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Demonstration of surface-enhanced Raman scattering by tunable, plasmonic gallium nanoparticles

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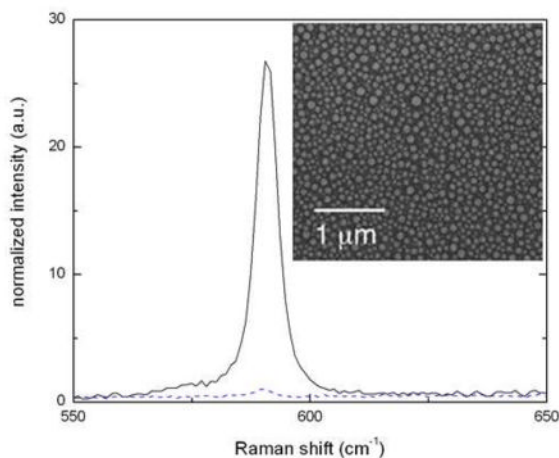
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Abstract



Size-controlled gallium nanoparticles deposited on sapphire are explored as alternative substrates to enhance Raman spectral signatures. Gallium's resilience following oxidation is inherently advantageous compared to silver for practical *ex vacuo*, non-solution applications. Ga nanoparticles are grown using a simple, molecular beam epitaxy-based fabrication protocol, and by monitoring their corresponding surface plasmon resonance energy through *in situ* spectroscopic ellipsometry, the nanoparticles are easily controlled for size. Raman spectroscopy performed on cresyl fast violet (CFV) deposited on substrates of differing mean nanoparticle size represents the first demonstration of enhanced Raman signals from reproducibly tunable self-assembled Ga nanoparticles. Non-optimized aggregate enhancement factors of ~80 were observed from the substrate with the smallest Ga nanoparticles for CFV dye solutions down to a dilution of 10 ppm.

Gallium, a standard metal used for optoelectronic devices, represents an alternative plasmonic material with attributes superior to traditional nanostructured silver and gold. Here we present the first demonstration of plasmonic Ga nanoparticle (NP) substrates for surface-enhanced Raman scattering.

Theoretical treatment by Zeman and Schatz reveals Ga's potential to support strong surface fields.¹ Plasmonic gallium NPs are promising for an array of applications because of their

broad plasmon tunability, stability across a wide temperature range, excellent plasmon resiliency when oxidized, and simplicity of deposition – even at room temperature.^{2, 3} Ga NPs can be tuned into the deep ultraviolet (UV), owing to its high plasma frequency, $\omega_p = 14\text{eV}$, with demonstrated tunability over a broad spectral range from 0.75–6.5 eV – a significant advantage over the limited range achievable by both Ag and Au, especially for simultaneous UV Raman/PL spectroscopy.^{2, 4, 5} Moreover, substrate-supported Ga NPs exhibit no post-deposition aggregation or attendant modification of the plasmon; therefore, the plasmon resonance is stable and reproducible. Unlike Ag and Au, Ga can be deposited directly onto solid supports, such as sapphire or Si, without an additional adhesion layer. Therefore, stable Ga NPs can potentially overcome the drawbacks associated with uncontrolled NP aggregation, yielding reproducibly tunable plasmonic substrates.

We have previously demonstrated that the Ga NP SPR is minimally redshifted and not quenched when exposed to air.² The Ga SPR remains stable and protected once oxidized even after over a year of air exposure. Conversely, Ag oxidizes excessively and becomes quenched within 36 hours of air exposure.⁶ In addition the Ga plasmon mode's remarkable thermal stability from 80K⁷ to 873K² foreshadows Ga's advantageous use for applications in thermally harsh and diverse environments. Given these promising and unique attributes, we demonstrate room temperature-deposited, tunable, plasmonic Ga nanoparticles and their applicability to surface-enhanced Raman scattering (SERS).

The Raman enhancement and longevity of Ga NPs substrates were tested using the standard Raman dye Cresyl fast violet (CFV). Ga NPs were grown by molecular beam epitaxy on inert, sapphire substrates to mitigate fluorescence interference in Raman measurements typically observed with glass substrates, but can be deposited on a wide variety of solid supports.² By adjusting the deposition time at a fixed beam flux, we modified the mean NP diameter and, therefore, tuned the surface plasmon resonance of three Ga NPs/sapphire substrates to (i) 2.9eV, (ii) 1.96eV, or (iii) 1.58eV, respectively, as shown in the pseudoextinction coefficient, $\langle k \rangle$, measured by *in situ* spectroscopic ellipsometry^{2, 8} (figure 1).

