Stretchable metal-elastomer nanovoids for tunable plasmons

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A range of flexible metal-elastomer nanostructures are fabricated using a self-assembly and casting technique. Such nanostructures support plasmons, which have energies and field distributions that are strongly dependent on the structure geometry or position within an array. In particular, truncated spherical metal cavities embedded within a flexible three-dimensional elastomer film can be elastically deformed without tearing, modifying their shape and mechanically tuning their resonant plasmon modes. Such structures make possible the fabrication of low cost elasto-optic films and tunable substrates for surface enhanced Raman spectroscopy. © *2009 American Institute of Physics*. [doi:10.1063/1.3247966]

Plasmons are trapped electromagnetic fields, bound by their interaction with free charges onto a metal surface. By fabricating appropriate nanostructures, plasmons can become localized on particles or within cavities, producing concentrated optical fields, which are utilized for applications such as surface enhanced Raman spectroscopy[1] and photoluminescence. The energy and field distribution of plasmons are strongly dependent on nanostructure geometry, and can be tuned by slight changes in nanostructure shape or volume.[2] For many applications it is desirable to actively tune the plasmonic properties of nanostructures, for example, to create low cost elasto-optic materials, plasmonic filters, and metamaterials.[3–5] While there have been many examples of nanostructures with plasmonic properties tunable by the fabricated structure geometry, *active* plasmon tuning has been limited in spectral range due to the optical,[6,7] electronic,[8] ferroelectric,[9] and thermal[10,11] tuning mechanisms involved. An alternative approach is to fabricate structures with *mechanically* tunable plasmonic properties. Relatively few mechanically tunable plasmonic structures have been demonstrated, with examples limited to tunable gratings[12,13] and plasmonic particle arrays embedded in a polymer matrix.[14]

Here we use a self-assembly and casting technique to fabricate a range of flexible metal-elastomer nanostructures, which have mechanically tunable plasmonic properties. A wide variety of nanostructures can exploit this fabrication procedure including [Fig. 1(a)] hemispheres, [Fig. 1(b)] voids, [Fig. 1(c)] tips, and [Fig. 1(d)] pyramidal pits. These structures consist of metal films or particles supported on or embedded within a flexible three-dimensional substrate. Both particles and cavities support plasmon modes with optical field distributions, which reflect the symmetry of the nanostructure geometry. The plasmonic resonances of flexible metal-elastomer nanostructures shift when mechanically stretched [Fig. 1(e)]. Changing the aspect ratio of these structures breaks the symmetry of the system and splits the plasmon modes. The key design constraint is preserving metal surface area (to avoid tearing), while changing the structure volume or aspect ratio. Stretching flexible nanostructures while fulfilling this constraint can tune the absorption of resonant plasmon modes across the visible spectral range, producing new types of elasto-optic materials and novel absorbers and emitters.

Although particles, tips and triangular pits have also been demonstrated, we here focus our discussion on the properties of flexible metal-elastomer nanovoids [Fig. 1(b)]. Nanovoids in solid-metal films have been investigated extensively elsewhere,[15] and support resonant plasmon modes within truncated spherical cavities which have energies and field distributions, which strongly depend on the structure geometry. Furthermore, the cavities of nanovoid structures are ideally suited to mechanical manipulation since the spherical geometry uniformly distributes the applied strain, minimizing the possibility of rupturing or tearing the cavity walls.

Metal-elastomer nanovoids are fabricated using a self-assembly and casting procedure [Figs. 2(a)–2(f)], producing structures ranging from shallow dishes up to fully encapsulated spherical cavities. A monolayer of polystyrene spheres is self-assembled on a gold-coated glass slide and a thin layer of transparent elastomer (Sylgard 182, refractive index[16] $n=1.41$ at 523 nm and 23 °C) is drop cast onto the spheres and left to cure. Upon curing, the elastomer film is peeled off the substrate with the spheres embedded in the film. The spheres are then removed by dissolving in dimethylformamide (DMF) solution. Finally a 100-nm-thick layer of gold is sputtered onto the elastomer substrate. It is convenient to define the normalized sample film thickness to describe the different sample geometries as $\bar{t}=t_{\mathrm{void}}/D_{\mathrm{void}}$, where D_{void} is

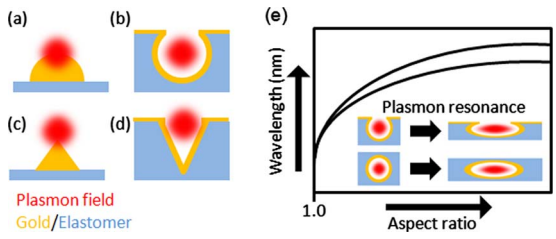

FIG. 1. (Color online) Hybrid metal-elastomer nanostructures and schematic resonant plasmon fields for (a) hemispheres, (b) voids, (c) tips, and (d) pyramidal pits. (e) Characteristic theoretical resonant plasmon wavelength dependence on structure aspect ratio (lines). As structures stretch, the broken symmetry results in plasmon splittings. Inset: schematic cavity with plasmon field distribution (shaded) when viewed from (top) side-on and (bottom) top-down.

