Stability Improved Stretchable Metallic Gratings With Tunable Grating Period in Submicron Scale

Da Yin, Jing Feng, Rui Ma, Xu-Lin Zhang, Yue-Feng Liu, Tong Yang, and Hong-Bo Sun, *Member, IEEE*

***Abstract*—We demonstrate a stretchable metallic gratings by fabricating an ordered buckling surface structure on an elastomeric substrate. Through oxygen plasma treatment of a prestretched elastomeric membrane, polymer gratings as templates are formed spontaneously after releasing the strain. The template gratings with different initial periods at submicron scale have been achieved simply by controlling the duration of the oxygen plasma treatment. Tunable surface plasmon-polariton (SPP) resonance can be excited in wavelength scale by depositing a thin metallic film on the template gratings. The stability of the metallic gratings' morphology has been improved by taking a template-restretching step before the metallic film deposition to weaken the Poisson effect. A tunable region of 90 nm for the SPP resonance has been achieved by stretching the metallic gratings up to 27.1% strain.**

***Index Terms*—Ordered wrinkles, stretchable metallic gratings, tunable surface plasmon-polaritons (SPPs).**

I. Introduction

GRATINGS are key components in a variety of devices such as DFB lasers [1], [2], thermal radiators [3], polariton lasers [4], light scanners [5], and optical fiber sensors [6]–[8]. Metallic gratings with proper periods by integrating the gratings with the metallic films have exhibited their effect in achieving surface plasmon-polariton (SPP) enhancement and improving the performance of optoelectronic devices [9]–[11]. The applications of the metallic gratings will be extended and more interesting when their periods can be dynamically tuned. However, their periods are fixed at the time upon fabrication and cannot be tuned externally for the metallic gratings fabricated on rigid substrates with conventional microfabrication process. Meanwhile, it has been reported that the metallic films rupture at strains of 1%–2% such as freestanding or polymer-supported gold, silver and copper [12], [13], which results in more difficult design and fabrication of tunable metallic gratings. A lot of efforts have been focused on realizing tunable metallic gratings with different tuning mechanisms. Olcum *et al.* [14] used template transferring methods to get elastomeric metallic gratings, and observed SPPs resonance and surface enhanced Raman spectroscopy. However, the original period of the stretchable grating was confined by the master grating, which limits its applications. Surface wrinkling [15]–[17] is an alternative for tunable metallic gratings fabrication. Yu *et al.* [18] achieved ordered surface wrinkles of thin metallic films on elastomeric substrates by a prestrain method. These ordered wrinkles were used as tunable diffraction gratings. However, the large period (d $\approx$1 um) of the metallic gratings is out of visible wavelength, which also limits their applications.

Besides above-mentioned limitations, it should be noted that Poisson effect is another problem for stretchable gratings. In a stretching-releasing cycle, the axis perpendicular to the stretching direction undergoes tensile strain upon releasing and compressive strain upon stretching. The tensile strain will result in cracks parallel to the stretching direction, which has been represented in previous reports [18], [19]. The compressive strain would deteriorate the gratings' morphology by compressing the gratings in the lateral direction. Creases would appear on the surface of the gratings, especially after the gratings undergo a number of stretching-releasing cycles.

In this work, submicron-scale metallic gratings with tunable period and improved stability of morphology have been demonstrated. Tunable SPP resonance in the wavelength scale is therefore realized. The submicron-scale periodic wrinkles on the surface of oxygen plasma treated elastomeric polymer are realized and used as the templates for the stretchable metallic gratings fabrication. The original periods of the wrinkles can be easily tuned by simply changing the duration of the oxygen plasma treatment, which results in a more flexible templates fabrication. A template-restretching step before the metallic film coating during the metallic gratings fabrication procedure has been taken to weaken the Poisson effect. The stability of the surface morphology for the submicron-scale metallic gratings is improved. The periods of the fabricated submicron-scale metallic gratings can be easily tuned by external mechanical strain. This facile and flexible method is more suitable for the fabrication of the stretchable metallic gratings.

