Silicene field-effect transistors operating at room temperature

Li Tao, Eugenio Cinquanta, Daniele Chiappe, Carlo Grazianetti, Marco Fanciulli, Madan Dubey, Alessandro Molle and Deji Akinwande

1. Raman Characterization of Silicene

Depending on whether silicon atoms are sequentially sitting in between or on top of Ag atoms, characteristic patterns of silicene domains with respect to the Ag unit cell include (4×4), (√13×√13) and (2√3×2√3) that have been well-distinguished by STM\textsuperscript{S1-3}. Raman spectroscopy is useful to understand such structures of silicene, which has a signature of broadened shoulder around 490-510 cm\textsuperscript{-1} (Supplementary Fig. 1a) compared to bulk silicon. The interpretation of silicene Raman signatures is based on previously reported self-consistent match between experimental data and the \textit{ab initio} model of the vibrational spectrum\textsuperscript{S4}. The decomposition of a measured Raman spectrum (Supplementary Fig. 1b) reveals $E_{2g}$ and $A_{1g}$ modes corresponding to (4×4) and (√13×√13) superstructures. In detail, the spectrum of the (4×4) superstructure is characterized by a remarkable intensity for the asymmetric shoulder, reflecting the high degree of intrinsic disorder due to the large amount of buckled atoms (30\%) present in its unit cell. With respect to the planar honeycomb lattice of graphene and the low-buckled honeycomb lattice of free standing silicene, the presence of a large amount of non-symmetric buckled atoms, makes these $A_{1g}$ modes Raman active for the (4×4) phase whereas they are silent for non-defected graphene and free-standing silicene thus resulting in a more pronounced intensity of the shoulder. This picture rules out in the silicene monolayer the possible assignment to locally oxidized silicon as recently proposed for the silicene bilayer\textsuperscript{S5}. On the other hand, the spectrum of the (2√3×2√3) is dominated by
E_{2g} modes at 522 cm\(^{-1}\), while the A_{1g} ones just bears a negligible intensity, reflecting a more pronounced planarity of this silicene superstructure\(^{34}\). Raman spectroscopy also allows us to distinguish silicene from amorphous silicon (a-Si), which usually has a broad bump <480 cm\(^{-1}\) that is over 10 cm\(^{-1}\) away from major components of the silicene signatures.

Supplementary Figure 1. Raman characterization on a) silicene compared to amorphous silicon (a-Si) and bulk silicon; b) decomposition of a measured Raman spectrum agrees with theoretical computation of E_{2g} and A_{1g} modes (centred at 517, 508 and 496 cm\(^{-1}\)) representing a mixed-phase silicene. Raman spectroscopy serves as a good cross-reference to STM for distinguishing silicene from a-Si phase.

2. Silicene transfer and device fabrication

As noted in our stability study (Fig. 3 in the manuscript), it is the encapsulated sandwich in between Al\(_2\)O\(_3\) capping and native Ag film that allows the preservation of pristine silicene during the delamination transfer (Supplementary Fig. 2a) in our SEDNE process. Atomic force microscope image in Supplementary Fig. 2b shows the surface morphology (RMS: 1-2 nm over the whole frame including highlighted particles on the surface) on a 3\(\times\)3 \(\mu\)m\(^2\) area of encapsulated silicene after delamination from growth substrate. The surface morphology of transferred Al\(_2\)O\(_3\)/silicene/Ag remains similar to its original condition on the growth surface.
Supplementary Figure 2. Encapsulated delamination transfer of silicene film stack. a) Optical and b) atomic force microscope image of Al₂O₃/silicene/Ag after delamination from growth substrate (mica).

After the transfer, a key step for successful fabrication of silicene devices is to define source/drain electrodes in native Ag film layer without attacking silicene underneath it. Commonly available Ag etchant is usually a strong oxidizer based chemical, such as nitric acid, and it attacks silicene film immediately upon contact. We explored alternative Ag etchant and found potassium iodide, KI, with a small addition of iodine could remove Ag film effectively without harm to Si in a time-controlled chemical etching\(^8\). SEM energy dispersive X-ray spectroscopy confirmed the complete removal of Ag in the silicene channel region during patterning of source/drain pads. Time-evolved Raman spectroscopy reveals a sufficient time window for controlled etch and subsequent electrical measurement.

