Plasmon resonances of aluminum nanoparticles and nanorods

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We report experimental and theoretical analysis of the plasmonic resonances of Al nanoparticles and nanorods. Ordered nanoparticle arrays with well-defined shapes and narrow size distributions are fabricated on quartz substrates over large areas using extreme ultraviolet interference lithography. The structures, which have sizes down to 40 nm, exhibit strong and sharp particle plasmon resonances in the near and deep-UV ranges. A comprehensive theoretical analysis carried out using dipolar approximation and finite-difference time-domain methods shows good overall agreement with measurements while revealing the dependence of the optical response of Al structures on the fabrication conditions. The results demonstrate the suitability of using Al as a plasmonic material in the UV range and the feasibility of extending applications of plasmonics, such as surface-enhanced Raman spectroscopy, down to the deep-UV range. © 2008 American Institute of Physics.

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I. INTRODUCTION

Metallic nanoparticles scatter and absorb light strongly at certain wavelengths due to the resonant excitation of charge density oscillations known as localized particle/surface plasmons.^{1,2} Potential applications of these plasmon resonances, such as in Raman and fluorescence spectroscopy, biochemical sensors, and nanophotonics, have led to an increasing interest in nanoparticles and their plasmonic properties.^{3–5} Although plasmonic properties of many metallic nanoparticles, in particular Au and Ag, have been investigated extensively, the literature on Al nanoparticles is surprisingly limited. Whereas Au and Ag exhibit interband absorptions below the wavelengths of about 590 and 350 nm,⁶ respectively, Al has low absorption down to a wavelength of 200 nm due to its free-electron-like character and high bulk-plasmon frequency.⁷ The accessibility of the spectrum in the 200–500 nm range makes Al an excellent and perhaps the only choice for applications such as broad-band wire-grid polarizers.^{8,9} Being considered as good free-electron metal, calculations on the plasmonic resonances of Al can be found in textbooks.^{1,2} For a comparison of Al to common plasmonic materials, the extinction spectra of spherical Au, Ag, and Al nanoparticles with diameters of 40 nm in a silica matrix are shown in Fig. 1(a). The spectra were calculated using Mie's theory, which provides exact analytical solutions for spherical particles.^{1,2} The extinction peaks in the blue and green regions result from the resonant excitation of the dipolar plasmon modes of Ag and Au nanoparticles. An Al nanoparticle of the same size exhibits a peak at about 250 nm due to the dipolar plasmon resonance and another peak at about 190 nm resulting from the quadrupolar mode. In Fig. 1(b), the extinction spectra of Al nanospheres with different diameters are presented. With increasing par-

ticle size, the Al spectrum exhibits a strong redshift and broadening due to retardation effects and emergence of higher order plasmon modes. Compared with Au and Ag nanoparticles of similar dimensions, the redshift of the plasmon peaks and observation of high-order plasmon modes are relatively significant for Al nanoparticles. For instance, for Au nanoparticles, the redshift of the dipolar resonance is only 150 nm when the particle diameter is increased from 20 to 140 nm as shown in Fig. 1(c).

Experimental studies on the plasmonic properties of Al face certain difficulties. Whereas chemical synthesis methods for Au and Ag have reached an advanced stage, providing particles of different sizes and shapes, the synthesis of Al nanoparticles with satisfactory size dispersion and without significant agglomeration remains a challenge. Pronounced plasmon peaks of Ag and Au can be obtained rather easily by roughening their surfaces or through island formation in thin films. Al particle plasmon resonance, however, has a stronger dependence on particle size and shape, as seen above, with strong redshift and emergence of broad features as the particle size grows. In random nanoparticle ensembles, inhomogeneous broadening as a consequence of shape and size variations smears out all the peaks. This is the reason for lack of any resonant features, unlike for Au and Ag thin films, for deposited Al thin films with significant island formation as reported even in recent studies.¹⁰ In the small-particle size limit ($d < 10$ nm), only the dipolar plasmon mode, which is rather insensitive to the size distribution, remains. However, the resonance peak is expected to occur at about 180 nm (in a silica matrix). Thus, for an explicit observation of the plasmon peak, optical experiments in the vacuum ultraviolet region are required. The recent availability of nanofabrication tools such as e-beam and focused ion beam lithography has enabled extensive experimental studies on the properties of nanoparticles. In general, ensembles of particle arrays have been fabricated and characterized with a microscope coupled to a spectrometer. However, these tools do not typically

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FIG. 1. (Color online) (a) Calculated extinction spectra of spherical Au, Ag, and Al nanoparticles with a diameter of 40 nm in a silica matrix. (b) Calculated extinction spectra of spherical Al nanoparticles with diameters of 20, 80, and 140 nm in a silica matrix. (c) Calculated extinction spectra of spherical Au nanoparticles with diameters of 20, 80, and 140 nm in a silica matrix. Calculations are based on Mie's formulae; for Au, Ag, and Al the optical constants provided in Refs. 6 and 7 were used.

cover the UV range needed for the measurements on Al nanoparticles. This problem can be circumvented by fabricating ensembles of nanoparticles over large areas, and thus the use of a UV-compatible microscope can be avoided. Nevertheless, this fabrication method is rather time consuming because of its serial writing nature.

