

Performance Enhancement of a Graphene-Zinc Phosphide Solar Cell using the Electric Field-Effect

Supporting Information

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Supporting Information Content

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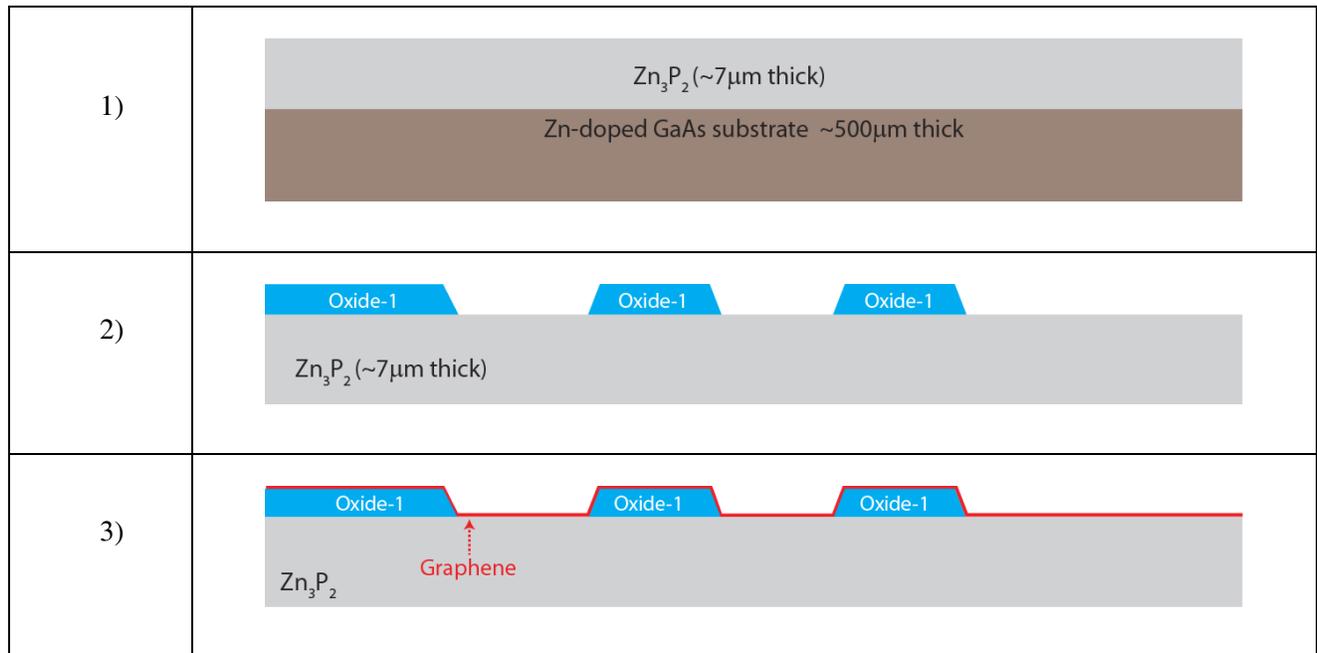
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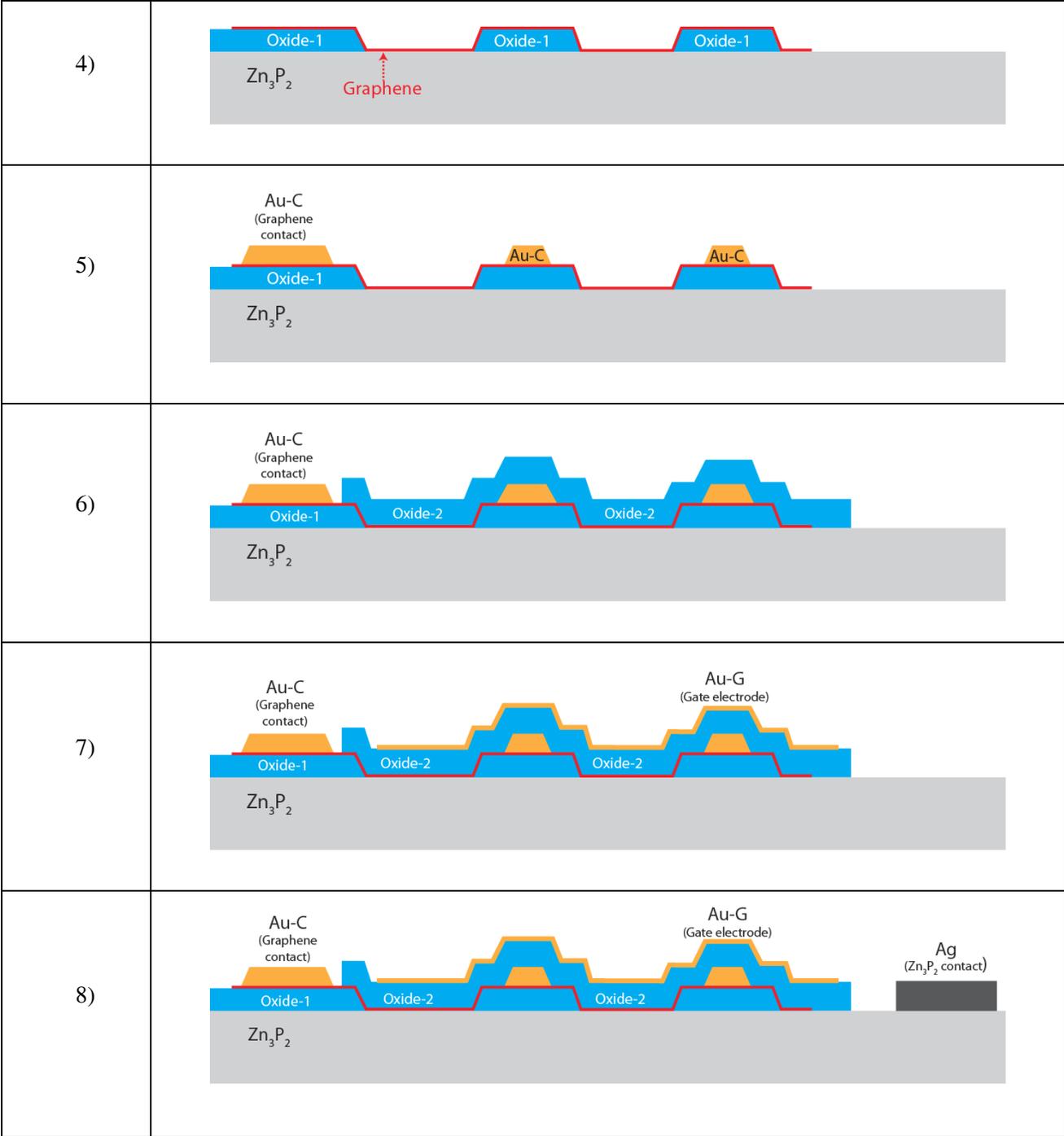
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A) Fabrication process

