Additive Manufacturing of Optical Devices using Inkjet Printing on Optical Nanostructures

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Abstract

We present a novel additive strategy to manufacture nano-optical devices using inkjet printing on nanostructured surfaces. To print optically variable devices, silver ink is jetted on the surface of nanopillar arrays to selectively activate or deactivate the structural color pixels. We study the effects of surface chemical properties on inkjet printing and two different printing modes: bright silver mode on hydrophilic surface and dark silver mode on hydrophobic surface. The printed silver film activates the structural color pixels in bright silver mode while deactivates the pixels in dark silver mode. Color images are printed in 120 pixels per inch resolution using both modes. 27 different colors can be achieved from bright silver mode and more than 512 colors from dark silver mode. The color images printed with bright silver mode show high color contrast owing to the index matching process that deactivates unwanted pixels. Color images printed from dark silver mode exhibit brighter colors owing to the high grating efficiency but lower color saturation due to the difficulty in completely deactivating pixels.

Introduction

Additive printing is a very powerful technique that can revolutionize many industries and research fields. The recent advancement of additive printing has proven the incredible diversity of products that may be printed, from automobile components [1] to replaceable artificial organs [2]. One distinctive advantage of additive printing, compared to conventional manufacturing techniques, is its flexibility to manufacture products with customer-defined input or personalized information. Fabrication of optical devices usually requires micro- and nano-patterning techniques. A wide range of patterning technologies has been developed such as optical lithography, electron beam lithography [3], diamond turning, laser ablation, micro-contact printing and nano-transfer printing. In recent years, inkjet printing has increasingly become popular as a scalable micropatterning technology due to its precise, flexible control and cost-effective additive process [4].

One type of optical device commonly used in anti-counterfeiting applications is the optically variable device (OVD) that can display shifting colors under different viewing angles. Conventional methods of manufacturing OVDs usually use expensive techniques (e.g. electron beam lithography) to fabricate a master stamp and replicate the OVDs into large quantity from the same stamp. Since the features on the stamps are not rewritable, it is very challenging to incorporate any personalized feature into the conventional OVDs.

Using additive printing on nanostructures, optically variable devices (OVDs) and other types of structural color images with personalized information can be efficiently manufactured. In our previous work, we have introduced the concept of inkjet-printed OVDs that produce color images [5]. The concept is shown in Figure 1. The surface of the substrate is patterned with bands of structural pixels composed of dielectric nanopillar arrays (NPAs) that give red (R), green (G) and blue (B) primary colors. One such substrate is referred to as a nanosubstrate. The size of the experimental nanosubstrate is 2.0 cm × 1.5 cm as shown on Figure 1(a), the pixel bands are repeated into a 1-D array, and each band is 70 µm wide as shown in Figure 1(b). The SEM images reveal the nanoscale details of the structures on the pixel band that each band contains NPAs of different periodicity. It is the periodicity of NPAs that leads light to diffract certain colors into certain direction as a 2-D grating. As shown in Figure 1(c), to print a color image, the RGB pixels on the nanosubstrate are selectively activated or deactivated using inkjet printing according to the desired color image. Different visual colors are achieved by properly adjusting the relative brightness of the individual RGB pixels.

The key aspect of our technology is to control the silver ink formation on the nanostructured surface in order to activate or deactivate the RGB pixels. Depending on the surface chemistry properties, printed silver can either form a thin layer or a thick layer on the NPAs. As shown in Figure 2(a), an unprinted NPA diffracts light into the viewer from the periodic structure of the nanopillars. Figure 2(b) shows the situation where the printed silver forms a very thin layer that is conformal to the nanostructured surface. After printing, the sample is laminated with a transparent film that has refractive index matched to the dielectric nanopillars. As a result, the NPAs not covered by silver cannot diffract light because the index matching optically annihilates the grating structure. In contrary, the NPAs covered with silver will remain active in diffracting light as the shape of the NPAs is preserved in the printed silver film and the silver provides enough optical contrast to diffract light. Since the printed silver in this case activates the pixel, this printing mode is referred to as *bright silver mode*. Figure 2(c) shows the situation where a very thick silver film is printed on the NPAs. In the region printed with silver, since the film is much thicker than the nanostructures, it only attenuates light by scattering and there is no diffracted color. In the region uncovered by silver, the dielectric NPAs still diffract light. Since the printed silver in this case actually deactivates the pixel, this printing mode is referred to as *dark silver mode*. It should be noted that, in dark silver mode, the printed sample shall not be laminated because the index matching deactivates the functioning dielectric NPAs.

