Localized surface plasmon resonances in the ultraviolet from large scale nanostructured aluminum films

Jérôme Martin,* Julien Proust, Davy Gérard, and Jérôme Plain
Laboratoire de Nanotechnologie et d’Instrumentation Optique, CNRS, Université de Technologie de Troyes, France
∗jerome.martin@utt.fr

Abstract: We report on a straightforward preparation method to obtain a dense layer of quasi-spherical aluminum nanoparticles over a large area. The method is based on rapid thermal annealing of a thin aluminum film deposited on a super-repellent substrate. Diameters ranging from 2 to 15 nm are obtained by varying the film thickness. Aluminum nanoparticles exhibit well-defined localized surface plasmon resonances in the ultraviolet range as revealed by extinction measurements and confirmed by Mie theory.

© 2013 Optical Society of America

OCIS codes: (310.6628) Subwavelength structures, nanostructures; (240.6680) Surface plasmons.

References and links
1. A. V. Zayats, I. I. Smolyaninov, and A. A. Maradudin, “Nano-optics of surface plasmon polaritons,” Phys. Rep. 408, 131–314 (2005).
2. A. V. Kabashin, P. Evans, S. Pastkovsky, W. Hendren, G. A. Wurtz, R. Atkinson, R. J. Pollard, V. A. Podolskiy, and A. V. Zayats, “Plasmonic nanorod metamaterials for biosensing,” Nat. Mater. 8, 867–871 (2009).
3. F. De Angelis, F. Gentile, F. Mecarini, G. Das, M. Moretti, P. Candeloro, M. L. Coluccio, G. Cojoc, A. Accardo, C. Liberale, R. P. Zaccaria, G. Perrozziello, L. Tirinato, A. Toma, G. Cuda, R. Cingolani, and E. Di Fabrizio, “Breaking the diffusion limit with super-hydrophobic delivery of molecules to plasmonic nanofocusing SERS structures,” Nat. Photonics 5, 682–687 (2011).
4. D. Gérard, J. Wenger, N. Bonod, E. Popov, H. Rigneault, F. Mahdavi, S. Blair, J. Dintinger, and T. W. Ebbesen, “Nanoaperture-enhanced fluorescence: towards higher detection rates with plasmonic metals,” Phys. Rev. B 77, 045413 (2008).
5. R. Mupparapu, K. Vynck, I. Malfanti, S. Vignolini, M. Burresi, P. Scudo, R. Fusco, and D. Wiersma, “Enhanced downconversion of UV light by resonant scattering of aluminum nanoparticles,” Opt. Lett. 37, 368–370 (2012).
6. S. K. Jha, Z. Ahmed, M. Agio, Y. Ekinci, and J. F. Löffler, “Deep-UV surface-enhanced resonance Raman scattering of adenine on aluminum nanoparticle arrays,” J. Am. Chem. Soc. 134, 1966–1969 (2012).
7. K. Ray, M. H. Chowdhury, and J. R. Lakowicz, “Aluminum nanostructured films as substrates for enhanced fluorescence in the ultraviolet-blue spectral region,” Anal. Chem. 79, 6480–6487 (2007).
8. M. H. Chowdhury, K. Ray, S. K Gray, J. Pond, and J. R. Lakowicz, “Aluminum nanoparticles as substrates for metal-enhanced fluorescence in the ultraviolet for the label-free detection of biomolecules,” Anal. Chem. 81, 1397–1403 (2009).
9. J. M. McMahon, M. Jeffrey, S. K. Gray, and G. C. Schatz, “Ultraviolet plasmonics: the poor metals Al, Ga, In, Sn, Ti, Pb, and Bi,” arXiv:0908.2000 (2009).
10. I. Zorić, M. Zäch, B. Kasemo, and C. Langhammer, “Gold, platinum, and aluminum nanodisk plasmons: material independence, subradiance, and damping mechanisms,” ACS Nano 5, 2535–2546 (2011).
11. C. Langhammer, M. Schwind, B. Kasemo, and I. Zorić, “Localized surface plasmon resonances in aluminum nanodisks,” Nano Lett. 8, 1461–1471 (2008).
12. K. Wu, Y. Lu, H. He, J. Huang, B. Zhao, and Z. Ye, “Enhanced near band edge emission of ZnO via surface plasmon resonance of aluminum nanoparticles,” J. Appl. Phys. 110, 023510 (2011).
13. A. Taguchi, Y. Saito, K. Watanabe, S. Yijian, and S. Kawata, “Tailoring plasmon resonances in the deep-ultraviolet by size-tunable fabrication of aluminum nanostructures,” Appl. Phys. Lett. 101, 081110 (2012).
1. Introduction

