

The surface passivation mechanism of graphene oxide for crystalline silicon

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Abstract — We have recently demonstrated that low surface recombination velocities on Si crystals are achievable from room temperature graphene oxide (GO) deposition. Intrinsic properties of this material make it an appealing candidate for surface passivation in solar cells. There is, however, very little literature on the passivation mechanisms of GO and further understanding is required. In this work we have thus studied GO/SiO₂/Si interface interactions by X-ray photoelectron spectroscopy (XPS). From our results we have confirmed that the passivation achieved by GO coatings do not result from chemical changes at the surfaces as has been previously suggested. In addition, close analysis of the spectra of GO coated silicon sample shows the elemental Si 2p peak is split into two doublets. We identify the appearance of this extra doublet to be the result of surface charging, and thus attribute the spectral change to formation of a depletion region at the silicon surface induced by GO's negative charge. Results in here presented may thus signify a significant step forward in the understanding of charged 2D materials passivation mechanisms and its use in advanced solar cell structures.

I. INTRODUCTION

The recombination of charge carriers at the surfaces of silicon crystals has become a characteristic of major relevance for high efficiency solar cell manufacture [1]. This recombination particularly affects the increasingly thinner wafers used for solar cell fabrication, cells made by the widely used Passivated Emitter and Rear Cells (PERC) concept and some other high-efficiency and passivated contact cell designs. Therefore, the use of new and improved materials, of low cost, for passivation are of paramount importance to the solar industry.

We have recently shown in Ref. [2] that GO can be readily applied on Si-crystal surfaces and effectively reduce recombination of carriers. Surface recombination velocities on

high resistivity materials down to 14.4 cm·s⁻¹ have been demonstrated and the high stability of the passivation discussed. Additionally, we have demonstrated that the passivation effect resulting from GO coatings is likely to be the result of the formation of a carrier depleted layer at the silicon subsurface due to the intrinsic negative charge of the GO. This conclusion was supported by the correlation between the extent of the passivation achieved by GO dispersions and their pH values and previous evidence that increased pH GO-dispersions present higher negative surface charge [3]. For such correlation we have used the microwave photoconductivity decay (μ PCD) technique, Kelvin Probe force microscopy (KPFM) and infrared absorption spectroscopy. Based on our results and the absence of evidence of chemical passivation observed in those studies we concluded that the passivation achieved by GO coating of Si was due to its negative surface charge, which during carrier excitation induced a depletion region preventing minority carrier recombination.

In this work we have gathered further evidence to support our hypothesis by means of XPS measurements. We show that there are no major changes in chemical composition on the Si/SiO₂ interface after GO deposition, discarding the possibility of a chemical surface passivation coming from the film as previously suggested [4]. Moreover, a major change in the Si 2p emission peak was detected upon GO coating of some of the studied samples together with a SiO₂ emission peak shift. The presence of GO splits the elemental Si peak into two doublets. As the elemental Si is protected from the GO by the native oxide layer this cannot be a chemical shift, so we hypothesize this shift arises from the formation of a depletion region on the Si subsurface.

II. EXPERIMENTAL DETAILS

Although we have demonstrated that the GO passivation methodology works effectively on p-type silicon in the resistivity range 1-1000 $\Omega\text{-cm}$, for the experiments described below we have used float-zone (FZ), lightly doped ($< 10^{13} \text{ cm}^{-3}$), $\langle 100 \rangle$ p-type silicon wafers which were “RCA 1” cleaned [5] as the baseline for sample preparation. Two sets of samples were then spin coated with 0.2 $\text{mg}\cdot\text{ml}^{-1}$ and 2 $\text{mg}\cdot\text{ml}^{-1}$ GO dispersions respectively. They were dried on a hot plate for 5 min at 200 $^{\circ}\text{C}$. Similar considerations on the sample processing and material preparation described in Ref. [2] were applied. The pH of the dispersions was measured to be 3.6 by a Mettler Toledo F20 pH meter.

Measurement of the effective minority carrier lifetime maps of the samples coated with the 2 $\text{mg}\cdot\text{ml}^{-1}$ GO solution were made on a Semilab WT-2000 PVN by the μPCD technique.

XPS experiments were carried out in a SPECS NAP-XPS instrument (under UHV conditions) equipped with a monochromated Al $K\alpha$ X-Ray source (SPECS Focus 500) and a Specs Phoibos 150 NAP hemispherical analyzer. The scans were acquired at a pass energy of 20 eV. Grazing emission scans were taken at a take-off angle of 20 degrees. All scans were charge referenced to adventitious carbon at 284.8 eV.