The process flow fabrication for the devices is illustrated below in Figure S1. We start with a Zn_3P_2 layer 7 μm thick on top a Zn-doped GaAs substrate $\sim 500 \mu\text{m}$ thick as shown in step 1 (from step 2 to 8 we only show the Zn_3P_2 and we omit the GaAs substrate). Then an oxide layer labeled Oxide-1 is deposited on the substrate and is composed of a 20 nm thick ZrO_2 film deposited by atomic layer deposition followed by a 40 nm thick SiO_2 layer deposited by electron beam evaporation (step 2). The oxide-1 layer is patterned by e-beam lithography and lift-off. Then a graphene layer, grown on copper by chemical vapor deposition, is transferred onto the substrate covering the entire chip (step 3). The graphene is then patterned by e-beam lithography and O_2 plasma (step 4). To make electrical contact to graphene, a Cr(10 nm)/Au(80 nm) thick layer labeled as Au-C is deposited on top of oxide-1 (step 5). The oxide-1 layer prevents an electric short between the Au-C and Zn_3P_2 . Then the gate oxide layer, labelled as Oxide-2, is deposited. It has the same composition as oxide-1, 20 nm thick ZrO_2 film deposited by atomic layer deposition followed by a 40 nm thick SiO_2 layer deposited by electron beam evaporation (step 6). As a gate electrode we use a thin Au layer consisting of 3 nm of Cr and 12 nm of Au (Au-G) deposited by thermal evaporation (step 7). Finally, an Ag electrode is deposited directly on top of Zn_3P_2 to make an ohmic contact with Zn_3P_2 .