Significant interest has been paid to the optical properties of Al nanoparticles in the far-infrared region. Al particles smaller than 10 nm exhibit anomalous far-infrared absorption,^{11,12} which has been attributed to quantum size effects¹³ and the effects of oxide overlayer.¹⁴ Another interesting effect that has attracted attention is the diminishing of the interband absorption at 850 nm wavelength in small Al clusters,^{15–17} resulting from the breakdown of the band structure. Broad absorption peaks attributed to surface plasmon modes were measured for nanoporous thin films,¹⁸ for thermally evaporated discontinuous films,^{19,17} and for hollow nanocaps.^{20,21} Surface plasmon modes were also observed in electron energy loss spectroscopy experiments of vapor-deposited Al nanoparticles.^{22,23} Recently, enhanced transmis-

sion through Al hole arrays has been observed and attributed to the resonant excitation of localized and extended surface plasmons.²⁴

In this paper we report our experimental observations on the plasmonic behavior of Al nanoparticles and nanorods. Nanostructures over large areas with well-defined shapes and narrow size distributions have been obtained using extreme ultraviolet (EUV) interference lithography. Fabrication of Al nanostructures with narrow size distribution is essential for obtaining sharp plasmon resonances because of the aforementioned significance of inhomogeneous broadening for Al nanoparticles. Moreover, this fabrication method provides large-area samples that simplify spectroscopic measurements in the UV region. The fabricated particles exhibit sharp particle plasmon resonances down to the deep-UV region. We compare experimental results with theoretical predictions obtained using dipolar approximation and finite-difference time-domain (FDTD) calculations and discuss the validity of the dipolar approximation. The effects of the natural oxide layer and the optical constants are investigated using these theoretical models.

II. EXPERIMENTAL DETAILS

To obtain Al nanoparticles we used EUV interference lithography,²⁵ physical vapor deposition, and lift-off techniques. Two-dimensional arrays of Al nanoparticles with different sizes, shapes, and periods were fabricated on quartz substrates. Sample preparation started with the spin coating of 80-nm-thick polymethylmethacrylate (PMMA) on silica (HPFS) wafers and with baking at 180 °C for 3 min. Subsequently, hydrogen silsesquioxane (HSQ) of 30 nm in thickness was spin coated on the PMMA film and the samples were baked at 90 °C for 3 min. The EUV exposures were carried out at the XIL beamline of the Swiss Light Source (SLS) at the Paul Scherrer Institute, Switzerland. The interference setup uses transmission gratings and coherent EUV light of 13.4 nm wavelength generated by an undulator source.²⁵ Following the EUV exposure, HSQ photoresist²⁶ was developed in a tetramethyl ammonium hydroxide (TMAH) solution with a normality of 2.6, resulting in hole patterns in HSQ. Reactive ion etching was used to transfer the pattern into the PMMA layer. This step produces a bilayer structure with an undercut that facilitates the subsequent lift-off process. Thermal evaporation of aluminum was performed at a base pressure of better than 1×10^{-6} mbar with a deposition rate of about 0.5 nm/s. Finally, the lift-off process was carried out in an acetone bath with ultrasonic agitation. Figure 2 shows scanning electron microscopy (SEM) images of typical samples. For all samples the metal thickness was kept constant at 30 nm. The size of the smallest fabricated particles was 40 nm. As seen in the figure, the particles possess some roughness due to the finite grain size of the Al crystals making up the nanoparticles. The area of the particle arrays varied in the 0.25–1 mm² range, which was large enough for characterization without any focusing optics. Extinction spectra (extinction = 1 – transmission) of the nanoparticle arrays were measured using a standard UV/visible/near infrared (NIR) spectrometer in the transmission

FIG. 2. SEM images of Al nanoparticle arrays (a) with an average particle diameter of 40 nm and unit cell dimensions of 90 and 100 nm, respectively; (b) with an average diameter of 138 nm and a period of 280 nm; and (c) with ellipsoidal particles with principle axes of 130×94 nm and a period of 200 nm. The particle thickness for all samples is 30 nm.

mode with a spectral resolution of 2 nm at normal incidence and with unpolarized light. The diameter of the light spot was always kept smaller than the sample size.

