Fabrication of ordered micro- and nano-scale patterns based on optical discs and nanoimprint*

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A simple method to fabricate one-dimensional (1-D) and two-dimensional (2-D) ordered micro- and nano-scale patterns is developed based on the original masters from optical discs, using nanoimprint technology and soft stamps. Polydimethylsiloxane (PDMS) was used to replicate the negative image of the 1-D grating pattern on the masters of CD-R, DVD-R and BD-R optical discs, respectively, and then the 1-D pattern on one of the PDMS stamps was transferred to a blank polycarbonate (PC) substrate by nanoimprint. The 2-D ordered patterns were fabricated by the second imprinting using another PDMS stamp. Different 2-D periodic patterns were obtained depending on the PDMS stamps and the angle between the two times of imprints. This method may provide a way for the fabrication of complex 2-D patterns using simple 1-D masters.

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Materials with ordered one dimensional (1-D) and two dimensional (2-D) micro- and nano-scale patterns surface are important to a host of scientific and commercial applications. For example, they can be used for surface-enhanced Raman scattering substrate[1], extraordinary optical transmission[2] and antireflective coatings[3]. The conventional techniques to fabricate ordered patterns are electron beam lithography, focused ion beam lithography, and photolithography[4,5]. However, they are extremely expensive and time-consuming for fabricating patterns with large areas. Nanoimprint techniques and various soft lithography methods, such as capillary force lithography, micro-molding in capillaries, nano-transfer printing[4,6], are low cost and rapid for fabrication on large areas. However, original masters are still needed which are often fabricated by the conventional electron beam lithography or focused ion beam lithography.

Commercial “write once read many” type optical discs, such CD-R, DVD-R and BD-R, are usually used for data storage. In these discs, a single spiral track is drilled on the polycarbonate (PC) layer. As the radius of the disc is much larger than the gap between two adjacent turns of the spiral, the patterns on the PC layer of different kinds of discs appear as one-dimensional (1-D) gratings with different periods[7,8]. Recently, these discs have been used as masters widely for the fabrication of periodical ordered nanostructures[9-12].

However, when the PC part of optical discs is used as master for fabrication of patterns, it usually sticks to the substrates. Polydimethylsiloxane (PDMS) is heat resist, elastic and highly hydrophobic and was used as soft stamps in soft lithography and nanoimprint[6,13]. In this work, the PC part of CD-R, DVD-R and BD-R is used as original 1-D master. PDMS is used to replicate the negative image of the 1-D grating structures on the masters, respectively, and then the PDMS with 1-D ordered patterns is used as stamps for nanoimprint. Three 1-D grating structures can be obtained on PC substrate, and six kinds of basic 2-D ordered patterns can be produced after the second imprint using different PDMS stamps.

The patterned PC parts of three kinds of optical discs CD-R (Kodak, 650 MB), DVD-R (HP, 4.7 GB) and BD-R (Philips, 25 GB) were used as initial masters. Small pieces were cut from CD-R, DVD-R and BD-R, respectively, and then the PC layers were separated from the reflective layer manually. For CD-R disc, scotch tape was used to peel off the printing layer, protective layer and reflective layer. The organic dye layer was dissolved by ultrasonic treatment with ethanol and the PC master with 1-D grating from CD-R disc was obtained[12]. DVD-R consists of two PC surfaces that sandwich a reflective layer and dye layer between them. The two PC layers can be manually separated by splitting the DVD-R along the cut edge by a scissor, and the PC layer with

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grating was then immersed into ethanol to remove the dye layer on the grating side[12]. For BD-R piece, it was put into the concentrated hydrochloric acid for 3 h to remove the aluminum coating on the PC layer.

Fig.1 shows the schematic of the fabrication processes of 1-D and 2-D ordered patterns on a blank PC layer by nanoimprint using a 1-D PC grating of CD-R as the master. As shown in Fig.1, a PDMS stamp was firstly fabricated by replica molding against the patterned PC masters from CD-R disc with a 12.5:1 (weight ratio) mixture of elastomer and cross-linker of sylgard 184 (Dow Corning, USA). The prepolymer solution, after degassing, was poured onto the master and was thermally annealed at 80 °C for 60 min for completing cross-linking, after which the PDMS stamp with negative patterns image of the master formed and was manually peeled off.