Figure S1: Fabrication Process Flow

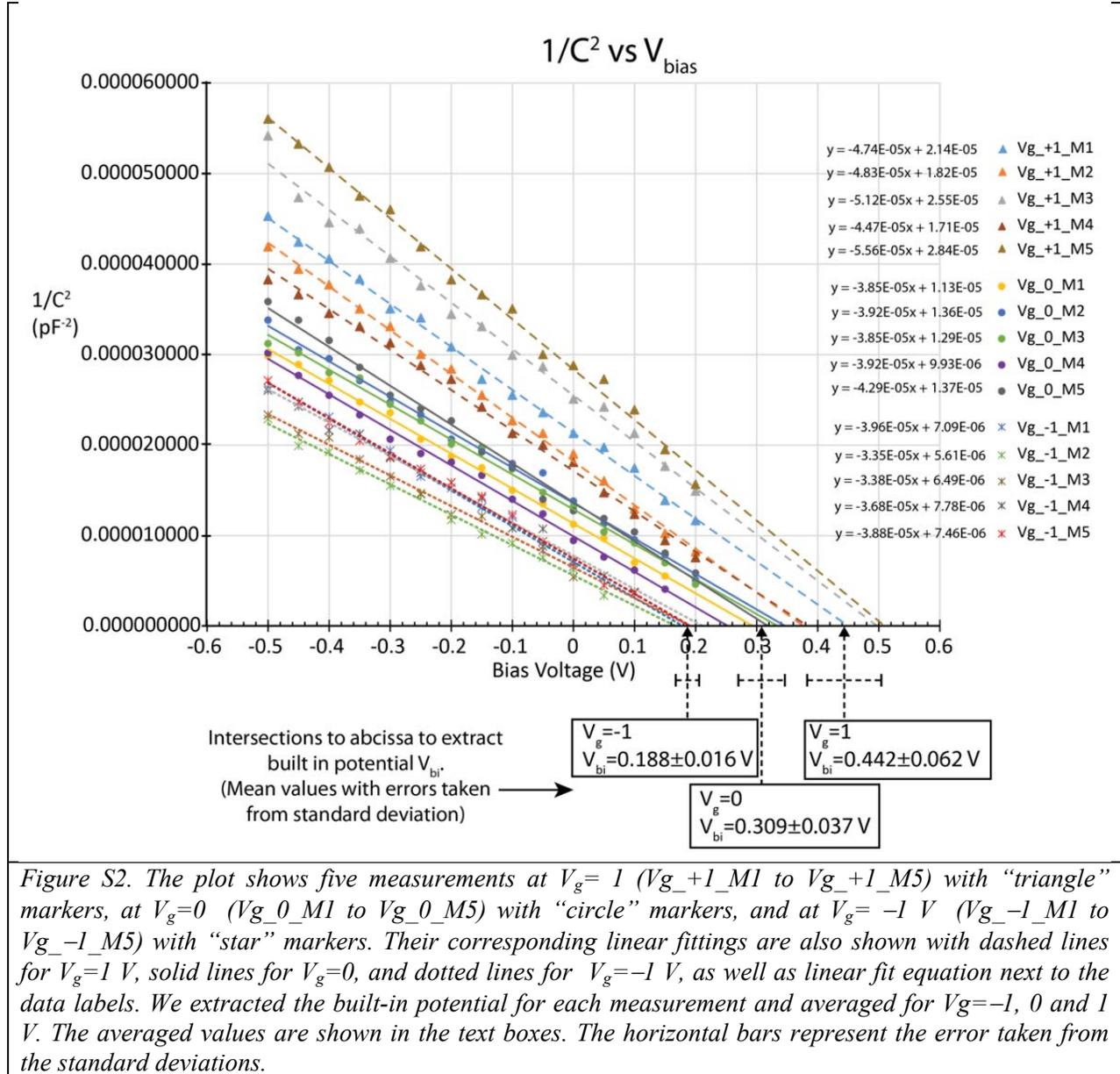




B) Series of capacitance measurements

The capacitance measurements were performed using an HP4192 LF Impedance Analyzer with an excitation of 50 mV @ 10⁵ Hz.

