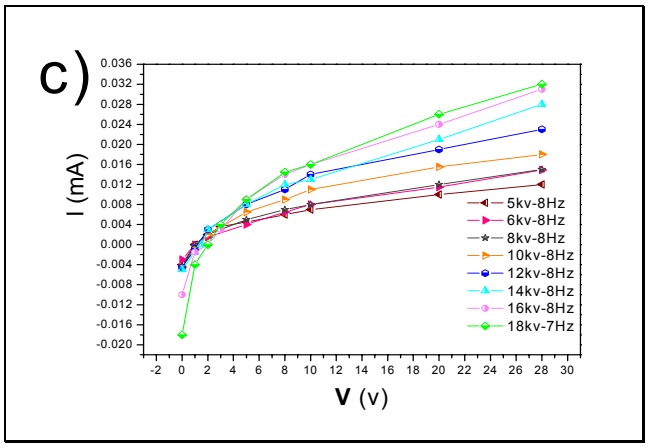
During the process of PED, an electron field was designed to penetrate the 4H-SiC substrate (Fig. S2a and Fig. S2b). If silicon ions are positive charged, they will be forced to cathode once available.

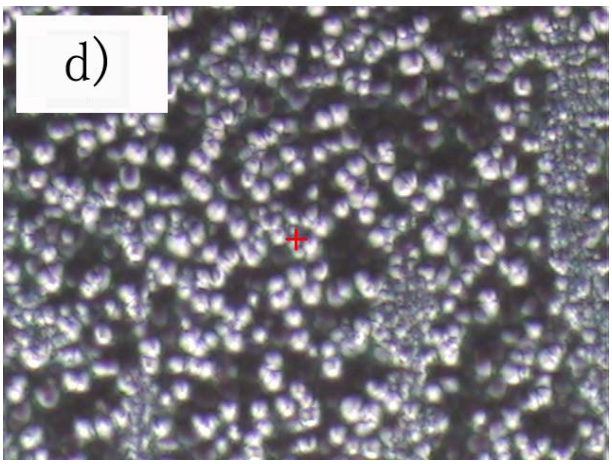
An outer extra-electric field is imposed as a field ion emission resource in the vacuum chamber. Fig.S2a exhibits the circuit diagram in detail. In the vacuum chamber, once substrate is bombarded by incident electron beamline (red arrow), the electrons will agglomerate on the surface of semiconductor substrate (SiC) for an instant immediately after a pulse. Therefore the substrate and the ground connection point will constitute a circuit protected by a protection resistance (R), the extra electrons on the substrate will transfer to the ground and the intensity of current detected by amperometer (blue circle) will be negative. When the field voltage ε is tuned to zero, the original current created by incident beamline completely can be measured using the circuit shown in the Fig.S2a. Subsequently the electrode reverses and the circuit changes as shown in Fig.S2b. With the field voltage increasing, the current value changes from negative through zero to positive, moreover the absolute value of positive is much larger than that of negative. The result was demonstrated in the Fig.S2c. If the field voltage is less than 2V, the current value in circuit will be negative, which states that no positive ions reach cathode. With the increasing of field voltage, the current values will evolution to positive, even a linear dispersion relationship between current and field voltage available, which states that large quantity of positive ions reach cathode. It is obvious that the silicon ions will be only possible case when the SiC irradiated by electron as the only target.

After the target is irradiated by electron beam line, the cathode of $SrTiO_3$ is checked with optical dark field microscope and XPS, and the concentration of silicon on the surface of cathode is detected (Fig.S2d and Fig.S2e).


a)
Incident
Beamline
SiC Substrate
Vacuum
Chamber
A
R
ε


b)
Incident
Beamline
SiC Substrate
Vacuum
Chamber
A
R
ε


c)
I (mA)
V (v)
5kv-8Hz
6kv-8Hz
8kv-8Hz
10kv-8Hz
12kv-8Hz
14kv-8Hz
16kv-8Hz
18kv-7Hz


d)

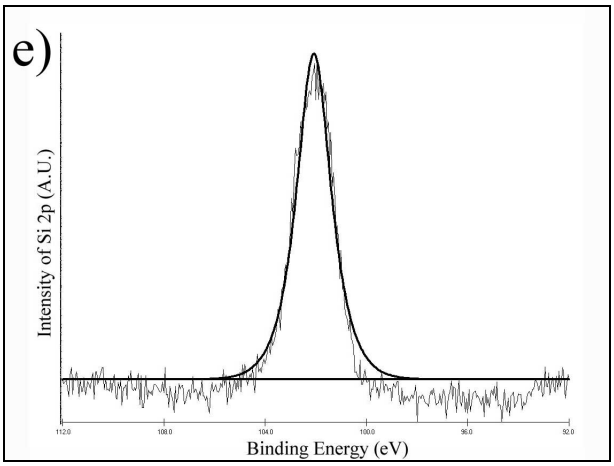

e)
Intensity of Si 2p (A.U.)
Binding Energy (eV)

Figure S2 The analysis of sublimation of silicon. a) Circuit diagram of field ion emission for probing the original electric current at different gun voltage where field voltage ε=0. b) Circuit diagram of field ion emission for probing the emission current changing with different gun voltage at different field voltage. c) The curves of current stimulated by PED and field ionized changes with electrode voltage. d) The optical topographic image of $SrTiO_3$, where the substrate of $SrTiO_3$ is coated with silicon-contained particles. (e) The XPS spectrum of Si 2p demonstrates that the silicon can be detected obviously.[3]

4. The optimized conditions for EG by PEI

With the incident energy promoting, the penetration depth of incident electrons will increase and finally lead to the epitaxial graphene (EG) distribution inhomogeneously. For example, the perturbation of the number of EG layers can reach 6 ML, if incident energy (10 keV) is employed. Higher incident energy can even result in more obvious indentation on the surface.