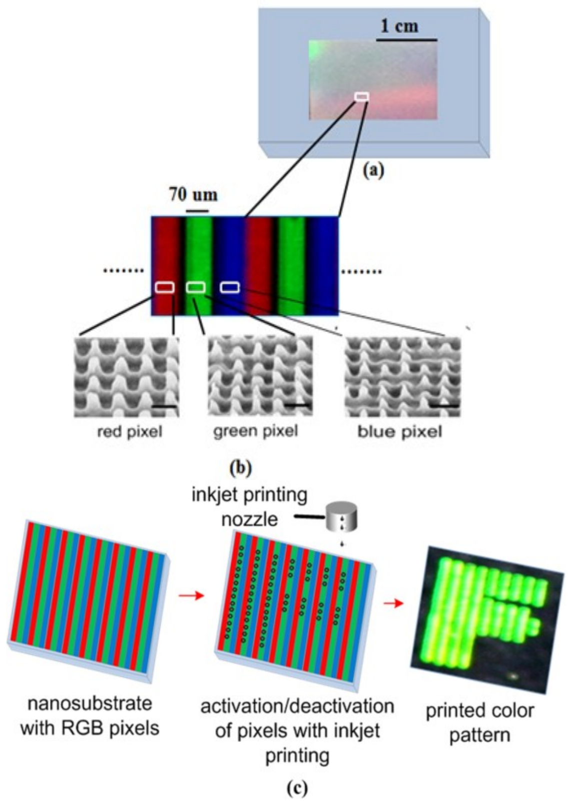

***Figure 1**. Schematic of inkjet-printed OVDs on nanopillar array pixels. a) The configuration of a nanosubstrate. b) Scanning Electron Microscope (SEM) images of the nanopillar array pixels. The length of scale bar is 500 nm. (c) Schematic process to print a color pattern on the nanosubstrate by selectively activating or deactivating pixels.*

In this paper, we study the bright silver mode and dark silver mode by modifying the chemical properties of the nanosubstrate surface. The objective of this work is to study the relationship between the characteristics of silver (Ag) inkjet printing and the surface conditions controlled by surface chemistry, thereby obtaining a technical solution for controlling the feature size in inkjet-printing-based on microfabrication of optical devices. The effects of controlling feature size on the chemically treated nanosubstrates are examined and the key characteristics, including pixel brightness and color levels, are presented.

Experimental Methods

Inkjet printer may be operated either in continuous mode or drop-on-demand mode. Unlike continuous inkjet printer, in drop-on-demand printer, dots of ink are precisely controlled which yielded high resolution. The small amount of ink is jetted onto a specific position on the any type of substrate on demand and the desired patterns are fabricated. We used Fujifilm Dimatix materials printer DMP-2831 with 16 nozzle cartridges of 1-picoliter drop volume. We use alcohol-based silver ink with 30-35% nanoparticle weight percentage. In the process of inkjet printing, inks of silver nanoparticles are jetted from the nozzles and deposited on the nanostructured surface. The binary printing pattern is generated using a custom-written MATLAB script based on the configuration of the nanosubstrate and the given color image.