Substrates were half metallized and half unmetallized for direct comparison between the Ga NPs' influence and the bare sapphire. A 1 μL volume of 100ppm CFV in ethanol was dropwise placed on fully oxidized Ga NPs/sapphire substrates and dried for approximately 15 minutes to ensure complete EtOH evaporation and to minimize the distance between the CFV molecules and the metal NP surfaces.

CFV and sapphire possess distinct, strong, and well-separated Raman active modes. EtOH easily wets the substrate surface and the solution spreads over a circular area of approximately $5 \times 5 \text{mm} = 25 \text{mm}^2$.

The strong Raman-active CFV mode at 590cm^{-1} was measured by an inVia Raman Renishaw Raman system with a 50 \times objective ($\sim 2 \mu\text{m}$ diameter beamspot) and a 0.2mW 633nm (HeNe) laser. A 100 ppm solution of CFV in EtOH was deposited on both the metallized and bare halves of each sample. The aggregate Raman enhancement for a given sample is simply the ratio of these two measurements, $R = (I_{NP}/I_{bare})$, repeated and averaged for five different locations, then divided by the fraction of the surface area covered by nanoparticles (f_{NP}) in the SEM image (*viz.* R/f_{NP}). The clear difference with and without Ga NPs on the surface indicates that the nanostructured Ga induces an enhancement of the Raman signal (figure 2). The 2.9eV SPR sample exhibits the strongest aggregate SERS enhancement ($\sim 30/0.37 = 80$), followed by the 1.58eV and 1.96eV samples. Although we have not attempted to discern the enhancement factor^{9, 10}, an unknown fraction of the heterogeneously distributed particle sizes and spacings enhance the Raman signal and it is clear the enhancement factor will be orders of magnitude larger when the few regions responsible for the enhancement are identified.

To quantify the sensitivity and post-oxidation stability of enhanced Raman signal from the 2.9eV NPs, CFV solutions ranging from 10–200ppm were deposited onto Ga NPs on sapphire for Raman measurements (figure 2, inset). As expected, the Raman intensity weakens linearly with decreasing CFV concentration, but even the 10ppm sample exhibits a measurable Raman signal. In stark contrast to Ag nanostructures used for SERS substrates, the Ga NP-enhanced Raman signal did not degrade even after several days of air exposure.

Several factors contribute to the varying enhancements among the three plasmonic Ga NP/ sapphire substrates. Enhanced Raman signals arise from strong localized surface modes of plasmonic NPs. Since all Ga NPs are spheroidal, the plasmon resonance of these samples tunes with NP size. Inspection of the Ga NP imagery supports a correlation between NP size and enhanced Raman signal: the 2.9eV sample, whose NPs had the smallest mean diameter (88nm), contributed the strongest Raman response. In addition, the high density of NPs associated with the smallest mean diameter increases the opportunity for interparticle electromagnetic coupling and field concentration between the NPs. The interparticle spacings in the 2.9eV sample are most narrowly distributed around a mean separation of 16nm, small enough to induce strong interparticle E-field coupling to enhance the local fields, ultimately strengthening the already enhanced Raman signal.¹¹ As the NPs increase in size, so does the interparticle spacing – 20nm for the 1.96eV substrate and 40nm for the 1.58eV substrate – weakening any enhancement derived from interparticle electromagnetic coupling. Taken together, the large number of small, similarly sized, closely spaced NPs enables the 2.9eV sample to produce the strongest Raman signal for a given concentration of CFV. Importantly, tuning the Ga NP diameter and spacing during growth can optimize the NP-induced enhancement.

Plasmonic Ga NPs can be flexibly applied to a variety of applications owing to their tunability over a broad spectral range, liquid phase, and attendant thermal and chemical stability. In a self-assembled, room temperature, UHV evaporation process, Ga NPs are tunable to specific plasmon resonances ranging from 0.75eV to 6.5eV. Although the enhancement factor for these Ga NPs is smaller than reported for Ag nanostructures, it is important to emphasize that enhanced Raman signals were observed even though room temperature deposition produces non-optimized NP density and size distributions. The tremendous control afforded by MBE deposition and Ostwald ripening to tailor Ga NP distribution – with more uniformly sized NPs or more controllable NP densities – heralds the potential of reproducibly self-assembled plasmonic Ga NPs for SERS.

