Tunable surface plasmon resonance on an elastomeric substrate

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Abstract: In this study, we demonstrate that periods of metallic gratings on elastomeric substrates can be tuned with external strain and hence are found to control the resonance condition of surface plasmon polaritons. We have excited the plasmon resonance on the elastomeric grating coated with gold and silver. The grating period is increased up to 25% by applying an external mechanical strain. The tunability of the elastomeric substrate provides the opportunity to use such gratings as efficient surface enhanced Raman spectroscopy substrates. It's been demonstrated that the Raman signal can be maximized by applying an external mechanical strain to the elastomeric grating.

OCIS codes: (050.2770) Gratings, (240.6680) Surface Plasmons, (240.6695) Surface-enhanced Raman Spectroscopy, (250.5403) Plasmonics

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1. Introduction

The surface plasmon resonance (SPR) phenomena observed on noble metal surfaces or nanoparticles has been a great interest in several fields of research such as nanoscale photonics and biological sensing [1]. SPR can simply be defined as collective oscillations of free electrons coupled to the metal-dielectric interfaces. Metal nanoparticles such as nanospheres, nanorods, thin film nanoislands or nanoshells show strong extinction and scattering spectra when excited at the SPR condition. On the other hand, continuous metallic films possessing a periodic perturbation also exhibit similar effects at the SPR condition. The challenge of designing effective structures to manipulate plasmonic fields and utilize them in functional devices still remains. In particular, the use of SPR in surface enhanced Raman spectroscopy (SERS) and biological sensing require an intelligent design in order to maximize the plasmonic enhancement. In general, there is a need to optimize the correlation between the SPR and the excitation laser line in the case of SERS applications. A similar optimization is needed to be done for sensing applications of the presence of a particular biological molecule or a chemical reaction. In this regard, the tunability of the SPR wavelength provides flexibility in many plasmonic sensing applications.

In recent years, several different tuning mechanisms have been demonstrated such as controlling the interior cavity sizes of nanospheres [2], changing concentrations of core-shell nanoparticles [3], length of the nanochain gold nanoparticles [4], thermal deposition parameters of silver nanoislands [5], using nanocomposite systems [6], controlling the size, height and shape of silver nanospheres [7]. However, many of the above mechanisms require the parameters to be fixed during the fabrication. On the other hand, flexible designs utilizing electronic [8], ferroelectric [9] or thermal [10, 11] tuning mechanisms are also reported in the literature. Those methods are reversible and can be applied after the plasmonic structure is fabricated. Such a repeatable process can find wide applications in the field of Raman spectroscopy and plasmonic sensing.

The tunability of SPR wavelength on nanoshells was demonstrated [12] and a maximum SERS signal was achieved by optimizing the SPR wavelength. A similar approach for maxi-

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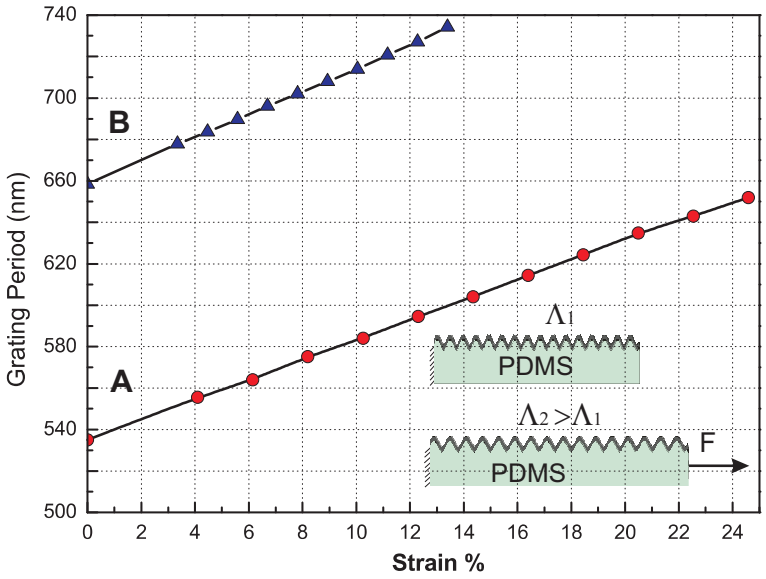

Fig. 1. Apparent grating period as a function of the applied mechanical strain for gratings with periods of 530 nm (**A**) and 665 nm (**B**). Both elastomers are coated with 55 nm of silver.

mizing the SERS signal was demonstrated on biharmonic grating structures by changing the grating strength and tuning the SPR wavelength [13]. It was reported that by controlling the geometry of the nanoshells, the SERS enhancements can be optimized [14]. A repeatable thermal tuning mechanism using silver nanoparticles for achieving a tunable SERS substrate was reported by Lu, et al. [15].