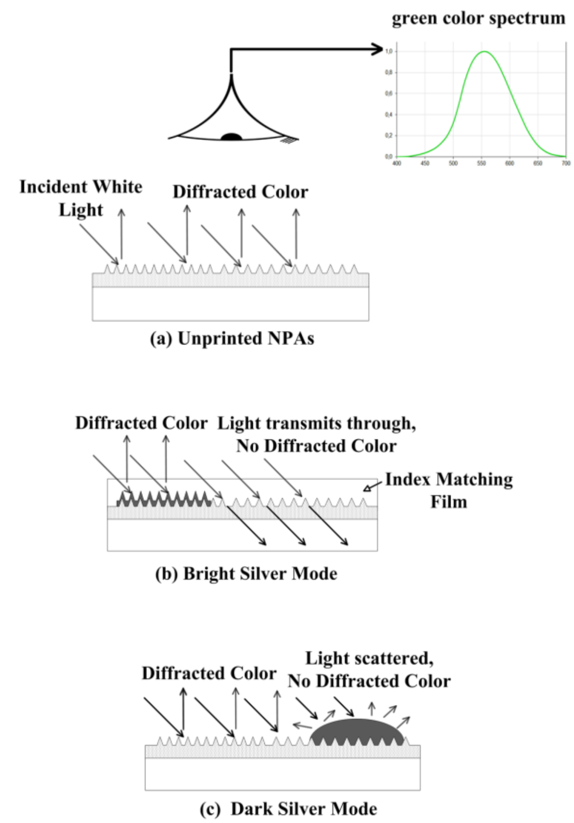

***Figure 2**. Schematic of bright silver mode and dark silver mode for printing colors on NPAs. (a) Unprinted NPAs and schematic of the diffraction colors. (b) NPAs printed with bright silver mode in which the pixel under the printed silver dot is activated while other regions are deactivated by lamination. (c) NPAs printed with dark silver mode in which the pixel under printed silver dot is deactivated while other unprinted regions remain active in diffracting light.*

When ink droplets meet the surface, they may splash or retract. Other group addressed this challenge by investigating the influence of substrate temperature and over printing [4]. They demonstrated the impact of substrate temperature on the shapes of dried and sintered inkjet-printed dots of nanosilver suspension. It is cited that the average dot thickness in first printing step on hydrophobic and hydrophilic surfaces reduces with increasing substrate temperature. They also found that there is an increase in average overprinted and dried dot thickness at lower temperature and even larger increase at higher temperature.

As previous research has shown, the shapes of droplets on the solid surfaces varied from oblate to spherical according to the dynamic contact angle at the three phase contact line [6]. Droplets tend to spread on a wetting surface [7], whereas they tend to rebound up on a non-wetting surface [8]. Therefore, modifying substrate with proper chemicals is not only useful to control the wetting behavior of printed dots on the surface, but also crucial to the printing resolution [7, 10].

In our experiments, we control the surface wettability using vapor phase deposition of monolayer on the nanostructured surface. Hexamethyldisilazane (HMDS) is applied to obtain a hydrophilic surface on which the silver ink splashed over the surface to form a thin film (bright silver mode). Perfluorodecyltrichlorosilne (FDTS) is used to obtain a hydrophobic surface on which the silver ink retracts to form a thick silver layer (dark silver mode). The contact angles of the HMDS and FDTS coated surface are measured to be 90.6° and 144.8°, respectively.

In our experiments, the effective brightness of the subpixels is evaluated by capturing the optical microscope images from the printed samples and image analysis using custom-written MATLAB script. The discernible color levels and resolution are of main interest. For the sake of brevity, only the results for silver printed on green pixel bands are presented in this paper. The trend is the same for inks printed on red and blue pixel bands.

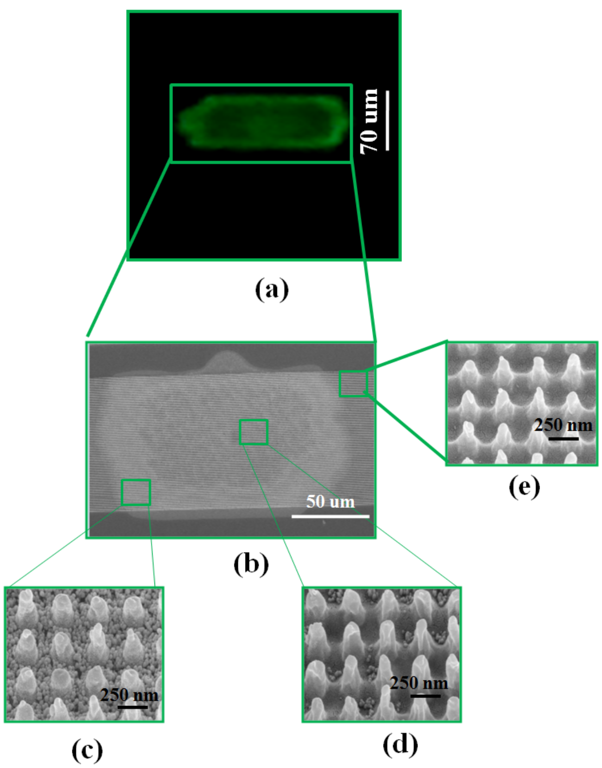

***Figure 3**. Silver ink printed with bright silver mode on hydrophilic surface. (a) Optical microscope image of one printed dot on green pixel band after laminating the sample. (b) SEM images of the silver dot printed on the hydrophilic surface and (c),(d) and(e) are inset images to show details in different regions.*

