Ultraviolet Nanoplasmonics: Materials and Applications

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The last decade has seen an explosion in the development and exploitation of nanometer scale (subwavelength) metallic structures because of their remarkable plasmonic ability to enhance local electromagnetic fields.[1-7] Plasmonic research and applications based on silver or gold nanostructures are rapidly maturing at visible and near infrared wavelengths. The degree of enhancement depends strongly on two principal characteristics: the conductivity and size of the nanostructure. Silver has been widely used for visible or near-infrared wavelength applications because of its very high electron density. Gold is a popular alternative, in spite of its lower conductivity and greater interband absorption, because it does not oxidize as rapidly as silver.

Although ultraviolet (UV) plasmonics is still in its infancy, opportunities abound for applying plasmonic techniques in the UV region: Raman scattering cross sections are dramatically higher, spontaneous emission rates are much faster, photocatalytic processes are currently inefficient, and improved electron photoemission sources are possible. For example, the Raman scattering intensity for excitation frequency f scales as f^4, so Raman spectra taken at ~250 nm will be 81 – 256 times stronger than spectra taken at the traditional wavelengths of 750 – 1000 nm.

To explore these opportunities, the ideal UV plasmonic material must be identified. Although the plasmonic properties of aluminum (Al) and gallium (Ga) nanoparticles (NPs) are potentially as compelling in the UV as the respective properties of silver (Ag) and gold (Au) in the visible, there has been surprisingly little research into Al or Ga nanoplasmonics. This presentation will explore the potential of Al and Ga NPs for UV plasmonic applications.

We have investigated the growth kinetics of Al and Ga NPs synthesized by molecular beam epitaxy (MBE) and demonstrated that significant UV local field enhancements are possible with Ga NPs.[8-12] Because of its low melting point (30°C), Ga forms a close-packed array of smooth hemispherical NPs when fabricated by room temperature MBE. The arrays exhibit remarkable long-term stability because of the rapid formation of a monolayer-thick, self-terminating oxide layer. By contrast, Al has a higher electron density with a bulk plasmon resonance deeper into the UV. However, its thick native oxide (Al_2O_3) diminishes its plasmonic properties: the local field enhancement falls exponentially with plasmon - emitter/analyte separation.

Specific applications to be discussed include enhanced or suppressed spontaneous emission and surface-enhanced Raman spectroscopy of nearby emitters and analytes, respectively. Excitonic mission rates from a quantum well emitter have been accelerated by a factor of 92 through resonant coupling to a nearby surface plasmon (Fig. 1),[13] while spatially averaged Raman signals from cresyl violet have been amplified in the visible and UV by nearby Ga NPs (Fig. 2).[12] A theoretical analysis using the discrete dipole approximation reveals how the plasmon resonance shifts polarimetrically as a function of NP size and shape (Fig. 3).[14]

References

[1] W. Barnes, J. Lightwave Tech. **17** (1999) 2170–2182.
[2] C. Haynes and R. van Duyne, J. Phys. Chem. B **105** (2001) 5599–5611.

[3] J. Jackson and N. Halas, Proc. Natl. Acad. Sci. U. S. A. **101** (2004) 17930–17935.
[4] K. Kneipp, Phys. Today **60**, 40–46 (2007).
[5] S. Lal, N. K. Grady, J. Kundu, C. S. Levin, J. B. Lassiter, and N. J. Halas, Chem. Soc. Rev. **37** (2008) 898–911.
[6] J. Vuckovic, M. Loncar, and A. Scherer, IEEE J. Quantum. Electron. **36** (2000) 1131–1144.
[7] Z. Wang, S. Pan, T. Krauss, H. Du, and L. Rothberg, Proc. Natl. Acad. Sci. U. S. A. **100** (2003) 8638–8643.
[8] S. Choi, T.-H. Kim, A. S. Brown, H. O. Everitt, M. Losurdo, G. Bruno, and A. Moto, Appl. Phys. Lett. **89** (2006) 181915.
[9] S. Choi, T.-H. Kim, H. O. Everitt, A. Brown, M. Losurdo, G. Bruno, and A. Moto, J. Vac. Sci. Tech. B **25** (2007) 969.
[10] S. Choi, T.-H. Kim, P. C. Wu, A. S. Brown, H. O. Everitt, M. Losurdo, and G. Bruno, J. Vac. Sci. Tech. B **27** (2009) 107–112.
[11] P. C. Wu, T.-H. Kim, A. S. Brown, M. Losurdo, G. Bruno, and H. O. Everitt, Appl. Phys. Lett. **90** (2007) 103119.
[12] P. C. Wu, C. G. Khoury, T.-H. Kim, Y. Yang, M. Losurdo, G. V. Bianco, T. Vo-Dinh, A. S. Brown, and H. O. Everitt, J. Am. Chem. Soc. **131** (2009) 12032–12033.
[13] A. Neogi, C. Lee, H. Everitt, T. Kuroda, A. Tackeuchi, and E. Yablonovitch, Phys. Rev. B **66** (2002) 153305.
[14] P. Albella, B. Garcia-Cueto, F. Gonzalez, F. Moreno, P. C Wu, T.H. Kim, A.S. Brown, Y. Yang, H. O. Everitt, and G. Videen, NanoLetters **11** (2011) 3531-3537.