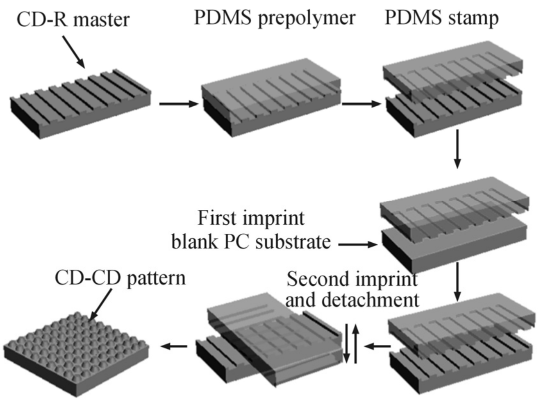


Fig.1 Schematic of the fabrication processes for 1-D and 2-D ordered patterns

The blank PC substrate was placed under the PDMS stamp with a pressure of 2.23 MPa at a temperature of 150 °C for 5 min, which is above its glass transition temperature[14]. After detachment, the PDMS stamp was rotated about 60° and a second imprint was performed with a pressure of 0.031 MPa at 140 °C for 3 min, yielding 2-D ordered pattern on the PC layer. These morphologies of the patterns were characterized by atomic force microscope (AFM) (Bruker, dimension EDGE).

As shown in Fig.2, the AFM image and the cross-section analysis of the CD-R master indicate that the 1-D grating structure of CD-R has a period of ~1 547 nm and height of ~163 nm. The corresponding PDMS stamp exhibits nearly a negative replica of the CD-R master with a period of ~1 572 nm and height of ~107 nm. The height of the grating in PDMS stamp is smaller than that of CD-R master, which can be attributed to that the viscosity of PDMS limits the penetration depth and the valley of the grating was not fully filled by PDMS during the replica molding process, so only the top part of the grating was replicated. After the nanoimprint process using the PDMS stamp, a 1-D grating structure formed on the blank PC substrate, and it has a period of ~1 621 nm and height of ~104 nm. Compared with the PDMS stamp, the height is nearly the same, but the period becomes larger due to the lateral deformation of PDMS under pressure[15].

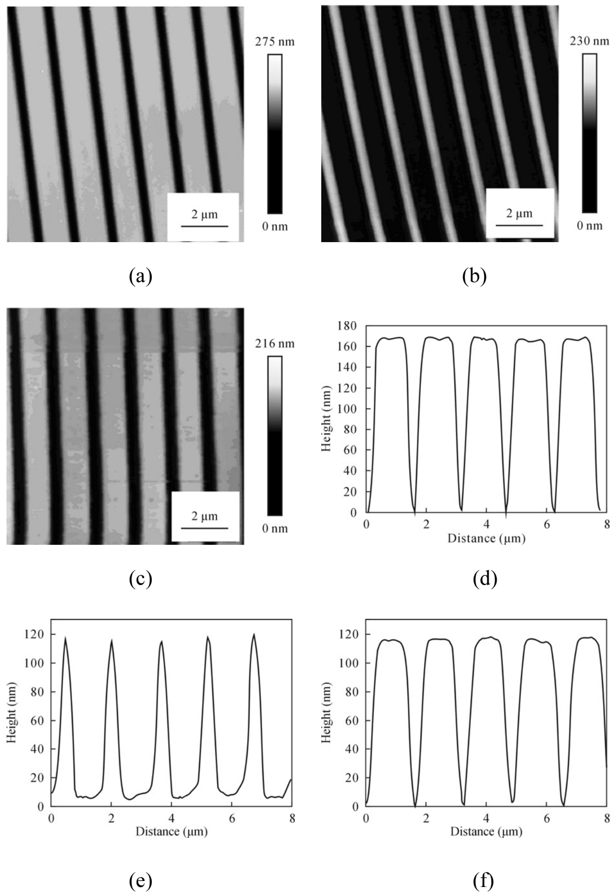


Fig.2 AFM images of (a) the pattern on the PC master of CD-R, (b) the corresponding PDMS stamp and (c) the imprinted pattern on the PC substrate; Morphology curves of the cross-section of (d) the master of CD-R, (e) PDMS stamp and (f) imprinted pattern