Experimental Results

Bright Silver Mode Printing on Hydrophilic Surface

Figure 3 shows the results of a single green color dot printed with bright silver mode on hydrophilic surface. Hydrophilic treatment assists the spreading of the silver ink, which can form into a thin film conformally coated on the NPA surface. After lamination, only the printed region remains active in diffracting light as it preserved the periodic morphology. As shown in Figure 3, NPAs are partly covered with silver ink and there is no close-packing of the silver nanoparticles at center of dot. The shape of the printed dot on hydrophilic surface is anisotropic as the ink tends to spread along the nanostructured surface rather than enter the empty gap between pixel bands.

Dark Silver Mode Printing on Hydrophobic Surface

Hydrophobic treatment leads to the formation of large aggregates silver nanoparticle on the surface as shown in the Figure 4. These particles block the NPAs and deactivate light diffraction. The printed silver film is too thick optically (> 400 nm thick) and therefore no periodic morphology from the NPAs can be preserved into the silver film. It is also observed in that the thickness of printed dots is decreased at the edge of the printed dots.

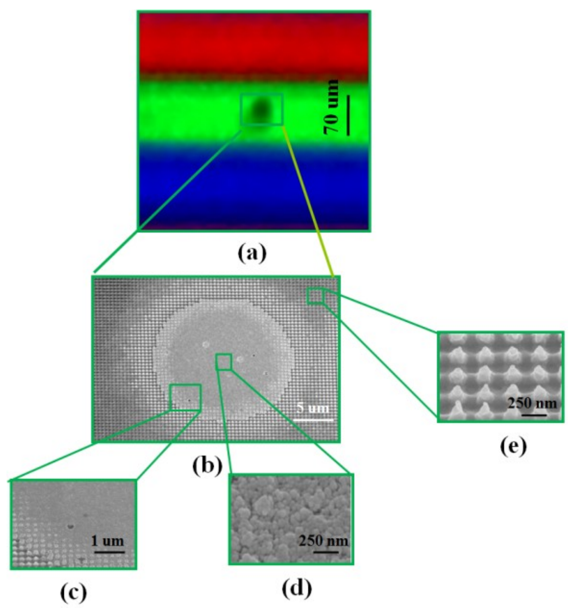

***Figure 4**. Silver ink printed with dark silver mode on hydrophobic surface. (a) Optical microscope image of one printed dot on green pixel band. (b) SEM images of the silver dot printed on the hydrophobic surface and (c),(d) and(e) are inset images to show details in different regions.*

Resolution and Discernible Color Levels

In our technology, the visual colors are controlled by the color levels of individual R, G, and B subpixels in each pixel and the resolution of printed image is determined by the inkjet printing process and the nanosubstrate pixel layout together. It is therefore of great interest to study the printing resolution and discernible color levels in each subpixel. In our experiments, we print different numbers of silver dots on one green subpixel to evaluate these characteristics. The color level is calculated by the number of dots that can be accommodated in one subpixel and the actual measurement of the effective brightness.

Hydrophilic Surface Behavior

The size of individual silver dot printed on hydrophilic substrate is around 147 µm long and 70 µm wide. As the droplet on hydrophilic surface tends to spread on the nanostructured surface, the shape of printed dot is much larger than printed dots on hydrophobic surface. By contrast, on hydrophilic surface, there is a slight increase in brightness until 2 printed dots as shown in Figure 5. It is found that more than 2 dots cannot contribute to more diffraction of color because of overlapping printed dots. Therefore, the brightness of printed silver dots saturates for more than 2 printed dots and the discernible color levels from bright silver mode is 3 levels (each subpixel can be occupied by 2 printed dots that is equivalent to 3 levels). 27 different colors can be printed in each pixel.

