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Influence of SiO₂ Layer on the Dielectric Function of Gold Nanoparticles on Si Substrate

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The dielectric functions of gold nanoparticle (Au NP) self-assembled on Si substrates without and with a SiO₂ layer (3, 10 and 30 nm in thickness) have been examined. For Au NP on Si substrate without a SiO₂ layer, a splitting in surface plasmon resonance (SPR) band in the imaginary part of the dielectric function ϵ_2 is observed, i.e., besides the typical SPR peak at ~ 2 eV, a pronounced peak at ~ 1 eV emerges, which is due to the hot spot, that is, a narrow gap between the Au NP and the mirror image. The splitting in the SPR band is greatly suppressed for the 3 nm SiO₂ layer and disappears for the 10 nm and 30 nm SiO₂ layers, showing that the resonant intensity from the hot spot rapidly attenuates with the gap distance. In addition, the SiO₂ layer also has significant influence on the interband transitions of Au NP. These observations are discussed in terms of the image charge effect and the formation of the percolated conductive Au layer on the SiO₂ layer.

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Surface plasmon resonance (SPR) interpreted as coherent oscillation of the conduction-band electrons induced by the interaction with an electromagnetic field has long been research interest since several decades ago.¹ The structural effects (size and shape of the metallic nanoparticle) on the movement of SPR band have been reported extensively, through both experimental measurements and numerical simulations.²⁻⁵ Furthermore, the substrate effect on the manipulation of the SPR band is normally considered as an additional mirror image of the nanoparticle inside the substrate.^{6,7} The modified polarization in both parallel and perpendicular directions along the major particle axis can be calculated in order to estimate the strength of particle-substrate interaction.^{7,8} This image charge effect was reported to be dependent on the size of the nanoparticle, the separation between the nanoparticle and its image in the substrate, and the dielectric constant of the substrate.⁶⁻⁹ Previous discussion on the image charge effect is mainly focused on the varied polarization, and its contribution to the interband transition of the metallic nanoparticles is still under debate. On the other hand, SiO₂ layer is generally considered as a barrier to isolate the influence from the substrate.¹⁰ However, the isolation effect of a SiO₂ supporting layer as a function of its layer thickness has been less covered. To better understand these issues, we have examined the influence of SiO₂ supporting layers with various thicknesses on both the SPR band and the interband transitions based on the dielectric function study.

In this work, the effective dielectric functions of the self-assembled gold nanoparticles (Au NPs) on Si substrate and SiO₂ layers with different film thicknesses, which are well modeled by a Drude term and three (or four) Lorentz oscillators, have been determined from spectroscopic ellipsometric (SE) measurement.^{11,12} The structural properties of the nanoparticles were obtained using atomic force microscope (AFM). Influence of the Si substrate and SiO₂ layers on the Lorentz oscillators has been investigated.

Experimental

The self-assembled Au NPs were fabricated by the deposition of an ultrathin gold film with electron-beam (e-beam) evaporation followed by rapid thermal annealing (RTA). The substrates were prepared from single crystalline Si wafers with (100) orientation polished on one side. Prior to the gold film deposition, the substrates were chemically cleaned using an aqueous mixture of H₂SO₄/H₂O₂, followed by buffered hydrofluoric acid and rising with deionized water.

