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Broadband radiative energy absorption using a silicon nanowire forest with silver nanoclusters for thermal energy conversion

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ABSTRACT

Heat transfer based on radiative energy absorption and thermal dissipation is important in the design of energy conversion and transfer systems. We studied in the design of radiative energy absorber for efficient energy harvesting and transfer using a nanoscale interface modification technology. We presented that silver nanoclusters assisted silicon nanowires (SiNWs) forest could be feasible for radiative energy absorption in a broadband spectral region. A drastic increase of radiative energy absorption could be obtained in the near infrared wavelength region with accompanying quasi-perfect absorption (higher than 95%) of ultra-violet and visible range of the irradiation spectrum. All of surface manipulations were based on top-down metal-assisted chemical etching feasible under room-temperature conditions to synthesize SiNWs with silver nanoclusters. The spectral absorbance characteristics were elucidated for characteristic lengths of SiNWs, clustering of silver nanoparticles, orientation of the substrate, and single as well as double-sided silver nanoclusters orientations dominate in spectral absorbance characteristics. The results were also presented for guaranteeing efficient solar-thermal converting components with 92.4% solar absorption performance under AM1.5D condition. Surface modification and optimization will be helpful to improve the performances of solar energy conversion systems and various heat transfer systems.

1. Introduction

Solar-thermal energy conversion is one of the most intriguing applications of renewable and sustainable energy supply. The solar-thermal conversion efficiency definitely depends on the radiative solar absorption at a solid interface and subsequent conductive heat transfer through the solid media [1–7]. Especially for efficient solar absorption, modern nanotechnology has suggested a feasible way to drastically increase radiative solar absorption performances [8,9]. Design changes to the interface surface have been attempted by structural modification with respect to 3-dimensional structure formation including meta-materials with novel architectures [10–12] as well as surface roughening [13–17], modulation of the refractive index [18], and reflection control [19]. Through the recent research, it has been confirmed that light scattering and trapping within the manipulated interfacial solid media increase the radiative absorbance, and it could be possible by manipulating exquisite architectures with the characteristic lengths below the wavelength of irradiation.

To meet the requirements for efficient photo-thermal conversion systems, we have to select an appropriate material at first for the solid substrate, which have a high thermal conductivity and feasibility to realize the interfacial structures. Considering the backgrounds and effectiveness, silicon (Si) can be one of the promising elements most responsible for the next generation of sustainable energy-harvesting technology and to power generation due to its intrinsic band-gap property, thermal conductivity, manufacturing feasibility, and abundance on the earth. However, there is room for improvement in Si-based substrates [20–23]. It has almost transparent characteristics under infrared (IR) irradiation due to its intrinsic band-gap properties. Even though most solar-irradiating energy is concentrated in the ultra-violet (UV) and visible (VIS) wavelength spectra, the resulting limitation in the performance of thermal-conversion systems as well as solar-absorbing systems could be resolved by extending the high-absorbance domain to complementary parts of the irradiation spectrum in the IR region [24].

In this study, we present that highly efficient radiative energy absorption in the near-IR (NIR) region can be realized with accompanying quasi-perfect absorbance in the UV–VIS spectrum. The structure- and material-induced light-trapping method, which is

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attributable to a forest of vertically aligned silicon nanowire arrays (SiNWs) in the form of 'black silicon' and silver nanoclusters (Ag-NCs) as a 'plasmonic light confiner', is discussed. We also highlight the role of Ag-NCs as a plasmonic light confiner; the presence of Ag-NCs at the base of the SiNWs. The radiative absorption characteristics are elucidated with respect to the characteristic dimensions of SiNWs, clustering of Ag, and structure of the absorbing system, in terms of the orientation of the substrate and double-side effects. A feasible and simple top-down method that is appropriate for room temperature processing is proposed, and it could be used for reliable mass production of large-areal synthesis. The characteristics and demonstrated strategies on efficient absorption of radiative energy can also widen its application fields towards heat transfer and cooling systems such as heat sinks, thermal spreaders, and heat exchangers [25,26].