Metallic nanoparticles (NPs) can support localized surface plasmon resonances (LSPRs) due to the coherent, collective oscillation of their surface conduction electrons [1]. When optically excited at the resonance frequency, LSPRs result in a strong and locally confined electromagnetic field in the vicinity of the NP. Thanks to this phenomenon, light is intensively absorbed and scattered by nanoparticles. The resonance properties, frequency and linewidth, depend on the NP’s material, shape, and the refractive index of the surrounding medium. Consequently, NPs exhibit extremely attractive nano-optical properties allowing various technological applications such as ultra-sensitive sensing [2], surface enhanced Raman spectroscopy (SERS) [3], and metal-enhanced fluorescence [4].

For several decades the properties of LSPRs have been almost exclusively studied in the visible region by using nanoparticles made of gold or silver. These noble metals support LSPR in the visible and near-IR range. Emerging applications will require the extension of nanoplasmonics toward higher energies, in the UV-range. For instance, plasmonics coupled with wide bandgap semiconductors, such as ZnO or GaN, could lead to more efficient light emission or harvesting devices [5]. Other applications include SERS [6] (the intensity of Raman emission increases with the fourth power of the frequency of the source) or fluorescence enhancement [7, 8]. However, only a few studies of LSPRs in the UV region have been reported, implying that UV plasmonics is still in its infancy. The reported works related to UV LSPR use metals such as Ga, In, Pd [9], Pt [10] or Al [7, 8, 11–14]. The real part of the dielectric function of aluminum is negative in the visible and UV regime, down to a wavelength of 100 nm, with low losses. The excellent optical properties of aluminum have already been exploited to create UV optical antennas [14, 15] and to enhance the fluorescence of wide bandgap semiconductors [12]. Aluminum nanostructures are generally designed with the help of electron beam lithography in order to obtain well-controlled nanostructures [11, 14]. Such techniques are limited to the patterning of relatively small areas. Other techniques allow large scale patterning at the price of poorly-defined resonances, such as the evaporation of very thin layers of metal [7]. The fabrication of metal nanostructures supporting well-defined UV LSPRs over a large scale has yet to be demonstrated.

In this paper, we report on a straightforward preparation method to fabricate a dense monolayer of aluminum nanoparticles (Al-NPs) directly on a quartz or silicon substrate. We have developed a large-scale patterning technique that allows tunable nanoparticle size. The method is based on the rapid thermal annealing of a thin layer of aluminum that has been evaporated on a substrate. This process is well known and widely used for the fabrication of gold and silver nano-islands [16, 17]. The adhesion of the metal film to the substrate is a key parameter for this fabrication technique. Gold and silver exhibit poor adhesion, yielding to a natural dewetting of the metal film during annealing, which leads to the formation of nano-islands. A chemical functionalization of the substrate has been reported that improves gold adhesion [16], leading to ultra-thin islands. Aluminum exhibits a high adhesion coefficient [18], which con-
siderably hinders the dewetting process, yielding to poor-quality aluminum nanostructures (see the micrograph in Fig. 1(a), left panel). To circumvent this issue, we propose a substrate preparation method that dramatically decreases the adhesion of aluminum to the substrate. A well-chosen chemical functionalization leads to a super-repellent substrate and allows for the efficient dewetting of aluminum. This results in the formation of high-quality aluminum nanoparticles, that are not nano-islands but aluminum nanospheroids (see Fig. 1(a), right panel). Optical characterization of the obtained nanoparticles demonstrates well-defined localized surface plasmon resonances in the ultraviolet range and good nanostructure homogeneity over the whole surface.