A SiO₂ layer with various thicknesses was thermally grown on Si substrate with dry thermal oxidation. The thicknesses of the SiO₂ layers were determined by a spectroscopic ellipsometer (J. A. Woollam, Inc). The thicknesses obtained for the nominal values of 3, 10 and 30 nm are 3.40 ± 0.22 , 10.38 ± 0.11 and 30.30 ± 0.53 nm, respectively. In addition, a Si substrate without a SiO₂ layer was prepared also by removing its native oxide with diluted HF solution. Then, all samples were transferred into a vacuum chamber with a base pressure of 5×10^{-6} mbar, equipped with an electron gun where gold deposition was controlled with the use of quartz crystal monitor. The thickness of the deposited Au film was 3 nm. After that, the Au film was heat-treated in nitrogen ambient by rapid thermal annealing at 550°C for 30 sec. An atomic force microscope (AFM) with tapping mode was used to characterize the structural properties of the Au NPs formed on the substrates with and without a SiO₂ layer. The SE measurements were performed using a variable angle spectroscopic ellipsometer (J. A. Woollam, Inc). The ellipsometric angles (Ψ and Δ) were measured in the wavelength range of 300–1100 nm with the step of 5 nm at three different incident angles (i.e., 65°, 70° and 75°).

Modeling and Discussion

The effective dielectric function of gold nanoparticles are related to free and bound electrons transitions, which can be represented by the Drude term and Lorentz oscillators, respectively, and the corresponding energy-dependent function is described by¹⁰

$$\epsilon(E) = \epsilon_{\infty} + \sum_{i=1}^n \frac{A_i}{E_i^2 - E^2 - i\Gamma_i E} - \frac{E_p^2}{E^2 + i\hbar \frac{E}{\tau_D}} \quad [1]$$

where ϵ_{∞} is a background constant or an offset, A_i is the amplitude of the i^{th} oscillator with the unit of (eV)², E_i is the resonance energy of the oscillator with the unit of eV, Γ_i is the damping factor of the oscillator with the unit of eV, E_p is the unscreened plasma energy with the unit of eV and τ_D is electron relaxation time with the unit of fs. Owing to the presence of the SiO₂ supporting layer, a four-phase model (i.e., air/gold-nanoparticle layer/SiO₂ film/Si substrate) is used in this SE analysis. Note that for the case of Au NPs on Si substrate, a three-phase model (i.e., air/gold-nanoparticle layer/Si substrate) should be used.^{11,12} The number (n) of Lorentz oscillators was determined to be 4 for Au NPs synthesized on Si substrate, where two oscillators are due to the interband transitions, while the other two Lorentz oscillators are required to describe the SPR band splitting. However, for gold nanoparticles formed on a thicker SiO₂ film (e.g., 10 nm), the split of

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Figure 1. Spectral fittings of $\text{Tan}(\Psi)$ at three different incident angles.

Figure 2. Spectral fittings of $\text{Cos}(\Delta)$ at three different incident angles.

the SPR band cannot be observed, thus only three Lorentz oscillators are used to describe the typical SPR band and the two interband transitions. Spectral fittings to the SE measurements at various angles of incidence were carried out based on Eq. 1 and the SE models (i.e., either the three- or four-phase models). The spectral fittings to the measured $\text{Tan}(\Psi)$ and $\text{Cos}(\Delta)$ (Ψ and Δ are the ellipsometric angles) are shown in Figs. 1 and 2, respectively. As shown in the figures, all spectral features can be fitted excellently for all the three angles (65° , 70° and 75°) of incidence. The values of the model parameters and the effective thickness of the gold-nanoparticle layer yielded from the fittings are given in Table I.

Figure 3 shows the plane-view AFM images of the gold nanoparticles formed on the Si substrate and the SiO_2 supporting layers with different thicknesses. As shown in Fig. 3, the nanoparticle formed on the Si substrate has a larger size distribution as compared to those synthesized on the SiO_2 supporting layers; and the NPs on the SiO_2 supporting layers also have a more perfect spherical shape. Based on our previous study on the movement of the SPR band due to the structural modification of the gold nanoparticles,¹³ the size variation observed in Fig. 3 should have little influence on the variation of the SPR band, although larger size distribution may result in a larger band-width. Thus, we believed that the evolution of the SPR band is mainly due to the presence of the SiO_2 supporting layers.