Figures

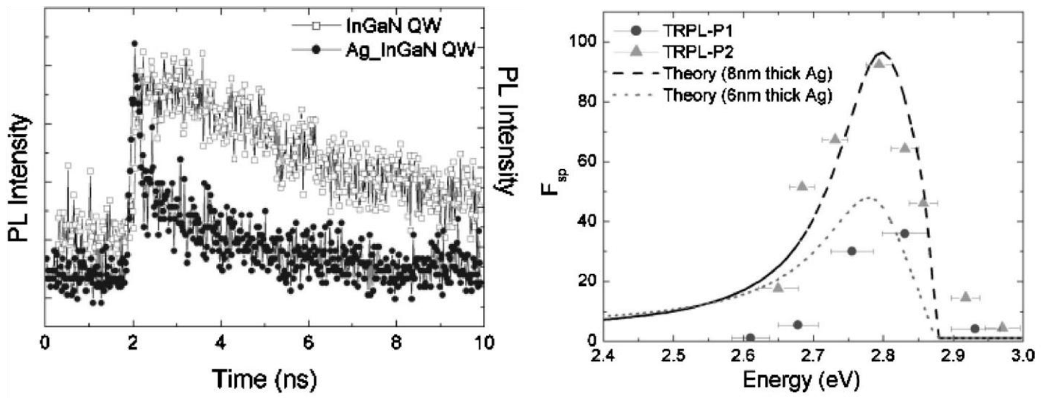

Figure 1. a) TRPL spectra of the InGaN QW emission into free space and altered by the nearby silver plasmon. b) The Purcell enhancement factor of the emission rate as a function of emission energy, showing that the enhancement is greatest when the emission is resonant with the LSPR at 2.85 eV.

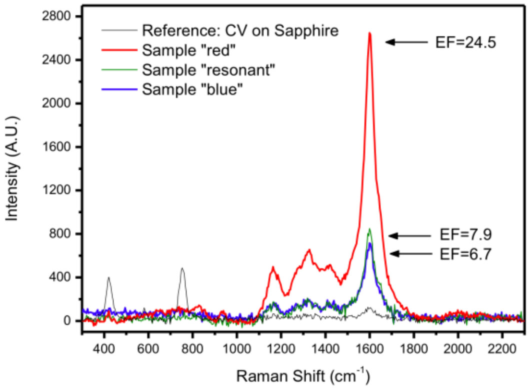

Figure 2. Demonstration of UV SERS of CV by Ga NPs on a sapphire substrate, compared to the Raman signal of CV on bare sapphire for laser energies red of (1.95 eV), resonant with (3.8 eV), and blue of (4.5 eV) the plasmon resonance.

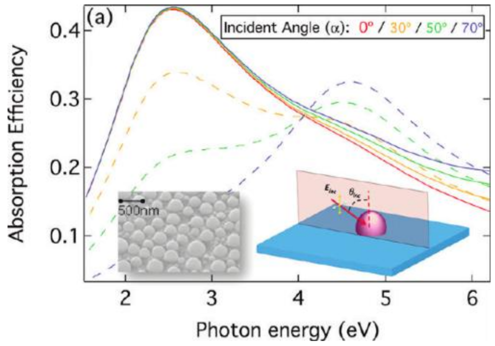

Figure 3. Absorption efficiencies as a function of incidence angle α for a hemispherical Ga NP having a 20 nm radius on a plane sapphire substrate and illuminated by S-polarized (solid lines) or P-polarized (dashed lines) Gaussian beams. Inset shows a scanning electron microscope of Ga NPs deposited by MBE.