

Graphene as transparent conducting layer for high temperature thin film device applications



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ABSTRACT

The use of graphene as transparent conducting layer in devices that require high temperature processing is proposed. The material shows stability upon thermal treatments up to 1100 °C if capped with a sacrificial silicon layer. The use of Cu foil or evaporated Cu as catalysts in Catalytic-Chemical Vapor Deposition growth gives rise to graphene of similar properties, which represents a promising result in view of its direct integration in microelectronic devices. Photovoltaic p–i–n thin film devices were fabricated on the as-deposited or annealed graphene membranes and compared with similar devices that incorporate as-deposited Indium Tin Oxide. No degradation in series resistance is observed for the annealed device. A 3.7% and 2.8% photovoltaic conversion efficiency is observed on the devices fabricated on as-transferred and on annealed graphene respectively. The major limitation derives from the high sheet resistance of the as-transferred state-of-the-art material. The results opens the way to the use of graphene in applications that require transparent conducting layers resistant to high temperature processing.

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1. Introduction

Single or multi junction thin film solar cells [1] in superstrate configuration, often identified as second generation solar cells, require the use of a transparent conducting layer (TCL) covering the transparent substrate, to access the top contact of the device [1,2]. Typical TCL materials are transparent conducting oxides (TCOs) such as F-doped SnO₂, Indium Tin Oxide (ITO), Al-doped ZnO, or MgO [1,2]. As the device is deposited on top of the TCL/substrate stack, the TCL has to withstand the maximum process temperature. This is normally not an issue, as the process temperature for such kind of devices is typically below 250 °C [1]. More recently, the third generation solar cells concept has been introduced, that envisages the use of material engineering in association with the use of abundant raw materials, in order to achieve sustainable high solar conversion efficiency [3]. Third generation solar cells may require the introduction of a nanostructured material [4] treated at temperatures up to 1000 °C or more. A typical example is the case of silicon nanodots in dielectric matrix [4–6]. With reference to Fig. 1, starting from the transparent substrate, the process sequence implies the fabrication of

the TCL, the deposition of the p-type semiconductor, and the fabrication of the dielectric material that includes the nanodots. The process continues with the fabrication of n-type contact, tunnel junction, bottom junction diode, and back contact. In such a sequence, the TCL must be tolerant to the fabrication temperature of silicon nanodots, that, if based on the Zacharias' approach [7], is typically around 1100–1150 °C [8,9], which represents an issue as the use of TCO at high temperature in p–i–n devices has not yet been demonstrated. The lack of such temperature resistant TCL is the reason why the structure illustrated in Fig.1 cannot be currently fabricated.

Several approaches are currently being investigated to overcome this issue. Löper et al. [6], mainly for research purposes, propose the use of membrane solar cells, with TCO deposited after the nanodot material has been fabricated. Allegrezza et al. [10] investigated the use of capped ITO, and demonstrated that temperatures up to 900 °C can be safely reached; Janz [5] makes use of c-Si as bottom device also used as deposition substrate, circumventing the need of temperature resistant TCL, but with the introduction of stringent constraints in the device design. An innovative approach is represented by the use of graphene (G).

G is thermally stable, and it was already proposed as a substitute of TCO's in photovoltaic and other optical devices [11,12]. Sheet resistances as low as 30 Ω/□ have been obtained on p-doped

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few layer G films, with 90% optical transmittance [13] which is competitive with the best results obtained on standard ITO. Moreover, G does not suffer for the same drawbacks, namely brittleness under bending and scarcity of the raw material. G is expected to outperform ITO as transparent conductive film in the field of stretchable and flexible electronics, and in organic photovoltaics [11,14,15] due to its mechanical and chemical stability. G has also been applied as active material in G-based heterojunction solar cells [16].

In this paper, we propose the application of G membranes as high temperature compatible TCL for the fabrication of third generation solar cells based on Si nanodots. Issues related to the preservation of G electrical quality when inserted within a film stack and annealed at high temperature have been addressed. G membranes have been synthesized, then transferred on quartz, capped by hydrogenated amorphous silicon (a-Si:H) and annealed at temperatures up to 1100 °C. The capping layer was then removed and the membranes characterized. p–i–n solar cells, incorporating not-annealed and annealed G as TCL, as well as not-annealed ITO for comparison, were fabricated. The *J–V* characteristics under illumination of devices are reported and discussed. The experiments are focussed on standard low-temperature p–i–n device design (275 °C maximum process temperature), as this allows the impact of the TCL to be identified. Including the high temperature nanostructured material in the p–i–n structure will first require solving specific device and material issues (see Section 4), which is beyond the scope of this work.

