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Synthesis and characterization of plasmon resonant gold nanoparticles and graphene for photovoltaics

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ABSTRACT

Here we discuss the use in solar cells of graphene grown by chemical vapor deposition (CVD) and of plasmonic gold nanoparticles (Au NPs) deposited by sputtering. The Au NPs have been coupled with a-Si heterojunction solar cells, with an organic active layer used in organic photovoltaics, and with graphene. Extensive characterization of those three systems by the optical technique of spectroscopic ellipsometry, which is suitable to monitor and analyze the plasmon resonance of the Au NPs, by the microstructural technique of Raman spectroscopy, which is suitable to analyze graphene properties and doping, and by atomic force microscopy has been carried out. Those techniques highlighted interactions between Au NPs and silicon, polymer and graphene, which lead to variation in the plasmon resonance of Au NPs and consequently in the characteristics of the Au NPs/Si, Au NPs/polymer and Au NPs/graphene hybrids. Specifically, we found that an optimal size and density of Au NPs are able to enhance the efficiency of c-Si/a-Si heterojunction solar cells and that exceeding with Au NPs size and density causes device shortcut because of interface interdiffusion between silicon and gold. To discuss organic photovoltaics, Au NPs have been combined with an electro-donating conjugated polymer, the poly[1,4bis(2-thienyl)-2,5-bis-(2-ethyl-hexyloxyphenylenes)]. We found that there is a strong correlation between the thickness and morphology of the organic active layer, which affects the energy and amplitude of the Au NPs plasmon resonance. Finally, Au NPs have been deposited on graphene. We found that Au NPs show the plasmon resonance in the region where graphene is transparent and also yield p-type doping of graphene decreasing its sheet resistance.

1. Introduction

Two main research and technological areas of development in both organic and inorganic solar cells are the inclusion of plasmonic metal nanoparticles to boost the efficiency of thin-film solar cells by increasing light absorption and the incorporation of graphene as transparent conductive electrode to replace indium tin oxide (ITO) films.

In the case of silicon based solar cells, the significantly reduced thickness of the silicon wafer or layers leads to insufficient sunlight absorption and inevitably to low energy conversion efficiency. Similarly, the poor charge transport of organic semiconductors limits the final thickness (and hence optical absorption) of the active layers. The use of a thick active layer leads to increased light absorption but inevitably increases the device resistance, while thinner organic layers favor effective charge collection due to shorter carrier pathways and the resulting reduction of recombination losses [1]. Therefore, efficient light absorption and coupling mechanisms are needed to improve the photon absorption efficiency, while keeping the thickness of the active layer thin enough to sustain carrier mobilities.

In this context, light trapping technologies are of paramount importance to increase efficiency.

Recently, metal nanoparticles supporting localized surface plasmon resonance (LSPR) [2] have attracted intensive research interest as an effective way of enhancing light absorption and, hence, energy conversion efficiency in both silicon [3–6] and organic solar cells [7–10]. Nanoparticles can also be used to effectively scatter the incident light into the intrinsic absorbing layer, increasing the optical path length in the thin film solar cells [11]. High coupling efficiency, large-angle scattering and low parasitic absorption in the metal are some necessary conditions for effective plasmonic light trapping [12]. To meet these criteria, the metal type, location, size and geometry of nanoparticles and the condition of the local dielectric environment have to be optimized [13,14]. Ag and Au NPs are the most widely used materials due to their surface plasmon resonances located in the visible range. Al and Cu, which have resonance in the ultraviolet and visible range, respectively, are also interesting because they are less expensive but they quickly oxidize with an unstable plasmon resonance [15]. Moreover, for organic solar

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cells, the choice of the metal has also to match the bandgap of the absorbing layer to provide appropriate overlapping between the plasmonic resonance and the absorption spectrum. In order to achieve this matching, size and shape of the metal nanoparticle are tailored by processing [16,17]. Kim et al. [8] showed the effect of Au and Ag NPs size on the optical absorption enhancement of an organic solar cell. They achieved a stronger optical absorption enhancement with larger Ag NPs compared with Au NPs, and attributed this to the Ag weaker self-absorption by interband Ag transitions. An enhancement of 34% in the optical absorption of the active layer was observed with Ag nanoparticles of 50 nm diameter. Oo et al. [7] integrated Au nanowires in organic solar cells and found an improvement of the current density and efficiency with a power conversion efficiency (PCE) of 2.72%.

As far as concerns cost reduction, an attractive approach is the use of novel transparent conductive oxides (TCOs). Currently, ITO is used as holes collecting electrode. However, drawbacks using ITO are three-fold: (i) indium is expensive and scarce; (ii) preparative methods such as sputtering, evaporation, pulsed laser deposition and electroplating can be costly; (iii) ITO is a brittle crystalline material and films under stressed may fracture [18], irreversibly dropping the conductivity by several orders of magnitude and, hence, limiting its exploitation in flexible solar cells [19,20]. Therefore, other TCOs are being explored to meet the ever-increasing demand. Over the last decade, thin metal foils [21,22], metal grids [23,24], ZnO [25] and carbon nanotubes [26–28] have all emerged as candidates for transparent conductors. Very recently, graphene — a single layer of carbon atoms arranged in a honeycomb lattice — is attracting interest in various electronics, optoelectronics and photovoltaic applications [29,30]. Graphene can perform multiple functions in inorganic and organic photovoltaic devices, such as semitransparent electrode and antireflection coating [31–35], photoactive material [36–39], bridge structure [40] and counter electrode [41,42].

