Gradient-Wrinkled Microparticle with Grayscale Lithography Controlling the Cross-Linking Densities for High Security Level Anti-Counterfeiting Strategies

Cheolheon Park,§ Hyung Jong Bae,§ Jinsik Yoon, Seo Woo Song, Yunjin Jeong, Kibeom Kim, Sunghoon Kwon,* and Wook Park*

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ABSTRACT: Physical unclonable functions (PUFs) enable different characteristics according to the purpose, such as easy to access identification, high security level, and high code capacity, against counterfeiting a product. However, most multiplex approaches have been implemented by embedding several security features rather than one feature. In this paper, we present a high security level anti-counterfeiting strategy using only labyrinth wrinkle patterns with different complexities, which can be used as unique and unclonable codes. To generate codes with different levels in a microtaggant, we fabricated wrinkle patterns with characteristic wavelength gradients using grayscale lithography. The elastic modulus of the polymer substrate and corresponding wavelength after the wrinkling process were controlled by designing the gray level of each subcode region in a gray-level mask image for photopolymerization of the microparticle substrate. We then verified the uniqueness of the extracted minutia codes through a cross-correlation analysis. Finally, we demonstrated the authentication strategies by decoding different minutia codes according to the scanning resolution during the decoding. Overall, the presented patterning method can be widely used in security code generation.

1. INTRODUCTION

Encoded microparticles have been fabricated for various applications, including cell carriers,1,2 multiplex bioassay platforms,3−8 and anti-counterfeiting strategies.9−13 Among the various nondeterministic encoding methods, including physical unclonable functions (PUFs),14,15 wrinkling is valuable where a large code capacity is required or for security purposes because a myriad of irreproducible topographical codes can be generated in a high-throughput manner. In our previous study, we utilized a labyrinth wrinkle pattern with a homogeneous ridge periodicity (characteristic wavelength) throughout the microparticle for an unclonable code.12

For anti-counterfeiting methods, several security features are generally introduced on a single product because one authentication layer is vulnerable to an attack as counterfeiting techniques become more sophisticated.16 In addition, a one-layer system cannot simultaneously perform simple identification and powerful authentication because of the trade-off between the security level and code readability. Consequently, multiplex approaches are universal to satisfy various authentication requirements for given purposes in the markets. For example, a banknote has more than 10 features, including a holographic image and watermark for overt authentication and fluorescence fibers for covert authentication. However, these approaches require different encoding mechanisms or mixing of different materials, which increases the production cost or complexity of the decoding system. Therefore, a gradient-wrinkled microparticle with one security feature is more effective for application to the actual market.

To achieve high security level anti-counterfeiting on a single microtaggant using only wrinkles, wrinkle patterns with different complexities need to be created so that users can read different codes according to the resolution of the decoding optic system. For example, a higher security level code with a wavelength of a few microns requires a higher resolution of the reading system, such as a confocal laser scanning microscope with a low scanning speed. As the code complexity or security level is determined by the wavelength, it is necessary to generate several wrinkle patterns with different characteristic wavelengths in a single taggant.

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To fabricate heterogeneous random wrinkle patterns in a single structure, the elastic modulus of the substrate or film thickness in the structure must be designed differently because the wavelength of the wrinkle pattern in a bilayer structure is determined by

$$\lambda = \frac{2\pi}{\pi - \nu_s E_s \nu_f E_f} \left[ \frac{(1 - \nu_f^2) E_f}{3(1 - \nu_s^2) E_s} \right]^{1/3} \tag{1}$$

where $E_s$ and $E_f$ are the elastic moduli of the substrate and film, respectively, $\nu_s$ and $\nu_f$ are Poisson’s ratios of the substrate and film, respectively, and $t$ is the thickness of the film. Various fabrication techniques for simultaneous patterning of wrinkles with different periodicities have been developed by utilizing geometric gradients, film thickness gradients, elastic modulus gradients, or both thickness and modulus gradients. However, these methods are inappropriate for the fabrication of numerous microparticles encoded with different wrinkle gradients because (i) the realization of a certain wavelength in a certain location is challenging owing to the geometric gradient or film thickness gradient and (ii) repetitive modification processes are required to fabricate heterogeneous patterns using the modulus gradient.

