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Topographic control on silicone surface using chemical oxidization method

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Abstract

The paper describes a wet process for modifying the surface of polydimethylsiloxane (PDMS) using H_2SO_4/HNO_3 solutions. The oxidation on the surface of PDMS was confirmed by the examinations of Fourier transform infrared spectrometry (FTIR), contact angle of water drop and X-ray photoelectron spectroscopy (XPS). The hydrophobic surface of pristine PDMS was not only changed to hydrophilic, but also formed wrinkles on it after chemical modification. Bilayer systems, stiff oxidized PDMS layers were capped on soft PDMS foundations, would generate easily compressive stresses due to the large difference in volumetric contraction rates and led to form wrinkles on the surface. Experimental results demonstrated the periodicity of wrinkles was controllable by controlling the duration of oxidation. Therefore, wrinkles could be arranged orderly by the guidance of external forces before oxidization. The potential technology for generating and ordering wrinkles on the PDMS surface is valuable in the applications of pressure sensors, biology, micro-optics and nano-/micro-fabrication in the future.

Keywords: Wrinkles; PDMS; Chemical modification

1. Introduction

The rubbery material, polydimethylsiloxane (PDMS), has attracted the attention of many material scientists recently as there are potential applications ranging from microelectromechanical systems (MEMS) to biology, due to its excellent physical and chemical characters [1–3]. Surface treatments are known to affect the physical and chemical properties of polymers and modify their performance, which is an important concern to be studied. Wrinkles are often observed on the surface of PDMS covered a thin metallic films or exposed to oxygen plasma or irradiated with high energy ions/electrons, which is interesting for their potential applications in pressure sensors, biology, micro-optics and nano-/micro-fabrication [4–14]. For example, nanostructured rod-like metallization layers with a tunable gap width can be generated by depositing platinum on high oriented surface undulation and subsequently mechanically strained it [14]. The formation mechanism of wrinkles developed by depositing metal films or oxidizing PDMS surfaces has been demonstrated when compressive stresses on a stiff layer were induced into an elastic layer, by the large difference in volumetric contraction rates on a bilayer system [4–11]. To compare with other ways, the use of high energy irradiation is quite unique, which is because this technology is the only known without the need of stiff layers generation. Under the bombardment of high energy electrons/ions, some bonds in PDMS chains were broken to generate mobile free radicals and then these radicals would recombine other chains to result in an increase of the molecular weight and a decrease of the chain-scission [13]. In refs. [4,5], the periodicity of waves on the surface of PDMS could be adjusted by controlling the thickness and deposited temperature of metallic films. In refs. [9,10], the periodicity could be controlled by adjusting the power and duration of plasma treatment. In refs.

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[12,13], the wavelength of the undulations could be changed by modulating the energy of argon plasma. Four approaches for aligning the waves have been also demonstrated as follows : (1) the waves are ordered by introducing bas-relief patterns into the PDMS. The waves align perpendicular to the steps in the surface [4]; (2) the waves are ordered by oxidizing a thin layer of PDMS on a cylindrical surface. The PDMS expands in one direction and the waves align parallel to the axis of the cylinder [9]; (3) the waves are ordered by compressing a flat slab of PDMS after it has been oxidized. The compressive stress is unidirectional and the waves align parallel to one another [9] and (4) the waves orient perpendicular to the border between treated and untreated regions, wherein the untreated/treated regions were defined through a mask [13]. Although the periodicity and orientation of waves can be effectively controlled by the above-mentioned technologies, low-cost methods for generating well-controlled and high-quality surface wavy structures are still very much expectable.

For the molecular structure of a PDMS polymer, it consisted of (-SiO(CH_3)$_2$) repeated units and is a helical structure, where the inner part of the helices is composed of siloxane units and outer part is composed of methyl groups [15]. Some literatures regarding the surface modification of carbon nanotubes have been reported that a strong acid solution was often used to attack or modify carbon atoms and then –OH and –OOH groups could be grafted onto carbon atoms [16–19]. Hence, we tried a chemical approach to modify the surface state of PDMS and to oxidize the carbon atoms in PDMS chains by dipping into a strong acid solution during few seconds to several minutes in this study. We found that wrinkles developed spontaneously on the PDMS surface after chemical modification and the periodicity of wrinkles, ranged from few ten to hundred micrometers and changed obviously with the increase of dipped time. By the use of Fourier transform infrared spectrometry (FTIR) the contact angle measurement of water drop and X-ray photoelectron spectroscopy (XPS), we would make every effort to guess the oxidized mechanism of PDMS surfaces. In addition, we tried to arrange regularly wrinkles on the PDMS surface by the presented approaches which have been reported in refs. [4,9]. Therefore, the optical performance of disordered or ordered wrinkles was also examined by an optical set-up.

