Ultralow Broadband Reflectivity in Black Silicon via Synergy between Hierarchical Texture and Specific-Size Au Nanoparticles

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Antireflectivity is one of the critical factors defining the performance of black silicon in optical, photothermal, photochemical, and optoelectronic applications. The photonic applications under visible light illumination are commonly tuned through surface texturing; however, their promising performance under longer wavelength (>1100 nm) requires either intrinsic lattice modifications or additional substance enhancement. Recent advances in microfabrication and material engineering have enabled in-depth exploration into the synergy between surface texturing and material reinforcement. In this study, black silicon with novel chimney-like hierarchical micro/nanostructures is fabricated via two-step reactive ion etching, and subsequently gold nanoparticles (Au NPs) are loaded on the black silicon by magnetron sputtering deposition. The micro/nanostructures result in synergy effect with the Au NPs on suppression of light reflection. An ultralow broadband reflection (<1%, wavelength 220–2600 nm) is achieved from the Au-loaded black silicon substrates. The impact of Au NPs and structural design such as size, spacing, shape, and etching duration on antireflectivity of black silicon is investigated. This study opens up new avenue for high-efficiency disordered applications of black silicon in the fields of sustainable energy and photonics/microelectronics.

1. Introduction

Black silicon is expected to be a promising material for photovoltaic,[1] photothermal,[2,3] and photoelectrochemical applications[4] due to its remarkably low optical reflectivity. Such behavior is attributed to the presence of light-trapping[5–7] structures such as pores, pillars, cones, and wires.[8,9] These surface structures vary in size and geometry, and they are categorized as micro/nanoscale[10–14] and order/disordered forms.[15,16] Noteworthy, the structures with high aspect ratio[7,17–19] and size matching the wavelength of incident light[6,9,20] exhibit low reflectivity.[9,21] The former parameter extends the optical path of incident light,[7,19] while the latter dimension facilitates coupling between light and materials.[5,23] These effects allow the incident light to get trapped and decayed in the surface structures, giving rise to ultralow reflection at near-ultraviolet (UV) to visible (vis) wavelengths.[24–26] A series of fabrication approaches, including metal-assisted chemical etching,[27,28] electrochemical etching,[29,30] and reactive ion etching (RIE)[9] has been developed to create such surface textures. In particular, RIE enables highly selective etching and produces smooth, vertical profiles, as well as higher structural resolution and density.[31,32] Research into such processes has focused on mask-assisted[33–37] and maskless etching,[38–41] both of which can be effectively used to produce black silicon with micro/nanoscale features. Although a few studies have proposed the combination of micro- and nanostructures, they mainly focused on the suppression of light reflection at the wavelengths below 1100 nm. The antireflectance of black silicon in the near-infrared (NIR) range (over 1100 nm) is still weak due to silicon’s intrinsic bandgap of 1.12 eV.[5]

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Recent advances on microfabrication enabled us to conduct a study on intrinsic element change \cite{42,43} and extrinsic reinforcement \cite{44–46} to decrease reflectivity at NIR wavelengths. For instance, laser irradiation was used to bombard a silicon surface to generate nanostructures. Femtosecond laser treatment with chalcogenides was carried out to dope silicon with sulfur and oxygen, yielding impurity energy levels \cite{20,43,47}. These impurity bands allowed excited electrons to have an indirect bandgap transition by absorption of two NIR photons, providing strong trapping of NIR light \cite{20,48,49}. However, it was difficult to control the distribution of each level and the number of impurities. This doping process is susceptible to thermal annealing and intensity of laser impulses \cite{50} and it incurs high cost and requires significantly high fabrication time \cite{9,48}. Another approach involves collective oscillations of free electrons in metallic nanoparticles (NPs) to excite a localized surface plasmon resonance (LSPR), forcing optical extinction. Extinction capability is determined based on the sum of photons absorbed and scattered. According to Mie’s theory \cite{51,52}, the proportion of absorbed and scattered photons is strongly dependent on particle size and shape. NPs with size significantly smaller than the optical wavelength can interact with light to acquire electron-hole pair excitation and advance an increase in photon energy absorption. Instead, light scattering dominates the optical response on larger particles \cite{53}. The electric field generated due to the electron oscillations can directly confine photons near the NPs, which amplifies the absorption and scattering intensity. Such amplification can sharply be increased upon the isolated NPs \cite{54}. It is thus inferred that optical extinction is able to get reinforcement in smaller and separated NPs. Recently, LSPR induced by the type, shape, and composition of NPs has been exploited in conventional antireflective surfaces \cite{44,55,56}. Noble metallic particles and their alloys show the best activity due to their excellent optical properties stemming up from a high density of easily polarizable free electrons \cite{57–59}. Thus, it has a high potential to overcome the broadband reflection challenge in black silicon via the combination of hierarchical texture and decoration of absorption-dominant particles.