Since the imprinted pattern is dependent on the master, if master with smaller period was used, 1-D grating with sub-micrometer period will be obtained. Therefore, the PC masters from DVD-R and BD-R were used as initial masters, and the 1-D grating pattern with sub-micrometer period was obtained by the method used for CD-R. As shown in Fig.3(a) and (b), the period of the PC master of DVD-R is ~733 nm and the period of the corresponding imprinted pattern is 746 nm. As shown in Fig.3(c) and (d), for BD-R master and the corresponding imprinted pattern, the periods are ~330 nm and ~332 nm, respectively. There are also some differences between the periods of the master and the corresponding imprinted patterns, which are predictable and can be mainly attributed to the deformation of PDMS stamp[15]. So 1-D gratings with different periods can be fabricated by nanoimprint using different optical disc masters, respectively.

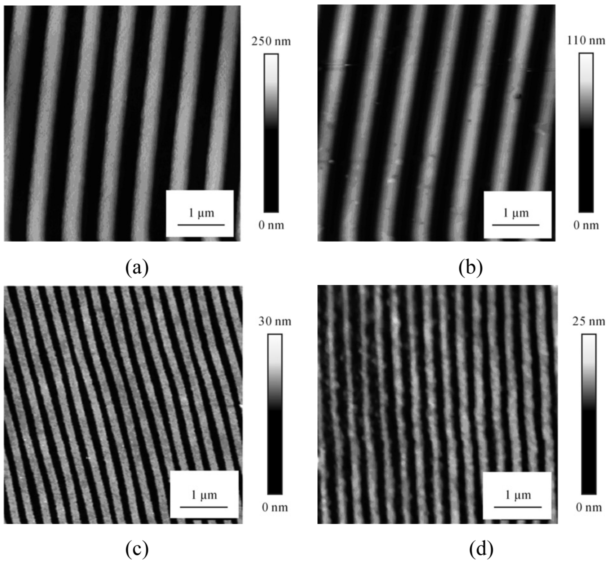
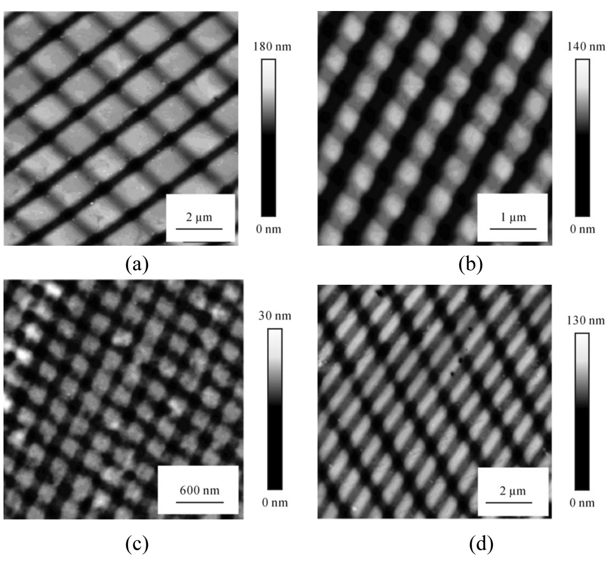


Fig.3 AFM images of patterns on the PC master of (a) DVD-R and (c) BD-R, the imprinted 1-D patterns on PC substrate corresponding to (b) DVD-R and (d) BD-R