2. Experiment

The liquid PDMS polymer that mixed PDMS silicone elastomer (Sylgard 184) and curing agent with the weight ratio of 10:1 was prepared. PDMS films with 100 μm thickness were deposited onto clean glass plates through a spin-coating process or coated with glass tubes by dipping into the PDMS liquids. In addition, PDMS films with step-like patterns were also prepared by casting against a PC-based mold fabricated by the micro-drill technology of excimer laser. These PDMS films were subsequently cured in an oven at 70 °C for 20 min. Simultaneously, a strong acid that mixed sulfuric acid solutions (H_2SO_4, content 95%) and nitric acid solutions (HNO_3, content 66–71%) with the volume ratio of 3:1 was prepared. Then, solidified PDMS films were immersed into H_2SO_4/HNO_3 solutions during few seconds to several minutes. Finally, the acid-modified PDMS films was dipped into clean water to remove the residual acid liquids and then dried by an air gun or an oven. Wrinkles could be found on the surface of PDMS.

3. Results and discussion

3.1. The surface character of the modification PDMS

PDMS silicone polymers have a strongly chemical stability to resist various acid solutions, such as hydrochloric acid (HCl), sulfuric acid (H_2SO_4), and nitric acid (HNO_3). Surprisingly, H_2SO_4/HNO_3 solutions seem to can react with PDMS polymers. After dipping H_2SO_4/HNO_3 solutions during few seconds, PDMS polymers started to change from transparent to white. An unknown white material which generated on the surface of PDMS polymers was supposed to be the product of chemical reaction after dipping in HNO_3/H_2SO_4 solutions. In order to verify what the white material was, FTIR, which is a useful instrument for the investigation of changes in the chemical structure of polymers, was utilized to analyze the difference between the pristine and the modified PDMS. Fig. 1(a and b) shows respectively the FTIR spectra of the modified and pristine PDMS and every characteristic peak is assigned corresponding groups on it. We found that absorption peaks of C–H groups changed obviously from a shape peak to a broad band and other absorption bands of C=C, C–O, C=O

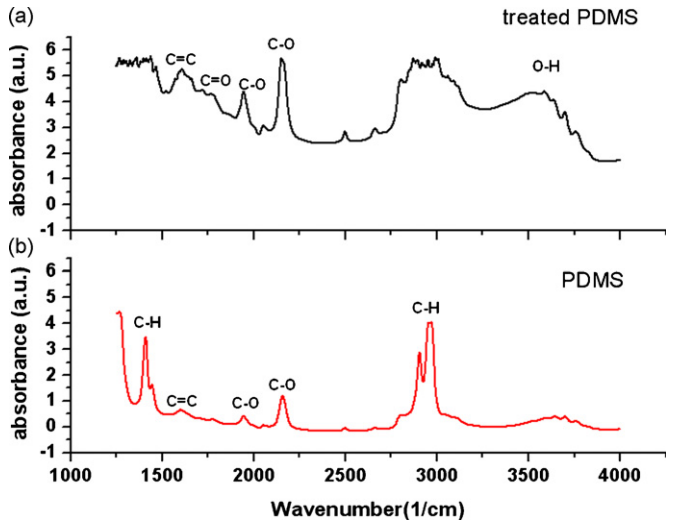

Fig. 1. FTIR spectra of (a) the oxidized PDMS surface modified by dipped H_2SO_4/HNO_3 liquids and (b) the pristine PDMS surface.

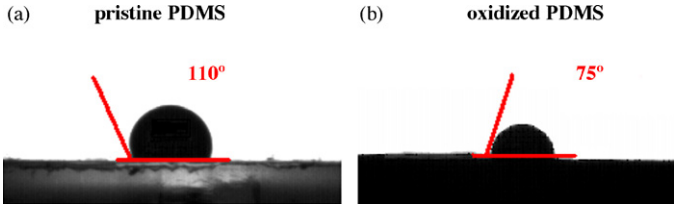

Fig. 2. Photo of water drop on (a) the pristine PDMS surface and (b) the oxidized PDMS surface.

groups strengthened strongly after chemical modification. It suggested that hydrogen atoms in methyl groups were abstracted from the polymer chains to generate radical within the polymer chains located at the surface. Some of carbon radicals in the polymer chain combined with oxygenic radicals formed in the acid-modified process.

