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# Optically tunable metal-dielectric diffractive structures

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Hybrid metal-polymer micro-pillar arrays are elaborated by solvent-assisted embossing techniques and subsequent gold deposition. The polymer is PMMA grafted with DR1 azobenzene derivatives. This photochromic material exhibits spectacular photomechanical properties. Under off-normal p-polarized illumination in the absorption band of the DR1, the metal-polymer hybrid micro-pillars bend in a direction determined by the light polarization. The deformation remains stable when the light excitation is turned off. The optically driven modification of the pillar shape allows to tune the optical properties of the pillar arrays. Very large intensity changes are measured in the diffraction spectra at zero order (specular reflection), first order and second order, with almost on and off switching of the diffraction efficiency. The photo-induced bending of the micro-pillars can be fully reversed by switching the linear light polarization to the orthogonal s-polarization state. This allows to recover the initial optical properties of the pillar array. The polarization-controlled reversibility of the pillars deformation suggests a complex photo-induced deformation mechanism involving stress and stress release assisted by the change in the visco-elastic properties of the polymer under illumination in the absorption band of the DR1 chromophore.

## I. INTRODUCTION

Micro- and nano-structuration is a major route to produce materials and devices with tailored properties for various applications such as smart coatings [1]. A current challenge is to incorporate active materials which can respond to an external stimulus, either optical, electrical, magnetic or mechanical, in order to control the structure shape and to tune the material/device properties. To address this issue, light-responsive materials are particularly attractive because optical stimuli enable non-contact operation, fast and easy addressability down to submicron scale, compatibility with various environments and selectivity through different parameters (wavelength, polarization, power). In this context, azobenzene-containing materials are under investigations for their specific ability to mechanically respond to a light excitation [2–8]. Their photomechanical properties are related to the photoisomerization of the azobenzene units. When the chromophore exhibits a push-pull character, like the Disperse Red 1 (DR1) compound, illumination in the molecule absorption band induces repeated trans-cis-trans cycles which lead to spectacular deformation of the host material [2, 3]. This photo-induced deformation involves several mechanisms: photo-expansion [9], light-induced change in mechanical properties [10–12] and polarization-directed mass motion [13–19]. Efficient structuration of the azobenzene-containing materials can thus be simply achieved by projection of an optical pattern. The photo-induced deformation process

can be controlled over a wide scale range, from a few tens of nanometers [15] to several microns [19]. However, the produced pattern shapes are limited to rather smooth relieves.

On the other hand, various embossing techniques were developed to pattern soft materials [20–25]. These techniques were in particular applied to azobenzene-containing polymers and allowed for the fabrication of micro- and nanostructures with large aspect ratios and abrupt shapes that cannot be elaborated by holographic inscription methods exploiting the photo-induced mass motion. The photomechanical response of the produced structures was then investigated and spectacular modifications of the initial pattern shape due to the photo-induced mass motion were evidenced [26–30]. As for thin films, adjusting the illumination parameters, in particular the light polarization, allows controlling the pattern deformation. These photoactive structures showed potential applications as tunable diffractive devices [31], light-controlled hydrophobic layers [32, 33] or active mechanical substrates in biology [34–36]. A further challenging issue is to associate the azobenzene-containing materials with non-photoactive materials in order to elaborate a hybrid structure with tunable properties. Recent works were reported on metal / azo-material structures [26, 37, 38]. Although these studies show the potentiality of this approach for designing devices with tailored optical and plasmonic properties, the tunability of the hybrid structure shape was not exploited.

In this paper, we report on the fabrication and study of metal/dielectric hybrid micro-pillar arrays which possess tunable optical properties. These micro-pillar arrays are obtained by solvent-assisted molding of an azobenzene-containing polymer and subsequent metal deposition by

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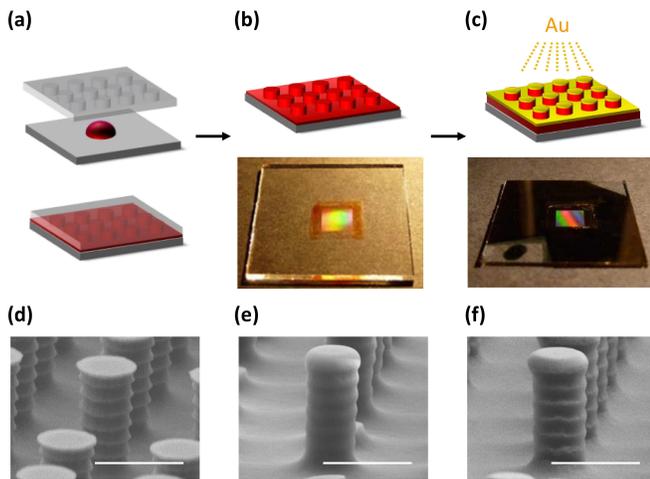


FIG. 1. (a) Schematic of the solvent-assisted embossing process of the PMMA-DR1 polymer dissolved in NMP using a PDMS mold. (b) and (c) PMMA-DR1 pillar array replicated on a  $2.5 \times 2.5 \text{ cm}^2$  glass substrate, respectively, before and after deposition of a 50 nm-thick Au layer. (d-f) SEM images of a pillar array on the silicon master, of the bare PMMA-DR1 replicate and of the metallized PMMA-DR1 replicate after deposition of the 50 nm-thick Au layer. The pattern period is  $3 \mu\text{m}$ , the pillar diameter and height are respectively  $1.2 \mu\text{m}$  and  $2.5 \mu\text{m}$ . The scale bar on the SEM images is  $2 \mu\text{m}$ .