III. RESULTS AND DISCUSSION

Figure 1 show the minority carrier lifetime map of one of the wafers used for the XPS studies, with an inset of a token cut off from the wafer which was spun coated with GO for surface passivation. Effective lifetimes of approximately 1 ms were obtained from the GO coated samples clearly demonstrating its passivating effect. Smaller tokens (1 cm x 1 cm) were cut from the same wafer and their X-ray photoemission spectra recorded. One sample was coated with 0.2 $\text{mg}\cdot\text{ml}^{-1}$ GO and another sample was left with only the thin oxide grown by the RCA clean and both spectra compared.

We have analyzed the C 1s and Si 2p core levels for Si/SiO₂ samples with and without deposited GO films. Figure 2 shows

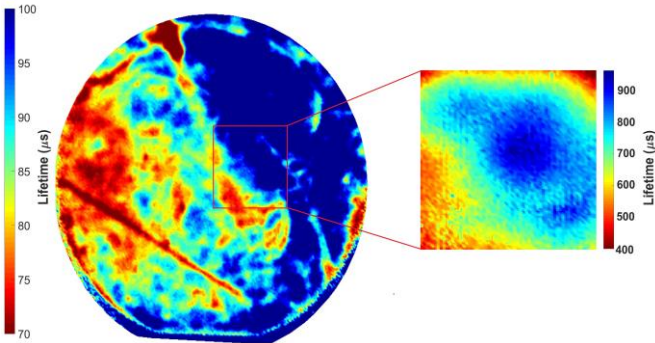


Fig. 1. Effective minority carrier lifetime map of a RCA cleaned and bare FZ p-type wafer (left), and a token sample from the highlighted area after 2 $\text{mg}\cdot\text{ml}^{-1}$ GO coating.

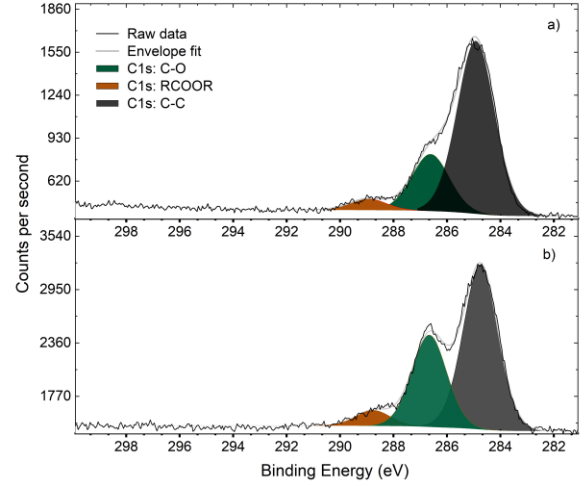


Fig. 2. C 1s spectra of a GO coated Si/SiO₂ sample. (a) Grazing emission. (b) Normal emission.

the grazing and normal emission of the C 1s peak of the GO coated sample which display the normal characteristic of a slightly reduced GO [6]. The envelope peak fits to three peaks, one corresponding to C-C bonds (black), one corresponding to carbon bonded to a single O (green) and one for the carboxyl/ester groups (orange). At grazing emission where there is a greater surface sensitivity, the black peak is enhanced relative to the other two. This suggests there is an overlayer of adventitious carbon over the top of the GO film due to the contact of the sample with air.

Figure 3 shows the 2p silicon peak from the GO coated sample (top) and the uncoated sample (bottom). From the same figure we can observe that the highest energy peak

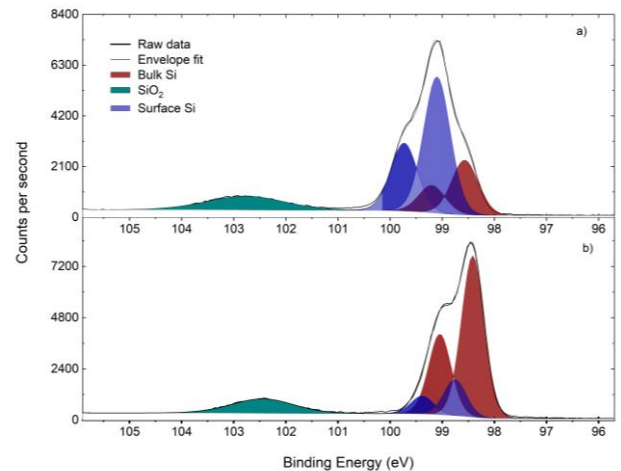


Fig. 3. Si 2p spectra of (a) GO coated Si/SiO₂ sample and (b) uncoated Si/SiO₂ sample showing a shift from the oxide peak on the coated sample and the shift and splitting of the Si 2p_{3/2,1/2} peak.