When low energy incident (5.0keV) is employed, more pulsed times are needed for formation of EG on SiC substrate. This low incident energy in irradiated area distributes more inhomogeneously than higher one, which can be inferred from Fig. S3a. When most of the irradiation area undergoes reconstruction of carbon atoms by PEI, some sporadic areas has been overheated by electron bombardment. Fig.S3a shows the morphology of overheated area, which has the similar topographic morphology to that overheated by TA mode (Fig. S3b), The impurities masked on the surface of EG have been characterized by Raman spectra(Fig.S3c)，where the peak ~520cm^{-1} indicates Si, [4] and XPS Si 2p (Fig.S3d), which demonstrates components including Si and its compounds.[5,6,7]

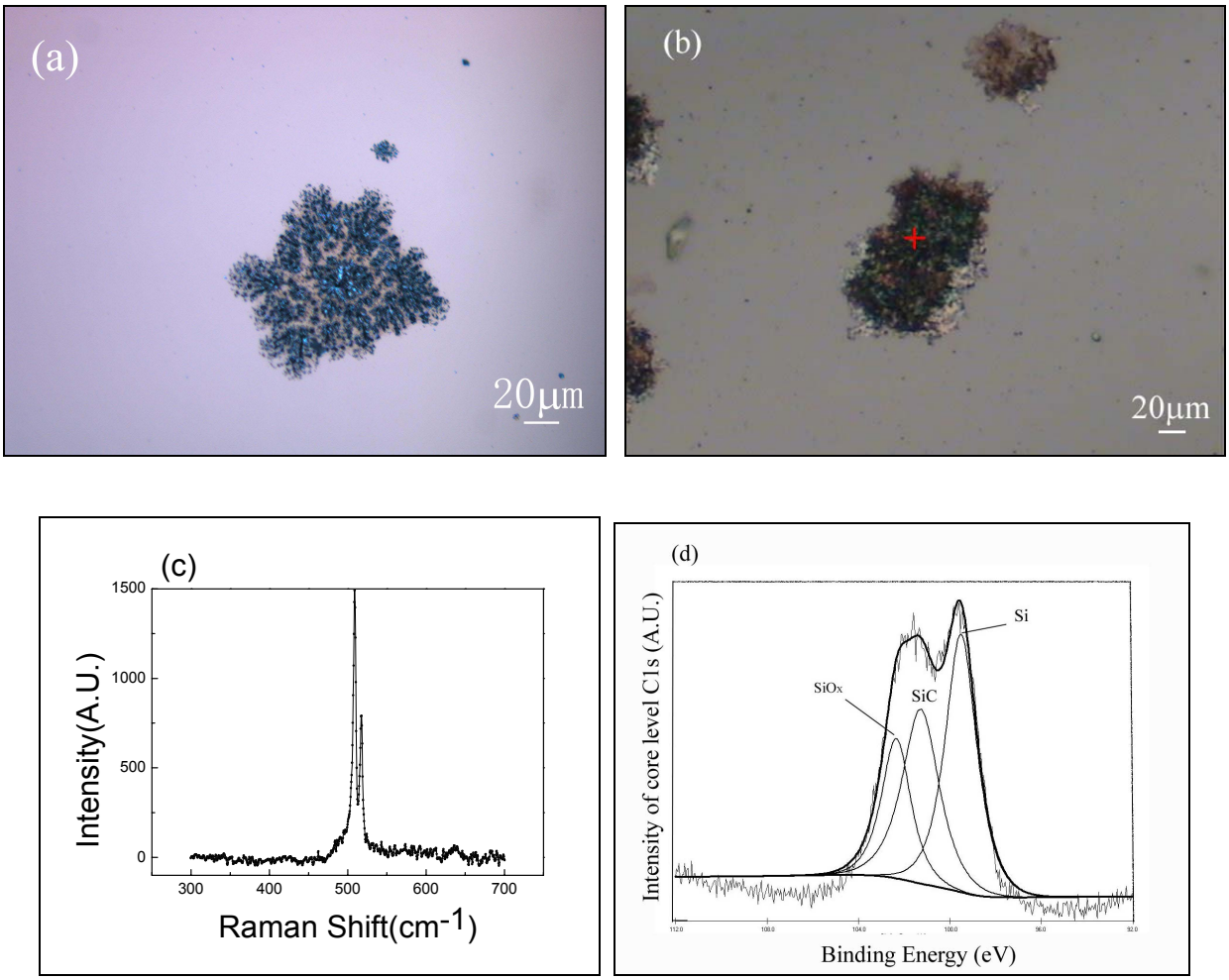


Figure S3 (Color online) the epitaxial graphene prepared by different routes on 4H-SiC. (a,b) optical topographic images of EG by PED (5keV, 2Hz,1000 times) or TA mode (1300ºC, annealing 6min with Argon pressure 0.1atm) respectively, and it is obviously that the EG was masked by the Si or its compounds. c) Raman Peaks of Silicon and other compounds have been observed under the same condition as a). d) Si 2p has indicated that the impurity masked on the surface of EG by TA mode includes Si or its compounds.

Supplementary Reference

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