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On-chip energy storage integrated with solar cells using a laser scribed graphene oxide film

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We demonstrate an on-chip concept of the energy storage integrated with crystalline silicon solar cells using a laser scribed graphene oxide film, which can lead to the miniaturization in size and the minimization in cost of optoelectronic devices. The integrated solar supercapacitor with 62% columbic efficiency is directly written on the reverse side of solar cell without any loss in the solar cell performance. The energy and power density of the obtained energy storage devices are comparable to those of electrolytic capacitors even after a number of charging-discharging measurements.

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The rapid development of micro-electronics, especially portable electronics, enhances the demand for on-chip energy storages. However, it is a challenge to scale down the size of the traditional energy storage devices to be suitable for the planar geometries of micro-electronic devices. Advancement of micro-fabrication technologies, especially the simple and cost-effective direct laser writing,^{1,2} has led to the development of high quality planar energy storage devices like micro-supercapacitors using graphene^{3–6} with the CO₂ laser printers and DVD burners. The achieved laser scribed graphene oxides (LSGOs) result in porous reduced GO (RGO) structures, which can hold the ions during the charging process due to the photo thermal reduction. This planar and scalable supercapacitor structures pave the way for the possibilities of directly integrated energy storage device with silicon wafer-based as well as the thin film amorphous silicon solar cells.

Recent reports on photo-charged energy storages with organic solar cells represent a promising direction towards this effort.^{7–11} But the efficiency and stability of these solar cells are not competitive; on the other hand, crystalline silicon (c-Si) solar cells dominate 90% of the current market.¹² An attempt to develop an integrated Si based supercapacitor by etching away the reverse side of c-Si solar cell does not facilitate the working condition of solar cell since the back contact was etched away, which inevitably affects the current collection.¹³

In this work, we manifested an on-chip integrated energy storage with c-Si solar cells using a LSGO film in an area of $3 \times 3 \text{ cm}^2$, as shown in Fig. 1(a), without the requirement of any extra foot-print. The analyses performed before and after the integration show that the obtained energy density and power density of the devices are comparable to those of electrolytic capacitors but with a long self-discharge time.

The integration of supercapacitors with commercially available c-Si solar cells was achieved by using a CO₂ laser beam of wavelength $10.6 \mu\text{m}$ (Versalaser) to scribe the

drop-casted GO film (Fig. 1(b)) with $6 \mu\text{m}$ in thickness and a concentration of 1.2 mg/ml on the reverse side of c-Si solar cells. The constructed supercapacitor has 16 electrodes with an average thickness of $16 \mu\text{m}$ and an ionogel electrolyte, as shown in Fig. 1(b). The thermal effect of the laser beam induces the reduction of GOs to RGOs (Fig. 1(c)).

Various laser powers were used to optimize the threshold power required to reduce the GO, as shown in Fig. 2(a). From the scanning electron microscopy (SEM) image (Figs. 2(b) and 2(c)), the threshold power of 1.9 W was found to be effective in reducing the GO film, resulting in porous structures. The unusual photothermal effect proceeds to the high intensity absorption evolving the formation of lattice vibrations in the structure during the laser-GO interaction. The highly localized temperature generated during the reduction results in the breakage of oxygen bonding in the material leading to defect induced graphene. Porous structures are expected due to the release of gases during the decomposition process of the functional groups like C–O, C=O, and

FIG. 1. (a) Schematic of the solar-charging in integrated energy storage with c-Si solar cells. (b) Laser scribing process for the reduction of GOs on the reverse side of a c-Si solar cell using a CO₂ laser beam. (c) The reduction of GO to RGO during the laser scribing process.

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FIG. 2. SEM images of LSGOs using various laser powers. (a) At 1.5 W, (b) at 1.7 W, (c) at 1.9 W, and (d) at 2.4 W. From the different laser reduction conditions, an optimum condition was obtained at 1.9 W as shown in (c).

water.³ The purity of the obtained RGOs depends on the amount of oxygen removal from the lattice, which can be adjusted by the laser power.

From Fig. 3(a), it can be seen that the I_G/I_D ratio obtained from Raman spectroscopy measurements (Reinshaw instruments) on LSGOs reduced at 1.9 W is around 2.72, which indicates the formation of highly crystalline RGOs.¹⁴ In Fig. 3(b), the electrical conductivity of the obtained LSGOs using the four-probe measurement (Jandel instruments, RM3000) and their thickness is presented as a function of the laser power. As expected, the conductivity increases with the laser power, reaching a maximum when the oxygen groups are removed to the largest extent before the GO breakdown threshold. Besides, the thickness also increases with the increase of laser power until the threshold condition for GO is reached leading to a supercapacitor with the decent performance before the GO breakdown threshold. At 1.9 W, the porous LSGOs attained a maximum conductivity of 10^4 S/m, which is comparable to that in the literature.³

The RGO films were then coated with ionogel electrolyte (fumed silica-1-butyl-3-methylimidazolium bis (trifluoromethylsulfonyl) imide) and were allowed to dry to remove any water left behind in the electrolyte for 3 h under the room conditions. To ensure the high performance of the integrated device, a layer of the SU8 photoresist with a thickness of 1 mm was used to insulate between the solar cell reverse side and the supercapacitors in order to avoid the impact

FIG. 3. (a) Raman spectrum of LSGOs obtained at a laser power of 1.9 W. (b) The thickness and electrical conductivity of LSGOs using various laser powers.