The effective dielectric functions of the gold nanoparticles on Si substrate and SiO_2 layers with different thicknesses are shown in Fig. 4. Both real and imaginary parts (ϵ_1 and ϵ_2 , respectively) of the dielectric functions are strongly dependent on the supporting substrate/ SiO_2 layers. The magnitudes of ϵ_1 and ϵ_2 of the Au NP formed on Si substrate are much larger than that of the Au NPs on SiO_2 supporting layers, and the amplitudes of ϵ_1 and ϵ_2 are inversely proportional to the thickness of the SiO_2 supporting layer. In addition, some characteristic features of ϵ_1 become less pronounced and gradually vanished with a thicker SiO_2 supporting layer. A peak at ~ 2 eV can be identified in the ϵ_2 spectra for all samples, and it is not largely affected by the presence of a SiO_2 layer. However, the prominent peak at ~ 1 eV can only be observed from the Au NP formed on Si substrate.

It has been reported that Au NP formed on Si substrate shows splitting in the SPR band with a strong resonance peak located at ~ 1 eV besides the typical SPR band at ~ 2 eV in the imaginary part ϵ_2 due to the image charge effect.^{11,12} The induced anisotropic polarizations in the directions parallel and perpendicular to the Si substrate are due to the strong interaction between Au NP and its mirror image.¹² Figure 5 shows the dielectric functions of the Lorentz oscillator (Lorentz oscillator 1) modeling the resonance peak located at ~ 1 eV as a function of photon energy for the Au NPs deposited on either

Table I. Values of the parameters of the Lorentz oscillators and the effective thickness of the gold-nanoparticle layer yielded from the spectral fittings.

Process	Lorentz parameters	Au NPs on Si substrate	Au NPs on 3 nm SiO ₂	Au NPs on 10 nm SiO ₂	Au NPs on 30 nm SiO ₂
Image charge effect	A1 (eV ²)	20.60	0.18	N.A.	N.A.
	E1 (eV)	1.15	1.11	N.A.	N.A.
SPR band	Γ 1 (eV)	0.31	0.86	N.A.	N.A.
	A2 (eV ²)	2.98	3.05	0.52	0.69
	E2 (eV)	2.16	2.27	2.48	2.12
Interband transition 1	Γ 2 (eV)	0.75	0.36	0.32	0.34
	A3 (eV ²)	21.22	3.86	2.67	3.46
	E3 (eV)	3.28	3.28	3.06	3.26
Interband transition 2	Γ 3 (eV)	0.80	1.26	1.25	1.80
	A4 (eV ²)	12.21	1.21	1.12	1.27
	E4 (eV)	3.92	4.12	4.11	4.13
Drude term	Γ 4 (eV)	0.66	0.20	0.89	0.53
	E _p (eV)	8.8	8.8	8.8	8.8
	τ_D (fs)	0.034	0.016	0.005	0.006
	Thickness of Au NP layer (nm)	11.15	15.81	18.36	16.15

the Si substrate or the 3 nm SiO₂ supporting layer. As can be observed from Fig. 5, the oscillator has a similar pattern in the dielectric function for the two samples; however, the inclusion of the 3 nm SiO₂ supporting layer has greatly suppressed this resonance peak (the amplitude of the oscillator is reduced from 20.60 eV² for the Au NP on Si substrate to 0.18 eV² for the Au NP on the 3 nm SiO₂ supporting layer, as shown in Table I). For Au NP on a thicker SiO₂ supporting layer (10 and 30 nm), this resonance peak disappears. The disappearance of the splitting in the SPR band of silver particles on thermally oxidized substrate has been reported.¹⁴ As proposed by Wormeester et al.⁹ the image charge contribution from the Si substrate is inversely proportional to the height of the nanoparticles above the substrate. Therefore, a SiO₂ supporting layer enlarges the separation between the nanoparticles and the Si substrate, and thus reduces the image charge contribution.

