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Realization of diverse displays for multiple color patterns on metal surfaces

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ABSTRACT

Enhanced colors can be formed when white light is irradiated on the surface ripples induced by femtosecond laser. In this paper, we have demonstrated the ability to display the diverse colors by simultaneously adjusting the incident white light angle and the ripples orientation. Furthermore, our investigation revealed that multi-patterns constituted by ripples with different orientations could be designed on metal surfaces. The diverse display for the desired ones can be realized by exquisitely varying the incident light angle and rotating sample angle. More interestingly, it is found that, although the same patterns could be displayed under different conditions, the colors might be different. These findings can provide a novel method to carry and identify high quantity of information, which may find potential applications in the fields of information storage, identifying codes and anti-counterfeiting patterns.

1. Introduction

The creation of colorful metals produced by Laser Induced Periodic Surface Structures (LIPSS) has drawn considerable attention in recent years [1–6]. These LIPSSs can be considered as a kind of grating structures, which could play important roles in modifying the optical properties of metal surfaces in a very versatile way [1–6]. The widely accepted theory believed that the formation of LIPSSs was the result of the interference between the incident laser beam and the surface-scattered wave [5–20]. In addition, it is indicated that the ripples (LIPSSs) orientation usually is perpendicular to the polarization of laser pulse [1,5]. The correlation of ripples orientation and laser polarization offers us an opportunity to skillfully utilize the laser polarization as a control parameter to write diverse displayed patterns on metal surfaces [5,6]. Specific color patterns can be generated due to the diffraction of light by producing polarization dependent structures [5,6]. Color effects can be diversely displayed by altering the incidence angle of white light, which is used to irradiate the patterns constituted by ripples with different orientations [6]. Although many works have been reported to explore how to use the laser polarization dependent ripples to obtain the needed optical diffractive effects, there are still few researches on systematical study of the combined influence of incident light angle and the ripples orientation on the color effects. Also there are few reports on the diverse displays for multi-patterns which are fabricated in the adjacent locations on the metal surface and constituted by ripples with different orientations.

In this paper, we not only discussed the combined influence of incident light angle and the ripples orientation on the diversity of structural colors, but also proposed the possibility of realizing the carry and diverse display of multi-patterns. Our investigation may find applications in the fields of information storage, identifying codes and anti-counterfeiting patterns and so on [5,6,13].

2. Experimental

The fs laser-induced surface ripples experiments were conducted by employing a femtosecond laser micro/nano machining system, as shown in the schematic diagram of the experimental set up (Fig. 1(a)). The linearly polarized pulse, delivered from a regenerative amplified Ti: Sapphire femtosecond laser system (Coherent) at the repetition rate of 1 kHz, central wavelength of 800 nm, was focused onto the mirror polished 316 L stainless steel surface. Before the laser irradiation, the polarization direction of the laser pulse was adjusted by a linear Glan–Taylor polarizer. The scanning was realized by using a computer controlled high precision *x*–*y* galvo mirror. The beam diameter focused onto the sample surface was about 20 μm. The laser induced surface structures

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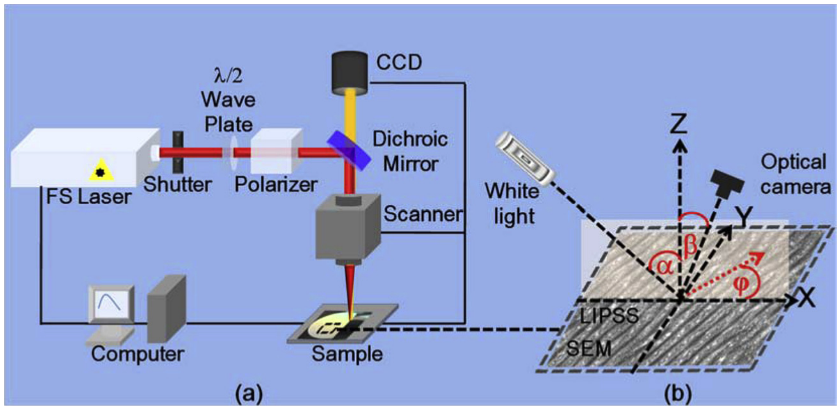