TABLE I. The solar cell performance under different conditions.

Condition	V_{oc} (V) ^a	I_{sc} (A) ^b	J_{sc} (mA cm ⁻²) ^c	FF ^d	η (%) ^e
Initial	0.614	0.469	34.28	70.79	14.9
After encapsulation	0.622	0.488	35.61	70.81	15.69
After 3 min charging	0.623	0.482	35.17	71.17	15.60
After 6 min charging	0.623	0.478	34.93	71.21	15.5

^a V_{oc} is the open circuit voltage.

^b I_{sc} is the short circuit current.

^c J_{sc} is the current density.

^dFF is the fill factor.

^e η is the efficiency.

from the laser scribing, which might influence the solar cell performance. On the other hand, the choice of electrolyte was made due to the non-liquidic and non-volatile nature of ionogel.¹⁵ Finally, another microscopic glass slide was used to encapsulate the integrated device to further improve the overall performance.

The characterization of the obtained integrated device was performed along with the individual analysis of solar cells and supercapacitors. It has been found out that the performance of the solar cell was not reduced, as shown in Table I. Instead due to the antireflection effect from the encapsulation layer, the conversion efficiency was improved slightly, as shown in Fig. 4(a). The performance remains stable even after the 6 min charging with the solar simulator (Oriel 3 A) under the one-Sun (1000 W/m^2) condition at the room temperature, as shown in Fig. 4(a). The temperature change observed during the charging of the supercapacitor was negligible. It was observed that the maximum V_{oc} obtained was around 0.38 V, which leads to a columbic efficiency of 62%. The major loss factor in the reduction of the supercapacitor output compared with the solar cell V_{oc} was

FIG. 4. (a) Solar cell performance before and after charging. (b) CC behaviour at a current load of $0.33 \mu\text{A cm}^{-2}$. (c) Areal capacitance obtained from the CC curve. (d) Self-discharge curve of the integrated device using solar and DC charging.

contributed by the contact resistance between the current collection tape and the LSGO.

The galvanostatic charge-discharge (CC) studies using a load of $0.33 \mu\text{A cm}^{-2}$ with a cut-off of 0.38 V similar to the solar cell output was performed, as shown in Fig. 4(b), in order to verify the ability of the supercapacitor in withstanding the number of cycles under the solar charging. The capacitance of the integrated supercapacitor is calculated from the measurements using the formula $C_A = \frac{I}{\frac{dV}{dt}}$, where I is the current and dV/dt is the slope of the discharge curve (Fig. 4(c)).⁴ The volumetric energy density is around $5 \mu\text{Wh cm}^{-3}$ from the formula $E = \frac{1}{2} \times C_V \times (U)^2 / 3600$, where E is the energy density in Wh/cm^3 , U is the electrochemical window of the electrolyte, C_V is the volume-based specific capacitance in F/cm^3 , and the power density is around 4.6 W cm^{-2} . The capacitance is mainly contributed by the geometry of the design, which decides the ionic mobility and transport distance of ions from the electrolyte between the electrodes.⁴ Currently, the continuous wave direct laser writing using 3D printers is limited by the diffraction limit to have electrodes closer to sub micrometer level. This issue can be overcome by the use of direct laser writing with advanced facilities like femtosecond laser writing as well as simulation emission depletion (STED) based nanofabrication techniques.²

As solar cells have to be exposed under the atmospheric conditions for years, we have to ascertain how each component will behave in the specified conditions even after the encapsulation. Device fabrication and encapsulation under inert conditions can improve the performance of supercapacitors. The self-discharge potential is studied (Fig. 4(d)) and found that the charge is held for more than 10 days with negligible loss of less than 1% after 5 h of discharge contributed by impurities left behind in the RGOs and leakage current.¹⁶ This is not common for commercial supercapacitors, which is restricted to 2 or 3 days to reach half maximum potential ($1/2 V_{\text{max}}$). Also the behaviour is a proof of high quality RGOs obtained during the laser reduction with little amount of oxygen groups left behind.

In order to have a comparison, DC charging using the same voltage as the V_{oc} of the solar cell was performed and we observed that a different behaviour of charging with a maximum of 0.28 V but the discharge behaviour remains the same as that for the solar charging. Basic theoretical circuit analysis of a DC charging (voltage constant) and a solar (current constant)¹⁷ charging was performed to get a better

understanding regarding the additional losses contributed to the integrated device. The internal losses within the DC charger circuit were higher in comparison to the solar cell, which result in higher voltage loss in the effective charging of supercapacitor using the DC charger.

In conclusion, we have designed and fabricated an energy storage device with long self-discharge time integrated with solar cell using LSGOs without sacrificing the performances of both the solar cell and the supercapacitor. This integration concept could lead to standalone Photovoltaic (PV) systems. The cost-effective and high efficiency supercapacitors have comparable performance to the existing photo-supercapacitors with the extended potential of remote area usage and building integration.

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