The other evidence for the modification of the methyl groups was the change of contact angle. The pristine PDMS surface has a low surface energy to cause the hydrophobic nature, which is due to methyl groups located on the out part of a PDMS chain (water drop contact angle is 110°). As a contact angle changed from 110° to 75°, we believed that parts of methyl groups in PDMS chains should be fractured after chemical modification. The contact angle image for a pristine and modified PDMS surface is respectively shown in Fig. 2(a and b). In addition, the IR spectra of treated PDMS polymers exhibited an OH absorption broad band from 3250 to 3900 cm^{-1} and a characteristic peak corresponding to OH groups of silanol moeties was also found at around 3750 cm^{-1}[20].

Besides, the element quantification of an oxidized PDMS was determined by X-ray photoelectron spectroscopy (XPS). The composition of the surface was $Si_1O_{1.493}C_{1.58}$ before oxidation and was $Si_1O_{1.763}C_{1.6}$ after oxidation. The oxygen content in PDMS polymer only increased, but carbon content was almost invariable. It implied that carbon atoms in PDMS chain were merely grafted other oxygenic groups. However, the composition of the oxidized surface in chemical treatment was obviously different from that in oxygen plasma treatment. After oxygen plasma treatment, oxygen content in PDMS polymer increased but carbon content decreased, resulting in the formation of silica-like structures on the surface of PDMS [9].

On the other hand, a diluted H_2SO_4/HNO_3 solution (H_2SO_4/HNO_3 mixtures with three volumes of water) was also examined through the following experimental steps. Under the same experiment condition, we found no any change in the appearance of PDMS. It indicated that the acid concentration was an important factor for the generation of an oxidized PDMS.

3.2. The surface topography of the modification PDMS

A stiff film (oxidized PDMS polymers) was capped on the soft foundation (pristine PDMS polymers) that was confirmed in the study. Bilayer systems such as Al/PS films [5], Au/PDMS films [4] and SiO_x/PDMS films [9] have been demonstrated by the formation mechanism of wrinkles by several research groups. The young's modulus of a stiff layer mismatched greatly with that of an underlayer elastical materials. The mismatched young's modulus would lead to the generation of compress stress. In order to release the compress stress, the surface would form wrinkles and remain eventually at the incompressible status. Because one of formation methods for wrinkles is a thin metallic film covered with an elastomer, we used only optical microscopy (OM) to observe the modified surface of PDMS in order to avoid the influence of a metal/elastomer system. Fig. 3(a) shows that OM image of disordered wrinkles formed by dipping into H_2SO_4/HNO_3 solutions during