2. Sample preparation

The preparation method is illustrated in Fig. 1(b). The surface of a quartz or silicon substrate is activated using piranha solution. Then perfluorosilane molecules (1H,1H,2H,2H-perfluorodecyltrichlorosilane from abcr GmbH) are grafted onto the surface. This drastically changes the surface wettability as verified by measuring the contact angle of a water droplet on the surface. An increase from 30° on quartz or silicon to 116° was observed after surface functionalization. A thin layer of aluminum is then evaporated onto the functionalized substrate, immediately followed by a rapid thermal annealing (RTA) for 10 minutes at 800°C. The RTA is done under primary vacuum followed by a 25 sccm argon flux to prevent oxidation of Al. During annealing, quasi-spherical aluminum droplets are formed due to the super-repellent property of the substrate. At approximately 400°C the bond between perfluorosilane molecules and the surface begins to break [19], at which point the molecules sublime and are vented from the chamber. The aluminum droplets retain their shape and crystallize as the temperature is slowly decreased from 800°C to room temperature. The whole annealing process is done in an oxygen-free environment so oxidation occurs only after the crystallization of the Al-NPs. Previous studies [11] have shown that oxidation on crystalline aluminum is limited to a 2-3 nm thick surface layer. This alumina shell acts as a passivation layer preventing further oxidation.

The crucial role played by the surface functionalization is illustrated in Fig. 1(a). The left panel shows a micrograph of a 5 nm aluminum film after annealing and without the surface functionalization step. We observe aluminum nano-islands with various sizes and shapes. When the surface is functionalized (right panel in Fig. 1(a)), well-defined quasi-spherical nanoparti-

![Fig. 1. Schematic of the method to obtain Al-NPs. (a) Comparison between a thin film evaporated on a substrate without (left panel) or with (right panel) a super-repellent surface functionalization. Scale bars on the SEM micrographs are 100 nm. (b) Detailed fabrication steps.](image-url)
Fig. 2. Morphological characterization of Al-NPs obtained with three different initial film thicknesses: 2.5 nm (left panel), 5 nm (center panel) and 8 nm (right panel). Images are obtained using (a-c) atomic force microscopy (AFM) and (d-f) scanning electron microscopy (SEM). Scale bars are 100 nm. The size histograms (g-i) are obtained from the corresponding SEM images. The blue lines correspond to a Gaussian fit of the experimental data: $y = \exp\left(-\left(\frac{x-x_0}{w}\right)^2\right)$. Fit parameters are for 2.5 nm thick film, $x_0 = 5.1$ nm and $w = 1.3$ nm; for 5 nm thick film, $x_0 = 6.9$ nm and $w = 2.9$ nm; for 8 nm thick film, $x_0 = 11.6$ nm and $w = 4.5$ nm.

icles of homogenous sizes are obtained. A complete characterization of the morphology of the nanostructured film is presented in Fig. 2 for three different film thicknesses (2.5, 5 and 8 nm). The nanoparticle diameters have been systematically measured from scanning electronic microscopy (SEM) images, yielding the Gaussian size distributions presented in the lower panels. The 2.5 nm film (Fig. 2(g)) gives rise to Al-NPs with a mean diameter of 5.1 nm and a relatively narrow distribution width (FWHM = 2.1 nm). When the film thickness increases, the mean diameter increases (6.9 nm for the 5 nm thick film and 11.6 nm for the 8-nm thick film) and the size distribution becomes broader, as observable in the SEM images. This is the result of a larger initial volume of matter leading to a wider distribution of NP sizes (FWHM = 4.8 nm for a 5 nm thick film and FWHM = 7.5 nm for an 8 nm thick film) during the annealing process. The particles are spheroids with a small aspect ratio, as confirmed by atomic force microscopy (AFM) and SEM imaging.