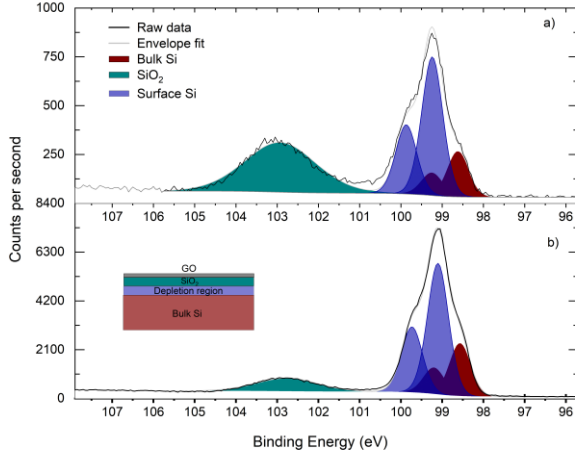


Fig. 4. Si 2p spectra of a GO coated Si/SiO₂ sample at (a) grazing emission showing a surface to bulk doublet ratio of 3, and (b) at normal emission showing a surface to bulk doublet ratio of 2.4. The inset depicts the suggested model of peak assignments.

(cyan), which corresponds to the SiO₂ at the surface, shifts towards higher binding energies whenever the GO film is present. Such an effect has been previously observed to be the result of surface charging [7], [8]. Nevertheless, in Ref. [8] the peak shift towards higher binding energies is attributed to a positive surface charge whereas the opposite occurs for negatively charged surfaces. This observation therefore contradicts our expected low energy shift caused by the GO's negative charge. Further, a rather unusual shape of the Si 2p core level peak was found on every lightly doped FZ GO coated sample in the presence of the thin native oxide layer. By comparing both (bare and coated) samples it is observed that the "bulk" component of the Si 2p peak (red doublet, Figure 3) reduces its magnitude after the GO deposition, whereas the appearance of what we consider to be a second doublet at higher binding energies dominate (blue). Further, we have compared the normal and the grazing emission of the unidentified Si 2p peak and found that the blue component of the fitted data in Figure 3 is enhanced relative to the red at grazing emission which allows us to conclude it is closer to the surface (see Figure 4). It is unlikely that the observed emission is caused by a chemical or crystallographic change as the silicon surface is protected by the SiO₂ layer which was the same for both samples. Moreover, due to GO's characteristics and deposition method it is also improbable that its presence causes any chemical interaction with the silicon underneath.

Even though we have not been able to strongly correlate the observed extra peak to any of the previously reported XPS emission data, some authors have demonstrated that similar changes in Si/SiO₂ interface band-bending can be probed by XPS measurements of the Si 2p peak shifting [7], [9]–[11]. In our case we do observe a slight shift from the Si 2p peak upon GO deposition, but it is rather a strong peak splitting what we believe to exhibit the differential charging at the interface. We

thus suggest that this extra doublet results from the formation of a depletion region induced by the surface charge. If our assignment is correct it may be possible then to correlate the depth of the depleted region to the surface/bulk doublet ratio and perhaps aid the current limitation of the proposed method in Ref. [11].

It seems as though this measurable effect on silicon have been largely overlooked in literature, with one possible reason for this being that the depth of the depletion region induced by thin SiO₂ layers alone is rather small leading to almost undetectable doublet formation in most reported studies. Similarly, a plausible explanation could be that the observation of the doublets in most other studies has not been clear due to the commonly used doping levels of Si which are in the order of 10¹⁴ cm⁻³ or higher, requiring large quantities of charge density for a strong enough field to deplete the subsurface region of the material [12].

A depiction of our suggested model is shown as an inset in Figure 4. This model agrees well with the theory of GO being able to reduce surface recombination in silicon by the formation of an electric field which repel charged carriers by means of the so-called "field-effect passivation". Therefore, if well understood, this passivation mechanisms may be then optimized for its application in high performance passivated-contact photovoltaic (PV) devices.

IV. CONCLUSIONS

It has been recently suggested that graphene oxide can be used for the surface passivation of Si crystals. Despite some current limitations of such passivation, GO's intrinsic properties and room temperature processing results in a very appealing material for a plethora of novel applications that require high throughput manufacture. Mechanisms responsible for the effectiveness of GO's passivation are still poorly understood, hence in this work we present advances on the identification of these mechanisms. By means of X-ray photoelectron spectroscopy we have studied the changes on the Si/SiO₂ surfaces after GO deposition. It is observed that no chemical changes occur on the surface upon deposition. Shifts on the SiO₂ XPS peaks measured from GO coated samples indicate that a surface charge exists. Furthermore, the appearance of an unexpected and poorly documented feature on the Si 2p peak has been observed on every lightly doped Si crystal coated with GO. We attribute this extra emission to result from the formation of a depletion region at the Si subsurface. It is such a depleted region which is aiding the reduction of charge carrier recombination at the surface of the studied silicon material. All these observations are in good agreement with our previously reported hypotheses. We believe that our findings are of significance not only to the PV community working with advanced 2D materials, but they are also likely to impact the wide scientific community working on Si/SiO₂ interfaces for various other applications given the lack of literature in the reported observations.

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