evaporation under vacuum. The photomechanical properties of the azobenzene-containing material enable to control the deformation of the pillars by an optical stimulus. We demonstrate that the photo-induced change in the pillar shape allows for the fine tuning of the optical properties of the metal/dielectric pillar array. The process is shown to be almost fully reversible by using an appropriate sequence of polarized illumination. Simulations of the optical properties of the metal/dielectric structures before and after photo-induced deformation are performed based on the rigorous coupled-wave analysis (RCWA). Numerical results show good agreement with the experimental data.

## II. SAMPLE PREPARATION

Our fabrication process of hybrid metal/photoactive polymer structures is schematized in Fig. 1. It is based on solvent-assisted embossing with a PDMS (PolyDiMethyl-Siloxane) stamp, a well-known approach now for the replication of patterns on soft materials [20–25]. Arrays of micro- and nanostructures with high aspect ratio can be elaborated this way [33].

The PDMS stamps were prepared from silicon masters fabricated by a customized Bosch process. Bosch process is a dry etching technique that consists of cycles alternating isotropic etching under SF<sub>6</sub> plasma and sidewall passivation/protection using C<sub>4</sub>F<sub>8</sub> plasma. This method inherently induces surface scalloping, which here can be

as large as 200 nm. It is a direct consequence of the alternating deposition and etching cycles, and depends on the timing of the steps in each cycle and on the etching rate. A Rapiertool was used, with 2.5 kW of 13.56 MHz RF power. The temperature of the wafer was controlled using an electrostatic chuck. An oxygen cleaning procedure was performed to remove polymers from the sidewalls of the reactor, minimizing contamination. The details of the process have been reported elsewhere [39]. A silanization treatment of the patterned Si surface was subsequently performed with TMCS (TriMethylChloroSilane) in gaseous phase in order to minimize the adhesion of the PDMS stamp to the Si surface when unmolding. The PDMS solution was prepared by mixing a PDMS prepolymer and an initiator (Memorive RTV615) with a 10:1 weight ratio, and subsequently outgassed under vacuum. The outgassed solution was then carefully poured onto the patterned master to prevent the generation of bubbles. Finally, the PDMS solution was cured at  $60^\circ\text{C}$  in an oven for 3 h. After complete reticulation, the PDMS stamp was detached from the Si master.

The PDMS stamp was then gently put on a small droplet of an azo-polymer solution deposited on a freshly cleaned glass substrate [Fig. 1(a)]. After drying the solvent at  $50^\circ\text{C}$  during 12 h, the PDMS was peeled off, leaving the azo-polymer transferred pattern on the glass substrate [Fig. 1(b)]. The azo-polymer is prepared from a 30 mg/mL solution of PMMA-DR1 (Poly-methyl-methacrylate-co-Disperse Red 1, from Sigma Aldrich) dissolved in NMP (N-methyl-2-pyrrolidone).

Figure 1(d-e) show SEM images of the pillars respectively on the silicon master and on the processed PMMA-DR1 layer. The period of the pillar array is  $3 \mu\text{m}$  and the characteristic dimensions of the PMMA-DR1 cylindrical pillars are  $1.2 \mu\text{m}$  in diameter and  $2.5 \mu\text{m}$  in height, leading to an aspect ratio slightly larger than 2. SEM analysis of the silicon masters, the PDMS stamps and the PMMA-DR1 structured films were performed for various pillar arrays with different characteristic dimensions to investigate the quality of the pattern transfer. We observed a good match between the geometrical parameters of the silicon master pattern, the PDMS mold and the PMMA DR1 replicate, leading to the conclusion that the technique is robust for a large range of structure dimensions. Annular structures observed on the side walls of the silicon pillars and of the PMMA-DR1 replica are due to the successive steps of the Bosch lithography process.

A 50 nm gold layer is deposited by evaporation in vacuum at normal incidence on the patterned PMMA-DR1 thin films [Figure 1(c)]. In this configuration, only the top of the PMMA-DR1 pillars and the surface of the residual PMMA-DR1 base layer are covered with gold while the pillar sidewalls mainly remain bare, except the annular protrusions induced by the Bosch lithography process [Figure 1(f)].