II. Experimental Details

Various approaches such as plasma oxidation [17], thermal evaporation deposition [18], focused ion beam exposure [20], and UV-curing [21] can be employed to produce stiff films on the surface of soft substrates. Polydimethylsiloxane (PDMS) is the most frequently used material as elastomeric substrates due to its characteristics of biological compatibility, high transparence, and high elasticity. We fabricated stretchable gratings with plasma oxidation on prestrained PDMS sheets. Fig. 1 shows the procedure to fabricate stretchable metallic gratings. The

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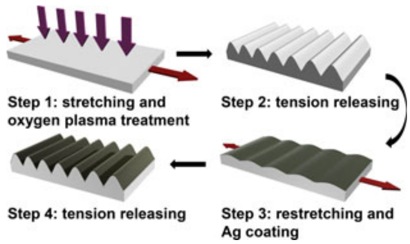

Fig. 1. Schematic illustration of procedures used to fabricate stretchable metal gratings: step 1, stretching the PDMS sheet and oxygen plasma treatment; step 2, releasing the pretension to form ordered wrinkles template; step 3, restretching the wrinkles template and coating Ag film; step 4, releasing the second tension to finish the metallic gratings fabrication.

transparent PDMS substrates were prepared by casting a mixed and degassed PDMS pre-polymer (Dow Corning Sylgard 184, with a ratio of base to curing agent of 10:1 by weight) on the polished surface of a silicon wafer. Curing at 95 °C for 1 h produced a PDMS sheet with a thickness of 400–700 um. After peeling off the PDMS sheet from the silicon wafer, we cut it to rectangles with desired sizes (5 cm $\times$ 1 cm). Then the PDMS strip was prestretched of 35% strain by a homemade stretching stage and treated with oxygen plasma to create a stiff skin (step 1). After releasing the prestrain, wrinkles with desired periods were generated on the surface of the PDMS strip (step 2). Then we use the polymer wrinkles (to be called gratings in the following text) as templates for metallic gratings fabrication. In step 3, the PDMS template was restretched with 30% strain and a thin silver film with a thickness of 25 nm was deposited. The second strain (30%) was less than the prestrain (35%), so that the gratings did not disappear after the restretching process, which would act as a template for the metallic grating. The Ag-coated PDMS sheet contracted after releasing the second strain and the metallic gratings were formed (step 4).

III. Results and Discussions

By simply varying the duration of the oxygen plasma treatment, the PDMS templates with different periods can be obtained. Fig. 2(a)–(d) shows the atomic force microscope (AFM) images of the templates with periods of 470, 560, 610 and 670 nm corresponding to oxygen plasma treatment duration of 2, 3, 4 and 5 min, respectively. It should be noted that the grating periods mentioned above are average values. The method using wrinkles for grating fabrication is not as precise as other proven techniques such as photolithography. The maximum fluctuating value of the grating period is about 35 nm for the case of 2 min oxygen plasma treatment. For other cases, the fluctuating values are smaller than 30 nm as can be seen in Fig. 3. The peeled-off PDMS sheet from the silicon wafer has a smooth surface near that of the silicon wafer, so that a smooth surface for the gratings can be obtained. In addition, homogeneous oxygen plasma treatment on the PDMS sheet ensures a uniform morphology of the gratings. The grating with a period of 560 nm as showed in Fig. 2(b) is chosen as the template to fabricate stretchable metallic gratings. Fig. 4(a) shows the AFM image of the template with an amplitude of 150 nm. Fig. 4(b) shows the AFM image of the grating after restretching with a second strain of 30% and