Hydrophobic Surface Behavior

The size of printed single dot on the hydrophobic substrate is about 18 µm. The surface behavior affects the geometrical shapes of printed silver dots as the shapes of printed dots are circular in dark silver mode. In this work, we print on one green subpixel band from 1 dot to 7 dots to evaluate the effective brightness of the green subpixel. Up to seven silver dots can be accommodated within each subpixel without overlapping. In other words, color images can be printed with 8 color levels and 512 (8×8×8) different colors in dark silver mode. As shown in Figure 5, subpixel brightness on hydrophobic surface declines as the number of printed silver dots increases. It should be noted that the printed pattern could not be laminated as the index matching deactivates the functioning NPAs that were not covered with silver dots.

Key characteristics of bright silver mode and dark silver mode are compared in Table 1. The resolution defined as pixel per inch (PPI) is actually determined by the substrate layout on which each pixel is 210 µm×210 µm in size. The resolution in dots per inch (DPI) is defined as the number of dots that can be printed without overlapping in each subpixel.

Table 1: Comparison of performance between bright silver mode and dark silver mode

surface	PPI	DPI	Color levels	Number of colors
hydrophobic	120	847	8	512
hydrophilic	120	290	3	27

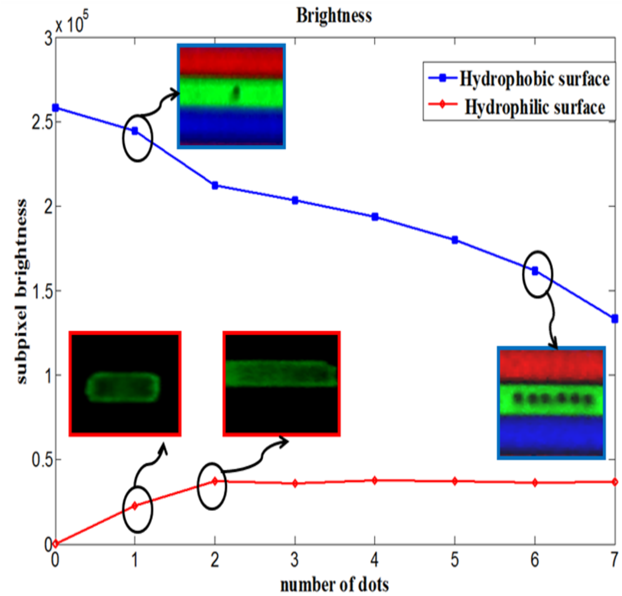

***Figure 5**. Effective subpixel brightness v.s. number of printed silver dots on hydrophilic and hydrophobic surface. The inset optical microscope images show the patterned subpixels in the corresponding data points.*

Examples of Printed Color Images

To further illustrate the bright silver mode printing and dark silver mode printing, we also printed two color images. To implement the experiments, hydrophobic substrate and hydrophilic substrate are produced and then generated binary patterns are inkjet-printed with respect to the nanosubstrate layout. Figure 6 shows the result images. Based on the data from Figure 5, the printed dots experienced no further increase in brightness on hydrophilic surface while increasing the number of printed dots beyond 2 dots printed. Thus, we successfully print a color pattern with only 27 different colors (3 levels in each subpixel) shown in Figure 6(a). Then, index matching is used to form the desired color pattern. The result exemplifies the bright printed pattern. In case of dark silver mode, silver inks were printed with 10 µm spacing and we managed to print a color portrait photo as shown in Figure 6(c). We observe overlapped printed silver dots at some region of the nanosubstrate, but the brightness of the subpixel is effectively attenuated by the printed silver dots. If we assume the subpixel brightness monotonically decreases with increasing number of dots, we may achieve 22 discernible color levels on each subpixel and 10,648 different colors using such configuration.

It can be observed that the color image printed with bright silver mode has a better color contrast than that with dark silver mode because there is no 'true black' in latter mode. In dark silver mode, it is very challenging to fully deactivate one subpixel as it requires the thick silver film to accurately cover the entire subpixel. Considering ink positioning errors and ink spreading behaviors, attempts to cover the entire subpixel would very likely affect neighboring subpixels. In bright silver mode, however, black color is easily achieved because the index matching of the unprinted regions completely deactivates diffraction. It should also be noted that, the image printed with dark silver mode is brighter than bright silver mode because in our NPA gratings, the uncovered dielectric NPAs give higher grating efficiency (unprinted regions in dark silver mode) than those covered with a thin silver film (printed regions in bright silver mode). By modifying the nanostructure configuration, we could potentially achieve equal brightness from both two modes.

