Enhancing the Interaction between High-Refractive Index Nanoparticles and Gold Film Substrates Based on Oblique Incidence Excitation

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ABSTRACT: We investigate the coupling of dipole resonances induced in a heteromaterial system composed of a high-refractive-index nanoparticle and a highly reflective substrate. A broad scattering signal and strong electric near-field enhancement in the near-infrared region are generated by a hybrid Si nanoparticle on a gold-film system under oblique illumination. Dark-field microscopy investigations of the scattering signal measurement reveal the resonance shifts of the dipole mode of silicon nanoparticles on gold films. Further, the scattering signal is enhanced for p-polarized illumination in the near-infrared region. The results indicate that the coupling of Si nanoparticles on a gold-film system facilitates a possible application for both surface-enhanced fluorescence and surface-enhanced Raman scattering.

INTRODUCTION

Electromagnetic scattering from nanostructures made of high-refractive-index materials has received considerable attention in the field of nanophotonics toward the control and manipulation of light in the near and far fields.1,2 Such nanostructures afford a simple approach to generate magnetic resonances at optical frequencies in addition to dominant electric resonant modes in metal plasmonic materials.1 It is well known from Mie theory that light incident on high-refractive-index dielectric nanoparticles induces a strong magnetic dipole (MD) and electric dipole (ED) in the nanoparticles. The frequency of the dipole resonances are dependent on the particle sizes3,4,9,13 and shapes.9 In this context, it has been recently demonstrated that MDs parallel to the magnetic field of light incident on silicon nanoparticles can generate a ring-shaped electric field distribution.12,15,16 The most common example of MD radiation is the induction of electromagnetic waves by excited metal split-ring resonators.14 The MDs of high-refractive-index particles provide convenient magnetic scattering, which can be utilized for applications such as nanoantennas, metamaterials,15 and metasurfaces. Although the near-field enhancement in metallic nanostructures utilized in plasmonics is stronger than that with high-refractive-index nanostructures,16 the far-field scattering signal is fairly strong for high-refractive-index materials. In comparison with metal nanostructures,16−25 the primary advantage of high-refractive-index materials is reduced heat generation because of the low-loss characteristic26 of such materials, which aids in increasing the reliable response of the target molecules with reduced heating and quenching in surface-enhanced spectroscopies.

The scattering patterns of high-refractive-index nanoparticles have been investigated with regard to coupling between EDs and MDs toward yielding single-directional scattering.1,6,9,12,20,27−29 The silicon asymmetric dimers have been demonstrated to enhance and guide forward scattering in both theory and experiment.30,31 In addition, Janus dimers with two different materials, such as dimers composed of gold and silicon, have also been observed to enhance forward scattering.12 However, it is difficult to fabricate such asymmetric dimers and heterodimers, and, further, the influence of the substrates on which the particles are deposited has not thus far been considered. In fact, the resonance of nanostructures will shift as a result of the effect of the substrate with different incident polarizations.32 In this regard, several recent studies have focused on the coupling effect of high-refractive-index nanoparticles with various films deposited on substrates. For instance, silicon nanoparticles placed in air, on glass, on silicon, and on a perfect electric conductor (PEC) yield different scattering performances.33 The influence of substrates with high reflectivity is significant because of the additional dipole resonance induced by the mirror effect.34 As regards structures comprising high-refractive-index nanoparticles on metal substrates, silicon nanoparticles on silver substrates have chiefly formed the focus of many studies.7 However, the different modes of dipoles interacting with metal films have not thus far been analyzed in detail. Previous studies have mainly focused on in-plane EDs under normal light
incidence. With dark-field microscopy measurements under oblique incidence, the reduction in the strength of the in-plane EDs becomes significant. Therefore, scattering from Si nanoparticles under oblique excitation can provide strong electric near-field enhancement generated by out-of-plane EDs in the small gap between the nanoparticles and the metal films.

In this study, we utilize the interaction of silicon nanoparticles with metal films under oblique excitation to enhance the electric near-field. We systematically describe the highly localized electric-field enhancements generated by strong dipole resonances between the silicon nanoparticles and the metal film. As per our finite element method (FEM) calculation results, the dipole resonances coupling between silicon nanoparticles and metal films are dependent on the dielectric constants of the films. Moreover, the electric-field enhancement at the interface between the nanoparticles and the films is affected by the direction of the dipole. In our experiments, we acquire the scattering spectra and images of scattering with dark-field microscopy under both p-polarized (p-pol) and s-polarized (s-pol) excitations to probe the existence of dipole resonances. We also discuss the scattering cross-section spectra of silicon nanoparticles placed on a gold film at different angles of incidence in both p-pol and s-pol illumination.