3. Transport Measurement of Silicene Field-Effect Transistors at Room-Temperature

Device #3 with \((2\sqrt{3} \times 2\sqrt{3})\) silicene exhibited similar ambipolar behaviour and more symmetric bell shape resistance profile (Supplementary Fig. 3) compared to devices #1 and #2 mixed-phase silicene described in the main text. Particularly, an \(I_{\text{MAX}}/I_{\text{MIN}}\) of \(~11\) and extracted field-effect mobility \(~35\ \text{cm}^2/\text{V-s}\), with residual carrier concentration at the Dirac point of \(8-9 \times 10^9\ \text{cm}^{-2}\) were obtained based on a well-accepted diffusive model\(^9, 10\). This observation on device #3, together with device #1 and #2, supports the predicted Dirac electronic structure of silicene. The lower mobility with respect to devices #1 and #2 (Fig. 5
in the manuscript of mixed-phase silicene) can be due to a more pronounced tendency for the 
\((2\sqrt{3}\times2\sqrt{3})\) superstructure to show defects and clustering due to the higher formation 
temperature and dewetting, therein conferring a relatively lower degree of long range 
structural order.

\[ \text{Supplementary Figure 3. Electrical characterization of a silicene transistor.} \]

Resistance versus gate overdrive voltage \((V_g-V_{\text{Dirac}})\) on silicene device \#3 \((2\sqrt{3}\times2\sqrt{3} \text{ silicene})\) with 
\(R_{\text{MAX}}/R_{\text{MIN}} \approx 11\). The extracted low-field carrier mobilities are 33 and 36 \(\text{cm}^2/\text{V-s}\) for electrons 
and holes respectively with residual carrier concentration at the Dirac point of \(8-9\times10^9 \text{ cm}^{-2}\).

To rule out the possibility of ambipolar transport behaviour from a-Si, Al\(_2\)O\(_3\), Ag residue and 
SiO\(_2\) pathways that may exist in our device configuration, we fabricated and examined 4 
control groups. As a control group sample, a-Si film was deposited and capped with 5 nm 
Al\(_2\)O\(_3\) at room temperature under the same flux parameters in the UHV chamber adopted for 
the silicene growth. Supplementary Fig. 4a&b shows that no additional streaks appear in the 
RHEED pattern after the a-Si deposition, at complete variance with the silicene case (Fig. 
2a&b in the manuscript). \textit{In-situ} scanning tunnelling microscopy (Supplementary Fig. 4c&d) 
confirms the formation of amorphous structures as a cross reference to RHEED. This a-
Si/Al\(_2\)O\(_3\) film stack was subjected to the same SEDNE process demonstrated in the 
manuscript for silicene devices, and electrical transport measurement shows negligible
current with no gate control (Supplementary Fig. 5a). Similarly, another control group sample with only 5 nm Al₂O₃ capping layer was prepared in the same UHV chamber under the same condition as for silicene samples, and then subjected to the same SEDNE process to make transistors that exhibit open circuit according to the statistics from a dozen devices (Supplementary Fig. 5b). As a result, Al₂O₃ capping layer or a-Si film is not responsible for the ambipolar behaviour observed in Fig. 5 from the manuscript or Supplementary Fig. 3.

Supplementary Figure 4. In-situ characterization of the a-Si layer. Real-time reflection high-energy electron diffraction on a) Ag(111), and b) a-Si on Ag(111) (the azimuth is along the [11-2] Ag surface direction). c) 100×100 nm² and d) 30×30 nm² in-situ scanning tunnelling microscopy (STM) images show the amorphous structure of deposited Si film. The STM images were acquired with a sample bias of -1.3 V and tunnelling current of 0.4 nA.
Supplementary Figure 5. Electrical characterization of control group devices on a) monolayer a-Si film plus 5 nm Al₂O₃ capping film and b) 5 nm Al₂O₃ capping film only. A dozen devices in each group exhibited negligible drain current within the same order of magnitude as the noise level of the measurement equipment.

In the case of possible thin Ag residue that might remain during the final etching step to pattern the native Ag as contacts, a control group of Ag thin film (~1 nm thick) devices with the same configuration as silicene FETs yielded three orders higher metallic current output with no ambipolar behaviour or appreciable gate modulation (Supplementary Fig. 6).

Supplementary Figure 6. Electrical characterization of control group devices with 1-2 nm residual Ag. a) Smooth drain current (I_D) versus voltage (V_d) curve showing linear metallic behaviour with a resistance of ~570 Ω. b) I_D-V_g curve showing no ambipolar feature, negligible gate control and negligible gate leakage current (I_g).
Real-time Raman observation reveals that the Ag-free silicene in device #2 still exhibits ambipolar transport in ~40 seconds, and then degrades afterwards within ~2 minutes when exposed to air after Ag removal (Supplementary Fig. 7). This additional observation agrees with the spontaneous structural transitions\textsuperscript{511} and local reconstruction\textsuperscript{512} of silicene suggested in recent fundamental studies. Further experimental studies are essential for ensuring long-term device stability for practical applications under ambient operation. Promising research avenues include controlling the intrinsic structure (i.e. phase and the number of layers) of silicene, and immediate thin film capping of post-fabrication silicene devices.

**Supplementary Figure 7.** Air-stability of silicene device #2: a) Raman spectroscopy and b) electrical measurement of the Ag-free mixed-phase silicene channel observable immediately after Ag removal. The silicene channel exposed on the top-side to ambient conditions degrades in about 2 minutes.