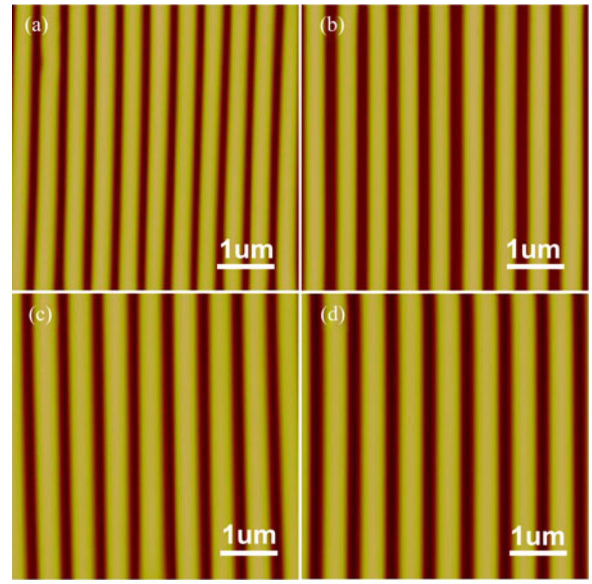

Fig. 2. AFM images of PDMS templates with different periods fabricated by different duration of the oxygen plasma treatment. (a) 2 min; (b) 3 min; (c) 4 min; (d) 5 min.

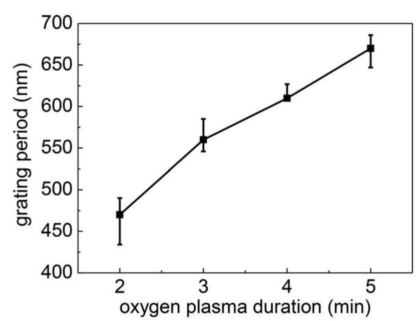

Fig. 3. Error bar plot of periods of PDMS gratings fabricated by different durations of oxygen plasma treatment. The black squares show the average values of the grating periods.

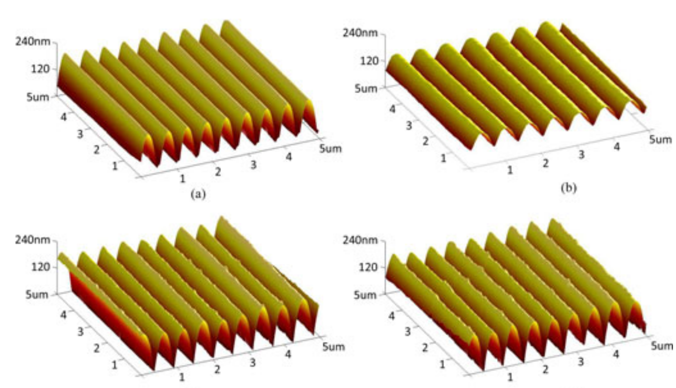

Fig. 4. AFM images of the PDMS template with an amplitude of (a) 150 nm and period of 560 nm, (b) restretching the PDMS template with a strain of 30% and coating Ag film, and (c) releasing the second tension. (d) AFM image of the metallic gratings after 30 stretching-releasing cycles.

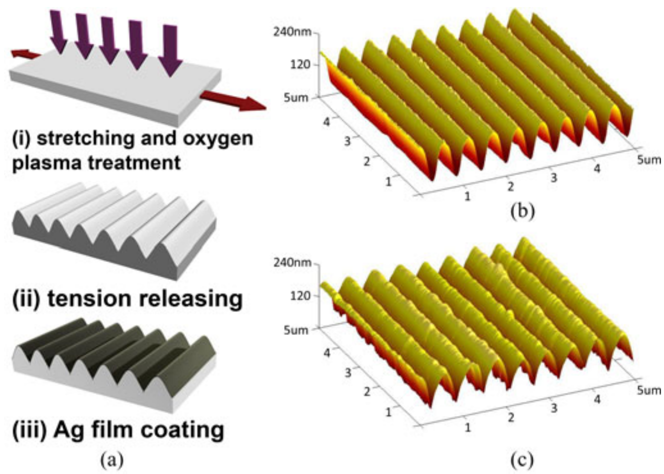

Fig. 5. (a) Fabrication procedure of the stretchable metallic gratings without the restretching step. AFM images of the metallic gratings fabricated (b) without the restretching step and (c) after 30 stretching-releasing cycles.