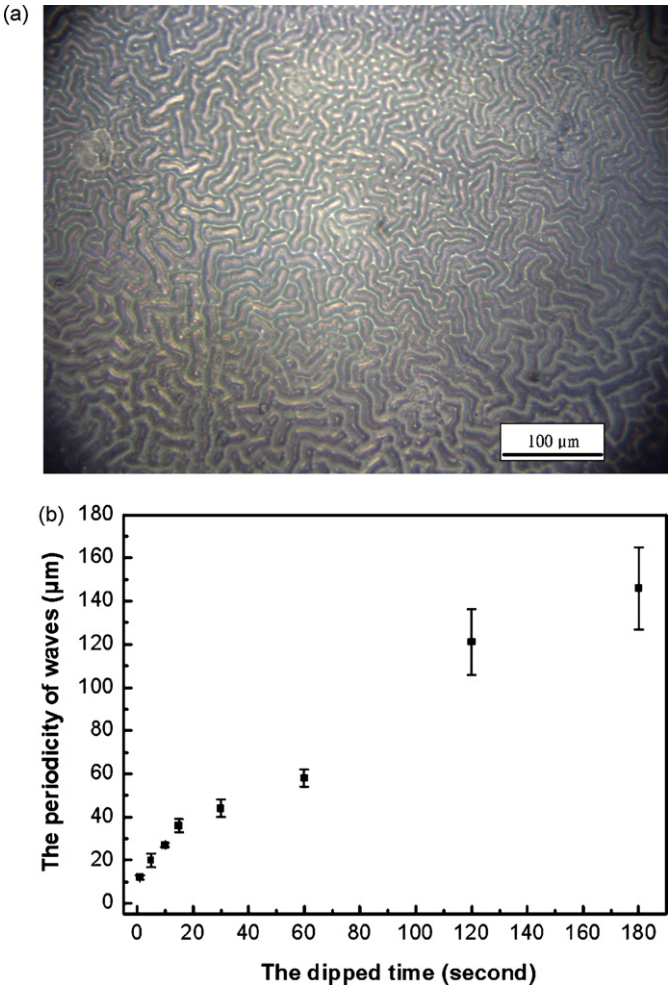

Fig. 3. (a) OM image showing wrinkles formed by dipped into H_2SO_4/HNO_3 liquids during five seconds on the PDMS surface and (b) the dipped time as a function of the periodicity of wavy structures.

five seconds. Fig. 3(b) shows that the dipped time as a function of the periodicity of wavy structures. The periodicity ranged from 11 to 165 μm during 1 s to 3 min was increased very rapidly with increasing the dipped time. Wrinkles generated in a wet process were discontinuous and bug-like in initial stages, but were continuous in later stages, which is because growing wrinkles would merge smaller ones. However, wrinkles generated in metal/elastomer systems were continuous in initial stages and these wrinkles grow hardly into several ten micrometers. For wrinkles on bilayer systems, the periodicity (λ) of the buckles can be expressed as Eq. (1) [4],

$$\lambda = 4.36t\left\langle \frac{E_s(1-v_p^2)}{E_p(1-v_s^2)} \right\rangle^{1/3} \quad (1)$$

where t, E_s, v_s E_p and v_p are the thickness of stiff layer, the elastic modulus and Poisson's of the stiff layer and the soft foundation layer and the thickness. Because we had only a very limited knowledge about the oxidized PDMS layer, we could not judge whether Eq. (1) described wrinkles on the surface exactly. However, this equation could explain the reason for the increase of wavelength with the increase of dipping time. In this

Eq. (1), the wavelength of wrinkles depended mainly on the thickness of the capped layer. In other words, the thickness of oxidized PDMS layer grew rapidly with the increase of dipping time.

3.3. The control for the arrangement of wavy structures

Some reports have been verified that the arrangement of waves formed on the bilayers system could be effectively controlled. There are mainly four approaches to align waves: (1) the arrangement of waves was always perpendicular to the surface of bas-relief patterns; (2) waves were ordered on a cylindrical surface; (3) waves are ordered after releasing a prestretched substrate and (4) waves orient perpendicular to the boundary between treated and untreated regions. In this study, we tried these approaches to arrange wrinkles on the modified PDMS surface.

To study the effect of the pattern on the orientation of the wrinkles, a single circular step-like pattern was first examined. The circular pattern shown in Fig. 4(a) was with a diameter of

