Nano Energy 34 (2017) 172–180

Contents lists available at ScienceDirect

Nano Energy

journal homepage: www.elsevier.com/locate/nanoen

Communication

Sub-nanometer planar solar absorber

Dong Liu*, Qiang Li

MIIT Key Laboratory of Thermal Control of Electronic Equipment, School of Energy and Power Engineering, Nanjing University of Science and Technology, Nanjing 210094, China

ARTICLE INFO

Keywords:
Sub-nanometer film
Two-dimensional material
Simple planar structure
Optical absorber
Solar energy

ABSTRACT

Monolayer two-dimensional (2D) materials have promising optical properties and hold potential as solar absorbers for photovoltaic devices. Efficient solar absorbers should have high absorption especially for wavelengths slightly smaller than the semiconductor bandgap wavelength. In this spectrum, solar cells have higher internal quantum efficiency, lower energy loss to lattice vibration, and resultant higher power conversion efficiency. 2D materials have been integrated into nanophotonic structures to enhance their absorption, but fabrication challenges hindered practical applications of these structures. Here, we theoretically and experimentally demonstrated a simple methodology to design efficient 2D material, and more generally, sub-nanometer planar, optical absorbers by placing a sub-nanometer film either onto a transparent layer on a metallic film substrate (structure 1) or between the transparent layer and the substrate (structure 2) with oblique sunlight illumination. We show that there always exist a pair of transparent layer thickness and incident angle for which these structures achieve 100% absorption (broadband and angle-robust absorption for structure 1 and narrowband for structure 2). 92% absorption, which is 2.6 times greater than prior theoretical demonstrations, was achieved in monolayer MoS_2 at 660 nm near its band edge to demonstrate material versatility (even materials with very low losses, which is counter-intuitive to conventional absorber designs). 2D material solar cells were further designed with 4.4% power conversion efficiency, a four-fold increase compared to prior designs. Our proposed methodology is applicable to numerous materials with atomic-layer or sub-nanometer thicknesses and paves the way to efficient sub-nanometer-thick energy harvesting devices with simple planar structures.

1. Introduction

Monolayer two-dimensional (2D) materials have shown unique optical properties. 0.33 nm thick graphene has much broader band absorption than common semiconductors with graphene absorbing 2.3% of the visible light as much as 20 nm thick silicon absorbs [1]. Monolayer MoS_2, representative of 2D transition metal dichalcogenides, has a direct bandgap unlike the bulk material [2]. Black phosphorene, a newly discovered 2D material, has thickness-dependent direct bandgap range from 0.3 to 2 eV [3]. These remarkable properties render 2D materials promising for photovoltaic [3–5], hydrogen production [6–8], and other solar energy applications [9]. However, the efficiencies of 2D material devices are still very low because of their atomic layer thicknesses and the resultant weak light-matter interactions. For example, the power conversion efficiency of the WS_2/MoS_2 bilayer solar cell theoretically designed by Bernardi et al. [10] was approximately only 1%. In addition, simply adding a metallic reflector does not improve the performance of this solar cell.

Many studies have tried to integrate 2D materials into photonic crystals [11–13], plasmonic [14–16] and other nanophotonic structures to achieve high absorption. However, complicated nano-patterning steps are needed to fabricate these structures, hindering their practical applications. Other studies also sought to use simple planar structures to enhance optical absorption in 2D materials [17–20], but the enhancement, or band-width and incident-angle-range tunability was limited. For example the absorption in the MoS_2 monolayer at 660 nm increased to 0.35 by placing it on top of a planar one-dimensional photonic crystal [19]. Recently, Kats et al. [21] demonstrated that optical absorption can be greatly enhanced using a planar structure consisting of an ultrathin absorbing dielectric layer and a metallic substrate with finite optical conductivity. In this structure, the absorbing layer is much thinner than conventional quarter-wavelength-thick anti-reflection coatings because of the “non-trivial” interference between this absorbing layer and the metallic substrate. However, in their work and follow-up works [22–26], the absorbing layers were, although thinner than a quarter wavelength, much thicker

* Corresponding author.
E-mail address: liudong15@njust.edu.cn (D. Liu).

http://dx.doi.org/10.1016/j.nanoen.2017.02.027
Received 12 October 2016; Received in revised form 6 February 2017; Accepted 16 February 2017
Available online 20 February 2017

than an atomically thin layer or a sub-nanometer layer.