In this study, we use an elastomeric grating structure in order to excite surface plasmon polaritons (SPP) on its metallic surface. The mechanical tunability of such gratings are used in several applications such as dry adhesives [16] with tunable surface roughness and adhesion, light scanners [17], spectrometry [18], and for possible application to stretchable electronics [19]. Recently such elastomeric gratings are used for the excitation of SPP on flat metallic surfaces [20].

2. Fabrication

We report a way of tuning the SPR by applying mechanical strain on the elastomeric grating structure. The elongation of the elastomer effectively changes the period of the metallic grating. From the well known dispersion relationship [21], it can easily be seen that the SPR wavelength also shifts as the external strain changes the period of the elastomeric grating coated with a thin metallic layer. We fabricated two silicone elastomers (Sylgard 184, Dow Corning) with gratings on top using two different methods. We choose two different periods in order to cover a wide range of wavelengths. The first elastomeric grating was generated using holographic lithography. We recorded a master grating with the desired period —665nm— on top of a bare silicon sample using a holographic He-Cd laser beam with 325 nm wavelength exposure on a photoresistive polymer (AZ1505). After developing the sample, we achieved a grating with 665 nm period on the photoresist. The elastomeric grating is then obtained using the replication procedure: Liquid polydimethylsiloxane (PDMS) is poured on the master grating and cured at 75°C for at least 2 hours. Note that the thickness of the elastomer is kept around 5 mm. After the

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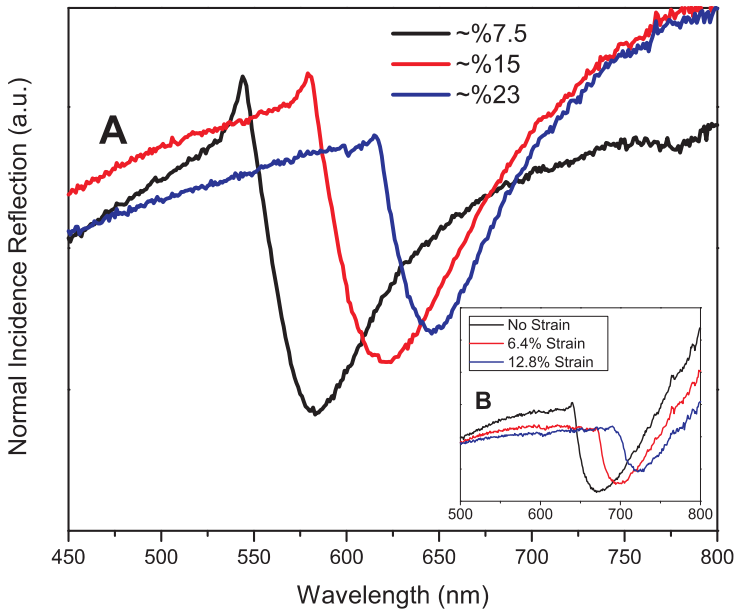

Fig. 2. The normal incidence reflection spectra for three different strain values of 7.5%, 15% and 23% for grating **A** (main) and no strain, 6.4% and 12.8% for grating **B** (inset).

curing procedure, the elastomeric stamp is peeled off from the master grating. Due to thermal contraction, there is a 1% decrease in the periodicity of the PDMS grating. To generate SPP, the PDMS grating is coated with an optimal 55 nm of silver [22] using thermal evaporation. For the second elastomer we used a commercially available ruled grating with 530 nm period as the master grating. The fabrication of the elastomeric grating is the same as in the first case. Similarly, this grating is coated with 55 nm of silver.

