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High-κ dielectric oxide as an interfacial layer with enhanced photogeneration for Gr/Si solar cells

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In recent years, graphene (Gr) based solar cells have attracted extensive interest because of their ability to produce low cost and highly efficient solar cells. Conventional Gr/Si Schottky junction based solar cells are mostly fabricated by transfer of graphene on silicon substrate. In current work the direct growth of graphene by using the Plasma Enhanced Chemical Vapor Deposition (PECVD) technique was demonstrated to make fabrication more practical on a large scale. Firstly Gr/Si Schottky junction based solar cells were fabricated, and by optimizing the growth process, power conversion efficiency (PCE) of about 3.5% was achieved. Additionally, we demonstrated a metal insulator semiconductor (MIS) structure by introducing hafnium oxide (HfO_2), and an enriched efficiency of 6.68% was reached. Furthermore, the chemical doping of Gr grown on top of HfO_2 passivated Si was done and the efficiency was further enhanced by 8.5%. This study also suggests that the V_{oc} of the Gr/HfO_2/Si solar cells strongly depends on the thickness of the HfO_2 interfacial layer. These solar cells proved reliable as their efficiency was still consistent even after four months. The current study envisions the use of graphene based solar cells for commercial application.

1. Introduction

Photovoltaics have the potential to replace fossil fuels and reduce the cost of materials. Traditional Si based solar cells providing a power conversion efficiency of up to 26% [1] are still dominant in the field of research and for commercial purposes. However, the most challenging task is to reduce the manufacturing cost of solar cells using fewer production material without compromising the efficiency [2–4]. In the past few years, Gr/Si (metal/semiconductor) solar cells have attracted great interest because of the ease of fabrication processes and low consumption of materials, which in turn lead towards lower cost solar cells. The two dimensional (2D) material and honeycomb structure of graphene make it unique in its physical, mechanical, electrical and optical properties as compared to other transparent and 2D materials [5,6]. Li et al., in 2010 reported the first Gr/Si solar cell with a power conversion efficiency (PCE) of about 1.5% [7]. Recently, much effort has been put into making high-efficiency Gr/Si solar cells. Chemical doping is one of the effective ways to achieve a high efficiency on these 2D graphene layers because pristine graphene has very high sheet resistance. The chemical doping method helps to reduce not only the sheet resistance but also change the built-in potential [8]. Usually, chemical doping on Gr is not stable, which makes it practically inapplicable [9]. In their search for a replacement for the chemical doping method, researchers have tried to enhance Gr solar cell efficiency using an interfacial layer between the graphene and silicon. Recently several researchers introduced different interfacial layers [10–14]. Most of this work is done on transfer graphene, which has some major problems during the fabrication of photovoltaic devices; firstly, handling of graphene monolayer can easily lead to damage and wrinkles while transferring the layer, which in turn directly affects the solar cell performance. Furthermore, the area of these devices is very small at around 0.1 cm^2, making it unsuitable for practical applications. The

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large-scale growth of graphene can be realized by using PECVD for photovoltaic applications. A high quality 2D graphene sheet made by using PECVD can be very attractive towards high performance graphene/silicon solar cells [15]. There is very little reported work on the direct growth of graphene on silicon substrate for the fabrication of photovoltaic devices [16–18] Liu et al. [16] reported the direct growth of graphene nano-walls for the fabrication of solar cells; the power conversion efficiency of these solar cells reached up to 5.1% after chemical doping. Chen et al. [17] demonstrated 2D graphene sheet based solar cells with a power conversion efficiency of about 0.078%. Jiao et al. reported the highest efficiency of 6.6% having cell area of 2.5 mm^2, by directly growing graphene nano-walls with PECVD technique [18]. Various oxides as an interfacial layer already reported for fabricating Gr/Si Schottky junction solar cells [11–13,19]. The lower PCE of above-mentioned Gr/Si solar cells can be attributed to a variety of reasons such as, the non-uniformity of the graphene layer, high sheet resistance, and the top electrode contact not being suitable for collection of electrons and holes generated by incident light. It can be improved by optimizing the growth process of graphene to achieve high quality 2D graphene layers and by using an appropriate solar cell structure.