Therefore, we are motivated to investigate how to enhance absorption in 2D materials, and more generally, in sub-nanometer films using simple planar structures, and to further increase the power conversion efficiency of 2D material solar cells. Here, we both theoretically and experimentally demonstrate a simple and powerful methodology to achieve near perfect absorption in a sub-nanometer film by placing it either onto a transparent layer on a metallic film substrate or between the transparent layer and the substrate with oblique sunlight illumination. We further demonstrated the material versatility of this methodology and its application in 2D material solar cells.

2. Results and discussion

2.1. Proof-of-concept for the methodology to enhance optical absorption in sub-nanometer planar absorbers

In our previous work [22], we found that the two-dimensional condition, $r(r_{Re}, r_{Im}) = 0$ (r_{Re} and r_{Im} are the real and imaginary component of total reflection coefficient), should be satisfied to achieve perfect absorption as shown in Fig. S1, but the absorbing layer thickness is the only one tunable parameter; and thus, the optical absorption of the structure in Fig. 1a highly depends on the intrinsic material properties of the absorbing layers. In the case with a sub-nanometer absorbing layer, the tunability of the absorbing layer thickness is further limited; thus, achieving high absorption in sub-nanometer layers is even more challenging. In this work, our designed sub-nanometer planar absorbers consist of a sub-nanometer film placed either onto a transparent layer on a metallic film substrate (Fig. 1b) or between the transparent layer and the substrate (Fig. 1c) for the oblique sunlight illumination condition. Methodologically, both structures provide two tunable parameters, the transparent layer thickness and the incident angle; thus, they both can achieve perfect total absorption.

To prove the effectiveness of our proposed methodology, we analyzed the ideal complex refractive indices needed to achieve 100% total absorption for the structures shown in Figs. 1b and 1c. The total reflection coefficient of these four-layer structures is expressed as [27].

$$r = \frac{r_{12} + r_{234} e^{2i\beta_2}}{1 + r_{12} r_{234} e^{2i\beta_2}} \quad (1)$$

where

$$r_{234} = \frac{r_{23} + r_{34} e^{2i\beta_3}}{1 + r_{23} r_{34} e^{2i\beta_3}} \quad (2)$$

In Eqs. 1 and 2, for transverse-electric (TE) polarized light with incident angle θ_1 (results for the transverse-magnetic (TM) polarization are presented at the end of this section)

$$r_{pq} = \frac{m_p \cos(\theta_p) - m_q \cos(\theta_q)}{m_p \cos(\theta_p) + m_q \cos(\theta_q)} \quad (3)$$

where $m_p = n_p + i\kappa_p$ is the complex refractive index of medium p (n_p is the refractive index and κ_p is the extinction coefficient), $\theta_p = \arcsin(m_1 \sin(\theta_1)/m_p)$, $\beta_p = (2\pi d_p/\lambda) m_p \cos(\theta_p)$, and d_p is the thickness of medium p. Setting reflectivity $R = |r|^2$ equal to zero for perfect absorption gives

$$r_{12} + r_{234} e^{2i\beta_2} = 0 \quad (4)$$

Eq. (4) was numerically solved to obtain the ideal complex refractive index of the absorbing dielectric. Without losing generality, alumina (Al_2O_3) was used for the transparent layer with silver (Ag) for the substrate, and Eq. (4) was solved at 500 nm wavelength. The complex refractive indices of Al_2O_3 and Ag used in the calculations were measured using the ellipsometry method (see Methods for details).