3. Results and discussions

For a demonstration of the tunable periodicity of the elastomeric grating, we performed a diffraction experiment [23]. We measured the angle of the diffracted beam when the grating is excited by a 514.5 nm Ar^{+} laser for the case of 530 nm grating (A) and by a 632 nm He-Ne laser for the case of 665 nm grating (B). The initial length of the elastomer has been measured using a caliper and the length increments are recorded using the micrometer of the mechanical stage. The mechanical strain is applied using a precision mechanical stage. The angle of the diffracted beam is recorded as a function of the applied mechanical strain. It's been shown in the literature that the thin metallic films on elastomeric substrates can be stretched reversibly without any plastic deformation up to 3% [24]. Elastic deformation for metallic films is important for maintaining the electrical interconnects on elastomeric substrates. In this work we deal with the grating periodicity of the metal layer. In the diffraction experiments, we have seen that the cracks on the metal surface do not change the effective grating period, but lower the quality factor of the surface plasmon resonance condition. In Fig. 1 the linear change in the periodicity of the grating is plotted up to 25% of mechanical strain.

To demonstrate the tunability of the SPR condition we used both gratings, A and B. The optical normal incidence reflection spectrum of the PDMS gratings is measured using an ellipsometer (JA Woolam VASE). As seen in Fig. 2, the SPR wavelengths on 55 nm silver coated gratings A and B are approximately 560 nm and 670 nm, respectively, in the absence of applied

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strain. As the elastomeric grating is stretched, SPR wavelength red shifts due to the increased grating periodicity. Note that the mechanical integrity of the silver film on top of the elastomeric grating may be degraded, if the strain is high [24]. The normal incidence reflection spectra are recorded for different applied mechanical strain values and plotted in Fig. 3. The shift in SPR wavelength follows the linear pattern as measured in diffraction experiments.

The elastomeric grating with 530 nm period is used as a SERS substrate to measure SERS signal of Rhodamine 6G (R6G) molecule. The grating is coated with 120 nm of gold layer by thermal evaporation. Raman spectra were obtained with a Jobin Yvon LABRAM Raman Spectrometer equipped with a He-Ne laser which gave an excitation line at 632.81 nm. 20 mW incident laser beam is focused by a 10x objective lens. The scattered radiation was collected by the same objective lens and sent through a Raman notch filter to a Peltier cooled CCD detector. 10 μl of 1.0×10^{-6} M R6G solution is drop-coated onto the elastomer and is then allowed to dry. The precision mechanical strain setup is used under the objective of the spectrometer. The elastomeric grating with R6G sample is stretched with the mechanical strain device until the Raman signal starts to increase. In Fig. 4, the Raman spectra of R6G are plotted for three different strain values. Raman signal is maximized when the strain is 20.8% which corresponds to a 633 nm grating period. The Raman signal drops immediately when the strain is further increased. Although the 18.8% and 22.9% strains are equally spaced from the optimal 20.8% strain, the enhancement factor drops faster in the latter case. This can be attributed to the shape of the absorption curves seen in Fig. 2, where the reflection spectrum of the grating is not symmetrical with respect to the resonance wavelength. The variation at the short wavelength side is faster than the variation at the long wavelength side.

After subtracting the background, the empirical signal enhancement factors were determined using the ratios of peak integrated surface enhanced Raman vibration to the corresponding unenhanced signal from 55 nm thick gold metal surface coated on silicon surface. An enhancement factor of more than 10^5 is achieved when the grating period is approximately 633 nm at