Fig. 1. (a) Experimental setup for stainless steel surface structuring. (b) Schematic illustration of color measuring system.

morphology was observed by a Field Emission Scanning Electron Microscopy (FESEM) (JSM-6700F). Schematic illustrations of measuring the optical properties were shown in Fig. 1(b). A digital optical camera (Cannon) was used to take the pictures of the structural colors. During the process of taking pictures, the surface ripples were irradiated by an unpolarized white light source from a LED lamp. For an objective evaluation of color effect, a spectrometer (Ocean Optics, USB2000) was used to measure the reflectance spectra diffracted by the formed ripples, if necessary. All measurements were carried out in dark to avoid stray lights from the surrounding environment.

3. Results and analysis

Based on experimental investigation, a series of processing parameters were optimized to satisfy the optimum condition for generating ripple structures. In this experiment, the pulse overlap was set to 32%, the line space was fixed at 20 μm, and the laser fluence was chosen as 1.1 J/cm^2. Under the processing parameters, a circle pattern with diameter of 6 mm was fabricated on the stainless steel surface. The SEM images indicate that periodic ripples with period of d = 540 nm, and orientation to be perpendicular to the polarization orientation of laser pulse were formed [5,6,14–17].

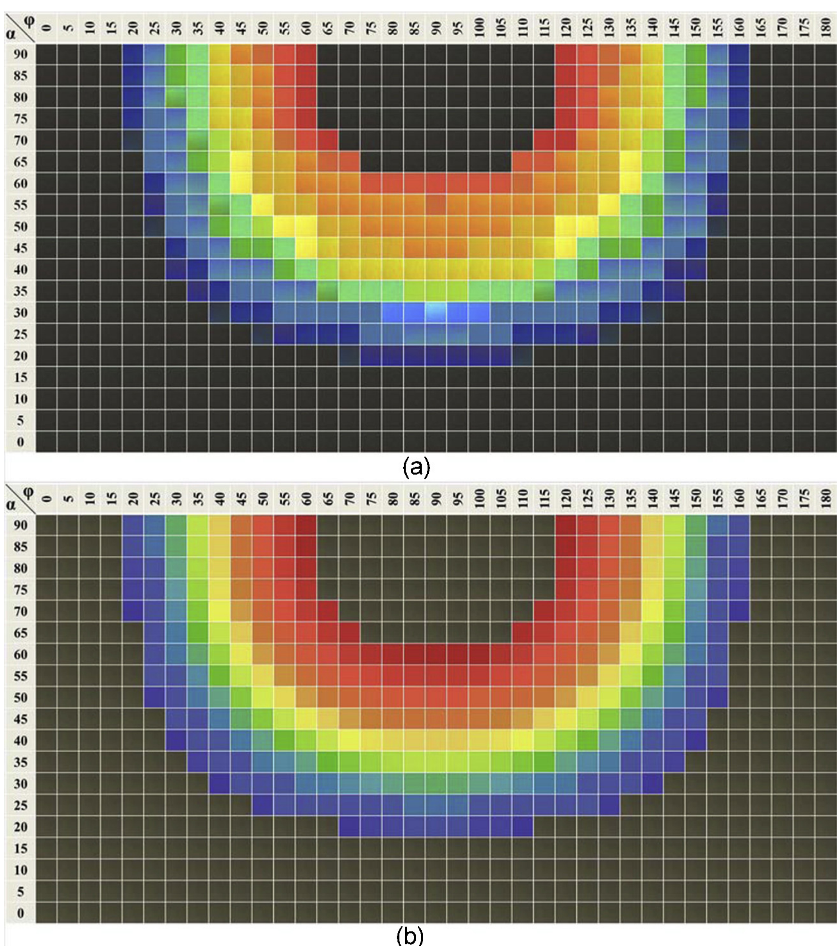

Fig. 2. (a) Photograph of the structural colors observed at different incidence angles and ripples orientations. (b) The simulation results of the structural colors.