In the first step, we investigated the normal incident case to show that near-perfect absorption cannot be achieved in sub-nanometer films using only one tunable parameter (the thickness of the transparent layer). Eq. (4) was solved for various absorbing dielectric thicknesses increasing from 1 to 20 nm with a step of 1 nm and for various Al_2O_3 thicknesses. The calculated ideal complex refractive indices of the absorbing dielectric are shown in Fig. 2a and b for structures shown in the inset.

The results show that all curves are almost linear with each curve referring to specific Al_2O_3 thickness (the linear dependence between the ideal extinction coefficient and refractive index was explained in Park et al. [25]). These curves follow similar trends for the two structures, so we then take Fig. 2a as an example. The red curve shows the ideal m_2 for d_3=0 (without a transparent layer like the structure in Fig. 1a). The structure has 100% absorption if (n_2, κ_2) of the absorbing dielectric is on the curve, but very few materials have such complex refractive indices in the nature (some materials may have the ideal complex refractive indices for limited numbers of wavelengths). Nevertheless, the ideal complex refractive index curves move up with increasing Al_2O_3 thicknesses. Therefore, mathematically the structure can always achieve 100% absorption for a specific pair of (d_2, d_3) if (n_2, κ_2) is above the red curve. We further observed that curve slopes increase with increasing Al_2O_3 thicknesses in Fig. 2a, with slopes nearly unchanged in Fig. 2b. Thus, the absorbing dielectric is thinner in the structure in Fig. 2a than in the structure in Fig. 1a when these two structures resonate at the same wavelength, while structures in Figs. 1a and 2b have absorbing dielectrics with nearly the same thickness to resonate at the same wavelength.

To validate previous analysis, germanium (Ge) was used as a representative absorbing dielectric. The measured complex refractive index of Ge (see Methods for details) is above the red curve as shown in Figs. 2a and 2b. We both experimentally and theoretically characterized absorbers with 13 nm Ge on top of 150 nm Ag (13 nm Ge/Ag),

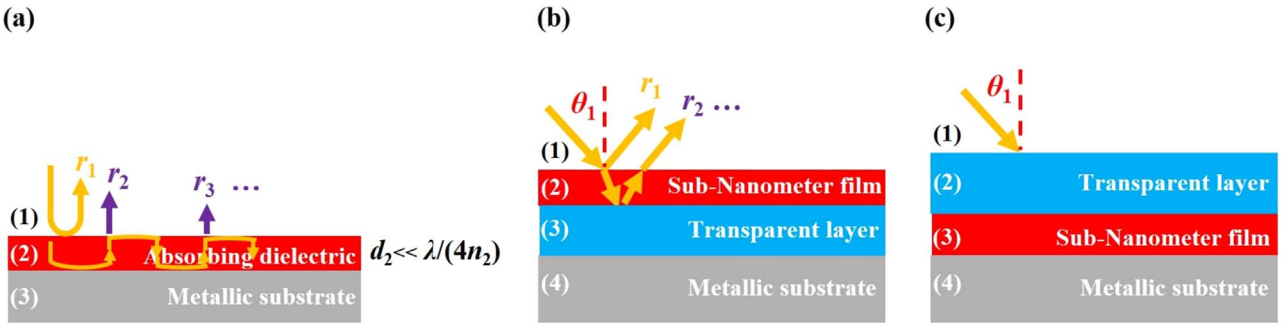

Fig. 1. Illustration of sub-nanometer planar solar absorbers with various structures. (a) Ultrathin planar absorber structure in previous works with an absorbing dielectric layer coated on a metallic substrate with finite optical conductivity. Our designed sub-nanometer planar absorbers consist of a sub-nanometer film placed either (b) onto a transparent layer on a metallic film substrate or (c) between the transparent layer and the substrate for the oblique sunlight illumination condition.