III. RESULTS AND DISCUSSIONS

The measured extinction spectrum of an Al nanoparticle array with particle diameter of 40 nm and lattice constants of 90 and 100 nm in the two orthogonal directions [Fig. 2(a)] is plotted in Fig. 3. The spectrum exhibits a sharp and narrow peak at about 270 nm. This resonant peak can readily be attributed to the dipolar mode of the surface plasmon resonance of the nanoparticles.

We calculated the extinction spectra of the structure using the FDTD method.²⁷ FDTD calculations were made us-

FIG. 3. (Color online) Experimental and theoretical extinction spectra of the Al nanoparticle array with a diameter of 40 nm, a thickness of 30 nm, and lattice constants of 90 and 100 nm. For FDTD calculations, the optical constants tabulated in Ref. 7 were used.

ing a code that employs monochromatic plane-wave excitation. Along the axes parallel to the surface plane, periodic boundary conditions were set at the boundaries of the simulation domain, which is equivalent to a single unit cell of the periodic particle array. Absorbing boundary conditions at both ends of the cell along the propagation axis were realized by using perfectly matched layers.²⁷ The grid size of the simulation domain was 1 nm. The Al nanoparticles were modeled as cylinders of 40 nm in diameter and 30 nm in height on a semi-infinite quartz substrate. Tabulated values of complex dielectric constants of Al given in Ref. 7 were used in the calculation. A comparison of the experimental and theoretical spectra plotted in Fig. 3 reveals a good agreement in general, notwithstanding a small discrepancy of 40 nm in the peak position.

The difference may be due to material properties and/or geometrical factors. The dielectric constants used in the FDTD calculations occasionally differ somewhat from the actual dielectric constants of the sample. Moreover, in the FDTD model, the nanoparticles are assumed to be identical and perfect cylinders, whereas the fabricated ones have some shape variations due to the finite grain size of evaporated aluminum. In addition, there is about 5% size dispersion over the entire area of the particle array. The finite size and shape dispersion lead to inhomogeneous broadening in which the experimental peak width is slightly broader than the theoretical one, as seen in Fig. 3. Moreover, in the FDTD model, the natural oxide layer of Al is not taken into account. From optical measurements on Al surfaces²⁸ and transmission electron microscopy (TEM) analysis of Al nanoparticles,²⁹ it is well known that a thin oxide layer of about 2–3 nm thickness forms on the metal surface upon exposure to air. Modeling a thin oxide layer in FDTD calculations would have required subnanometer grid sizes and thereby impractically long computing times.

To investigate the potential role of the aforementioned factors to the observed discrepancy between experiment and theory, we performed further calculations using different approaches. In Fig. 4, extinction spectra calculated with various theoretical models are shown, and the FDTD calculations are also plotted for comparison. Note that the spectral range is 160–500 nm in this figure and FDTD calculations show a new peak that emerges from quadrupolar resonance with a shorter resonance wavelength than the dipolar resonance. Dipolar approximation in the quasistatic limit is a commonly used method to explain the optical properties of metallic particles with sizes much smaller than the wavelength.^{1,2} Analytical formulae are available for spherical and elliptical particles as well as core/shell structures.^{1,2}

The calculated extinction spectrum of Al nanoparticles with an oblate shape with principle axes of 40 and 30 nm using dipolar approximation is shown in Fig. 4. The spectrum shows a single peak at about 210 nm wavelength while the quadrupolar resonance is missing because this method takes only the dipolar mode into account. In this model, nanoparticles are single and isolated particles, and therefore the coupling between the nanoparticles is neglected. Dipolar coupling between the particles is expected to cause small peak shifts at present particle separation distances.^{30,31} More-

FIG. 4. (Color online) Comparison of the theoretical extinction spectra of Al nanoparticles with an oblate shape with principle axes of 40 and 30 nm calculated using different models. The solid line (black) denotes FDTD calculations; the dash-dotted (green) line denotes the calculations based on dipolar approximation; the dashed line (red) denotes dipolar approximation calculations with MLWA correction; the dotted line (blue) denotes dipolar approximation with MLWA correction and assuming that the nanoparticle of same total size is coated with 3-nm-thick Al_2O_3 . The optical constants provided in Ref. 7 were used.