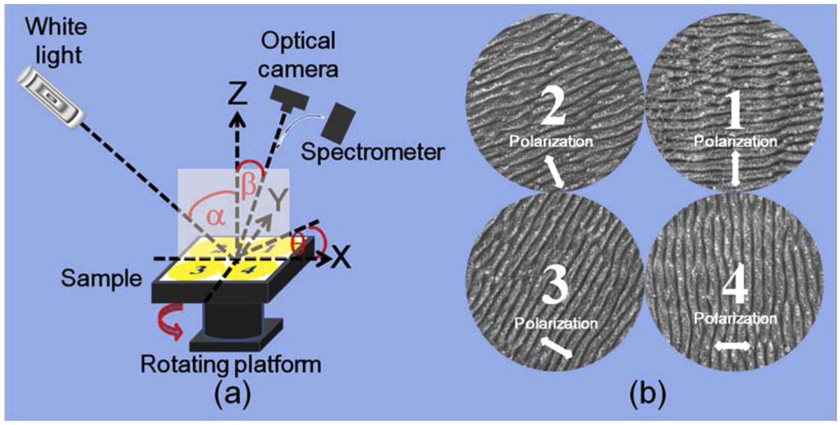

Fig. 3. (a) Schematic illustration of measuring the optical property. (b) SEM images of the ripples with orientations of 0°, 30°, 60°, 90°, respectively.

In order to systematically investigate the influence of the incident angle of white light and the ripples orientation on the formation of structural colors, a color measuring system was configured as presented in Fig. 1(b). Fig. 1(b) illustrates that the incident white light and the optical camera were placed in the *XZ* plane, with α and β orientation to the *Z*-direction on both sides, respectively. The sample constituted by the ripples with φ orientation to the *X*-direction was located in the *XY* plane. The range of α was from 0° to 90°, and that of φ was from 0° to 180°. The optical properties of the ripples can be considered to be close to those of reflective diffraction gratings. When white light is shined on the sample surface, diffraction gratings divide incident light into spectra with different wavelengths. The spectra are reflected differently by virtue of its wavelength-dependent refractive index. In this case, the lights with certain wavelengths are deflected from reaching the optical camera owing to the presence of structures. As a result, the reflected light with particular wavelength captured by the digital camera becomes sources of structural colors [21].

As the clarity of the taken colors depend on the observation angle to some extent, many measurements were performed to find the optimal location of the digital camera. It was found that the shadow of the camera could be seen in the sample surface when the viewing angle β was less than approximately 20° for the specular reflection of the mirror polished stainless steel surface. On the other hand, if the viewing angle was larger than approximately 60°, part of the taken colors was dim, which was unsatisfactory. Hence, observation of the clearest color on the basis of analyzing the optical images was adopted as a criterion for the optimal viewing angle. On this basis, an angle of about 25° was chose, and this was kept constant for all measurements.

Under different incident light angle α and ripples orientation angle φ, the pictures of the diverse colors were taken. The pictures were cropped and arranged in order, as shown in Fig. 2(a). It is revealed that the colors are strongly dependent on the incident light angle α and ripples orientation angle φ. In addition, it is noticed that the colors mainly appear in the central zone, with "V" shaped profile, nearly spanning the whole visible spectrum. On the contrary, in other regions, the colors disappear, or display completely dark.

To explain this phenomenon, the ripples are regarded as rectangular reflection grating, and the theoretical analysis based on the grating diffraction is performed. The diffracted light wavelengths λ that match the different colors can be calculated with the following diffraction equation [13]:

$$m\lambda = d(\sin\ \alpha \cdot \sin\varphi + \sin\beta). \quad (1)$$

Here m is the order of diffraction, which is an integer. λ is the wavelength of white light wavelength, and the range is from approximately 400–700 nm, to cover the visible color spectrum. d indicates the period of the grating (540 nm). The range of the $d(\sin\alpha{\cdot}\sin\varphi + \sin\beta)$ in our case is from 228 nm to 768 nm, hence only the first-order diffraction from the grating can be selected, namely $m = 1$. Then the calculated wavelengths are transformed into the corresponding colors, and the result is presented in Fig. 2(b). Obviously, for each specific incident angle of white light, diverse colors can be viewed at different angles.