3. Optical properties

Optical properties of the Al-NPs have been analyzed using extinction measurements performed in a UV-Visible spectrophotometer (Cary100 from Agilent Technologies). Figure 3 shows a comparison of the extinction spectra of thin film and NPs, i.e. before and after RTA. Spectra have been obtained from different areas of the substrate that demonstrate the overall ho-
mogeneity of the sample. The thin films exhibit spectra characteristics similar to that of bulk aluminum [7]. After annealing and creation of Al-NPs, the bulk metallic aspect of the film disappears and the sample becomes transparent. The spectra show a well-defined UV resonance around $\lambda = 210$ nm. This resonance is the signature of the localized surface plasmon supported by the Al-NPs and the FWHM is related to the size distribution of the NPs. The 2.5 nm film presents a single peak, in the range of 200-400 nm, associated with its narrow NP size distribution. In contrast, the thicker films exhibit a broader peak, at $\lambda \approx 210$ nm, as well as other features at longer wavelengths. These features will be discussed in detail below. Let us emphasize that the plasmonic optical properties are temporally stable: after 5 days the Al-NPs exhibit the same extinction spectra, while an unprocessed aluminum film oxidizes and the absorption peak disappears. This is strong confirmation of the crystalline nature of the Al-NPs since oxidation on crystalline aluminum takes place only at its surface. In contrast, the polycrystalline Al film allows for oxidation through its grain boundaries, resulting in a pure alumina film within a few days.

To confirm the plasmonic origin of the resonances observed in Fig. 3, we performed numerical simulations based on Mie theory using a freely available code [20]. Results are presented in Fig. 4 for the 2.5 nm thick film which resulted in Al-NPs with a mean diameter of 5.1 nm. The Al-NP is modeled as an aluminum sphere coated with a shell of alumina representing the oxidation layer. The total diameter of the oxidized particle is taken as 5.1 nm, which corresponds to the experimental value. An effective medium with refractive index of $n_{\text{ext}} = 1.32$ was used to account for the quartz substrate and surrounding air. The thickness of the alumina shell was tuned in order to match the simulated spectrum to the experimental spectrum. We found an excellent agreement for a shell thickness of 1.1 nm, giving us a first estimate of the oxidation layer thickness. This value is slightly lower than the 2-3 nm thick layer reported in studies on lithographically fabricated Al-NPs [11]. This may be due to a higher crystallinity of our Al-NPs leading to less oxidation, but further studies are required to support this assumption. For larger Al-NPs the resonance around $\lambda = 210$ nm broadens and other peaks appear at longer wavelengths (Fig. 3(b)). We explain the broadening of the first peak by the larger size distributions of the particles. The other peaks can be explained by considering electromagnetic interactions between neighboring Al-NPs leading to the appearance of coupled plasmonic modes.
Fig. 4. Blue line: Mie theory extinction spectrum for a single Al sphere (radius $a = 1.45$ nm) coated with 1.1 nm of alumina (total radius $b = 2.55$ nm). The surrounding effective medium has a refractive index of $n_{\text{eff}} = 1.32$ and the refractive index of alumina is $n_{\text{Al}_2\text{O}_3} = 1.83$. Red marks: corresponding experimental extinction spectrum for Al-NPs from a 2.5-nm thick aluminum film (mean diameter 5.1 nm).

4. Conclusion

In conclusion, we have proposed an original method allowing for large-scale preparation of aluminum nanoparticles on a substrate. The method is based on the rapid thermal annealing of a thin aluminum film deposited on a super-repellent substrate. The obtained NPs exhibit a relatively homogeneous size distribution depending on the initial thickness of the Al film. The resulting Al-NPs have well-defined surface plasmon resonances in the ultraviolet as shown by extinction measurements and confirmed by Mie theory. The samples are stable over time as bulk oxidation is prevented by the formation of a passivation layer. To the best of our knowledge, this is the first time that an annealing method is successfully used to create aluminum nanoparticles (and not nano-islands). They could be used as substrate for metal-enhanced fluorescence, UV-SERS, or coupled to a wide bandgap semiconductor for enhancing the efficiency of optoelectronic devices operating in the ultraviolet regime.

Acknowledgments

We thank Stephanie Dodson for proofreading the manuscript. This work has been supported by the French National Research Agency (grants HYNNA ANR-10-BLAN-1016 and TWINS ANR-11-BS10-002) and the Labex ACTION. Financial support of NanoMat (www.nanomat.eu) by the “Ministère de l’enseignement supérieur et de la recherche,” the “Conseil régional Champagne-Ardenne,” the “Fonds Européen de Développement Régional (FEDER),” and the “Conseil général de l’Aube” is acknowledged. JM acknowledges support from the “Conseil régional Champagne-Ardenne” under grant PlasmUV.