### 2. MATERIALS AND METHODS

#### 2.1. Silica-Coating Process for Formation of Gradient-Wrinkled Microparticles

In this paper, we present a designable and scalable patterning method with gradient wrinkles for a novel high security level anti-counterfeiting strategy using random wrinkles by controlling the elastic modulus of a substrate using grayscale lithography. The microparticles with inhomogeneous wrinkle patterns were fabricated using a grayscale optofluidic maskless lithography system and subsequent wrinkling process. We generated wrinkle patterns with wavelength gradients in a single microparticle using a gray-level mask image that divided the particle into an array of subcode regions with gray levels in the range of 95 to 255 (distance between gray levels: 8) (Figure 1a). The height of each subcode region in the gradient-wrinkled microparticle was synthesized differently according to the gray level chosen for the region, and 15 gray levels, for example, 239−255, can be captured at a time at a specific focal height. The grayscale color creator from a decimal code (Figure 1b) was used to generate the UV power for each gray level (Figure 1d). The microparticles were synthesized by reflecting UV light through a gray-level mask image with a gradient gray level. After the synthesized microparticles were coated with silica, they were dried to generate surface wrinkles by shrinking, and then exposed to UV light. The heights of the bars are digitalized by the UV power (Figure 1c). The grayscale colors were designed to allow for decoding at a single focal height, allowing for at most 15 gray levels to be used within the same microparticle. The particles were produced using wavelengths for each of the gray levels, as shown in Figure 1d, to create the range of 21 possible gray levels, ranging from 95 to 255, each being eight gray-level units apart. The grayscale colors...
were converted from a decimal code (Figure 1b). For the microparticle synthesis, we prepared a photocurable prepolymer mixture consisting of ethoxylated trimethylolpropane triacrylate and 3-(trimethoxysilyl)propyl acrylate. Using grayscale lithography, the intensity of ultraviolet (UV) light reflected from a digital micromirror device was controlled according to the gray level of the loaded gray-level mask image (Figure 1c,d). The number of particles that can be silica-coated at a time, with a TEOS reaction time of 160 min, was about 5000, and photolithography took about 1 h to manufacture 5000 particles. Consequently, we can simultaneously expose a single microstructure to several UV intensities during photopolymerization, which enables the control of the cross-linking density of the synthesized polymeric microparticles in specific regions. After the synthesis of the polymeric microparticles, patterned with different elastic moduli, they were incubated in an aqueous solution for a silica-coating process with tetraethyl orthosilicate (Figure 1b). A thin silica layer was formed on the surface of the polymeric microparticles, yielding a core–shell-type microstructure. By drying these silica-coated microparticles immersed in the solution, wrinkle patterns were generated on the microparticle surface due to the mismatched strain between the core and shell layers during shrinking (Figure 1c). The silica-coated microparticles consist of a shell formed from silica and a core synthesized from monomers. Since silica is relatively more rigid than the synthesized monomers, there is a mismatched strain between the core and the shell during shrinkage. The shell cannot shrink much due to its lower elasticity relative to the core. By applying this to eq 1, the UV power changes as the gray level changes, and the values of $E_s$ and the wavelength are changed. In this wrinkling process, the characteristic wavelength of the wrinkle pattern was determined by the elastic moduli of the core ($E_s$) and shell ($E_f$) and the shell thickness ($t$), as shown in eq 1. $E_s$ can be controlled by changing the cross-linking density with the UV intensity during photopolymerization, while $t$ can be controlled by changing the silica-coating conditions. Consequently, under the same silica-coating conditions, various wavelengths could be easily generated within each subcode region based on the gray level and corresponding $E_s$, all in a single fabrication process, which was quite desirable in previously developed control techniques using geometric, thickness, or modulus gradients.

2.2. Array of Gradient-Wrinkled Microparticles with Grayscale Lithography. We then quantitatively analyzed the fabricated gradient wrinkles in terms of both the wavelength and minutia (ridge ending or ridge bifurcation point) density to verify code control mechanisms based on the gray level. By fabricating four subcode regions with different gray levels in each microparticle, we covered 20 levels between 103 and 255, with five types of microparticles (Figure 2a–e). We used the same particle synthesis (UV power: 80 mW/cm²; 0.2 s illumination with a 20× objective lens (numerical aperture: 0.45, Olympus)) and silica-coating conditions for this experiment.12 After imaging of these wrinkled microparticles using CLSM, we extracted the wavelength values in each code region using a fast Fourier transform analysis. Overall, the wavelength exhibited an inversely proportional relationship with the gray level (Figure 2f) because $E_s$ decreased with the decrease in the gray level, while the corresponding wavelength increased, as shown in eq 1. The wavelength maintained similar values in the upper two levels (Figure 2a) because the polymer monomers were fully cross-linked with the corresponding gray levels. In contrast, the patterns were incomplete in the lower two levels (Figure 2e) because the UV doses were not sufficient to polymerize the monomers. We also utilized the distribution of minutiae as a code in this chaotic wrinkle pattern and verified that the minutia...
density was proportional to the gray level (Figure 2f). Consequently, we could control the code complexity in each subcode region by changing the gray level because the minutia density determines the complexity.

3. RESULTS AND DISCUSSION

3.1. Decoding and Correlation with 30 Subcodes. Finally, we demonstrate the decoding of the minutia code using three types of encoded microparticles with different gray-level distributions (Figure 3a). As shown in Figure 3b, we extracted minutia information in each subcode region after processing of the CLSM images. The subcodes were then merged into a single code with the same position as the gray-level array shown in the mask image in Figure 3c. Using this processed code information, we performed a cross-correlation analysis to verify the uniqueness of the code. For this purpose, we transformed the merged minutia position information into a binary matrix in each encoded microparticle and calculated the cross-correlation values between matrices. The particle analysis using CLMS-based imaging takes about 7 s per image when processed in the environment of an Intel Core i3-1005G1 processor (1.20 up to 3.40 GHz 4 MB L3 Cache). The correlation values were obtained from a total of 30 microparticle samples, 10 samples in each group. The heat map in Figure 3c shows that intercorrelation values (correlations among different microparticles; mean value: 0.12) were distinguished from intra-correlation values (correlations between the same microparticle). This verifies that the four subcodes had different codes, although they were represented as one encoded microparticle. Thus, we can use a merged minutia code as a unique identification.