over, the inhomogeneous dielectric environment of the nanoparticle cannot fully be taken into account. Therefore, the weighted average of the dielectric constants of the air and the substrate is taken as the dielectric constant of the immediate environment of the nanoparticle. This approximation is found to be successful for describing the experimental data of nanoparticles on substrates.³¹ The quasistatic dipolar model results in a narrower and blueshifted peak in comparison to the FDTD model (see dashed-dotted line in Fig. 4). Since this quasistatic approximation ignores dynamic effects, it holds only for small nanoparticles. Although this approximation is widely used to describe the plasmonic resonances of Au and Ag nanoparticles of similar size, size-dependent factors such as retardation effects are relatively significant for Al nanoparticles, as demonstrated in Fig. 1(b). An accurate approximation to correct the particle size and radiation damping effects is the so-called modified-long-wavelength approximation (MLWA),^{31,32} which provides simple expressions for extinction cross sections. The quasistatic result obtained in Fig. 4 is corrected with the MLWA model and plotted as dashed-line curve in the same figure. This correction leads to redshift and broadening of the plasmon peak. Despite differences in modeling such as particle shapes, coupling with neighboring particles, and presence of an inhomogeneous medium, the modified quasistatic dipolar approximation is in good agreement with the FDTD model, which is a more realistic method. These results show that the MLWA method is as good as the FDTD method to account for the optical properties of the present structures.

Owing to the relative simplicity of the MLWA method, we can go one step further by including a correction for the natural oxide layer. The calculated spectrum of the particles coated with a 3-nm-thick aluminum oxide layer is plotted as dotted-line curve in Fig. 4. The inclusion of the natural oxide layer, while keeping the total thickness constant, leads to a redshift in the peak position of about 5 nm. The redshifting due to the oxide layer is largely compensated by the shrink-

FIG. 5. (Color online) Calculated extinction spectra of Al nanoparticles of 40 nm total diameter and 30 nm total thickness with a 3 nm natural oxide layer using various optical constants. MLWA calculations are based on the optical constants reported in Refs. 7 and 33 (dotted line) and Ref. 34 (dashed line). The solid line curve represents the best fit to the experimental data presented in Fig. 3.

ing size of the metallic core, showing that the existence of the natural oxide layer has a small effect on the peak position. Ruling out these effects as possible sources of discrepancy between experiment and theory in Fig. 3, the only remaining factor is a possible difference between optical constants in experiment and theory.

In order to investigate the effect of the optical constants, we made further calculations based on various dielectric constants reported in literature, and the resulting spectra are plotted in Fig. 5. The optical constants used are extracted from optical measurements carried out by Shiles *et al.*³³ and Ehrenreich *et al.*³⁴ on clean and unoxidized thin films deposited and kept in UHV conditions. The results of the experiments by Shiles *et al.*³³ were also adopted by the widely used reference book edited by Palik.⁷ Note that the dotted-line curves in Figs. 4 and 5 are identical in which both MLWA approximation and oxide-layer correction are incorporated. As seen in Fig. 5, the spectra based on different values of dielectric constants show significant variation. Within the range of wavelengths of 160–600 nm we obtained best-fit Drude parameters with a plasmon energy of $\hbar\omega_p=15.6$ eV and an electron relaxation time of $\tau=1.1$ fs for the values of Shiles *et al.*,³³ while the best-fit parameters are reported as 12.7 eV and 5.12 fs in the optical frequencies by Ehrenreich *et al.*³⁴ In fact, a survey of reported optical constants in the literature reveals an even greater variation than the values selected here.^{7,35} Since the dipolar model with the MLWA approximation is a simple analytical model, we carried out a best-fit procedure to the position and width of the experimental peak shown in Fig. 3 by changing the Drude parameters. The Drude parameters obtained with this procedure are $\hbar\omega_p=13.1$ eV and $\tau=1.0$ fs. These are reasonable values and within the range of experimentally reported data in literature. It should be noted that the obtained Drude parameters are simply fit parameters and this fitting procedure, which makes many assumptions, cannot be used for accurate determination of the optical properties of the real material. Nevertheless, the results demonstrate that the optical constants reported in literature show significant variations and

FIG. 6. (Color online) (a) Measured and (b) calculated extinction spectra of Al particle arrays with various diameters as provided in the figure. The array period is 280 nm and the metal thickness is 30 nm. For the FDTD calculations the optical constants listed in Ref. 7 were used.

that the actual optical constants of a structure are subject to change depending on fabrication procedure. In particular, bulk oxidation during the deposition and electron scattering by the grain boundaries substantially change the optical properties of physically deposited Al. These properties are highly sensitive to the deposition rate and the base pressure of the deposition chamber.³⁶ In conclusion, the optical constants of deposited Al films can vary and the discrepancy of 40 nm in peak position between theory (FDTD) and experiment can be attributed to the changes in optical constants. It should be noted that size effects, i.e., reduced relaxation times due to small particle size, become important at diameters below 20 nm and are negligible in the present case. However, the relaxation time can be reduced due to grain boundaries, defects, and roughness.