For the data from Figure 3.D we apply a top gate voltage with a Keithley sourcemeter. We observed variations in the measurements, so we performed a series of 5 measurements at each gate voltage of -1 , 0 and 1 V that are shown in Figure S2.



These data were taken as follows. We apply a $V_g = -1$ V and ramp V_{bi} from -0.5 to 0.2 V. From this data we obtain our first data for $V_g = -1$ ($V_{g_-1_M1}$ in previous plot). Then we left V_g and V_{bi} electrically floating for ~ 30 min. After the 30 min we applied again $V_g = -1$ V and ramp V_{bi} from -0.5 to 0.2 V to obtain our second set of data for $V_g = -1$ V ($V_{g_-1_M2}$). We repeated the same process 3 more times to obtain our 5 sets of measurements for $V_g = -1$ V. This procedure was repeated again for $V_g = 0$. We left the device electrically floating, then apply $V_g = 0$ and ramp V_{bi} from -0.5 to 0.2 V. Then we float again V_g and V_{bi} , wait 30 min, and then set again $V_g = 0$ and ramp V_{bi} from -0.5 to 0.2 V until we get 5 data sets.

The same was done for $V_g = 1$ V. In this way we got 5 measurements for each of the gate voltages of -1 , 0 and 1 V, with ~ 30 minutes between each measurement leaving the device floated (disconnecting our probes from the device).

The mean value with error tolerances obtained for the built-in potentials are:

$$\text{At } V_G = -1 \text{ V} \rightarrow V_{bi} = 0.18 \pm 0.02 \text{ V}$$

$$\text{At } V_G = 0 \text{ V} \rightarrow V_{bi} = 0.31 \pm 0.04 \text{ V}$$

$$\text{At } V_G = +1 \text{ V} \rightarrow V_{bi} = 0.44 \pm 0.06 \text{ V}$$

C) Calculation of carrier concentration, change in graphene Fermi level and built-in potential

C.1) Carrier concentration in Zn_3P_2 extracted from Figure 2.B:

The total capacitance C_T , measured in Figure 2.B, is equal to the equivalent capacitance of the oxide capacitance C_O in series with the capacitance C_D from the depletion zone in Zn_3P_2 ($1/C_T = 1/C_O + 1/C_D$).

At negative voltages, in the accumulation mode, $C_T \sim 58$ nF/cm². Since, $C_D \rightarrow \infty$ because there is no depletion width, then $C_O = C_T \sim 58$ nF/cm².

At positive voltages, in depletion mode, $C_T \sim 40$ nF/cm². Since $1/C_D = 1/C_T - 1/C_O$, then $C_D = 128$ nF/cm².

Since $C_D = \epsilon_{sc}/W$, where W is the depletion width, and $\epsilon_{sc} = 11 \times 8.85 \times 10^{-14}$ F/cm, then $d = 76$ nm.

From the depletion width we can estimate the carrier concentration through the expression:

$$W = 2 \sqrt{\frac{\epsilon k T \ln\left(\frac{N_A}{n_i}\right)}{q^2 N_A}}. \text{ Substituting for } n_i = 3.5 \times 10^{20} \text{ m}^{-3} \text{ (Springer database) and } N_A = 6 \times 10^{22} \text{ m}^{-3} \text{ gives } W \sim 73 \text{ nm.}$$

Thus the estimated carrier concentration in Zn_3P_2 is $\sim 6 \times 10^{16} \text{ cm}^{-3}$.