In this study, research on black silicon fabricated via a two-step RIE process was reported. This procedure can be successfully used to fabricate a hierarchical 3D texture comprising micrometer hollow cylinders and nanopores. The microstructures have advantages of the order distribution as well as smooth and vertical sidewalls. The nanopores randomly distributed throughout the top and bottom of the hollow cylinders, lead to the increase in the structural density and aspect ratio. Such a design allows multiple wavelengths of incident light to be reflected along the sidewall in the depth direction. The light gets diffusely reflected at the bottom of the structure, which results in quadric reflections and stronger light–material coupling. This 3D structure enlarges the loading area of Au film and diversifies its thickness. Thermal-annealing treatment was applied to form NPs with a size gradient below 20 nm, on which light absorption becomes the dominant extinction factor. Synergy effect was observed to occur through the interaction of light-propagation in the hierarchical texture and the energy decay caused by nonpropagating excitation of NPs. Finally, broadband ultralow reflectivity of less than 1.0% was observed in the wavelength range from 200 to 2600 nm.

2. Hierarchical Design and Antireflectivity

Various emerging microfabrication technologies allow the machining of the surface texture of black silicon from nanometer \cite{57} to micrometer scale \cite{16,60,61}. A variety of black silicon samples have been created by optimizing the surface structures \cite{6,10–12,18,60} however, the ultimate objective is to fabricate a geometry that provides strong light trapping performance. The light trapping is manipulated through extension of optical path caused by multiple reflections and refraction, as well as energy decay through the light–silicon coupling \cite{7,22,23}. For the nanostructures with size much smaller than the wavelength, reflection is suppressed through a sudden change in refraction. In microstructures with the size comparable to the wavelength; multiple internal reflections accompanied with light–material coupling causes light trapping. Nowadays, the suppression of light reflection in hybrid structures has attracted significant attention \cite{6,10,12,61}. The configuration of micro/nanoscale hybrid structures is a prospective approach to further decrease the reflectivity of black silicon. It is worth assuming that perpendicular or inward sloping sidewalls help directing light along the depth direction, which inspired us to explore the antireflective properties of hierarchical design that integrates vertical micrometer-sized structures with nanometric decorations.

Figure 1 shows schematic illustration of the fabrication process. The process involves four significant steps as follows: 1) mask-assisted etching (Bosch RIE) to machine hollow cylinders; 2) cleaning the residual photoresist; 3) maskless RIE (SF6/O2) to decorate top and bottom surface with nanopores; and 4) deposition of Au NPs via magnetron sputtering and subsequent thermal annealing. This research focuses on the structural design related to shape, distribution, depth, and exploration of the optimal configuration of Au NPs required to produce ultralow reflection.