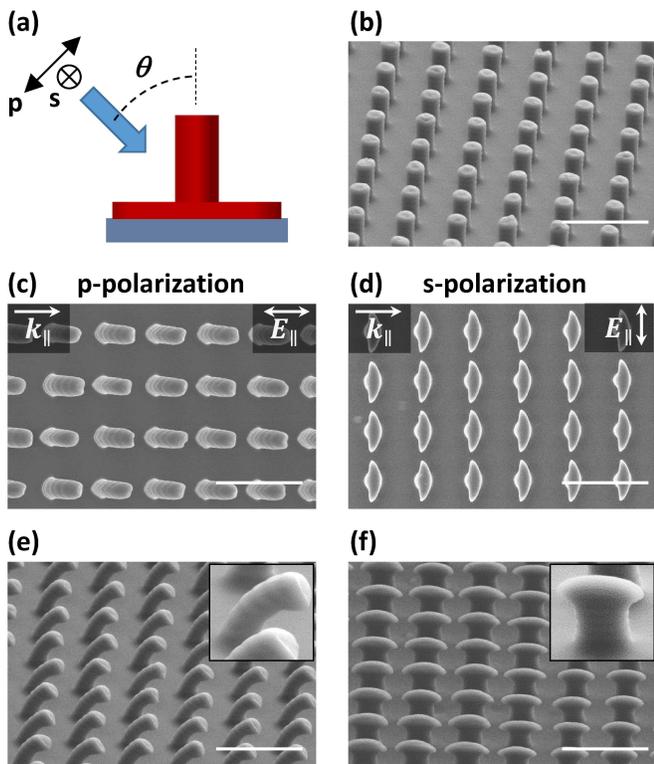


FIG. 2. (a) Schematic of the pillar illumination geometry. (b) SEM image of the bare PMMA-DR1 pillar array. (c) and (e) top and oblique views of the same pillar array after 10 min illumination by a p-polarized laser beam of wavelength 488 nm and power density  $2 \text{ mW/mm}^2$ , with an incidence angle of  $45^\circ$ . (d) and (f) same as (c) and (e) for an illumination with s-polarized light. Scale bar is  $5 \mu\text{m}$ . The orientation of the light wave vector and electric field in-plane components are indicated. Insets in (e) and (f) show a zoom of the pillar after deformation.

### III. PHOTOMECHANICAL RESPONSE OF PHOTOACTIVE PILLAR ARRAYS

The DR1 azobenzene derivative exhibits a blue absorption band. Illumination in this band efficiently excites the photoisomerization colorredbetween trans and cis forms. In the following, we use a laser emitting at 488 nm, very close to the DR1 absorption peak, to study the photomechanical response of the pillar arrays. In all experiments presented here, samples are excited with an incidence angle of  $45^\circ$ . Since the photoinduced deformation of azobenzene-containing polymers is known to be a polarization-directed process, we will study the photomechanical response of the pillar structures for linear p and s-polarization states.

Figure 2 shows the SEM images of the micropillar array before and after 10 min illumination with  $2 \text{ mW/mm}^2$  power density of the 488 nm laser.

When the light is p-polarized, the pillars are seen to bend as was already recently reported [40]. A slight change in the pillar top surface shape is observed. The

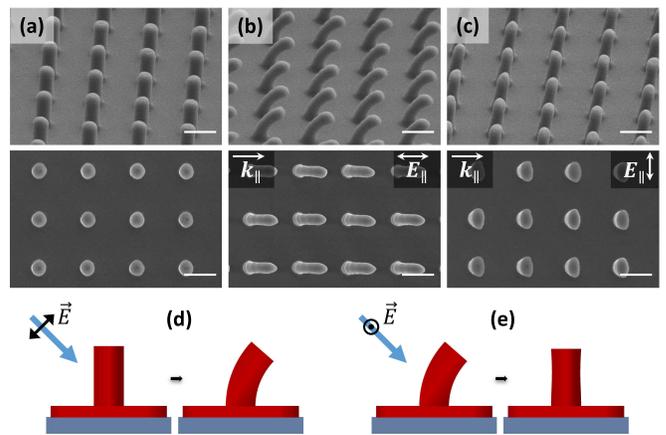


FIG. 3. SEM images (oblique and top views with  $2 \mu\text{m}$  scale bar) of (a) the pillar array before illumination, (b) after 10 min illumination with p-polarized light, (c) after subsequent 10 min illumination with s-polarized light. The laser excitation settings were identical to those of Figure 2. Under illumination with p-polarized light, pillars bend. Under subsequent illumination with s-polarized light pillars unbend and recover their initial vertical shape.

microscopic origin of the photo-induced deformation of azobenzene-containing materials is not fully elucidated but, as already mentioned, it is known to involve an efficient mass migration process mainly governed by the light polarization pattern [14, 15, 17, 41, 42]. In the present experiment, the pillar bending is directed by the light polarization. When the light polarization is rotated away from the p-polarization direction, the pillar bending direction is also rotated and the bending efficiency decreases.

When the light is s-polarized, the pillar does not bend. Instead a symmetric deformation of the pillar occurs, predominantly on the top face of the pillar, along the light polarization direction [Figure 2(d) and (f)]. Since the deformation originates from the photo-induced mass motion directed by the light polarization, s-polarization can only induce a symmetric deformation perpendicular to the pillar axis. The resulting deformation is thus not a bending of the pillar but appears as a transverse stretch which is more efficient on the free flat top surface of the pillar than on the curved pillar sidewall.

Therefore, p- and s-polarized illuminations induce completely different deformations. However, surprisingly, pillars that were bent by p-polarized illumination are seen to unbend and recover their initial vertical shape when subsequently illuminated with s-polarized light. This is shown in Figure 3 where are presented scanning electron microscopy images of the same pillar structure before illumination, after 10 min illumination with p-polarized light and after subsequent 10 min illumination with s-polarized light.