2. Experimentals

G membranes have been synthesized by Catalytic-Chemical Vapor Deposition (C–CVD), using Cu as catalyst. Besides the standard procedure based on Cu foil [17], evaporated Cu films on oxidized Si were also used [18,19]. The latter procedure is expected to allow for easier integration in microelectronic fabrication processes and direct patterning of the G-based TCL through catalyst definition. The fabrication details of G membranes are summarized in Table 1. For evaporated Cu films, G membranes were deposited

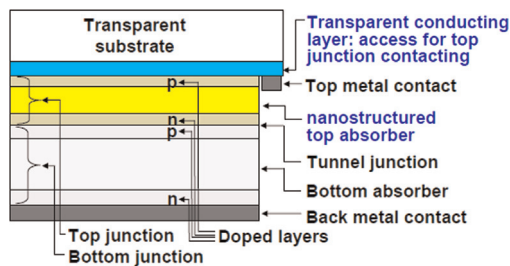


Fig. 1. Possible configuration for a 3rd generation solar cell: tandem cell in superstrate configuration, with nanostructured material as top absorber.

Table 1
G membranes fabrication.

Reactor:	Hot-wall CVD
Cu foil:	Sigma Aldrich, 99.8% pure, 25 μm
Cu film:	Evaporated, 700 nm thick
CVD on Cu foil:	0.66 hPa; CH ₄ :H ₂ = 144:10, 1000 °C
CVD on Cu film:	987 hPa; 7% CH ₄ in Ar/H ₂ , 1000 °C
Removal from substrate:	Wet etch and release of G on PMMA
Cu film, Cu removal:	FeCl ₃ /HCl solution
Cu foil, Cu removal:	HNO ₃ solution
Rinse of G on PMMA:	Deionized H ₂ O
Final PMMA removal:	Hot acetone and isopropanol

Table 2

PECVD deposition parameters: pressure, substrate temperature, thickness. Common to all layers: 13.56 MHz excitation frequency, 28 mW/cm² power density.

	pH (Pa)	T (°C)	t (nm)	Process gases (sccm)				
				SiH ₄	B ₂ H ₆ ^a	PH ₃ ^b	H ₂	CH ₄
Si cap:	1	275	40	20				
p-layer:	0.8	120	15	6	10		20	6
n-layer:	0.9	160	50	24		6	30	
i-layer:	0.6	160	315	20				

^a 0.5% diluted in H₂.

^b 2% diluted in SiH₄.

at atmospheric pressure in order to reduce sublimation of Cu during the synthesis.

After the synthesis, G membranes have been transferred on proper substrates, such as fused silica or grid substrates for electrical, optical and Transmission Electron Microscopy (TEM) characterization. Standard wet etching of Cu layers and subsequent releasing of the polymer-supported G [20] have been adopted to accomplish the transferring procedure (Table 1).

Before high temperature processing, the G membranes were covered by an a-Si:H capping layer deposited by plasma-enhanced CVD (PECVD), using the fabrication conditions reported in Table 2. During the annealing treatment, the capping layer undergoes crystallization and partial oxidation. The capping layer was etched off in 0.5% diluted HF, followed by a wet etch in tetramethyl ammonium hydroxide (TMAH), 2% diluted in deionized water and heated at 50 °C. Ultrasonic stirring was applied to the solution.

The G membrane structural quality was evaluated by means of micro-Raman spectra collected directly on the original Cu-based substrates using 633 nm excitation wavelength, and by TEM observations performed using a Tecnai F20 microscope equipped with Schottky emitter, operating at 200 keV.

The optical and electrical characterizations were carried out on G membranes both as transferred on quartz and after annealing either in N₂ atmosphere or in vacuum at temperatures in the range 400–1100 °C. The optical transmittance (*T*) was measured using an Avantes fiber optics spectrophotometer, while electrical measurements were performed on a G area of 1 cm², using evaporated Ni electrodes in Van der Pauw configuration.

The photovoltaic thin film devices were fabricated either on top of the G layers on quartz, or on ITO deposited on Eagle glass substrates for comparison. The p/i/n layer sequence was then deposited by PECVD. The deposition parameters are reported in Table 2. The back contact of the cell is realized by Ag evaporation through a shadow mask that defines the 0.07 cm² effective area of each device. The devices were characterised under AM1.5G illumination.

3. Results

3.1. As-prepared G membranes: fabrication and characterization

Micro-Raman spectra, collected directly on G membranes on the original Cu-based substrate, are reported in Fig. 2. In the figure, the parameters of G and 2D peaks, and the intensity and areal ratios I_{2D}/I_G and A_{2D}/A_G are also reported. The absence of the D peak in the spectra, and the high value of the I_{2D}/I_G ratio (3.22 and 1.08 for Cu foil and Cu film respectively) indicate high crystalline quality for the membranes [21–23]. The I_{2D}/I_G ratio and 2D-peak full width at half maximum (FWHM) can also be used to evaluate the number of G layers in the membrane [24]. The results are indicated in the inset of Fig. 2. Both Cu-foil and Cu-film synthesis processes result in the growth of continuous G membranes, as indicated by the Raman signal

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