Figures 2a,b shows tilted and top view scanning electron microscopy (SEM) images of the silicon surface textured with

![Figure 1. Schematic illustration of the fabrication process.](image-url)
maskless RIE (SF$_6$/O$_2$). These obtained nanopores have an average depth of 6.5 µm and a diameter of <450 nm. The surface texture can be machined from microporous to nanoporous with the increase in the SF$_6$/O$_2$ gas flow ratio.[41] In contrast to reported studies, the gas flow ratio of SF$_6$ to O$_2$ used herein was 36:47. The results of our previous research revealed that abundant O* radicals caused the rapid formation of a SiO$_x$ layer on the sidewalls during etching,[62] leading to intense selective etching downward, and ultimately, the formation of nanopores with high aspect ratio. Such nanopores could evolve into needle-like structures with the continuation of etching process. Figure S1 of the Supporting Information shows SEM images of black silicon with nanoporous needle-like structure with etching time increasing from 5 to 40 min and their corresponding reflection spectra. Maskless RIE with 5 min duration was selected for subsequent fabrication of hierarchical textures.

The smooth and vertical sidewalls guide incoming light toward the bottom of the structure. Therefore, it can be expected that a hierarchical design combining the micro- and nanostructures could further decrease reflection. Figure 2d illustrates the tilted view SEM image of the black silicon with nanopores on the top and bottom of the chimney arrays.

In addition to the micro/nanofabrication processes, optical measurements were recorded in different reflection modes to investigate the contribution of different structural designs on antireflectivity. First, a polished planar silicon wafer was used as a reference to evaluate antireflectivity of the textured samples. Figure 2e demonstrates that both the silicon samples with micro- and nanostructures, respectively, show lower reflectance than the planar silicon in the visible range, and the nanopore black silicon shows the lowest reflectance. The reflectance of the black silicon with hierarchical structures (chimney-like black silicon) is lower than that of the black silicon with only nanopores in the size range of 220 to 1100 nm, while they show similar reflective behavior at wavelengths greater than 1100 nm. Specular and diffuse reflectance spectra were recorded, respectively, to analyze the effects of the antireflectivity on the textured surface. Figure 2f shows that both samples with nanopores have nearly zero reflection from 220 to 2600 nm, while the reflectance of the sample with only chimney array structure is 40% less than the reflectance in the UV–vis range and less by 15% at other wavelengths. Figure 2g illustrates that diffuse reflection is observed in all cases, which indicates diffuse reflection is the dominant...
behavior on all textured silicon samples. The periodic fluctuation observed in the reflection spectra from the chimney array sample refers to porous silicon-based photonic crystal.[63] X-ray photoelectron spectroscopy (XPS) (Figure 2h) was used to analyze elemental existence of the planar and textured surfaces. The results show that silicon, carbon, oxygen, and fluorine are the primary components making up these surfaces. The existence of O\textsubscript{2} in maskless RIE resulted in an increase in the concentration of elemental oxygen on the nanoporous surface. The use of O\textsubscript{2} in the pretreatment step of the Bosch process also introduced elemental oxygen onto the surface of the chimney array. Similar concentrations of elemental oxygen were observed from the samples with nanoporous and hierarchical structures, indicating identical compositions for both of them. Figure S2 of the Supporting Information shows the X-ray photoelectron spectra of the chimney-like black silicon treated by buffered oxide etching (BOE) for 2 min. Figure S3 of the Supporting Information shows the related reflectance spectra, which reveal that there was no obvious difference in reflectance between the original black silicon and the BOE-treated one. Moreover, the energy dispersive spectrometry was employed to investigate the elemental compositions before and after the BOE treatment, as illustrated in Figures S4–S7 of the Supporting Information. A slight decrease of O\textsubscript{2} was observed after the treatment, but it still existed. It might be attributed to the natural growth of oxides during the testing. Therefore, the antireflectivity difference might have been originated from physical configuration of the hierarchical texture rather than lattice modifications. Figure 2i displays the photograph of the textured silicon with only micrometer chimneys structure. Figure 2j shows the photographs of the black silicon with only nanoporous structure (left) and micrometer chimney structure with nanopore decorations (right).