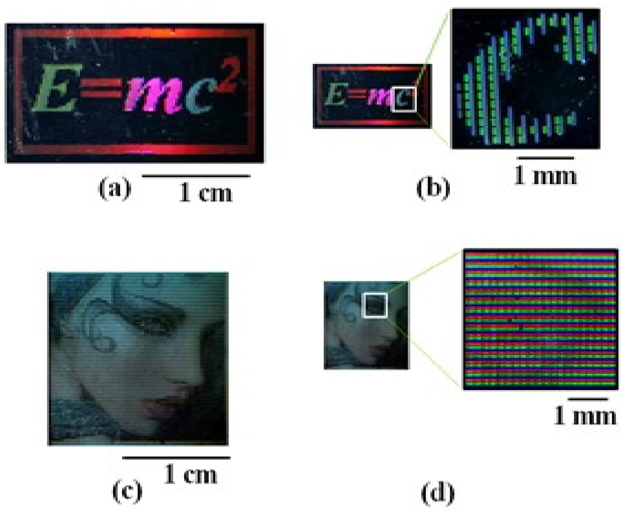

***Figure 6**. Photographic images of printed samples. (a) Color patterns printed with bright silver mode. (b) Zoom-in image of (a) to show the details on the printed color letter 'C'. (c) Color photo printed with dark silver mode. (d) Zoom-in image of (c) to show the details on the eye.*

Conclusion

We have demonstrated the concept and the experimental results of inkjet-printed optically variable devices to rapidly print any color images with structural coloration. By modifying the surface chemical properties, we can selectively control the activation or deactivation of the pixels and also the printing resolution and color levels. The presented technology shows promises in manufacturing personalized authentication devices.

An interesting question that still remains to be answered is whether the development of ink materials and formulation can influence the resolution of printed patterns. This will be addressed in a future study.

References

[1] E. Bassoli, A. Gatto, L. Iuliano, and M. G. Violante. "3D printing technique applied to rapid casting," Rapid Prototyping Journal, 13, 148 (2007).

[2] V. Mironov, T. Boland, T. Trusk, G. Forgacs, and R. R. Markwald, "Organ printing: computer-aided jet-based 3D tissue engineering," TRENDS in Biotechnology, 21, 157 (2003).

[3] A. M. Hung, C. M. Micheel, L. D. Bozano, L. W. Osterbur, G. M. Wallraff and J. N.Cha, "Large-area spatially ordered arrays of gold nanoparticles directed by lithographically confined DNA origami," Nature Nanotechnology, 5, 121 (2010).

[4] D. J. Lee and J. H. Oh, "Shapes and morphologies of inkjet- printed nanosilver dots on glass substrates," Surface and interface analysis," 42, 1261(2010).

[5] H. Jiang, S. Arabi, H. Shahbazegian, J. N. Patel and B. Kaminska, "Inkjet printed optically variable devices on a polymer Substrate patterned with nanoPillar array structural pixels," IEEE Nano 2015 conference, Rome, Italy (2015).

[6] D. Caviezel, C. Narayanan and D. Lakehal, "Adherence and bouncing of liquid droplets impacting on dry surfaces," Advanced Materials, 5, 469 (2008).

[7] H. Y. Ko, J. Park, H. Shin and J. Moon, "Rapid self-assembly of monodisperse colloidal spheres in an ink-jet printed droplet," Chemistry of materials, 16, 4212 (2004).

[8] C. Antonini, A. Amirfazli and M. Marengo, "Drop impact and wettability: from hydrophilic to superhydrophobic surfaces," Physics of Fluids (1994-present), 42, 1261 (2012).

[9] H. Y. Ko, J. Park, H. Shin and J. Moon, "Rapid self-assembly of monodisperse colloidal spheres in an ink-jet printed droplet," Chemistry of materials, 16, 4212 (2004).

[10] J. Z. Wang, Z. H. Zheng, H. W. Li, W. T. S. Huck and H. Sirringhaus, "Dewetting of conducting polymer inkjet droplets on patterned surfaces," Nature Materials, 3, 171 (2004).