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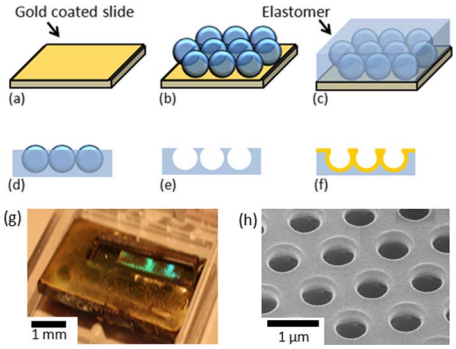

FIG. 2. (Color online) (a)–(f) Metal-elastomer nanovoid fabrication procedure. (g) Image of a typical sample, opalescent strip is nanostructured with nanovoid cavities. (h) SEM images of $\bar{t}=0.8$ structure.

the diameter of the void and t_{void} is the film thickness, so that the fully encapsulated void has $\bar{t}=1$. To fabricate a structure of a particular $\bar{t}$, metal is electrodeposited up to a height $\bar{h}=1-\bar{t}$ around the self-assembled spheres at step (b). If the height of metal deposited is greater than $\bar{h}\approx 0.3$, then spheres remain adhered to the metal template rather than lifting off with the elastomer film. This currently prevents the fabrication of elastomeric cavities in the range of $\bar{t}\approx 0.5-0.7$. Using this technique, it is possible to produce elastomer cavity samples of thicknesses $\bar{t}=0-0.5, 0.7-1$, yielding structures which support a wide variety of plasmon modes that are tunable by the thickness $\bar{t}$ and by active stretching.

Metal-elastomer nanovoid samples of cavity diameter 900 nm [Fig. 2(g)] appear opalescent due to diffraction by the periodic structure and absorption by plasmon modes. Scanning electron microscopy (SEM) imaging [Fig. 2(h)] reveals the smooth metal coating achieved by sputtering onto an array of nanovoids of thickness $\bar{t}=0.8$ and confirms a 100-nm-thick conformal metal coating within the cavities.

Nanovoid arrays support both propagating Bragg plasmons and localized Mie plasmon modes, both of which are sensitive to strain. Bragg plasmons are coupled by the periodicity of the structure and are observed for structures of $\bar{t}\leq 0.3$, for which the structure takes the form of a two-dimensional (2D) grating. Due to their delocalized nature, Bragg plasmons have energies which are strongly dependent on both the angle of incident light and the sample orientation. Mie plasmon modes are observed for structures of $\bar{t}\geq 0.6$, for which the structure takes the form of an array of truncated spherical cavities. The localized modes of nanovoids are referred to as Mie plasmons due to their similarity with the resonances of nanoparticles, and are labeled ${}^{m}L={}^{0,1,\cdots}P,D,F$ according to their angular states and in accordance with Mie theory.[17] Due to their localized nature, Mie modes have energies which are relatively independent of the angle of incident light and the sample orientation. Therefore, in general, angle-resolved reflectivity measurements are a key to distinguishing the plasmon modes of nanovoids. However for intermediate sample thicknesses ($\bar{t}\approx 0.3-0.6$), Bragg modes mix with weakly localized Mie plasmons producing mixed-states with more complicated dispersions.[18]

To produce elasto-optic effects in metal-elastomer nanovoids, both the Bragg or Mie plasmon resonances can be stretch-tuned. Due to their narrow absorption linewidths, it is expected that Mie resonances should produce the strongest

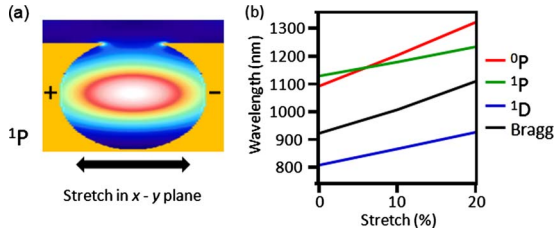

FIG. 3. (Color online) (a) Calculated field distribution of the ${}^{1}P$ cavity mode in a 900 nm diameter nanovoid, which has been stretched by 20% in the x-y plane. +/− indicate positions of charge nodes on the cavity walls. (b) Calculated energy of localized modes upon cavity stretching.