To better understand the effect of the hierarchical texture on antireflectivity, the microchimney structures were tuned with respect to various diameter, spacing, and height by the Bosch process. Then, maskless RIE (SF\textsubscript{6}/O\textsubscript{2}) process was performed on these chimney-like textures for 5 min. Figure 3 illustrates the SEM images of the chimney-like silicon and chimney-like black silicon samples with varied diameter, spacing, and height. Column (a) SEM images illustrate the tilted views of sample #3 with diameter, spacing, and height of 10, 2, and 18 µm (Bosch, left), respectively, and subsequent maskless RIE treatment with SF\textsubscript{6}/O\textsubscript{2} (right). The reflectance of samples #2 and #3 at the UV–vis range is lower than that of sample #1 because the larger diameter increases the pore proportion, allowing more light to enter the structure rather than coming out directly via specular reflection. However, samples #1 and #2 exhibit lower reflectance at IR wavelengths. The nanopore decoration brings about an identical decrease in reflection at UV–vis wavelengths to less than 1%. Column (b) illustrates the tilted SEM views

Figure 3. SEM images and measured reflection spectra of the chimney-like silicon surface after mask-assisted etching (tilted view, left) and the chimney-like black silicon surface after the follow-up maskless etching (tilted view, right). All scale bars are 20 µm. Notably, the samples treated with only Bosch etching are named as chimney-like silicon, while they are named as chimney-like black silicon after RIE treatment with SF\textsubscript{6}/O\textsubscript{2} to form nanopore decoration. Column a) SEM images and measured reflection spectra of the samples with diameter variation of 5, 8, and 10 µm. These samples have suffix serial number of 1, 2, 3, respectively. Column b) SEM images and measured reflection spectra of the samples with spacing variation of 2, 4, and 8 µm. These samples have suffix serial number of 2, 4, 5, respectively. Column c) SEM images and measured reflection spectra of the samples with height variation of 10, 22, and 31 µm. Notably, the chimney-like silicon No2 was selected to investigate the effect of height on the reflectance.
of sample #4 with diameter, spacing, and height of 10, 4, and 18 µm (Bosch, left), respectively, and subsequent maskless RIE treatment with SF₆/O₂ (right). The reflection spectra reveal that the smaller spacing indicates higher structural density, which is helpful to trap visible light, but does not work in NIR light. These black silicon samples with nanopore decoration show high antireflection capability in the UV–vis light range, which is still weak in infrared light. As shown in Column (c), the effect of height difference was also studied. The structures with height 10, 22, and 31 µm were used to study the antireflectivity, respectively. As expected, the higher sidewall allows more reflection of incident light along the depth direction, providing lower reflectance from 220 to ≈1100 nm. Subsequent decoration of the nanopore further reduces reflection, except at IR wavelengths. Thus, structural density and aspect ratio are both prominent in the hierarchical design, which is helpful for incoming light and extension of propagating path. This type of behavior also occurs in other micro/nanostructures as well, as illustrated in Figure S8 of the Supporting Information. SEM images show micrometer-sized honeycomb, square, and cylindrical arrays with the same nanopore surface.

The low reflection at UV–vis wavelength range is ascribed to the structural design rather than the bandgap modification. The configuration of microstructured silicon slightly influences the IR reflection due to the silicon bandgap energy of 1.12 eV. However, decrease in reflectance from black silicon beyond 1100 nm remains challenging. To address this issue, other researchers have proposed intrinsic bandgap regulation and external field-assisted enhancement (i.e., sulfur doping with femtosecond laser irradiation), and metallic particle deposition. The reduced reflection with the former method depends on the impurity formed in silicon and dark spot defects in the bandgap. The latter is ascribed to LSPR. Both approaches have attracted attention. However, the distribution and density of impurities are difficult to control precisely. Defects caused by random laser-induced etching are also a problem. In contrast to laser-induced treatment, the LSPR effect generated by metallic particles is primarily determined by the particle size, shape, and spacing, which are easy to control. Thus, apart from the structural design, the use of LSPR in black silicon with hierarchical texture is of great importance. The chimney-like black silicon sample #2 was used to study synergy effect between the hierarchical texture and Au NPs-induced LSPR.