In detail, we take the incident angle of 90° for example. In this case, the diffraction equation can be rewritten as

$$\lambda = 540\sin\ \varphi + 228. \quad (2)$$

The diffraction condition is $0.3 \le \sin\varphi \le 0.874$. Therefore, the corresponding range of φ is from 17.46° to 60.93°, and from 119.07° to 162.54°. For other orientation angle ranges, there is no visible wavelength found to fulfill the diffraction condition, hence no structural color can be observed.

A systemical comparison between the experimental results and the simulation ones reveals that some color differences can be found. This can be attributed to the following reasons: (1) even though the processing parameters were carefully chosen, LIPSS itself is not a very uniform periodic structure which has its intrinsic limitation in terms of grating uniformity. This nonuniformity can causes the differences in the light modulation; (2) the irregular nano-particles formed on the top of the LIPSSs can absorb or reflect certain wavelengths of light; (3) the discordance between environmental conditions and the measurement system; (4) the fluctuation and distortion of light source. Although the experimental results are not very perfect compared to the model, this colors reported in this work demonstrate angle sensitive.

From the above discussion, it is evident that the colors can be periodically displayed if ripples orientation angle φ is ranged from $-\infty$ to $+\infty$. Moreover, in this case, all the above-mentioned colors in Fig. 2(a) can appear at different locations if another viewing angle β is chosen.

The following section provides an example to illustrate a possible application of this finding, which is done by introducing the diverse display of multi-patterns. For this purpose, four numbered circle patterns, arranged in two rows and two columns, were fabricated on the stainless steel surface, as shown in Fig. 3. The diameter of each pattern is 6 mm. The surface structures are constituted by ripples with orientations of 0°, 30°, 60°, 90°, respectively, which are designed by controlling the laser polarization. The polarization angles for samples 1–4 are 90°, 60°, 30°, and 0°, respectively, as shown in the SEM images of Fig. 3(b). In the initial position, the ripples orientation of the No. 1 pattern is alignment with the *X*-direction.

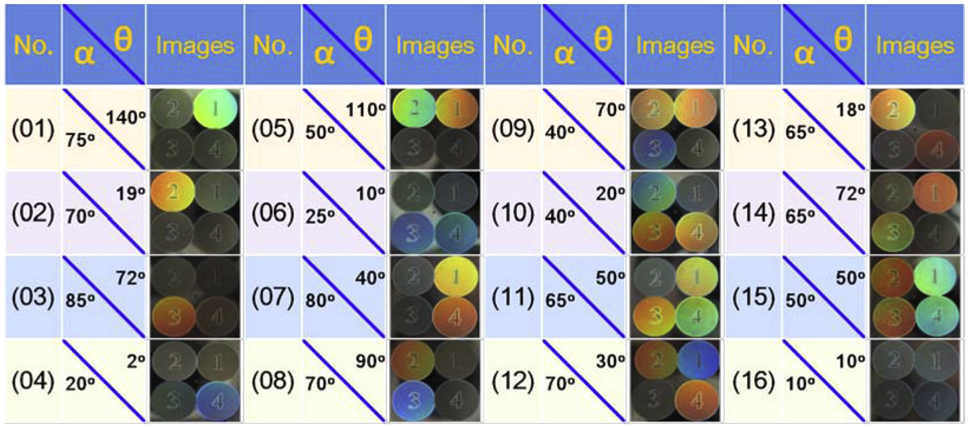

Fig. 4. Multi-patterns displayed with different structural colors.