Figure 1. Schematic of the physical system considered in the FEM simulations in this study. Silicon nanoparticles are placed on a glass substrate on which a gold thin film is deposited, and this system is illuminated by a polarized light wave.

Figure 2. Simulation spectra of scattering cross-section for a single silicon spherical nanoparticle on different substrates: free space (black), glass (blue), PEC (green), 40 nm silver film (orange), and 40 nm gold film (red). (a) Scattering cross-section spectra for p-pol incident light. (b) Scattering cross-section spectra for s-pol incident light. The radius of the nanoparticle is 65 nm in all cases, with the incident angle being 70°. Dashed lines indicate the ED perpendicular to the substrate (ED⊥).
In our study, light scattering from spherical Si nanoparticles is based on the Mie scattering theory. In addition, the scattering signal can be decomposed into multipolar contributions as follows:

$$C_{\text{sc}} = \frac{2\pi}{k^2} \sum_{n=1}^{\infty} (2n + 1)(a_n|\mathbf{E}|^2 + b_n|\mathbf{H}|^2)$$

Here, $k$ represents the wave vector, and $a_n$ and $b_n$ represent the scattering coefficients of the electric and magnetic multipolar contributions, respectively. For nanoparticles with sizes considerably smaller than the incident wavelength, only the first two terms are generally relevant. In our simulation study, it is assumed that the nanoparticles are made of crystalline silicon, and the ED and MD resonances are controlled in the visible region by varying the particle sizes. To acquire the scattering spectra of a single nanoparticle on the substrate, we performed numerical simulations using the commercial software package COMSOL Multiphysics v4.3b in the frequency domain. The simulation is separated into two procedures to determine the change of energy on the particle surface. First, the background of the light source is calculated without the presence of the silicon nanoparticle. Once the background is placed in the module, and the calculated nanoparticle is placed in the module, and the calculated background field is used to calculate the scattering field. After completion of the two procedures, the scattering cross-sections are defined by integrating the change of energy on the nanoparticle surface. In the simulations, the silicon nanoparticles placed on substrates were excited by p-pol and s-pol light (Figure 1), with the angle of incidence being set at 70°.

The scattering spectra of silicon nanoparticles with radius $r$ (=65 nm) on different materials are presented in Figure 2, including 40 nm thick gold, silver, and PEC films, all of which got deposited on a glass substrate (refractive index = 1.52). Those spectra indicate the distinct influence of the thin film on the scattering. The results indicate that the primary ED and MD resonances appear at 470 and 560 nm, respectively, on all substrates. Even for different polarizations, the resonance wavelengths of ED and MD do not shift. However, with the oblique incidence, the ED corresponding to the out-of-plane field component (ED⊥) is induced at around 500 nm due to resonance between the nanoparticle and the PEC. As the resonance wavelength of the MD is close to that of the ED, the total scattering cross-section significantly increases. From Figure 2a, it is evident that the contribution of ED⊥ from Si nanoparticles coupling with PEC and metals is a broadband signal. Despite the superposition of individual scattering signals, the MD can be observed clearly. Moreover, the MD perpendicular to the substrate (MD⊥) couples with metal films for s-pol illumination. In Figure 2b, the resonance wavelength of MD⊥ appears at 540 nm with sharper bandwidths.

To verify whether silicon nanoparticles could induce stronger scattering cross-sections of ED⊥ on a substrate with high reflectivity than on dielectric substrates, we particularly studied the cases of silver and gold thin films. For the case of a silicon nanoparticle on a silver thin film, the resonance of ED⊥ shifts to ~640 nm and generates broad scattering spectra. On comparing the spectra of silicon nanoparticles on silver and gold, we noted that ED⊥ on the gold thin film appears at a longer wavelength (Figure 2a) because the plasma frequency of gold is smaller than that of silver. The result shows that ED⊥ arises due to the strong interaction between the Si nanoparticles and the metal films.