3. Synergy Effect between Hierarchical Texture and Au NP-Induced LSPR

To identify an optimized design capable of providing hierarchical texture and containing LSPR particles, the mechanism governing antireflectivity in black silicon was analyzed. First, light propagation plays an important role in studying antireflection in black silicon with different textures. On the surface texture of the hollow cylinder arrays, the incident light is likely to undergo specular reflection from the flat top area, leading to undesirable reflection loss. The nanopores suppress the reflection behavior if they have a textured surface. Sharp configurations, together with uneven sidewalls, provide many propagation pathways for reflected light. Still, such nanopores have limited “windows” for long light wavelengths to enter the structure, which weakens reflection suppression. Nonetheless, mesopores and spacing between hollow cylinders with larger feature sizes provide access for optical waves. Their vertical walls allow incident light to be reflected in the depth direction, giving rise to more opportunities for light–material coupling. It enables that each surface texture acquires its own merits. Therefore, the hierarchical structure takes advantages of both micro- and nanostructures. In contrast to micro- or nanostructure, the hierarchical surface texture has large windows and vertical wells, leading to suppressed specular reflection and increased diffuse reflection. Figure 4a illustrates that such hybrid texture design reduces specular reflection loss and facilitates the light–material coupling effect while extending the optical path length, resulting in ultralow reflection below 1100 nm.

Second, metallic NP-induced LSPR is the key to address the challenge of high reflection above 1100 nm. The electric field of the optical waves can cover the metallic particles with a size much smaller than the wavelength. Such electric field polarizes conducting electrons in the metal lattice. When the frequency of incident light matches that of oscillating valence electrons, the incident light can stimulate a collective resonance oscillation of valence electrons in the solid state, yielding electric dipoles. The restoring force between the electric dipoles impedes electron displacement to form plasmon oscillations driven by resonant light waves. The wavelengths resonant with these oscillations can only excite the LSPR. The photon energy injected into the plasmon oscillation produces attenuation through either radiative scattering or nonradiative path. Radiative decay stems from photon emission caused
by electron–hole recombination\textsuperscript{[70]} and electron–phonon scattering,\textsuperscript{[71]} while nonradiative recombination causes the conversion of photons into heat.\textsuperscript{[72]} The relative weight between these two decay determines the relative contributions from scattering and absorption.\textsuperscript{[73]} This balance changes with NP size and tends to undergo radiative decay with the increase in size. According to the Mie theory regarding absorption and scattering in isolated Au NPs,\textsuperscript{[52,53]} the two effects are comparable when the size of the NPs is \(\approx 50\) nm, and absorption prevails when the size is less than \(50\) nm. For Au NPs with size of \(\approx 20\) nm, scattering phenomena account for only a few percent of the light attenuation.\textsuperscript{[69]} In particular, the light-to-heat conversion efficiency of these particles with the size above \(2\) nm can reach \(100\%\).\textsuperscript{[74]} Therefore, isolated Au NPs with size less than \(20\) nm were considered to be the best candidate for transferring photon energy to the black silicon. Figure 4b shows the absorption-dominant Au NPs with size smaller than \(50\) nm as well as the transit of thermal energy and hot carriers at the interface between a particle with LSPR and bulk silicon. The above mentioned investigation inspired us to explore the optimal configuration of Au NPs to further decrease reflectivity above \(1100\) nm through thermal-dissipation dominant energy decay. The advantages of hierarchical structures and specific Au NPs to reduce reflectance from black silicon were investigated herein for the first time.