Figure 6 shows the measured and calculated extinction spectra of Al nanoparticles with various diameters. The metal thickness and the period of the array are fixed as 30 and 280 nm, respectively, so that the evolution of the plasmon resonance peak with changing particle diameter can be demonstrated. With increasing diameter the peak position shifts to longer wavelengths and the peaks get broader due to increased retardation effects. The discrepancy in the peak positions between experiment and theory due to the optical constants is about 20–25 nm. Although other optical constants, as in Fig. 5, would have provided somewhat better agreement of the calculations with the experiment, we used the optical constants reported in Ref. 7 since they are generally accepted values. The calculated spectra show some

FIG. 7. (Color online) Measured extinction spectra of ellipsoidal Al nanoparticles of various sizes and aspect ratios. The perpendicular axis with respect to the substrate (film thickness) is 30 nm and the primary axes on the surface plane are provided in the figure. The period of the structures is 200 nm.

sharp modulations below 400 nm wavelength, which are not seen in the experiment. Both experiment and theory are zeroth-order transmission spectra, and the first-order diffraction channel is open at a wavelength of 410 nm. Sharp attenuations in the intensities around the critical angles of the diffraction channels are known as Wood's anomalies,³⁷ which are probably smeared out in the experiment due to inhomogeneous broadening.

Figure 7, finally, shows the extinction spectra of ellipsoidal nanoparticles with various sizes and aspect ratios. For the smallest particle, which has an aspect ratio close to unity, only one peak is visible. With increasing particle size and aspect ratio, two distinct peaks appear, which can be attributed to the plasmon resonances of the principle axes of the ellipsoids on the surface plane. The plasmon resonance associated with the short axis shifts from 310 to 380 nm with increasing length, whereas the long axis resonance shifts from 425 to 495 nm. Since there are equal numbers of nanorods along two orthogonal directions, as seen in Fig. 2(c), the two different modes cannot be excited independently by using polarized light. This type of multiple resonance associated with different plasmon resonances of the different axes of asymmetric particles provides great flexibility in tunability of the plasmon resonances over a large wavelength range and is also advantageous in some applications,^{4,38} for example, for the “lightning rod” effect in which near fields at the ends of nanorods are substantially higher than those of spherical nanoparticles. Whereas Au and Ag nanorods exhibit plasmon resonances in the NIR range, Al nanorods can be easily tuned to the wavelengths in the visible range. Al nanorods can thus be used for plasmon-enhanced spectroscopy experiments in this range instead of Au and Ag spherical nanoparticles.

IV. CONCLUSIONS

In summary, we have demonstrated the feasibility of achieving strong and sharp plasmon resonances in the UV region in Al nanoparticles and nanorods. Lithographic fabrication of nanoparticles with uniform size and shape properties was the key to avoiding severe broadening and redshift

that obscure such resonances in random ensembles. The retardation effects are relatively significant for Al nanoparticles and therefore quasistatic dipolar approximation fails to describe the measured spectra, whereas the MLWA (Refs. 31 and 32) is found to be successful. Analysis of the experimental results points to small but significant variation in the optical constants compared with previously reported values. We developed a fitting procedure to extract the effective optical constants of metallic nanoparticles from their plasmon resonances.

Most importantly, the observation of sharp plasmon resonances of Al nanoparticles shows the feasibility of extending plasmonics research down to the deep-UV region, which has remained relatively unexplored. Thus, new applications such as surface-enhanced Raman spectroscopy (SERS) in this spectral region may be conceivable. In fact, UV-SERS experiments have been performed by using transition metals that exhibit only moderate enhancement factors but are nevertheless better than Au and Ag.³⁹ In contrast, Raman scattering enhancement of Al nanoparticles was theoretically predicted to be as high as 10^5 and below 400 nm. Al outperforms all metals except Li in terms of near-field enhancement⁴⁰ (Li, however, is not a suitable material for practical applications due to its high chemical activity).

Other interesting applications of Al plasmonic resonance might be in energetic materials and propellants. Great advances have, for example, been made in the development of nanoenergetic materials and Al nanoparticles have attracted significant attention as a promising candidate.⁴¹ Thus, in investigating fundamental processes such as oxidation and rupture of Al nanoparticles, monitoring their plasmonic resonances may be used as a simple or even *in situ* method complementing SEM and TEM analyses.

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