3.2. Single Gradient-Wrinkled Microparticle that has Two Security Codes for High Security Level Anti-Counterfeiting. The random wrinkling pattern with homogeneous periodicity cannot achieve both high security level and simple decoding because of the trade-off between the security level and readability. For example, a high security level code with a wavelength of a few microns requires a higher resolution reading system, such as CLSM, with a low scanning speed. This enables the simultaneous generation of different codes in a single encoding process and reading of these codes using a microscope with different resolutions, which provides an efficient encoding and decoding of multiple codes without additional processes.

We fabricated a gradient wrinkling pattern onto a single microparticle, which can be precisely decoded at a specific focal height (Figure 4). Despite the use of the same particle, the decoding results can be changed by refocusing CLSM. As the height of the particles produced through grayscale lithography varies, the optimal focal height for decoding each area varies according to the gray level of the illuminated UV, even after the generation of wrinkles. Thus, unintended minutia codes can appear at any focal length among the detectable focal heights of gradient wrinkling patterns in a particle. The minutia code extracted without knowing the initial information is different from the intended minutia code, which is decoded by extracting all areas of information at a specific focal height (Figure 4b,d). It is challenging to evaluate the type of initial information to attempt replication. Thus, the gradient wrinkling microparticles can be used as a PUF for the high security level anti-counterfeiting strategy.

4. CONCLUSIONS

In summary, we developed a microtaggant with a high security level anti-counterfeiting strategy using gradient wrinkling based on grayscale lithography. We controlled the wavelength of the wrinkled patterns by changing the gray level in the gray-level mask image. For demonstration, we created microparticles having subcodes with different wavelength combinations. We then verified that the minutia code generated by merging minutia distributions extracted from each subcode region could be used as a unique code. Finally, by designing a mixture of wrinkled patterns with a large wavelength difference, we generated different codes in a single microstructure, according to the resolution of the reading microscope. Ultimately, we can provide a high security level anti-counterfeiting strategy enabling a simple, powerful authentication in a single anti-counterfeiting taggant, without additional fabrication processes, by sharing the encoding system. Moreover, using the developed encoding method, other encryption approaches can also be utilized to...

Figure 3. Decoding of minutia codes. (a) Designed gray-level mask images. (b) Extraction of minutia distributions from subcode regions. The left and right images are representative images of groups 2 and 3, respectively. The green and red points represent ridge ending and bifurcation points, respectively. Only the region corresponding to 60% of the entire subcode area was used as a code to minimize the undesired edge effect on the code region (scale bar: 100 μm). (c) Heat map of the cross-correlation values of the merged minutia codes. The correlation values were averaged after separately calculating those for the ridge ending and bifurcation points.
further increase the security level, which will be investigated in a future study.

AUTHOR INFORMATION

Corresponding Authors

Sunghoon Kwon — Department of Electrical and Computer Engineering, Seoul National University, Seoul 08826, Republic of Korea; Bio-MAX Institute, Seoul National University, Seoul 08826, Republic of Korea; orcid.org/0000-0003-3514-1738; Email: skwon@snu.ac.kr

Wook Park — Institute for Wearable Convergence Electronics, Department of Electronic Engineering and Department of Electronics and Information Convergence Engineering, Kyung Hee University, Yongin-si, Gyeonggi-do 17104, Republic of Korea; Email: parkwook@khu.ac.kr

Authors

Cheolheon Park — Institute for Wearable Convergence Electronics, Department of Electronic Engineering, Kyung Hee University, Yongin-si, Gyeonggi-do 17104, Republic of Korea; orcid.org/0000-0002-8254-628X

Hyung Jong Bae — Department of Electrical and Computer Engineering, Seoul National University, Seoul 08826, Republic of Korea

Jinsik Yoon — Institute for Wearable Convergence Electronics, Department of Electronic Engineering, Kyung Hee University, Yongin-si, Gyeonggi-do 17104, Republic of Korea; orcid.org/0000-0001-7756-9738

Seo Woo Song — Bio-MAX Institute, Seoul National University, Seoul 08826, Republic of Korea

Yunjin Jeong — Bio-MAX Institute, Seoul National University, Seoul 08826, Republic of Korea

Kibeom Kim — Institute for Wearable Convergence Electronics, Department of Electronic Engineering, Kyung Hee University, Yongin-si, Gyeonggi-do 17104, Republic of Korea

Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.0c05207

Author Contributions

C.P. and H.J.B. contributed equally to this study. The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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Figure 4. (a) Multiple-wrinkled particle observed by CLSM with a low resolution (256 × 256) (scale bar: 50 μm). (b) Minutiae at two low gray-level regions. (c) Multiple-wrinkled particle observed by CLSM with a high resolution (1024 × 1024). (d) Minutiae at all gray-level regions.
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