Photo-induced bending and unbending at a macroscopic scale were demonstrated in liquid crystal elastomer incorporating azobenzene moieties [43]. In that case,

the deformation was fully reversible as it was related to single photo-isomerization processes of almost bistable azobenzene derivatives: the transition from trans to cis states was induced with one wavelength and produced the film bending, and the back transition from cis to trans states was induced with another wavelength and produced the unbending of the film. In our case, the deformation process is much more complex because it involves repeated trans-cis-trans photoisomerization cycles and polarization-directed mass migration. Previous works have already shown that the deformation induced by linearly polarized light in pillars of materials containing azobenzene push-pull derivatives can be partially reversed by a subsequent illumination with the orthogonal polarization [30, 31]. However, this was achieved in the specific geometry where the sample was illuminated in normal incidence. In this case, the two orthogonal polarizations should both produce a stretch of the pillar top surface but along orthogonal directions. If the volume is conserved, one can reasonably assume that subsequent stretch along two orthogonal directions may compensate each other, at least to first order. In contrast, in the case of off-normal incidence that we use, illuminations with p- and s-polarizations do not induce equivalent deformations (Figure 3) and it is hardly conceivable that the bending induced by p-polarized illumination may be reversed by a subsequent stretch in the orthogonal direction induced by s-polarized illumination. We thus propose a different explanation. Illumination with p-polarized light produces at the same time a drop in the PMMA-DR1 viscosity [12] and a mass motion along the illuminated sidewall of the pillar. Since the absorption length of the exciting light in the PMMA-DR1 is smaller (200 nm) than the pillar diameter (1200 nm), the off-normal illumination produces a dissymmetric deformation which results in the pillar bending and induces a stress across the pillar. When p-polarized illumination is turned off, the material viscosity jumps up back to its initial value, which is too high for the stress to relax and the pillar deformation is frozen. Under subsequent s-polarized illumination, viscosity drops down again and the stress produced under p-polarized illumination is released which results in the pillar unbending.

It has to be noted that, according to this mechanism, the photoinduced deformation of the pillars is governed by the illumination of the pillar sidewall. Therefore, in the case of the metal-dielectric pillar arrays obtained by gold evaporation at normal incidence, since the pillars exhibit sharp edges and the pillar sidewall are thus not metallized [Figure 1(f)], it might be expected that the photomechanical properties of these structures is preserved. This contrasts with previous studies of metal-dielectric performed on gold-covered azo-polymer thin films [37, 38]. In these works, the photoactive polymer was patterned by holographic techniques to produce surface relief gratings, prior to the metal deposition. But once the layer was deposited all over the patterned azobenzene-containing polymer, the photome-

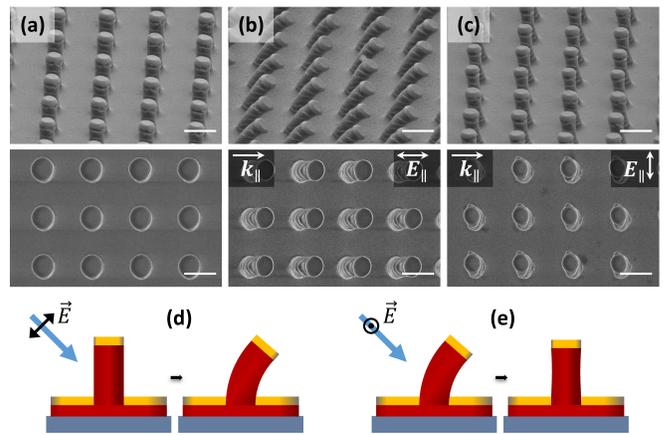


FIG. 4. SEM images (oblique and top views with 2  $\mu\text{m}$  scale bar) of (a) the pillar array coated with 50 nm of gold before illumination, (b) after 10 min illumination with p-polarized light, (c) after subsequent 10 min illumination with s-polarized light. The illumination power density was 20  $\text{mW}/\text{mm}^2$ . Excitation with p-polarized light induces pillar bending. Under subsequent illumination with s-polarized light pillars unbent and recover their initial vertical shape.

chanical properties of the photoactive material were inhibited and further photo-induced deformation of the structure was impossible. The optical properties of the device were thus not tunable.

When illuminating the metallized pillar array with p-polarized light, at an incidence angle of  $45^\circ$ , bending of the hybrid pillars is observed [Figure 4(b)]. Under subsequent illumination with s-polarized light, the gold-covered pillars unbend and almost completely recover their initial shape, as was observed on bare PMMA-DR1 structures [Figure 4(c)]. After the p+s illumination sequence, the pillars appear to be only a few percent shorter than before illumination. As expected, the photomechanical response of the photoactive structure is thus preserved although the photo-induced deformation process is significantly less efficient than on the non-metallized pillar array. Indeed, a deformation similar to the one of the non-metallized pillar structure is obtained with the same illumination time of 10 min but with a power density of 20  $\text{mW}/\text{mm}^2$ , i.e. 10 times higher. This might be due to slight metallization of the pillar sidewall in spite of the normal incidence geometry of the gold evaporation. Note that, since a 50 nm-thick gold film deposited on PMMA-DR1 precludes the photo-induced mass transport in the photoactive polymer, the gold-covered surfaces, at the top of the pillars and on the residual base PMMA-DR1 layer, are not modified by the illumination.