coating a 25 nm Ag film corresponding to the process from step 2 to step 3 shown in Fig. 1. The period of the grating increased to 700 nm and the amplitude decreased to 67 nm. It can be seen that after Ag film coating, the grating's surface roughness increased a little. Fig. 4(c) shows the final morphology of the metallic grating after releasing the second strain (from step 3 to step 4 in Fig. 1). The period of the grating decreased to 560 nm which was nearly the same as the selected template in Fig. 2(b), while the amplitude increased to 160 nm which was a little larger than that of the template. No obvious protuberances and changes of the morphology on the gratings can be observed and the root mean square (RMS) roughness value of the metallic gratings only has a small variation from 4.3 nm (see Fig. 4(c)) to 4.8 nm after 30 stretching-releasing cycles with strain of 30% as can be seen in Fig. 4(d).

The stretchable metallic gratings without the template-restretching step were fabricated for comparison, as shown in Fig. 5(a). The fabrication process is as follows: stretching with 35% prestrain and 3 min oxygen plasma treatment of the PDMS sheet (i), releasing the prestrain to form wrinkles template (ii), and coating a 25 nm Ag film (iii). Fig. 5(b) shows the AFM image of the metallic gratings fabricated by this scheme. The gratings' period and amplitude are nearly the same with those of Fig. 4(c). However, after 30 stretching-releasing cycles with 30% strain, the morphology of the gratings deteriorates obviously as can be seen in Fig. 5(c). More and larger protuberances and creases appear. And the RMS roughness value of the metallic gratings has increased obviously from 3.5 (see Fig. 5(b)) to 5.9 nm (see Fig. 5(c)).

The different phenomena between the two schemes can be attributed to the Poisson effect. The Poisson ratios of PDMS and Ag are 0.47 and 0.38, respectively. When the grating is stretched with a strain value of 30%, the compressive strain perpendicular to the stretching direction is about 14%. The Ag film is not stretched directly but deforming with the grating lines. For the metallic gratings fabricated without template-restretching step, the compressive stress forces the polymer template and metallic film to deform (such as wrinkling) together. And so the metallic film on the grating lines produces unrecoverable creases and protuberances after dozens of stretching-releasing cycles as seen in Fig. 5(c). For the metallic gratings fabricated with template-restretching step, restretching the PDMS template plays an important role in improving the stability of the metallic gratings. The compressive stress only acts on the polymer template instead of the metal film in the template-restretching step as seen in Fig. 1 (step 3), which means that the surface deformations (such as wrinkling) have arose on the polymer template before metal film coating. When releasing the 30% strain, the stretchable system recovers to its energy equilibrium state and the wrinkles on the grating lines disappear under the action of tensile stress. Bending, instead of stretching, is the main behavior during the wrinkles disappearing process. So the metal film is not stretched directly by the tensile stress but bending with the wrinkles. Although the tensile strain is as large as 16.3%, the metallic film does not creak (see Fig. 4(c)). In the following 30 stretching-releasing cycles, the applied strain was similar with the "restretching strain" of 30%, the effects of the Poisson effect was not larger than those from the restretching step. Therefore, the morphology of the metallic gratings did not deteriorate (see Fig. 4(d)). Further, a test of 500 stretching-releasing cycles with a strain value of 30% has been done, after which the morphology of the grating has almost no change. The test has indicated the mechanical robustness and stability of the metallic gratings, although more cycles are needed until the gratings break down to give the lifetime of the stretchable metallic gratings.

The SPP resonance properties of the tunable metallic gratings have been investigated. The metallic grating was fabricated with a period of 530 nm. The normal incidence absorption spectra at the Ag/air interface under five different external strain values, as well as that of planer sample (a 25 nm silver film coated PDMS sheet without wrinkles) are summarized in Fig. 6(a). During the absorption spectra measuring process, a PDMS sheet without wrinkles and metal film was used as background sample all the way. The SPP resonant wavelength at 0% strain was approximately 565 nm. As stretching the grating, the SPP resonant wavelength exhibited redshift as a result of the increased grating's period. The SPP resonant wavelength increased to about 581, 594, 630 and 658 nm at the strain values of 6.9%, 13.6%, 21.2% and 27.1%, respectively. The tunable wavelength range is around 90 nm, which demonstrates a wide optical tunability of the metallic gratings.