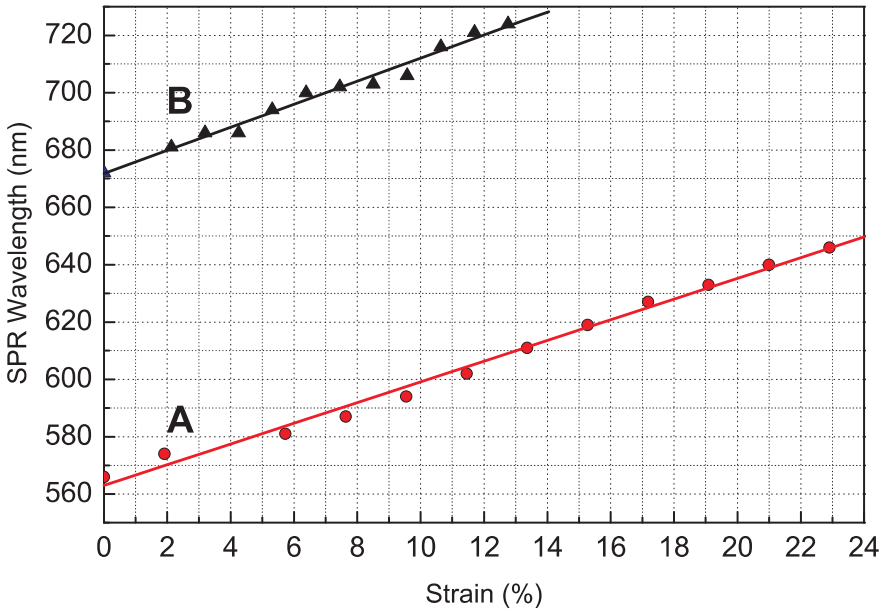

Fig. 3. SPR wavelength as a function of applied strain for grating **A** (circles) and **B** (triangles).

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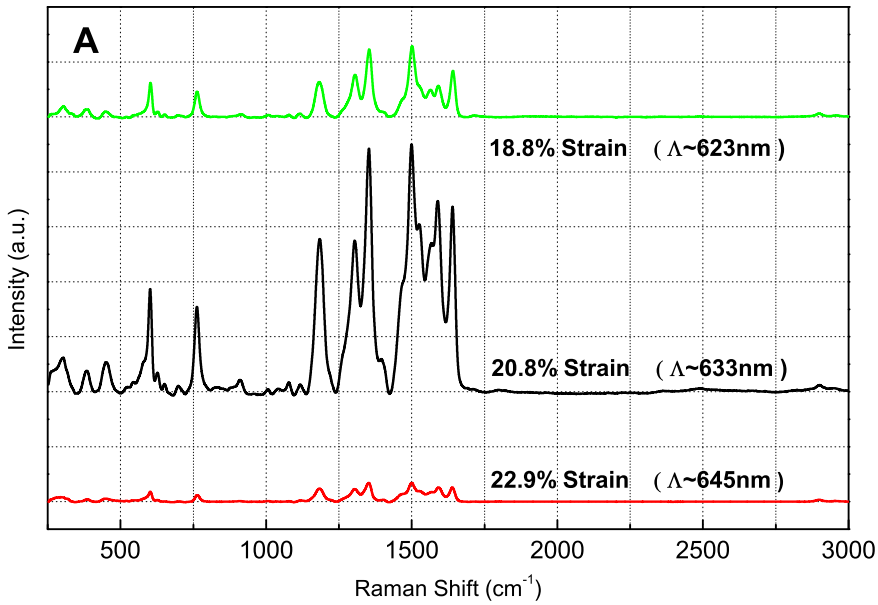

Fig. 4. SERS spectrum of R6G molecule taken from the elastomeric grating **A** surface coated with 120 nm gold for strain values of 18.8%, 20.8% and 22.9%. Background of the Raman signal is corrected.

the strain value of 20.8%. The enhancement factor is approximately constant for all the Raman peaks of R6G molecule, which shows the increase in the absorption of the excitation laser.

4. Conclusions

We have demonstrated the use of elastomeric gratings with tunable surface plasmon resonance condition. We have tuned the surface plasmon resonance wavelength by applying a mechanical strain on elastomeric gratings coated with a thin layer of metal. The shift of the SPR wavelength shows a strong correlation with the shift of the grating period. We have shown the use of the elastomeric grating with a SERS experiment of R6G molecule. It has been found that a maximum Raman signal can be reached by changing the surface plasmon resonance condition on the surface of the elastomeric grating. Note that the presented method is compatible with Raman and Micro-Raman Spectroscopy methods which utilize a fixed incident angle. It provides a simple way of excitation and tuning the surface plasmon resonance condition without using bulky prism couplers or complex scanning mechanisms required for changing the angle of incidence. Additionally, using the right angle reflection method provides a self aligned mechanism for incident and reflected beams. We believe that the method can be used not only in SERS experiments, but also in biosensing and plasmonic enhancement applications.

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