#### IV. TUNABLE OPTICAL PROPERTIES OF PHOTOACTIVE HYBRID PILLAR ARRAYS

Micro- and nanostructured metal/dielectric hybrid systems are widely studied and used for optics and plasmon-

ics applications [44, 45]. Their properties are governed by the geometrical characteristics of the pattern at the micro- or nanometer scale. Modifying the pattern shape should therefore allow for tuning their optical properties.

The change in the reflectivity spectrum of the gold-covered sample during the photo-induced pillar deformation is shown in Figure 5. In this experiment, an unpolarized collimated white light beam of weak power density (a few  $\mu\text{W}/\text{mm}^2$ ) is used as a probe. The reflected light is analyzed by a spectrophotometer. The incidence angle of the white light probe beam is fixed at  $10^\circ$ . The specular reflected beam at  $-10^\circ$  is focused on the spectrophotometer entrance slit with a convergent lens which matches the spectrophotometer aperture. The measured reflectance spectrum is normalized by the white light source spectrum measured with the same spectrophotometer. The structure is photoexcited with a low 488 nm-laser power density of  $0.25 \text{ mW}/\text{mm}^2$  at an incidence angle of  $45^\circ$ . The laser beam is p-polarized during the first 120 min, and s-polarized during the following 120 min.

Before excitation with the 488 nm laser, the reflectivity spectrum between 400 nm and 950 nm shows large modulations due to the interferences between the light reflected by the gold layer at the top and at the bottom of the pillar [Figure 5(b)]. The spectral positions of the modulation extrema essentially depend on the pillar height (here  $2.5 \mu\text{m}$ ) and the modulation amplitude on the filling factor (ratio between the pillar top surface area and the base surface area). The low reflectivity in the blue range is due to the decrease in the gold layer reflectivity. In Figure 5(e), the reflectance spectra  $R$  of the flat 50 nm-thick gold layer away from the pillar structure is plotted as a reference (dotted blue line).

During illumination with the p-polarized blue laser beam, a progressive destruction of the interferences is observed. This evolution is due to the pillar bending. After 120 min of illumination, the modulations in the reflectivity spectrum have almost completely disappeared. We performed RCWA calculations of the reflectivity spectrum of the metallized sample, using the values of the geometrical parameters of the pillars deduced from SEM observations. The refractive indices of the materials in the probed spectral range were measured (by ellipsometry) for PMMA-DR1 and taken from the literature for gold [46]. A good agreement is found between the simulations and the experimental results [Figure 5(e-f)].

After the modulations in the reflectivity spectrum have almost completely vanished, the blue laser beam polarization is switched to s-polarization in order to induce unbending of the pillars. As a result, the intensity modulations show up again on the reflectivity spectrum. We thus succeed in modifying reversibly the structure shape by an optical stimulus and to tune this way the optical properties of the hybrid pillar array. Note that, when p-polarized illumination is extended well beyond the suppression of the reflectivity spectrum modulation, the deformation of the pillars still continues but cannot be reversed anymore by subsequent s-polarized illumination.