Considering all possible device configurations in this study, supplementary Table 1 summarizes the distinct transport behaviours among silicene and control group devices, affirming that the transistor data (Fig. 5 in the manuscript and Supplementary Fig. 3) are indeed due to charge carriers in silicene rather than parasitic path through the Ag thin-film or other thin film layer such as a-Si, Al\textsubscript{2}O\textsubscript{3} or SiO\textsubscript{2}. 
Supplementary Table 1. Comparison of silicene transistors with 4 control group devices

<table>
<thead>
<tr>
<th>Device configuration</th>
<th>$I_d$-$V_d$</th>
<th>$I_d$-$V_g$</th>
<th>Key Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silicene</td>
<td><img src="image1" alt="Image" /></td>
<td><img src="image2" alt="Image" /></td>
<td>Ambipolar; $\mu \approx 100$ cm$^2$/V-s</td>
</tr>
<tr>
<td>Ag silicene</td>
<td><img src="image3" alt="Image" /></td>
<td><img src="image4" alt="Image" /></td>
<td>Metallic behaviour</td>
</tr>
<tr>
<td>2-Si silicene</td>
<td><img src="image5" alt="Image" /></td>
<td><img src="image6" alt="Image" /></td>
<td>Open circuits</td>
</tr>
<tr>
<td>Al$_2$O$_3$ silicene</td>
<td><img src="image7" alt="Image" /></td>
<td><img src="image8" alt="Image" /></td>
<td>Degraded silicene</td>
</tr>
</tbody>
</table>
4. Estimation of the Small Band Gap of a Dirac Semiconductor

The residual carrier density \( n_o \) is the total electron and hole density at the Dirac point. \( n_o \) of a Dirac semiconductor is given by the sum of the populated states, adapted from Chapter 3, Eqn. 3.44 in Ref.\textsuperscript{S13}:

\[
n_o = 2 \int_{\Delta / 2}^{E_{\text{max}}} g(E)F(E, E_F) dE \tag{1}
\]

where \( \Delta \) is the small band gap within an order of magnitude of thermal energy. The factor of two accounts for the contribution of electrons and holes, and \( E_{\text{max}} \) represents the maximum relevant energy. \( g(E) \) and \( F(E, E_F) \) are the energy \( E \) dependent density of states and Fermi-Dirac population function respectively. \( g(E) = \frac{8\pi}{(h v_F)^2} E \), and \( F(E, E_F) = \frac{1}{1 + e^{E/E_F}} \).

where \( h \) is Planck’s constant, \( K \) is Boltzmann’s constant, \( T \) is temperature, and \( v_F \) is the Fermi velocity. At the equilibrium Dirac point, \( E_F = 0 \) eV and the residual carrier density is due to thermal activation, assuming negligible impurity doping, which is the case for the silicene devices reported in this work. In addition, without loss of accuracy, the upper limit of Eq. (1) can be taken to infinity because of the rapid decline of the Fermi-Dirac exponential tail at high energies. It follows that Eq. (1) reduces to:

\[
n_o = \frac{16\pi}{(h v_F)^2} \int_{\Delta / 2}^{\infty} \frac{E}{1 + e^{E \over kT}} dE \tag{2}
\]

For the case of graphene with zero band gap, Eq. (2) simplifies to \( n_o = \frac{4 (kT)^2 \pi^3}{3(h v_F)^2} \), a quantity that depends only on a single material parameter, \( v_F \), and amounts to a constant \( \sim 1.5 \times 10^{11} \text{ cm}^{-2} \) at 20 °C room temperature\textsuperscript{S13}.

For the silicene devices reported in this work, the substantially lower residual carrier density indicates a small band gap is present. Solving Eq. (2) for experimental \( n_o \sim 8 \times 10^9 \text{ cm}^{-2} \) yields \( \Delta \sim 0.21 \text{ eV} \) within the range of band gap opening (0.0-0.4 eV) predicted by Pflugradt et al.\textsuperscript{S14}.

The Fermi velocity of silicene was taken from recent measurement to be \( v_F \sim 1.3 \times 10^8 \text{ cm/s} \textsuperscript{S15} \).

The value of \( \Delta \) calculated here must be considered a rough estimate particularly because we have assumed that the Dirac dispersion is largely preserved. While this is supported by recent density functional theory studies\textsuperscript{S14} and angle-resolved photoelectron spectroscopy (ARPES)
of silicene\textsuperscript{15}, specific studies are needed to understand the silicene–dielectric surface interaction, the nature, value and dependence of silicene’s electronic structure and band gap on temperature, substrates, and external fields. Most importantly, these studies are now in principle feasible based on the SEDNE concept described in this work that can enable the realization of experimental silicene devices.

References:


S7. Microtechnology/Etching Processes, Institute of Electronics and Nanotechnology, Georgia Tech, \texttt{http://grover.mirc.gatech.edu/processing/Etchants.pdf}