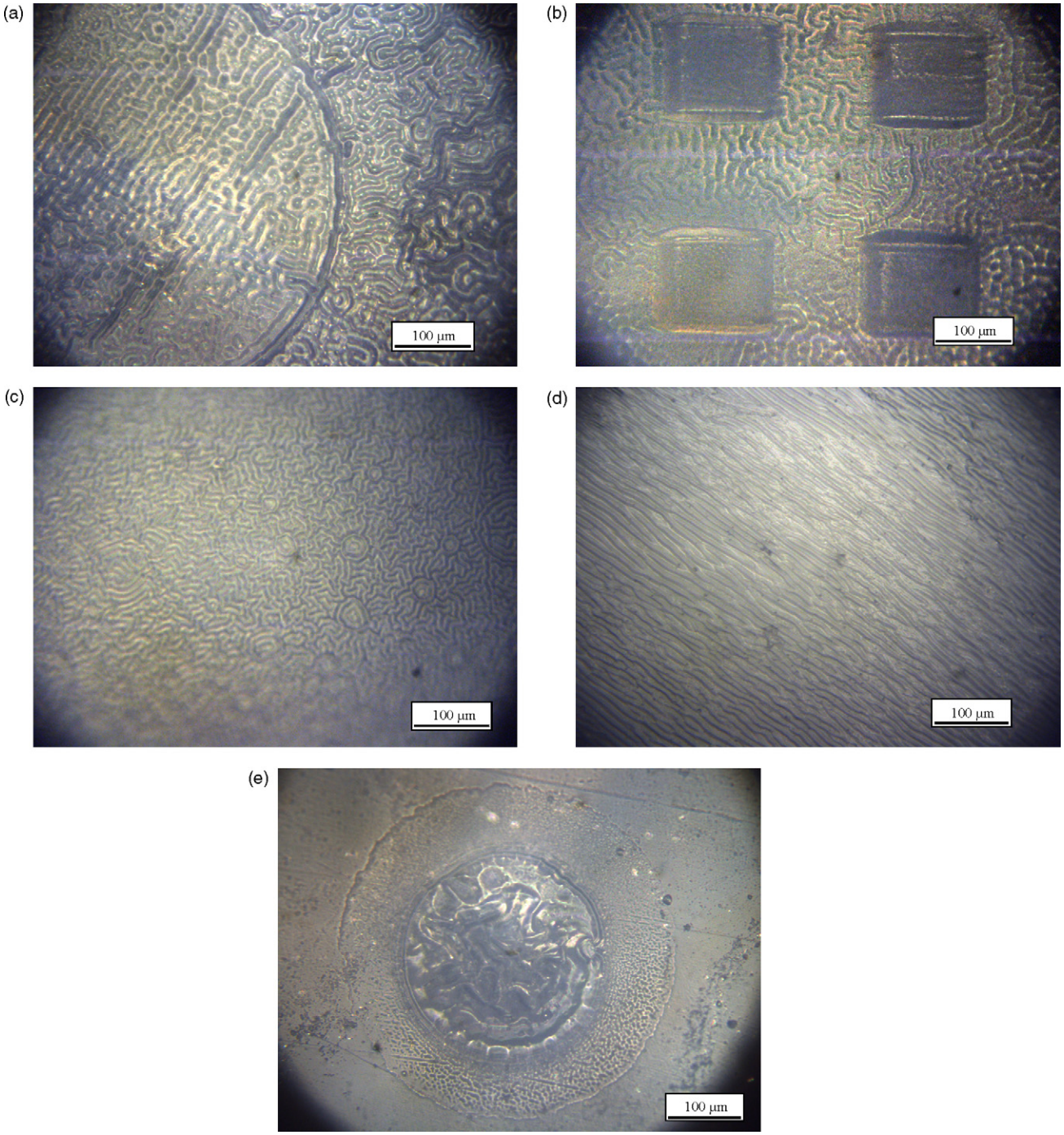

Fig. 4. OM image showing wrinkles (a) on a circular step-like pattern; (b) on a two by two square step-like patterns array; (c) on the surface of a glass tube covered a layer of PDMS films; (d) on the surface of a prestretched PDMS substrate and (e) on the defined region through a mask.

750 μm and height of 10 μm and disordered wrinkles were respectively found on the top and bottom of the step-like pattern on PDMS plates. Then, wrinkles on the PDMS plate with patterns in array were also considered. An array with two-by-two square patterns, each pattern having a side length of 100 μm, height of 10 μm, and pitch of 100 μm was studied. Disordered wrinkles were still found in this array. These wrinkles would not be regularly arranged along the sides of step-like patterns, regardless of the change of the size and shape of step-like patterns. The resultant image is shown in Fig. 4(b). Therefore, as the scale of wrinkles grew with dipped time and was bigger than that of step patterns, the patterns would be devoured by wrinkles.

Then, to study the effect of the curved surface on the orientation of the wrinkles, curved surface with different curvatures were respectively examined. Wrinkles which were still found on different curved surfaces arranged randomly with the change of curvatures. The resultant image is shown in Fig. 4(c). Although disordered wrinkles was formed on curved faces, the ring-like wrinkles which were different form the bug-like wrinkles on non-curved surfaces were first found on it.

Next, the effect of uniaxial forces applied to stretch a PDMS substrate before oxidization was studied. No wrinkles were found before releasing the oxidized substrate. But, ordered wrinkles, shown in Fig. 4(d), were found after releasing the oxidized substrate. Each of wrinkles faced almost a single direction, which was perpendicular to the stretched direction of a PDMS plate. The magnitude of the compressive stress on the oxidized PDMS/PDMS due to the substrate contraction was smaller than the stretched tension stress introduced by the preload, leading to be able to arrange regularly wrinkles on the surface.