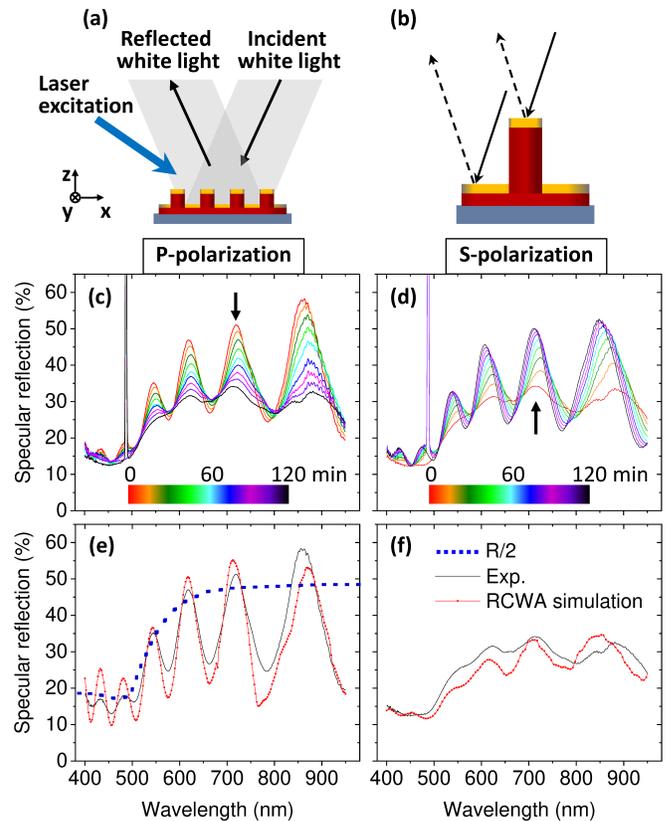


FIG. 5. (a) Schematics of the measurement configuration of the reflectivity spectrum during light excitation of the hybrid pillar array. The incidence angle of the probe white light is  $10^\circ$ . Specular reflection is collected by the spectrophotometer. The sample is excited with the 488 nm laser beam of power density of  $0.25 \text{ mW}/\text{mm}^2$  at an incidence angle of  $45^\circ$ . (b) Schematic of the interfering beams scattered on the pillar top surface and on the base plane. (c) Evolution of the reflectivity spectrum during p-polarized illumination of the pillar array. (d) Reverse evolution of the reflectivity spectrum during subsequent s-polarized excitation inducing the pillar unbending. In (c) and (d), the colour code indicates the exposure time to the excitation laser. The peak at 488 nm is due to the diffusion of the excitation laser. (e) and (f) Comparison of the experimental data with RCWA simulations of the reflection spectra of the initial and bent pillar array, respectively. In (e), as a reference, the dotted blue curve represents the reflectance spectra  $R$  of the flat 50 nm-thick gold layer away from the pillar structure (for the sake of graph readability  $R/2$  is plotted).

The evolution of the shape of the structures during p- and s-polarized illumination can be estimated by analyzing the change in the reflectivity spectrum. Figure 6(a) shows the variation of the reflectivity at 720 nm which corresponds to a maximum (constructive interference) in the reflectivity spectrum during the p- and s-polarized illumination sequence. The variation of the peak wavelength of the corresponding maximum is plotted in Figure 6(b). The intensity is somehow related to an effective filling factor of the structure while the spectral position

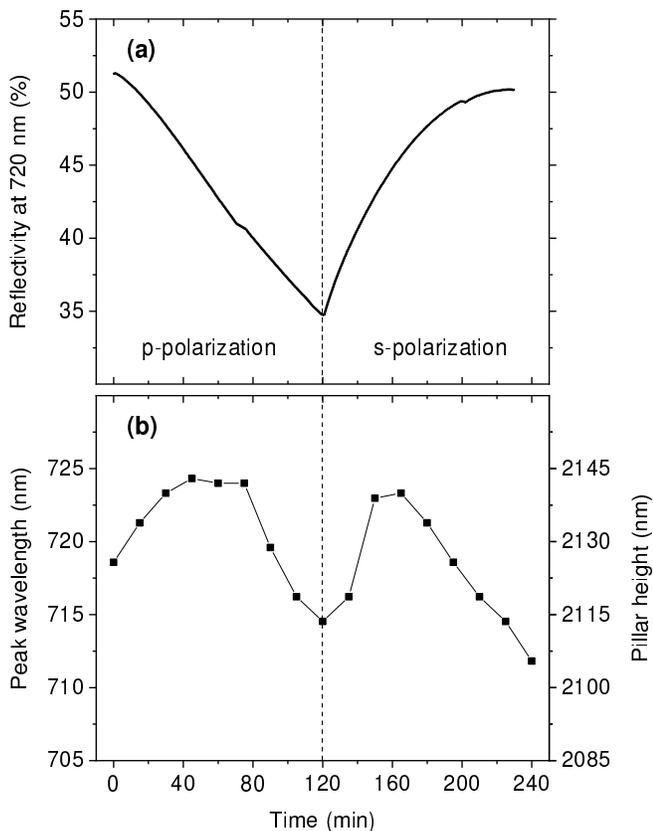


FIG. 6. Evolution of (a) the reflected intensity and (b) peak wavelength of the constructive interference feature indicated by the arrows in the reflectivity spectra of Figure 5(c-d) during p- and subsequent s-polarized illumination. The left axis in (b) indicates the pillar height that can be deduced from the position of the interference extrema in the reflectivity spectrum.

of the extremum is related to the pillar height. Under p-polarized illumination, the reflected intensity around 720 nm strongly decreases due to the diminution of the light scattered in the specular direction by the top of the pillars when the pillars bend. Interestingly, the spectral position of the reflectivity maximum only slightly changes, by less than 2 %, indicating that the height of the pillars remains almost the same. This shows that a moderate photo-induced deformation of the pillars produces a large change in the reflectivity spectrum.

Note that moderate deformations are favorable to achieve reversibility. When switching the excitation polarization from p to s, the reflectivity (i.e. the interference modulation amplitude) immediately starts to rise again, and reaches a value of 50 % very close to the initial one of 52 % (before p-polarized illumination). The illumination times are similar for suppressing the interference modulation with the p-polarized illumination and for restoring it with s-polarized illumination. During the unbending process with s-polarized excitation, a 10 nm red shift of the reflectivity maximum position from 715 nm to 725 nm is observed which is followed by a

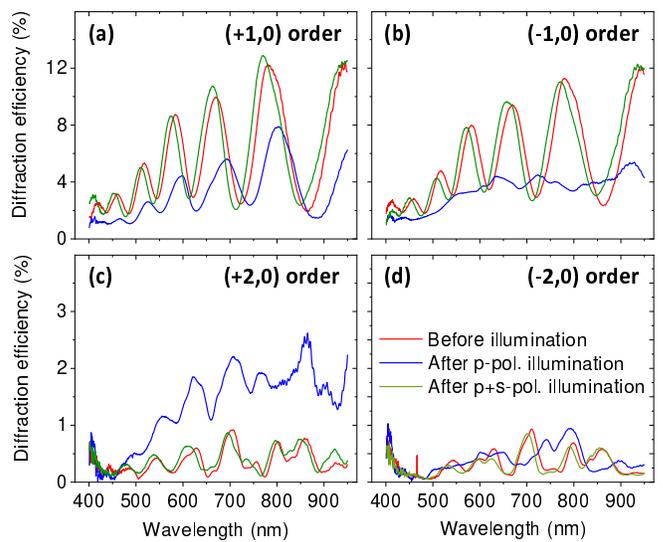


FIG. 7. Diffraction spectra of the first (1,0) and second (2,0) orders of the gold-covered pillar array before illumination (red curve), after 120 min p-polarized illumination (blue curve) and after subsequent 120 min s-polarized illumination (green curve).