Graphene offers several advantages over ITO including weight, robustness, flexibility, chemical stability and transparency. Graphene absorbs 2.3% of light per layer, less than the ITO and any other TCO layers [43]. Another important peculiarity of graphene is that it is an amphoteric material, and its work function can be changed by doping through charge transfer [43,44], implying that graphene can be used as both cathode and anode to match the HOMO–LUMO of a large variety of materials [43,45,46]. Moreover, doping of graphene is an effective approach for improving the conductivity without significantly deteriorating transparency [47]. As an example, Kim et al. [48] demonstrated the reduction in the sheet resistance by up to 77% when graphene is doped with $AuCl_3$, whereas Zheng et al. [49] used HNO_3 treatments of graphene to reduce the sheet resistance by about 20–50% improving its transmittance. Different approaches are used to dope graphene, such as heteroatoms doping [50,51], chemical modifications [28,52,53] and electrostatic field tuning [44]. Although substitutional doping results in a stable system, the honeycomb structure of graphene is inevitably disturbed by induced defects by the incorporation of foreign atoms. To circumvent this problem, the sensitivity of graphene to local perturbations, for example, by physically adsorbed gaseous molecules has been exploited, which is inherently a reversible process [43,54], and this reversibility makes it hard to achieve a stable doped graphene because the adsorbed species can desorb. In addition to adsorbed gases, simple molecules bearing electron withdrawing or donating functional groups have been adsorbed on graphene resulting in p- or n-doping [55]. Gold has also demonstrated by Raman spectroscopy to provide p-doping in graphene through the use of $AuCl_3$ and Au nanoparticles dopants [56].

In this paper, we report the synthesis of graphene by chemical vapor deposition (CVD) and of gold nanoparticles (NPs) by a sputtering methodology suitable for integration in photovoltaics and discuss some aspects related to their characterization and coupling with both silicon and organic solar cells. Specifically, considering the examples of Au NPs/silicon, Au NPs/polymer and Au NPs/graphene plasmonic hybrids, we investigate: (i) the impact of the nanoparticle size and interface reactivity when Au NPs are deposited on an a-Si/c-Si heterojunction solar cell; (ii) the effect of the polymer thickness and of its self-organization on the optical properties of the Au NPs/polymer plasmonic hybrids; (iii) the impact of Au NPs on graphene transparency and sheet resistance due to the Au doping effect. To study the absorption behavior of those systems, the optical techniques of spectroscopic ellipsometry and Raman spectroscopy are used and corroborated by morphological characterization using atomic force microscopy and by electrical characterization using Hall measurements.

2. Synthesis and characterization methods

2.1. Synthesis of gold nanoparticles

In order to fabricate plasmonic hybrids, we developed a plasma sputtering methodology compatible and integrable with the plasma fabrication of silicon thin film solar cells [57] and organic solar cells. Briefly, gold nanoparticles (Au NPs) were deposited by sputtering an Au target using an Ar plasma operated at 14 W and 0.3 Torr at different temperatures in the range 60–600 °C. The temperature was the parameter used to tailor the shape of the nanoparticles [58], whereas the sputtering time determined the Au coverage and Au NPs size.

We also explored solution-approaches based on colloidal Au NPs because sputtering may destroy the graphene structure [59]. Au nanorods of 25 nm × 50 nm size stabilized in CTAB/H_2O purchased by Aldrich with a longitudinal SPR at 575–625 nm and a transverse SPR at 505–555 nm were deposited by dropcasting on graphene. The sample was rinsed in H_2O various times to remove the CTAB.

2.2. Synthesis of graphene

For graphene fabrication, we exploited low pressure (1–4 Torr) CVD from CH_4/H_2 mixtures at a temperature of 900 °C [60]. Graphene was grown on 300 nm Cu/300 nm SiO_2/Si substrates, which were annealed at 900 °C in 1 Torr of H_2 for copper native oxide desorption and copper recrystallization.

After growth, graphene was transferred on other substrates and devices using the polymethyl-methacrylate (PMMA) method [61–63]. Specifically, a layer of PMMA was spin-coated on the surface of graphene, and the copper was then etched in ammonium persulfate (Transene APS-100), yielding a thin PMMA/graphene membrane suspended in the solution. The sample was subsequently rinsed in isopropanol and blown dry with nitrogen to prevent liquid from drying on the graphene surface. Finally, the graphene was transferred under dry conditions onto the target substrate.

2.3. Optical characterization of Au nanoparticles and graphene by spectroscopic ellipsometry

Investigation of the LSPR of Au NPs requires establishing the effect of nanoparticle shape, size and dielectric environment on the resonance energy, broadening and amplitude [64–66].

Spectroscopic ellipsometry (SE) [67] has been demonstrated to be a versatile technique to characterize optically and in real time Au NPs [58,68,69] and graphene layers [60,70]. SE measures the ratio, ρ, of the Fresnel reflection coefficients of the two components of the