In order to clarify the relationship between the grating period and the external strain, we firstly did some theoretical simulations. The corresponding grating period was simulated by finite-difference time-domain method according to the measured SPP resonant wavelengths. At the strain values of 0%, 6.9%, 13.6%, 21.2% and 27.1%, the simulated grating' periods are 525, 545, 555, 590 and 630 nm, respectively. The period variation is about 100 nm which is a little larger than that of the SPP resonant wavelength variation. Then we measured the grating periods at different strain values experimentally by diffraction method. The diffraction formula is

$$\mathrm{d}\sin\theta = \mathrm{k}\lambda \tag{1}$$

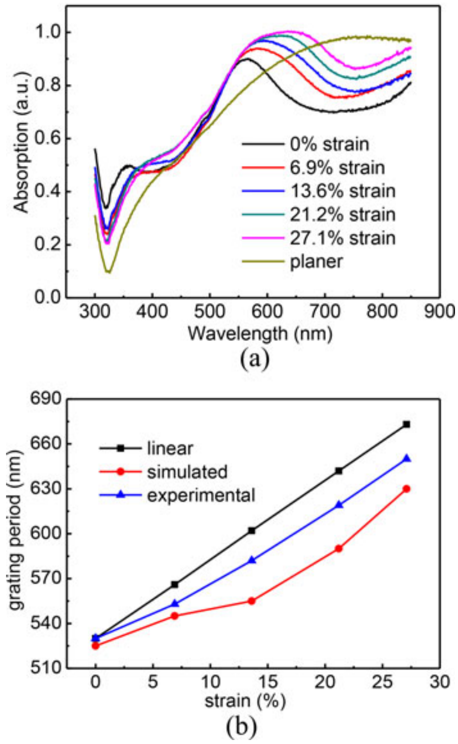

Fig. 6. (a) Absorption spectra of metallic gratings fabricated with "restretching step" at different external strain. (b) The relationship between grating periods and external strain values.

where d is the grating period, θ is the diffraction angle, and λ is incident light wavelength. The light source is a semiconductor laser with an output wavelength of 405 nm. With k values of ± 1, the measured grating periods are 530, 553, 582, 619 and 650 nm at above mentioned strain values. The period variation is about 120 nm. The relationship between the theoretically simulated and experimentally measured grating periods and the external strain exhibits a deviation from the linear relationship as seen in Fig. 6(b). The data appearing in the linear line is obtained by the equation of $d = 530^*(1+\text{strain value})$, in which the 530 nm is the period of the metallic grating at 0% strain and d is the grating period. For strain values of 6.9%, 13.6%, 21.2% and 27.1%, the calculated grating's periods are 567, 602, 642 and 674 nm respectively. Comparing the simulated and measured grating's periods with the linear values, it can be seen that the grating's periods presented a hysteretic increasing rate with the external strain. In addition, the SPP resonance is broaden with the increasing of the strain value as can be seen in the absorption spectra (see Fig. 6(a)). This may be caused by the twisty deformation and surface defects of the gratings under the high strain. The uniformity of the strains applied to the whole grating area is decreased with the increasing strains, which results in a ununiformity of the grating period. It is also noted that the intensity of the SPP resonance decreased with applied strain. Similar behavior has also been observed in previous report [22]. As the gratings were stretched, the amplitude of the sinusoidal gratings decreased, which contributed to the decrease of the intensity for the SPP resonance.

IV. Conclusion

In conclusion, submicron-scale metallic gratings with tunable periodicity and improved stability of surface morphology have been fabricated by using periodic PDMS wrinkles as templates. The template's original periods can be controlled easily and a period as small as 470 nm has been achieved. The Poisson effect on grating morphology has been weakened by employing a template-restretching step. The SPP resonance is tunable through tuning the grating periods by external strains. This method is demonstrated simple and flexible for fabricating tunable metallic gratings, and has potential to be used in not only SPP enhancement applications, but also in tunable diffractive gratings and stretchable electronic devices.

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