In this study, 2D graphene was grown by using PECVD directly on a silicon substrate to avoid the transfer method for solar cell application. Few layers of graphene with a film thickness of 1.5 nm, was observed by using an atomic force microscope. PCE of 3.5% was realized by optimizing the growth conditions to fabricate Gr/Si heterojunction solar cell with an active area of 0.3 cm^2. Furthermore, different layer thicknesses of Hafnium oxide (HfO_2) were introduced at the interface of Gr and Si, ranging from 1 nm to 2 nm HfO_2 is widely used in CMOS technology because of its good insulating properties, has good thermal stability at higher temperatures [20], and helps to reduce the leakage current [21]. The band-gap of hafnium oxide is 5.5–6.0 eV, which is pretty much aligned with the silicon for blocking the electrons generated from the silicon bulk material during illumination. The recombination process can be reduced effectively by introducing HfO_2 across the interface. It also has less structural defects with the graphene layer, and observed that HfO_2 makes a good interface with Gr [22–24], which helps to get more uniform and continuous film. It was observed when HfO_2 was introduced, the PCE of Gr/HfO_2/silicon (metal-insulator-semiconductor) solar cells increased from 3.5% to 6.68%. It is further increased to 8.5% by applying HNO_3 chemical doping as shown in Fig. 1 (b). This chemical treatment was done by exposing the device to the HNO_3 vapor for 3–4 min as reported [25]. The outcome of this research effort can lead to the commercialization of Gr/Si solar cells.

2. Materials and methods

2.1. Hafnium oxide (HfO_2) growth

HfO_2 growth of different layered thicknesses ranging from 1 nm to 2 nm was conducted using atomic layer deposition (ALD) on an n-type silicon substrate. Each nanometer film thickness required 8 cycles of ALD. No post annealing was done after the deposition of *HfO_2*.

2.2. Graphene growth

Afterwards, high quality graphene was deposited using PECVD directly on the HfO_2/n-type silicon wafer. Methane (CH_4) was the main precursor for the growth of graphene along with the hydrogen (H_2) environment. The total deposition time was 2 h using CH_4 and H_2 sources (2 sccm: 10 sccm) under the RF plasma power of 50 W. The substrate temperature was kept at 550 °C. Before the deposition of graphene, the substrate was annealed for 3 h in a vacuum within the chamber. More detailed characteristics of the quality of graphene deposited using PECVD can be found in our previous work [26].

2.3. Fabrication of photovoltaic device

The fabrication steps of Gr/HfO_2/Si solar cells are illustrated in Fig. 1. An n-type silicon substrate (1-5 Ω-cm) wafer was used for the fabrication of graphene based solar cell. HfO_2 was deposited using the ALD technique as mentioned earlier. Afterwards, the sample was placed in PECVD chamber for the growth of graphene. After completing the growth of HfO_2 and graphene, 400 nm of aluminum was deposited at a rate of 5 A/s as a back electrode using a thermal evaporator. It was followed by the deposition of Au/Cr (70 nm/10 nm) as a front electrode using an e-beam evaporator. The top electrode was deposited using shadow masking with an area of 6 mm × 5 mm, the shadow mask had a design of a bus bar with a thickness of 500 μm and a finger size was 100 μm. Fig. 1 shows the schematic diagram of fabrication process and photograph of Gr/HfO_2/Si solar cell with 0.3 cm^2 junction area. The purpose of a top electrode having finger bars and bus bar is to collect the photogenerated charge carriers efficiently and helps to enhance the PCE of Gr/Si solar cell.

2.4. Characterization

Surface morphologies of samples were observed by using an optical microscope (Olympus BX51 M), and surface topography were characterized using an atomic force microscope (AFM) (Nano Focus, n-Tracer). Structural analysis of graphene was carried out using a Renishaw RAMASCOPE 2000 Raman spectroscopy equipped with a He–Ne laser with a wavelength 632.8 nm. Current-voltage (IV) characterization was done using a Keithley 2400 model. The light IV was measured by using Newport solar simulator under 1.5 G and with an intensity of 100 mW/cm^2, which was calibrated with a standard solar cell prior to measurement.

3. Results and discussion

High dielectrics of hafnium oxide attract the greatest interest in research area because of its large band-gap, high thermal stability, high thermodynamic stability (especially in contact with silicon), and high energy barriers for blocking electrons with respect to silicon [22]. Additionally, it was reported that the interaction of HfO_2 with graphene results in less damage under plasma treatment. Due to these characteristics, the Gr/HfO_2/Si solar cell structure was fabricated.

The graphene layer deposited on hafnium oxide coated silicon substrate shows surface smoothness with no cracks despite being deposited at higher temperatures as shown in Fig. 2(b). Apparently, this shows that the interaction between the graphene and HfO_2 makes no physical damage to the graphene layer. Additionally, further detail of the surface morphology was analyzed using AFM characterization as shown in Fig. 2(a). AFM line profile shows the surface roughness of 1–2 nm. These surface characterization results show good surface smoothness of the graphene layer on top of HfO_2. Further surface quantification of Gr/HfO_2 thin-films on top of the polished wafer was done using a reflectance measurement as shown in Fig. 2 (c). Reflectance spectra were measured in the range of UV and visible range because that particular light wavelength range is viable for light to energy conversion for silicon base solar cells. Reflectance spectra is interesting, As shown in Fig. 2(c) and Fig. S1, Gr/HfO_2(1 nm)/Si shows lower reflectance at lower