2. Materials and methods

2.1. Fabrication method for top-down SiNWs w/Ag clusters

Vertically aligned SiNWs with and without Ag-NCs are synthesized by a metal-assisted chemical etching method (MaCE) [27–29]. A 525-micron-thick silicon substrate is immersed in a solution of 4.8 M HF and 0.005 M $AgNO_3$ to introduce the metallic ions of Ag^+ onto the substrate surface by galvanic displacement [30]. After the reduction of Ag for 1 min, the substrate is etched with an etching solution that is a mixture of 4.8 M HF and 0.1 M H_2O_2. In the solution, the oxidized area of Si just below the reduced silver particles is etched away by hydrofluoric acid, and those partial areas henceforth becomes deeper, forming nanoholes on the substrate. The residual area that does not undergo the etching process consequently forms vertically aligned SiNWs. The height of SiNWs, as a characteristic length of the structure, is principally controlled by changing the etching time of the Si substrates in the solution of HF and H_2O_2. However, the reduced silver particles remain at the bottom of the nanoholes as nanoclusters. These can be dissolved using nitric acid solution. For comparative demonstrations of the effect of Ag-NCs, additional samples with an intentional silver thin layer (40 nm) are fabricated by conformal Ag deposition using an E-beam evaporator on the synthesized SiNWs without Ag-NCs. The SEM images and apparent length of SiNWs (l), that is, the ratio of the total etched depth on both sides of substrate to the initial thickness of the substrate (525 μm), are presented in Table 1 and Fig. 1, respectively. The whole wet-bench procedure is conducted under room temperature and atmospheric pressure conditions.

2.2. Surface characterizations

The surface morphology was characterized by field emission scanning electron microscopy (FE-SEM, JSM-6700F, JEOL), and we confirmed the average height of the SiNWs with image processing. Composition analysis on the nanoclusters and conformally deposited Ag was conducted in the backscattered electron imaging mode, and images presenting the nanoclusters on the bottom of nanoholes between SiNWs were compared with the conformally Ag-deposited samples. The SEM images and apparent length of SiNWs (l) are presented in Fig. 1 and Table 1 in the manuscript, respectively.

2.3. Measurement of spectral absorbance

The spectral absorbance of the prepared samples was evaluated by measuring the spectral reflectance and transmittance. The total hemispherical reflectance and transmittance were measured using a spectrophotometer (Cary5000, Agilent) with an integrating sphere. The spectral range of irradiation was in a range of UV to NIR from 200 to 2200 nm, where effective energy transformation could be feasible with the high spectral irradiance of solar irradiation. The spectral absorbance was consequently evaluated based on the formula $\alpha(\lambda) = 1 - (r(\lambda) + T(\lambda))$, where $\alpha(\lambda)$, $r(\lambda)$, $T(\lambda)$ and λ represent spectral absorbance, spectral reflectance, spectral transmittance, and wavelength of irradiation, respectively.

3. Results and discussion

3.1. Structural light scattering characteristics and SiNWs dimension

Structural light scattering characteristics are principal factors for light absorbance. Fig. 2 presents that absorbance is greatly dependent on the effects of the characteristic dimension of interfacial structures, that is, the height of SiNWs. For efficient light absorption, the characteristic physical length of the superficial structures should catalyze light scattering to increase the optical path length. Vertically aligned SiNWs can play a role as an anti-transmission and anti-reflection layer, causing light scattering that disturbs the straight incidence of irradiating light. This makes the dense forest of SiNWs favorable for enhancing light-trapping performance [14,20,31]. The morphological characteristics of SiNWs are effective in realizing ultrahigh surface area, subwavelength structure, and compensative porosity gradient changing refractive index with depth, which are essential for an effective light-absorbing surface [12,13,16,26]. Based on those merits, we demonstrate that SiNWs in the form of black silicon have near-perfect light-absorption performance, especially in the region of UV to VIS spectra. All of the samples, from 2 to 22 microns in height, have high absorbance, α, namely over 90% from 200- to 1000-nm-wavelength incident light. However, silicon is an inherently IR-transparent material with low light-absorbing characteristics, thus the spectral absorbance in NIR from 1100 to 2200 nm is <40%. As we increased the characteristic length, h, of SiNWs, clear enhancement of absorption was apparent, especially in the NIR region. From the inset of Fig. 2, we can confirm that the increase in the characteristic length induced a definite improvement in absorption in the NIR region. Herein, the normalized efficiency, η, the ratio of the average

Table 1
Fabricated samples of SiNWs accompanying Ag treatments. The column marked 'Sides' shows the surface where SiNWs are synthesized. The apparent length of SiNWs, l, (the ratio of the total etched depth on both sides of the substrate to the initial thickness of the substrate) depends on the etching time during the synthesis of SiNWs and the sides. The initial thickness of the substrate is 525 μm.

Case	SiNWs			Ag	Case	SiNWs			Ag
	Sides	h (μm)	l			Sides	h (μm)	l	
Pl	–	–	–	–	*SN5*	Double	10.1	0.039	–
SN1	Single	2.4	0.005	–	*SN6*	Single	10.1	0.019	Ag-NCs
SN2	Single	7.1	0.014	–	*SN7*	Double	10.1	0.039	Ag-NCs
SN3	Single	10.1	0.019	–	*SN8*	Double	10.1	0.039	40-nm deposition, front
SN4	Single	21.1	0.040	–	*SN9*	Double	10.1	0.039	40-nm deposition, rear