Predictably, a synergistic effect could be induced due to light propagating in hierarchical structures and decaying in specific LSPR particles. Figure 4c shows the possible mechanism of such synergistic trapping of the incident light. Light incident on the top surface is less likely to experience specular reflection due to metallic particle-induced photon absorption and scattering. The portion of light incident on the sidewalls gets attenuated through plasmon oscillations on NPs and silicon absorption. Reflected or scattered light might be weakened again on the other sidewalls through interaction with their surface metallic particles. The nanopores and NPs at the bottom of the well can collect remnant reflected and scattered light. Based on the above-mentioned analysis, a broadband ultralow reflectivity is in prospect to achieve. A systematic investigation of synergy effect between the hierarchical texture and Au NP-induced LSPR is crucial to upgrade black silicon antireflectance.

4. Antireflection on Hierarchical Texture and Au NPs

Figure 5a shows SEM image of the hierarchical structure with Au NPs formed by thermal annealing of gold film with thickness of \(\approx 4\) nm. Figure 5b exhibits the existence of NPs on upper pores, chimney sidewall, and bottom pores. The Au NPs in these regions have diverse sizes, spacing, and concentration; however, they have a similar nanospheroid shape. Their dimension is distributed from 5 to \(20\) nm, and the particles at the bottom are smaller than those in the upper region. The 3D structure causes sputtered Au film to have a gradient thickness. Therefore, the formed NPs show size difference after annealing, leading to an LSPR particle size gradient on the hierarchical surface. All the Au NPs separate from each other and the spacing between adjacent particles is comparable to their size. The Au NPs can be attached to the silicon surface for a long time due to the formation of metal–semiconductor bonds during the thermal annealing, as shown in Figure S9 of the Supporting Information. Moreover, it also assists the hotspot formation\textsuperscript{[75]} and maximizes the number of particles. Such widespread isolated Au NPs lead to the increase in the occurrence of LSPR and also the local-field trapping large amount of light.
photons. Figure 5c demonstrates that spectrum of textured silicon presents a noticeable decrease of reflection, which is aided by the NPs deposited from 4 nm gold film. Instead, the black silicon with a hierarchical structure provides overall reflection below 1.0% in the wavelength range from 220 to 2600 nm. There are two possible reasons for the high reflection of wavelengths above 1100 nm on the nanopore surface. First, there are limited windows to take the incidence of IR light, leading to inevitable reflection loss. Second, a smaller amount of large-sized particles leads to lower LSPR intensity. The inset image shows that the average reflectance from chimney-like black silicon decorated with NPs is ~0.5% at above 1100 nm, and the maximum reflectance of 0.6% occurs at 1250 nm. Figure S10 of the Supporting Information shows reflection from Au NPs formed from 4 nm gold film on planar silicon as a reference. The transmittance spectra exhibit that the combination of hierarchical texture and Au NPs offers much lower broadband transmittance than the nanopore surface. Figure 5d exhibits that the overall transmittance is less than 0.5% from 220 to 2600 nm. It can be deduced that the energy decay occurring at the silicon/gold NP interface suppresses reflection of IR light, and the photons are most likely converted to heat. Thus, the hierarchical texture and Au NPs are responsible for the low broadband antireflectivity.

The Au films with thickness of 2, 4, 6, 8, and 10 nm were fabricated to investigate the effect of particle size on reflection suppression. Thermal annealing at 500 °C for 1 h was carried out in all cases to form the NPs. Notably, the samples with NPs formed with 8 and 10 nm gold film are out of reflectance measurement due to the appearance of an observable golden color on the surface. Figure 6a shows that the black silicon decorated with NPs formed with 4 nm film exhibits the lowest reflectance. By contrast, the 6 nm film-formed particles provide much lower reflectance than that of the 2 nm case. The fewer particles in the 2 nm case may cause relatively weak LSPR intensity. Figure S11 of the Supporting Information illustrates that the size of particles in the 6 nm case becomes larger than others, leading to more light scattering from these particles rather than absorption. As expected, the related reflectance spectra from the nanopore surface with different Au NP sizes also supports such an explanation, as shown in Figure S12 of the Supporting Information. Figure 6b illustrates the measured reflection spectra of hierarchical designs with different micrometer structures (i.e., honeycomb, triangle, square, and cylinder) and the Au NPs formed through 4 nm Au film. The reflectance is universally lower than 1% from 220 to 2600 nm. It is evident that the optimized particle size is lower than 20 nm and can be created by 4 nm film.