14 nm blue-shift. This is due first to the slight increase of the tilted pillar effective height when unbending and then to the slight diminution of pillar height after unbending due to the transverse stretch of the pillars induced by s-polarized illumination (see Figures 3 and 4).

The deformation of the pillars is also expected to modify the diffraction properties of the pillar array. Since the photo-induced pillar deformation under p-polarized illumination introduces both an asymmetry and an anisotropy in the structure, the change in the diffraction efficiency must be different for the different diffraction orders. We have measured the diffraction efficiency spectrum of the first and second diffraction orders (Figure 7). In this experiment, the probe white light beam illuminates the structure at normal incidence and the spectrum of each diffraction order is measured by detecting the light collected in the spectrophotometer as a function of the detection angle. The different diffraction orders are labeled (x,y) according to their respective coordinates in the xy plane of observation, parallel to the sample surface plane. The incidence plane of the excitation blue laser is the xz plane so that the (x,0) diffraction orders are in the plane of the pillar deformation. In the initial state, strong interference modulations are observed in the spectrum of the first diffraction orders, like in the specular reflexion spectrum. The efficiency of the second diffraction orders is one order of magnitude lower and exhibit a more complex interference modulation feature in the probed spectral range. Symmetric diffraction orders (x,0) exhibit similar diffraction efficiency spectra. After a p-polarized illumination, the change in the diffraction efficiency spectrum strongly depends on the order index. The interference modulations in the efficiency spectrum

of the (1,0) order are reduced by about a factor of two while they almost completely vanished for the (-1,0) order. The (2,0) order shows a large increase in efficiency while the (-2,0) order spectrum is only slightly affected by the photodeformation of the pillar array and remains weak. Illumination with s-polarized excitation almost restores the initial diffraction spectra. In Figure 8, these experimental results are compared with RCWA simulations. Before the photo-induced pillar deformation a very good agreement is obtained, as previously observed. After the photo-induced pillar deformation, the slight discrepancies between the calculated and measured diffraction spectra are due to the fact that the actual shape of the bent pillars are not easy to reproduce in basic RCWA simulations. In particular, the positions of the interference extrema are very much dependent on the pillar height which, as we have seen, may change non monotonously during the deformation process. However, the RCWA simulations reproduce quite well the trend in the change in the diffraction efficiency for the different orders.

The evolution of the different diffraction orders of the 2D pillar array can be measured during the photo-induced deformation process. In this experiment [Figure 9(a)], a 635 nm probe laser beam, out of the DR1 absorption band, impinges the sample surface at normal incidence and the diffraction pattern is projected on a screen. The intensities of the different diffraction orders are recorded by a CCD camera. A neutral filter is placed at the center of the screen in order to attenuate by a factor of 30 the first diffraction orders: (0,1), (1,0), (1,1), avoiding saturation of the camera. The sample is excited with a 488 nm laser power density of 0.25 mW/mm<sup>2</sup> at an incidence angle of 45° in the xz plane.

Clearly, the photo-induced pillar deformation mainly affects the (+1,0) and (+2,0) orders [black curves in Figure 9(b) and (c)]. The (+1,0) order intensity first increases reaches a maximum value and then decreases monotonously. At the same time, the (+2,0) order intensity increases spectacularly by a factor of 10 while the (-2,0) order remains almost unchanged. The variations of the (+1,0) and (+2,0) orders can be explained by a blazing-like effect. Bending of the pillars first improves the efficiency of the (+1,0) order up to an optimum effective blazing angle which is reached after about 40 min of illumination. Beyond this deformation, the diffraction efficiency decreases. For the (+2,0) diffraction order, the optimum effective blazing angle is about twice as large and the intensity reaches a maximum value after about 115 min of illumination. From SEM observations [top image in Figure 9], we measure a tilt of the pillar top surface of about 15° after 120 min of p-polarized illumination. For a grating of 3 μm period, blazed at 635 nm, the expected blaze angle is of about 6° at first order and about 12° at second order, which is in good agreement with the observed tilt of about 15°. Note that, after switching the excitation from p- to s-polarization, the deformation is reversed and the initial diffraction pattern