C.2) Carrier concentration in Zn_3P_2 extracted from Figure 3.D:

$1/C^2 = 2(V_{bi} - V)/q\epsilon N_A$, thus, the slope of the function is equal to:

$$\Delta(1/C^2)/\Delta V = -2/q\epsilon N_A, \text{ and}$$

$$N_A = 2/(q\epsilon) \times (\Delta V / \Delta(1/C^2))$$

Substituting that $\epsilon = 11 \times 8.85 \times 10^{-14}$ F/cm, and taking from Figure 3.D for $V_G = 0$ that for $\Delta V = -0.7$ V,

$$\Delta(1/C^2) = 90.9 \times 10^{-6} \text{ cm}^4/\text{nF}^2, \text{ we obtain } N_A = 9.88 \times 10^{16} \text{ cm}^{-3}.$$

C.3) Change in Fermi level in graphene induced by gate voltage:

The gate dielectric consists of a 20 nm layer of ZrO_2 with a 40 nm layer of evaporated SiO_2 . Our characterization of the films has given values of $\epsilon(ZrO_2) = 18$ and $\epsilon(SiO_2) = 5.6$. From here we can estimate the capacitance of the layer:

$$C(ZrO_2) = 18 \times (8.85 \times 10^{-14} \text{ F/cm}) / 20 \text{ nm} = 796 \text{ nF/cm}^2,$$

$$C(SiO_2) = 5.6 \times (8.85 \times 10^{-14} \text{ F/cm}) / 40 \text{ nm} = 123.9 \text{ nF/cm}^2$$

$$\text{Total capacitance (series) is: } 107.21 \text{ nF/cm}^2$$

The charge induced in graphene can be easily calculated from $Q=CV$, for a gate voltage of 1 V:
 $Q=C \times V = (107.21 \text{ nF/cm}^2) \times (1 \text{ V}) = Q = 107.21 \text{ nC/cm}^2 = 6.68 \times 10^{11} \text{ e}^-/\text{cm}^2$.

The corresponding change in Fermi level:

$$\Delta E_F \sim v_F \hbar \sqrt{(\pi n)} \approx (1.15 \times 10^8 \text{ cm/s}) \times (6.58 \times 10^{-16} \text{ eVs}) \times \sqrt{(\pi \times 6.68 \times 10^{11} \text{ cm}^{-2})} = 0.109 \text{ eV} \sim 0.11 \text{ eV}.$$

Thus, the estimated change in graphene Fermi level for $\Delta V_G = 1 \text{ V}$ is $\sim 0.11 \text{ eV}$.

Where $v_F = 1.15 \times 10^8 \text{ cm/s}$ is taken from Xu *et al.* Appl. Phys. Lett. **98**, 133122 (2011)

C.4) Built-in potential induced by gate voltage

The built-in potentials were extracted by extrapolating to the abscissa of $1/C^2(V_B)$ for each of the measurements and then averaging and setting the standard deviation as error tolerance. The mean values extracted are:

$$\text{At } V_G = 1, V_{bi} = 0.442 \pm 0.062 \text{ V}$$

$$\text{At } V_G = 0, V_{bi} = 0.309 \pm 0.037 \text{ V}$$

$$\text{At } V_G = -1, V_{bi} = 0.188 \pm 0.016 \text{ V}$$

The change in built-in potential when V_G goes from -1 to 0 V is:

$$\Delta V_{bi} = V_{bi}(V_G = 0) - V_{bi}(V_G = -1 \text{ V}) = (0.309 \pm 0.037 \text{ V}) - (0.188 \pm 0.016 \text{ V}) = 0.121 \pm 0.040 \text{ V}$$

The change in built-in potential when V_G goes from 0 to $+1 \text{ V}$ is:

$$\Delta V_{bi} = V_{bi}(V_G = +1) - V_{bi}(V_G = 0 \text{ V}) = (0.442 \pm 0.062 \text{ V}) - (0.309 \pm 0.037 \text{ V}) = 0.133 \pm 0.072 \text{ V}$$

D) Photovoltaic measurements instruments

Photovoltaic conversion was measured under an Oriel AM1.5 sunlight simulator (model 67005).