Finally, a defined region through a mask was selectively modified and studied. The circular pattern with a diameter of 400 μm was examined. After chemical treatment, the resultant image is shown in Fig. 4(e). Instead of a defined circular pattern, concentric circles were found in the modified region, wherein some tiny ripples were randomly located on the outer circular and disordered wrinkles were laid in the inner circular. For the occurrence of concentric circles, this is obvious evidence that wrinkles was formed due to surface contraction.

Experiment results revealed that wrinkles formed by a wet process were merely ordered through the guidance of external forces. These results were corresponding incompletely with previous literature regarding the arrangement of wrinkles formed through metal deposition or plasma treatments. We considered that metallic particles or plasma radicals merely deposited or implanted the surface of PDMS vertically by physical processes, which are unable to modify the sidewalls of steps on PDMS substrate. The generated compress stress, due to the surface contraction, in the sidewalls of steps was zero but was rapidly increased beyond the edge of steps. The gradient of stress would force to arrange regularly wrinkles. But, the orientation of wrinkles formed by a wet process were easily random because the foundation shrank homogeneously, included the surface of PDMS and the sidewalls of steps. Each part of PDMS surfaces in wet processes was uniformly oxidized, regardless of the sidewall of pattered steps or curved surfaces, leading PDMS surfaces that were simultaneously contracted without the generation of the gradient of stress. Hence, a wet process to modify PDMS surfaces can be regarded as an isotropy modification.

3.4. Optical performance of wrinkles

To investigate the optical performance of wrinkles, an experimental apparatus consisting of a laser diode as the light source, a PDMS plate with the generated wrinkles as the test sample, a screen and CCD camera as the imagine display and recording system was set up. As the laser beam passed through the PDMS plates, the generated diffraction patterns were projected on the screen and then they were captured and recorded by the CCD camera.

By this apparatus, a PDMS plate with disordered or ordered wrinkles were respectively examined. As the wrinkles were randomly arranged, the resulting diffraction pattern, shown in Fig. 5(a) was a series of concentric circles. It indicated the wrinkles had a characteristic average and no preferential orientation [5]; as the wrinkles were regularly aligned, the resulting diffraction pattern, shown in Fig. 5(b), would be a series of peaks. Although each of the ordered wrinkles, generated in a wet process through a pre-stretched step was slightly discontinued, there was not any influence for diffraction pattern of ordered wrinkles. With the change of dipped time, the diffractive order of optical gratings, which responded to the periodicity of wrinkles, could be adjusted. Hence, it seems to be a low-cost approach to generate optical gratings through a wet process without any instrument.

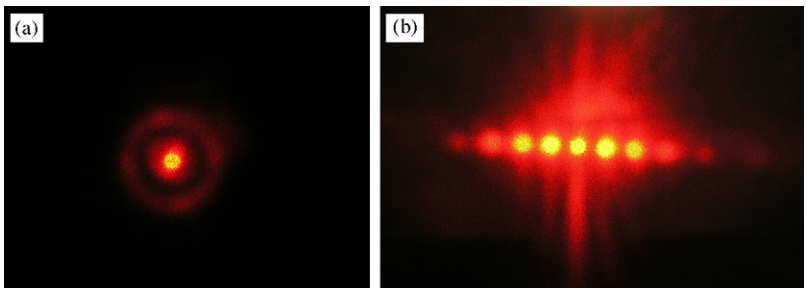

Fig. 5. CCD images showing the diffractive patterns for (a) disordered wrinkles and (b) ordered wrinkles.

4. Conclusions

The surface modification of PDMS was achieved by the treatment of H_2SO_4/HNO_3 solutions. The hydrophobic surface not only was changed to hydrophilic, but also formed wrinkles on it after chemical modification. The surface layer of PDMS was immediately oxidized, after it contacted with the acid solutions. The oxidization was demonstrated by the examination of FTIR, contact angle of water drop and XPS. A bilayer system, a stiff layer (an oxidized PDMS film) was capped on the soft foundation (a PDMS film), would lead to the formation of wrinkles and the wavelength of wrinkles increased with the increase of the dipped time. Wrinkles developed in wet processes were hard to arrange orderly in the surroundings of step-like patterns and on curved surfaces, which is due to oxidization uniformly. Ordered wrinkles, which were merely found through the guidance of external forces, were regarded as optical gratings and these examined their optical performance. We believe that this novel method for generating well-controlled and high-quality surface wavy structures is interesting in the applications of MEMS, micro-optics, biology, and nano-/micro-fabrication.

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