Moreover, except for ED⊥, the other resonance peaks do not shift when the metallic thin films are changed. The resonance of ED⊥ is affected not only by the polarization of incident light but also by the substrate material.
RESULTS AND DISCUSSION

As shown in Figure 3, three resonant wavelengths are observed clearly under both p-pol and s-pol illuminations for the case of a silicon nanoparticle on a gold thin film. In Figure 3a,d, the direction of the ED is aligned with the incident electric field, and the resonance wavelength is 470 nm. Similarly, the MD (560 nm) parallel to the incident magnetic field affords a ring-shaped distribution of the normalized electric field in the silicon nanoparticle. Importantly, on comparing the distributions of the electric fields at 700 nm between p-pol and s-pol, we noted the evidently distinct intensity difference at the interface between the silicon nanoparticle and the gold thin film. In Figure 3c, the electric fields perpendicular to the substrate correspond to ED⊥, and the electric field is strongly localized in the lower hemisphere of the nanoparticle.

Table 1 lists the intensity of the electric field at the gap between the silicon nanoparticle and the gold thin film for each resonance for both p-pol and s-pol illuminations. The intensity of the localized electric field is dependent on the dipole modes, reflectivity of the gold thin film, and polarization. As shown in Figure 3b, the localized electric field is enhanced in the gap. Because the MD parallel to the substrate induces an MD in the gold thin film in the same direction, an inverse MD is simultaneously induced in the interface. The induced MD generates a ring-shaped electric field and increases the intensity of the electric field in the gap. In contrast, the near-field of the normalized electric field at 700 nm is strongest for p-pol illumination because of the influence of the direction of the ED. In addition, because of the small distance between the Si nanoparticle and the gold film (Figure 3c), there is strong ED⊥ coupling with the gold film. However, there is no localized electric field enhancement for the case of the Si nanoparticle under s-pol illumination (Figure 3f).

Next, in the experimental phase of our study, we deposited a 70 nm thick gold film on indium tin oxide glass by means of electron beam evaporation. Silicon nanoparticles (Nanostructured & Amorphous Materials, Inc.) were mixed in deionized water and spin-coated onto the gold films. The scattering signal was acquired with the use of a customized microscope (modified Olympus BX51) equipped with confocal apertures, a monochromator (Andor SR303i), and an EMCCD (Andor iXon 888). The scattering spectra of nanoparticles were excited by white light from a 150 W xenon lamp and collected by the objective lens. Spectrum normalization was performed as per the following expression

$$\frac{S_{NP-film} - S_{film}}{S_{std}}$$

Here, $S_{NP-film}$ represents the scattering signal obtained from the area containing only one nanoparticle, and $S_{film}$ represents the background signal obtained from the area without the nano-
particle on the same sample. Further, $S_{nd}$ represents the reference spectrum of the light source as obtained from the surface of a reflectance standard. In the measurements, the excitation light was partially covered to generate the uni-azimuthal angle ($\sim 5^\circ$) excitation condition because the internal illumination built into the microscope when used under dark-field illumination was ring-shaped. A single Si nanoparticle placed on a gold film was illuminated at oblique angles ($64^\circ - 74^\circ$) with respect to the normal direction of the substrate surface. A polarizer was placed in front of the excitation ring to vary the incident polarization between p- and s-pol. The scattering signal was collected by a high-numerical-aperture objective (Olympus MPLFLN 100× BDP, NA = 0.9, WD = 1 mm).

To verify the presence of coupling between the ED$_\perp$ of the silicon nanoparticle and the gold thin film, we measured the scattering spectra for three different nanoparticle diameters (120, 150, and 195 nm), as shown in Figure 4. The resonance wavelengths exhibit a red shift with increasing particle diameter, which can be convenient for tuning the enhancement of the localized electric field at the desired wavelength. Importantly, the scattering spectra of the simulations and experiments exhibit a close agreement.

The dark-field color images were utilized to verify the presence of the polarization-dependent scattering signals. The scanning electron microscope (SEM) image of the 150 nm diameter Si nanoparticle is shown in Figure 5a. When the silicon nanoparticle is excited with p-pol light, it appears orange-colored due to the enhancement of the scattering contributed by ED$_\perp$ (Figure 5b).