5. Conclusion

In this study, mask-assisted RIE (Bosch process) was used to develop various chimney-like microstructures with smooth, vertical sidewalls. Then nanostructures with high aspect ratio and structural density were decorated on the chimney-like structure by maskless etching (SF6 + O2). These methods enabled an in-depth exploration of the hierarchical texture with micro/nanostructures and their antireflection properties. The fabricated hierarchical surface increased the length of reflection of incident light and diversified the propagating paths. The chimney-like black silicon substrate is beneficial to accommodate a large amount of LSPR particles, in which their size shows a gradient distribution from the top surface to bottom ends. The hierarchical hybrid structures exhibited a strong synergistic effect with Au NPs-induced LSPR to boost the antireflectivity of black silicon. For the optimized Au NPs (<20 nm), an ultralow broadband reflection of lower than 1% was achieved in the wavelength range from 220 to 2600 nm. The research results lay down new perspective for future studies of light manipulation and conversion in optoelectronic,[17,76–78] photocatalytic,[79,80] and photothermal[81] applications, such as Schottky photodetectors,[78,82] light-dependent disinfection,[83] liquid motion,[84] and photothermal-based antibacterial applications.[85,86]

6. Experimental Section

Fabrication of Chimney-Like Black Silicon with Hierarchical Texture and Au NPs: Polished (100)-oriented p-type silicon wafers with resistivity of 1–20 Ω cm and thickness of 500 ± 10 μm thickness were used to fabricate the hierarchical texture. All wafers were treated in a BOE solution at room temperature, followed by acetone, isopropanol, and deionized (DI) water to remove the natural oxide, residuals, and organic contamination.

Patterned masks were prepared by applying a positive photoresist (MICROPOSIT S1813, Germany) via photolithography (EVG 620, Austria). The diameter and spacing were defined by the mask design so that micrometer-sized profiles could be produced. Mask-assisted texturing was conducted by “Bosch etching” (SF6 + C4F8)9, while RIE with a mixture of SF6 and O2 was used for maskless engraving. Both steps of RIE were conducted in an RIE cluster (Plasma Pro100 Cluster,
Oxford Instruments, UK). Detailed etching parameters are listed in Tables S1 and S2 of the Supporting Information. After 100 to 350 Bosch loops, the samples were sonicated in acetone, isopropanol, and DI water to remove residual photoresist, followed by drying with nitrogen flow. The duration of the second etching was varied from 5 to 20 min. Au film was deposited at room temperature by DC sputtering (AJA International, USA). This sensor-based digital system allows precise control over the film thickness. Annealing was performed in a thermal furnace at 500 °C for 1 h in nitrogen to granulate the film.

Characterization of the Chimney-Like Black Silicon with Hierarchical Texture and Au NPs: The morphology of the surface texture was characterized by SEM (Hitachi UHR FE-SEM SU8230, Japan). The reflectance and transmittance of the samples were measured using a UV–vis–NIR spectrophotometer (Shimadzu UV 3600 plus, Japan). BaSO4 was used as a reference for reflectance measurements from the structured surface; however, an aluminum mirror was used as a reference for reflectance measurements from planar silicon. Total reflection, diffuse reflection, and mirror reflection measurements were recorded using an integrating sphere. XPS was performed (samples exposed in air) using an electron spectrometer (ESCALAB 250, Thermo Scientific Corporation).

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of interest
The authors declare no conflict of interest.

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