Acknowledgments

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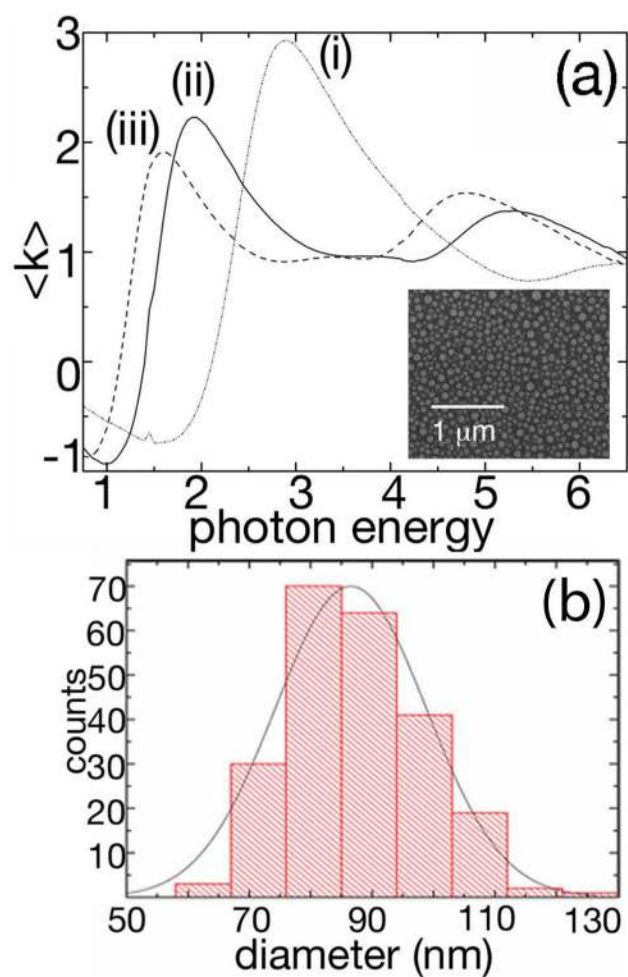


Figure 1. (a) Pseudoextinction spectra obtained by *in situ* spectroscopic ellipsometry corresponding to three Ga NP on sapphire samples. The SEM image (inset) and accompanying NP diameter distribution histogram (b) correspond to the 2.9eV SPR sample (curve (i) in (a)).

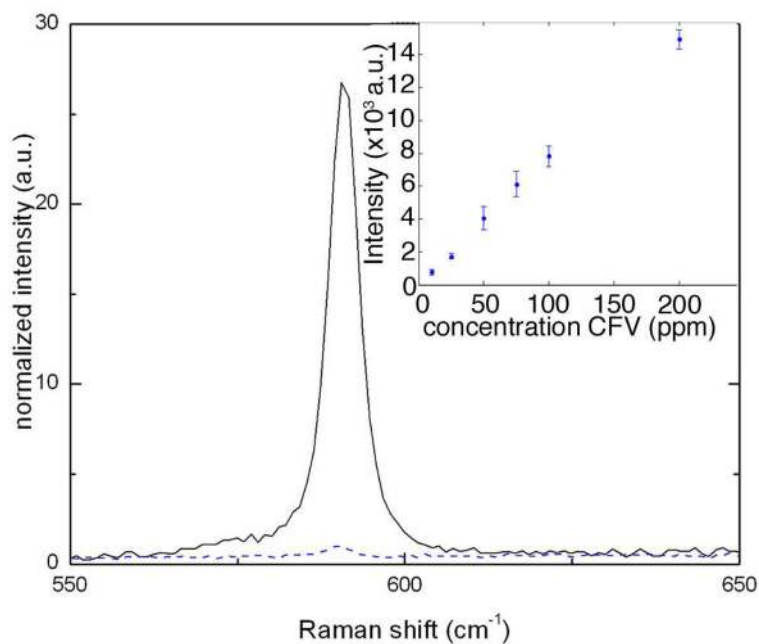


Figure 2. High resolution Raman spectra for the strongest CFV mode at 590cm^{-1} for Ga NPs with SPR at 2.9eV (solid) compared to the same CFV mode on bare sapphire (dotted). Decreasing CFV concentration in ethanol exhibits a linear correlation between CFV concentration and the Raman intensity. Calibration error bars, determined by the standard deviation of five measurement locations, range from 4–20%, quite small even at the largest concentrations, indicating reproducibility (inset).