In contrast, the dark-field microscopy image for s-pol illumination appears yellowish because the scattering signal is primarily due to MD$_\perp$ at shorter wavelengths (Figure 5c). Figure 5d,e shows the dark-field images of the Si nanoparticle excited with a 675 nm laser at an incident angle of 70°. The scattering images were collected by a long-focal-length objective (Olympus LMPFLN 100× BD, NA = 0.8, WD = 3.3 mm) and a digital camera (Canon EOS 750D). The intensity of scattering at 675 nm for p-pol is stronger than that for s-pol.

The scattering cross-section spectra of the Si nanoparticle ($r = 75$ nm) on gold thin film (70 nm thickness) at different incidence angles are shown in Figure 6a,b for different polarizations. At small incident angles ($0^\circ - 20^\circ$), there are two resonance peaks corresponding to the in-plane ED (ED$_h$) at 540 nm (Figure 7a) and the in-plane MD (MD$_h$) at 630 nm (Figure 7b), and the scattering spectra are similar for both polarizations. When the incident angle is greater than 20°, MD$_\perp$ at 600 nm becomes significantly stronger for s-pol. Furthermore, MD$_\perp$ produces a sharper scattering signal than that of the in-plane MD. For the p-pol case, when the incident angle is greater than 45°, ED$_\perp$, which generates a considerably broad scattering signal, is enhanced at 730 nm (Figure 7c). For both polarizations with incident angles greater than 75°, all resonances become fairly weak owing to decreasing total incident electric and magnetic fields (when the incidence angle approaches 90°, the reflection coefficients approach −1 for both polarizations, and, therefore, the total external electric and magnetic fields approach zero).37

Figure 5. (a) Scanning electron microscopy (SEM) image and dark-field scattering images under (b) p-pol and (c) s-pol for 150 nm diameter silicon nanoparticle. Scattering intensity under (d) p-pol and (e) s-pol illumination with 675 nm laser. Inset: the scattering images of silicon nanoparticle with 150 nm diameter.

In contrast, the dark-field microscopy image for s-pol illumination appears yellowish because the scattering signal is primarily due to MD$_\perp$ at shorter wavelengths (Figure 5c). Figure 5d,e shows the dark-field images of the Si nanoparticle excited with a 675 nm laser at an incident angle of 70°. The scattering images were collected by a long-focal-length objective (Olympus LMPFLN 100× BD, NA = 0.8, WD = 3.3 mm) and a digital camera (Canon EOS 750D). The intensity of scattering at 675 nm for p-pol is stronger than that for s-pol.

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CONCLUSIONS

In summary, we demonstrated a strong enhancement of the electric near-field under oblique p-pol illumination through coupling of the ED\(\perp\) of high-refractive-index silicon nanoparticles with gold thin films. The hybrid silicon nanoparticles coupled with gold thin film exhibited extraordinary field enhancement (\(~\times 1250\text{-fold enhancement}\) ). In addition, the ED\(\perp\) resonances were dependent on the type of metal films. The experiments and simulations of the scattering spectra, far-field images, and electric near-field distributions showed a close agreement. The near-field enhancement of silicon nanoparticles on a gold-film system under oblique illumination can be applied to other surface-enhanced spectroscopic techniques such as infrared spectroscopy, surface-enhanced fluorescence, and even silicon-tip-enhanced Raman spectroscopy.

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Author Contributions
K.P.C. conceived the design and supervised the whole project. Y.L.K fabricated the samples and performed the characterizations and simulation. S.Y.C and S.Y.C helped in the characterizations. K.P.C. and Y.L.K wrote the manuscript. All the authors reviewed the manuscript.

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Notes
The authors declare no competing financial interest.

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Figure 6. Two-dimensional mappings of scattering cross-section spectra (\(\times 10^3\text{ nm}^2\)) of silicon nanoparticles deposited on a gold thin film (nanoparticle diameter = 150 nm, gold-film thickness = 70 nm) at different incident angles for (a) p-polarization and (b) s-polarization illumination. Arrows indicate the main resonant contributions of the corresponding dipole moments. MD\(\parallel\) (ED\(\parallel\)) and MD\(\perp\) (ED\(\perp\)) denote the in-plane magnetic (electric) dipole and out-of-plane magnetic (electric) dipoles.

Figure 7. Illustration of EDs and MDs at different incident angles in p-polarization. (a) In-plane ED (ED\(\parallel\)) at 540 nm and (b) in-plane MD (MD\(\parallel\)) at 630 nm at normal incidence. (c) Out-of-plane ED (ED\(\perp\)) at 730 nm at oblique incidence.
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