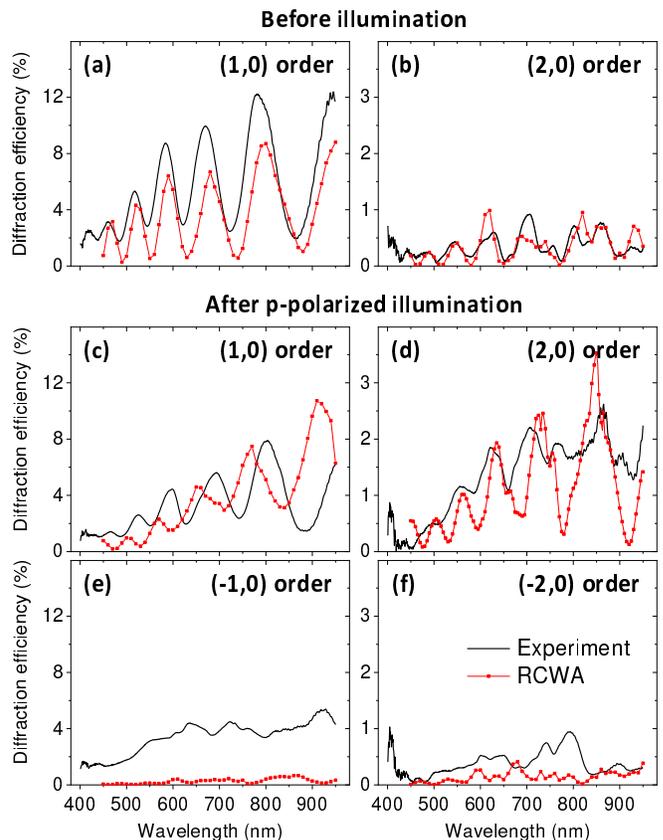


FIG. 8. (a) First and (b) second diffraction orders spectra of the 50 nm gold-covered sample before illumination: experiment (black curve) and RCWA simulation (red dotted curve). Only positive orders are shown due to the system symmetry. (c) and (d) Same as (a) and (b) after p-polarized illumination. (e) and (f) Same as (c) and (d) for negative first and second diffraction orders. The pillar bending produces an asymmetry between opposite diffraction orders.

is progressively almost fully restored within a similar excitation time. However, as clearly seen in Figure 9(c), the kinetics of the change in the diffraction efficiency under p-polarized excitation and of the reverse process under s-polarized excitation are not identical. The variation with exposure time of the (+2,0) diffraction order efficiency shows first a sigmoid-like increase under p-excitation, which is characteristic of the usual PMMA-DR1 photo-induced deformation process, and then an exponential-like decrease under s-excitation which suggests a relaxation process.

## V. CONCLUSION

In conclusion, we have demonstrated that azobenzene-containing materials can be used to elaborate micro- and nano-structured hybrid metal/dielectric devices with tunable optical properties. Micro-pillar arrays of PMMA-DR1 were prepared by solvent-assisted emboss-

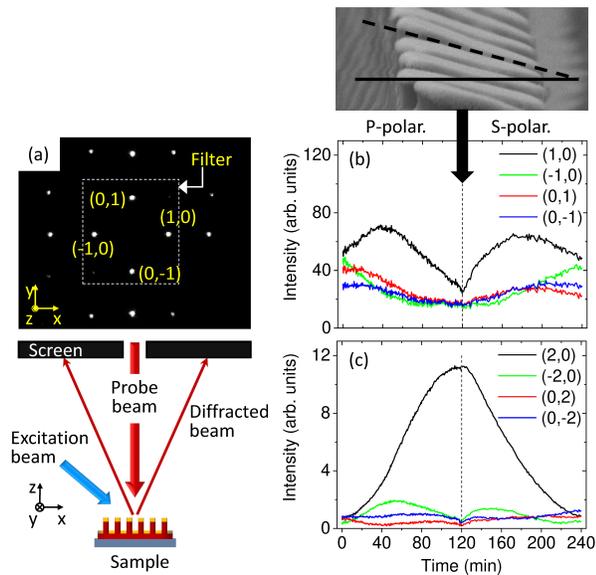


FIG. 9. (a) Schematic of the optical setup for measuring the intensity of the diffraction orders of the metallized pillar array as a function of photoexcitation time. The probe beam of 635 nm wavelength impinges the sample at normal incidence. Diffracted beams are projected on a screen. The diffracted pattern is recorded by a CCD camera. A neutral filter (dashed square) attenuates the first diffraction orders by a factor of 30 in order to avoid saturation of the camera. A linearly-polarized blue laser beam of 488 nm wavelength and  $0.25 \text{ mW/mm}^2$  power density excites the sample with a  $45^\circ$  incidence angle. (b) [resp. (c)] Evolution of the intensity of the first (resp. second) diffraction orders during excitation of the structure with p-polarization and subsequently with s-polarization. SEM image of the bended pillars after p-polarized illumination is shown in b.

ing. Thin Au layer was deposited by evaporation under vacuum. Areas of the embossed azo-polymer structure which were unexposed to the ballistic metal flux keep their photomechanical properties and photo-induced deformation of the hybrid structure remains possible under light excitation at oblique incidence. The direction of the deformation can be controlled by the incident light polarization. The optical properties (reflection and diffraction spectra) of the pillar arrays measured during the photo-induced deformation process exhibit very large changes. The reversibility of the photo-induced deformation is achieved thanks to a proper illumination sequence with polarized light which allows to recover the initial optical properties of the structure. The proposed approach is based on a very simple technological process and allows for the fabrication of a wide range of hybrid micro- and nano-structures which could potentially lead to the development of tunable optical and plasmonic devices.

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