With a sufficiently thick SiO₂ supporting layer (e.g., 10 nm), the image charge effect is insignificant, leading to the disappearance of the splitting in the SPR band. In this circumstance, the dielectric function of Au NP can be evaluated as an isotropic layer, where polarizations in both parallel and perpendicular directions are considered to be the same. Therefore, it is not necessary to use an additional Lorentz oscillator to model the isotropic polarization, since no SPR split will be induced. On the other hand, it may be also possible that disappearance of the Lorentz oscillator is related to the formation of a continuous Au layer (i.e., the gold film has percolated and formed a continuous conductive pathway on the SiO₂ layers). The growth of the Au NP formed on the SiO₂ layer is considered to be in Stranski-Krastanov mode, where a continuous film is followed by island growth.¹⁵ The image charge effect of the Au NP can be suppressed as a result of

Figure 3. Plane-view AFM images of the gold nanoparticles self-assembled on Si substrates without and with a SiO₂ layer.

Figure 4. Effective dielectric function ϵ of the gold nanoparticles formed on different substrates: (a) real part, ϵ_1 and (b) imaginary part, ϵ_2 . For a better visibility, the insets show the ϵ_1 and ϵ_2 of the gold nanoparticles formed on the SiO_2 supporting layers with various thicknesses.

Figure 6. Dielectric function of Lorentz oscillator 2 for Au NPs on the Si substrate and on the SiO_2 supporting layers with various thicknesses.

Figure 5. Dielectric function of Lorentz oscillator 1 for Au NPs on Si substrate. The inset shows the dielectric function for Au NP on the 3 nm SiO_2 supporting layer. The solid and dotted curves represent the Lorentz oscillator in the measurement range and beyond the measurement range, respectively.

the formation of the percolated conductive Au layer on the SiO_2 layer.

Unlike the resonance peak located at ~ 1 eV, the typical SPR band (at ~ 2 eV) is relatively less influenced by the presence of the SiO_2 layer. The dielectric functions of the Lorentz oscillator (Lorentz oscillator 2) modeling the typical SPR band as a function of photon energy are shown in Fig. 6 for all the samples. The amplitude and peak position of the Lorentz oscillator show a random or weak dependence on the thickness of the SiO_2 supporting layer. Nevertheless, the movement of the peak position can be attributed to the change in the average size of the nanoparticles, i.e., an increase in the Au NP size will lead to a red-shift in the SPR peak.¹³

As shown in Table I, the interband transitions of the gold nanoparticles can be modeled using two Lorentz oscillators: one oscillator (Lorentz oscillator 3) at ~ 3 eV corresponds to the transitions from the uppermost $5d$ -valence electron bands to states in the s , p bands just above the Fermi level; while the other (Lorentz oscillator 4) at ~ 4 eV represents the transitions from the lower-lying d bands to band 6 and from s , p states in band 6 to s -, p -like states in band 7.¹⁶ Figure 7 shows the dielectric functions of Lorentz oscillator 3 for all the samples. It can be concluded from Table I and Fig. 7 that the Si substrate greatly enhances the interband transition and the interband transition decreases with increasing the SiO_2 supporting layer thickness. Although the mechanism responsible for the substrate influence on the interband transition is still not clear, one may suspect that the influence could be related to the image charge effect from the Si substrate. In addition, the interband transitions could be also affected by the change in the structural properties of Au nanoparticles as the introduction of a SiO_2 supporting layer can significantly modify the structural morphologies of the Au nanoparticle.

Figure 7. Dielectric function of Lorentz oscillator 3 for Au NPs on the Si substrate and on the SiO₂ supporting layers with various thicknesses.

Conclusion

A strong splitting in the SPR is observed for Au NP on Si substrate; however, it is greatly suppressed for the 3 nm SiO₂ layer and disappears for the 10 and 30 nm SiO₂ layer. Besides, a SiO₂ layer also has a significant influence on the interband transitions of Au NP. These observations are discussed in terms of the image charge effect and/or the formation of percolated conductive Au layer on the SiO₂ layer.

Acknowledgments

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