The change of the rotating sample angle θ can be realized by rotating the platform anticlockwise around the Z-direction. In this way, ripples orientations of all these patterns can be varied. Correspondingly, the diffraction equation for each pattern can be written in sequence as

$$m_1\lambda_1 = d(\sin\ \alpha \cdot \sin\ \theta + \sin\ \beta) \tag{3}$$

$$m_2\lambda_2 = d(\sin\ \alpha \cdot \sin(\theta + 30^\circ) + \sin\ \beta) \tag{4}$$

$$m_3\lambda_3 = d(\sin\ \alpha \cdot \sin(\theta + 60^\circ) + \sin\ \beta) \tag{5}$$

$$m_4\lambda_4 = d(\sin\ \alpha \cdot \sin(\theta + 90^\circ) + \sin\ \beta) \tag{6}$$

It should be noted that enhanced colors can be observed on the pattern when the corresponding diffraction equations meet condition $400 \le m\lambda \le 700$ nm, ($m = 1$). In this way, one or more patterns can be distinguished selectively from all the patterns by the corresponding colors. It is desirable to use a computer to perfectly analyze this selectivity. In this analysis, four cases of "one out of four pattern", six "two out of four patterns", four "three out of four patterns", a "none" and an "all" can be obtained.

For verification, the related experiments are conducted by studying the structural colors of the patterns. The home-made setup is illustrated in Fig. 3(a). By conducting the experiment carefully, it is found that the desired patterns can be observed with enhanced colors by adjusting the incident light angle and the rotating sample angle, as shown in Fig. 4. Meanwhile, the rest cannot be observed for the colors disappeared.

In addition to the cases shown in Fig. 4, the sample can present the same patterns with different enhanced colors at other incident light angle and rotating sample angle. A typical experiment shown in Fig. 5 analyzes the impact of the angle sensitivity on the color effects for the same patterns.

In Fig. 5, the No. 1 pattern exhibits with blue, green, yellow and orange at the given angles. Since the main reason for the colors is the diffracted light received from the observed pattern by camera, the spectral properties for the pattern are investigated with a spectral measurement system (Fig. 3(a)). The reflectance spectrum of the pattern is made as a function of the visible wavelengths, as shown in Fig. 5. The measurements give the spectral information for the measured color. This experiment reveals that the desired patterns can be displayed with different enhanced colors, demonstrating strong angle sensitivity. Assuming that enhanced colors represent different information, multiple types of information stored with the mentioned method can only be correctly identified in certain condition. Such an investigation can provide a promising method to fabricate patterns containing security information with various colors which are not only readable but also difficult to be imitated. Hence, the technique may find applications in meeting the urgent requirements for forgery protection, information storage, and identifying codes and so on.

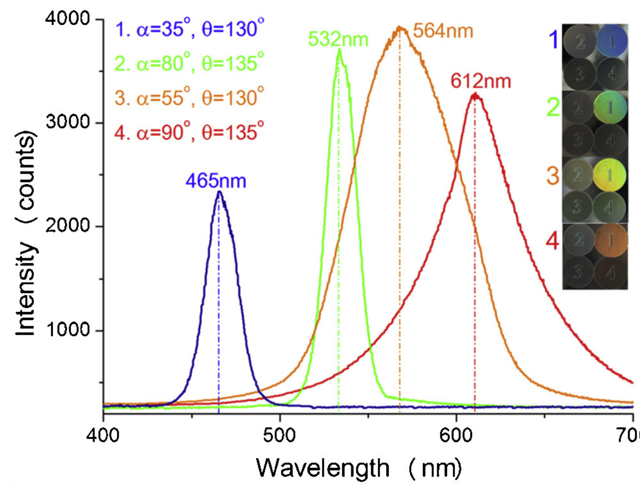

Fig. 5. Images and spectrum of No. 1 pattern measured at different angles.

4. Conclusion

In summary, this paper has reported the study of the combined influence of incident light angle and the ripples orientation on the diversity of colors. Furthermore, this work has researched the diverse display of multi-patterns with the discussed method. The novel marking way may find broader applications in the field of identifying codes, information storage and anti-counterfeiting and so on.

Acknowledgments

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References

[1] A.Y. Vorobyev, C. Guo, Colorizing metals with femtosecond laser pulses, Appl. Phys. Lett. 92 (2008) 041914.
[2] M.S. Ahsan, F. Ahmed, Y.G. Kim, M.S. Lee, M.B.G. Jun, Colorizing stainless steel surface by femtosecond laser induced micro/nano-structures, Appl. Surf. Sci. 257 (2011) 7771–7777.