2-D ordered patterns can be fabricated by imprint for the second time. As shown in Fig.4(a), 2-D ordered patterns were imprinted on the PC substrate by using the same PDMS stamps from CD-R master for the first and second time imprint, and this pattern was named as CD-CD pattern. Similarly, DVD-DVD and BD-BD patterns were imprinted, which are shown in Fig.4(b) and (c), respectively. If the two times of imprints were performed using different stamps, complex 2-D patterns can be fabricated on the substrate. As shown in Fig.4(d)—(f), the patterns of DVD-CD (DVD-CD means DVD stamp is used for the first imprint and CD stamp is used for the second imprint), CD-BD and DVD-BD were fabricated and they exhibit complex structures. For example, the DVD-CD pattern exhibits a period similar to DVD-R master in one direction, while it exhibits a period of CD-R master in another direction. More complex 2-D patterns can be fabricated by changing the angle between the two times of imprints.



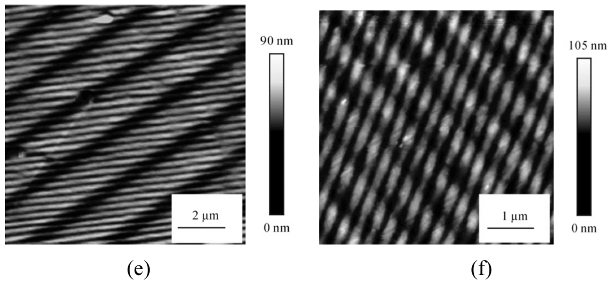


Fig.4 AFM images of the 2-D patterns of (a) CD-CD, (b) DVD-DVD, (c) BD-BD, (d) DVD-CD, (e) CD-BD, (f) DVD-BD on the PC substrate

To give a visual observation of the imprinted patterns, the method of diffraction of light was used. As shown in Fig.5(a), the patterned PC exhibits a “rainbow” shape due to the diffraction of sunlight. As shown in Fig.5(b), a hexagonal 1-order diffraction pattern was observed when the DVD-DVD pattern was irradiated by a laser with the wavelength of 405 nm. Since the ratio of the period of DVD-R to the wavelength of 405 nm is ~1.8, and the angle between the two times of imprints is about 60°, a hexagonal 1-order diffraction pattern can be observed.

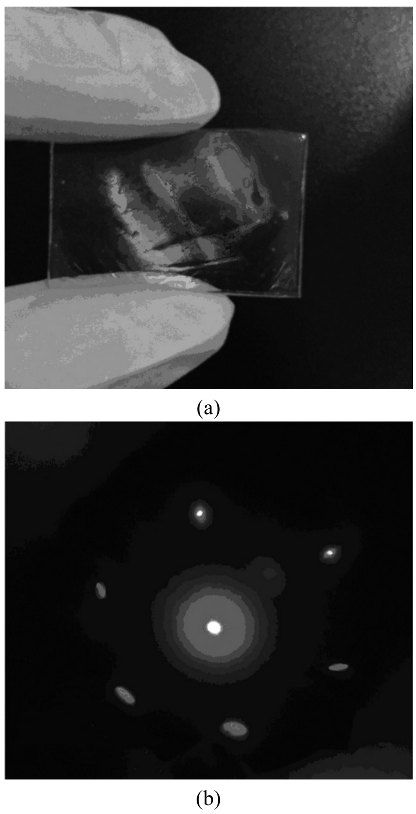


Fig.5 (a) The photo of the imprinted DVD-DVD pattern on PC substrate; (b) The laser diffraction on the screen for DVD-DVD pattern, irradiated by a laser with the wavelength of 405 nm

In summary, we have presented a simple and low-cost method to fabricate 1-D and 2-D ordered micro/nano patterns by nanoimprint technology, using soft stamp from the PC part of CD-R, BD-R and DVD-R. Although various 1-D and 2-D patterns can be obtained by using expensive custom-made stamps with 2-D patterns or by complex electron beam writing, the proposed method shows that some kinds of patterns can be produced without using such costly stamps or techniques. Further, though the experiments reported in this work were performed with PC substrate, the process is generic and can be implemented with films of other polymer materials as well, such as polymethyl methacrylate (PMMA) and polystyrene (PS).

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