observable elasto-optic effects. Calculations are performed to investigate the effect of stretching on the Mie resonances of a nanovoid using a boundary element scheme described in Ref. 19. The lowest energy Mie plasmon mode of nanovoids is the $m=1$, $l=1$ mode (${}^{1}P$) [Fig. 3(a)]. This mode has a field vector aligned in the plane of the surface and is strongly coupled to incident light. As strain is applied, the shape of the cavity is modified but the volume remains roughly constant. The cavity stretches along the axis parallel to the direction of applied strain but contracts along the axis perpendicular to the applied strain direction, breaking the axial symmetry of the cavity. Calculations [Fig. 3(b)] show that as a nanovoid cavity is stretched, Mie plasmon modes with field vectors aligned parallel to the stretch direction tune to longer resonant wavelengths, where for ${}^{1}P$ a 20% strain produces $\approx 10\%$ increase in resonant wavelength. The contraction of the cavity in the plane perpendicular to the direction of stretching tunes plasmons with field vectors aligned along this short axis to shorter wavelengths [represented in Fig. 1(b)]. Similar tuning behavior is expected for the ${}^{0}P$ and ${}^{1}D$ Mie plasmon modes. However, in general, the splitting and tuning of modes is found to be dependent on the precise plasmon field distribution of the mode within the changing cavity volume. In contrast, the tuning of Bragg plasmon modes is expected to be a linear function of the applied strain (for low strains) since these modes are supported on the 2D periodic top surface structure which deforms according to Poisson's equation.

Reflectivity measurements [Fig. 4(a)] for a 900 nm diameter metal-elastomer nanovoid cavity of thickness $\bar{t}=0.5$ [shown in Fig. 2(g)] reveal a plasmon absorption dip at 730 nm. Comparison with angle-resolved reflectivity data (not shown) indicate that the plasmon is a ${}^{1}D$ Mie mode mixed with a Bragg plasmon mode.[15] The sample was stretched on a translation stage while recording the normal incidence reflectivity using a 10× optical microscope collecting over a

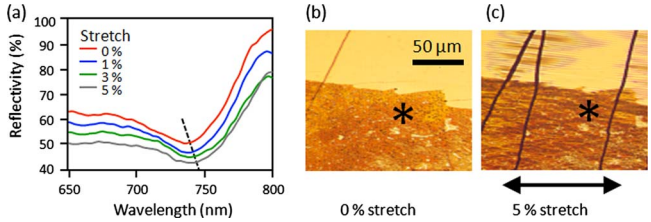

FIG. 4. (Color online) (a) Reflectivity of the metal-elastomer nanovoid structure with applied strain (dashed line indicates the wavelength of peak plasmon absorption). (b) and (c) Microscope images at 10× of (bottom) nanovoids and (top) flat metal on elastomer at strains corresponding to (b) 0% and (c) 5% stretching. Spectra in (a) taken at ∗.

range of angles $\theta \leq 5°$. The strain-dependent reflectivity shows that the plasmon resonance tunes from 730 nm at 0% applied strain to 745 nm at 5% applied strain. This represents the first observation of stretch-tuning of localized plasmons. The 3 nm/% is less than half than predicted in our models, indicating that the strain is not completely transferred across the metal film. Comparison of microscope images of the structure at 0% and 5% applied strain [Figs. 4(b) and 4(c)] shows the formation of cracks and ripples on the metal/polymer film, which absorb a fraction of the applied strain. Flat unpatterned thin metal films supported on elastomeric substrates fracture at strains greater than 2% (Refs. 20 and 21) and wavelike ripples form normal to the stretch direction due to the buckling instability of the film.[22] Correspondingly, the sample reflectivity drops as the rippled surface scatters and diffracts light and the substrate becomes semitransparent. As the strain is increased beyond 5%, the reflected light intensity drops rapidly as the number of defects increases and the plasmon resonances can no longer be accurately identified. In order to overcome such defects, the flat metal film must be removed from around the coated nanovoids. This can be achieved using a sacrificial aluminum layer, which is deposited before the removal of the spheres during fabrication (in progress). This process leaves gold only *within* cavities and ensures that the maximum possible strain is applied to the cavities and not to the surrounding flat surfaces, thereby minimizing the formation of cracks and ripples.

In these samples Mie plasmon resonances are not yet observed on thicker nanovoid structures of $\bar{t} \geq 0.7$. One explanation is that although sputtering coats the cavity conformally, it is unable to coat uniformly around the entire cavity (due to shadowing by the cavity lip entrance). Therefore the cavity may not provide sufficient confinement for strong localized plasmon resonances. Future experiments will investigate the role of the cavity rim on elastomer nanovoid substrates.

In summary, we present a simple self-assembly and casting procedure for fabricating metallic nanoscale cavities in a stretchable elastomer film. Upon coating with metal, structures support plasmon resonances which are stretch-tunable by applying strain to the structure. The fabrication procedure can be modified to produce alternative geometries, including gratings, pits, spikes, and particles, for use in applications from sensors to displays.

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