[3] G. Li, J. Li, L. Yang, X. Li, Y. Hu, J. Chu, W. Huang, Evolution of aluminum surface irradiated by femtosecond laser pulses with different pulse overlaps, Appl. Surf. Sci. 276 (2013) 203–209.
[4] A.A. Ionin, S.I. Kudryashov, S.V. Makarov, L.V. Seleznev, D.V. Sinitsyn, E.V. Golosov, O.A. Golosova, Y.R. Kolobov, A.E. Ligachev, Femtosecond laser color marking of metal and semiconductor surfaces, Appl. Phys. A 107 (2012) 301–305.
[5] B. Dusser, S. Sagan, H. Soder, N. Faure, J.P. Colombier, M. Jourlin, E. Audouard, Controlled nanostructrures formation by ultrafast laser pulses for color marking, Opt. Express 18 (2010) 2913–2924.
[6] J. Yao, C. Zhang, H. Liu, Q. Dai, L. Wu, S. Lan, A.V. Gopal, V.A. Trofimov, T.M. Lysak, Selective appearance of several laser-induced periodic surface structure patterns on a metal surface using structural colors produced by femtosecond laser pulses, Appl. Surf. Sci. 258 (2012) 7625–7632.
[7] J.E. Sipe, J.F. Young, J.S. Preston, H.M. Van Driel, Laser-induced periodic surface structure. I. Theroy, Phys. Rev. B 27 (1983) 1141–1154.
[8] J.F. Young, J.S. Preston, H.M. Van Driel, J.E. Sipe, Laser-induced periodic surface structuresII. Experiments on Ge, Si, Al, and brass, Phys. Rev. B 27 (1983) 1155–1172.
[9] J.F. Young, J.E. Sipe, H.M. van Driel, Laser-induced periodic surface structure. III. Fluence regimes, the role of feedback, and details of the induced topography in germanium, Phys. Rev. B 30 (1984) 2001–2015.
[10] S.E. Clark, D.C. Emmony, Ultraviolet-laser-induced periodic surface structures, Phys. Rev. B 40 (1989) 2031–2041.
[11] L. Qi, K. Nishii, Y. Namba, Regular subwavelength surface structures induced by femtosecond laser pulses on stainless steel, Opt. Lett. 34 (2009) 1846–1848.
[12] G. Miyaji, K. Miyazaki, Origin of periodicity in nanostructuring on thin film surfaces ablated with femtosecond laser pulses, Opt. Express 16 (2008) 16265–16271.
[13] H. Lochbihler, Colored images generated by metallic sub-wavelength gratings, Opt. Express 17 (2009) 12189–12196.
[14] J. Wang, C. Guo, Ultrafast dynamics of femtosecond laser-induced periodic surface pattern formation on metals, Appl. Phys. Lett. 87 (2005) 251914.
[15] A.Y. Vorobyev, C. Guo, Femtosecond laser-induced periodic surface structure formation on tungsten, J. Appl. Phys. 104 (2008) 063523.
[16] A.Y. Vorobyev, V.S. Makin, C. Guo, Periodic ordering of random surface nanostructures induced by femtosecond laser pulses on metals, J. Appl. Phys. 101 (2007) 034903.
[17] J. Wang, C. Guo, Formation of extraordinarily uniform periodic structures on metals induced by femtosecond laser pulses, J. Appl. Phys. 100 (2006) 023511.
[18] T. Tomita, Y. Fukumori, K. Kinoshita, S. Matsuo, S. Hashimoto, Observation of laser-induced surface waves on flat silicon surface, Appl. Phys. Lett. 92 (2008) 013104.
[19] B. Tan, K. Venkatakrishnan, A femtosecond laser-induced periodical surface structure on crystalline silicon, J. Micromech. Microeng. 16 (2006) 1080–1085.
[20] J. Bonse, A. Rosenfeld, J. Krger, On the role of surface plasmon polaritons in the formation of laser-induced periodic surface structures upon irradiation of silicon by femtosecond laser pulses, J. Appl. Phys. 106 (2009) 104910.
[21] S. Kinoshita, S. Yoshioka, J. Miyazaki, Physics of structural colors, Rep. Prog. Phys. 71 (2008) 076401.