Novel optically variable thin film based on a single silicon coating material

W. LI, L. CHEN, L. X. XIAO, N. CHEN, X. Z. WANG, Y. K. BU*
Department of Electronic Engineering, School of Information Science and Engineering, Xiamen University, Xiamen, 361005, China

Optically variable thin film plays an essential role in optical anti-counterfeiting field. In this paper, we proposed a new method based on single silicon material to obtain optically variable thin film, which is composed only of silicon and silicon compounds (silica and silicon nitride) for the first time. A five-layer optically variable stack /Si'/SiO_2/Si/SiO_2/Si'/ is designed and fabricated, the experimental results was in accordance with the design. Under D65 illuminant, the color of reflected light is kelly with 0° and blue with 60° observation angle, which proved optical thin film based on single silicon material can realize good color-shifting effect.

(Received November 28, 2016; accepted August 9, 2017)

Keywords: Metal-dielectric, Single-material, Optically variable thin film

1. Introduction

The rapid development of optical anti-counterfeiting technology brought new high-tech means to the field of security. The idea of using optically variable device (OVD) to prevent counterfeiting of valuable documents was first suggested by Dobrowolski 20 years ago [1]. In 1989, Dobrowolski, worked in the National Research Council of Canada, applied thirteen-layer dielectric film on Canadian currency [2]. Conventionally, the base design principle of optically variable thin films is using two or more materials. All-dielectric optically variable thin film generally composed of titanium oxide and silicon dioxide or tantalum oxide and silicon dioxide [3-4], and metal-dielectric optically variable thin film usually need three different materials including of metal chromium as absorption layer, silicon dioxide as dielectric layer, metal silver or aluminum as high reflector, respectively [5-6]. In 2008, a pair of metameric all-dielectric filters was firstly fabricated by dual ion beams sputtering, which respectively consists of nineteen and fifteen layers, and suggests poor metameric effect because of the deposition errors [7]. Moreover, a novel OVD integrates with electrochromic material was proposed for the first time in 2011 by previous research groups [8]. However, the diversity of the film materials in the traditional OVD easily leads to the increasing of manufacture errors. In this paper we are dedicated to study a method to realize optically variable thin film based on one coating material (silicon). Compared with the conventional design method of optically variable film, this method abandons the chromium, nickel and other heavy metal materials, and adopts silicon material as alternative material. This method is less pollution to the environment and the cost is lower. More importantly, this method uses only silicon coating material and breaks the traditional design principle that takes two or more coating materials in the fabrication process. In addition, only one coating materials is used to obtain some materials whose refractive index are different by controlling the working gas pressure. Guided by the explicit film-forming mechanism, the deposition process is easily controlled and the coating has high repeatability. In this study, we adopted the plasma sputtering to fabricate the thin film stack. Under D65 illuminant, the reflected color with 0° observation angle is kelly while the color becomes blue with 60° observation angle, which shows good color shift effect.

2. Design and fabrication

In deposition process, silicon is the only coating material and the other materials with different refractive index are synthesized by controlling the working gas (nitrogen or oxygen or others). In this research, the basic materials to design optically variable thin film are silicon and silicon dioxide. In view of the physical and chemical properties, silicon has become a kind of semiconductor material applied broadly. Due to the advantages of less use of material, low cost and mass production on substrate, silicon films have been regarded as the core materials of new solar cell. In addition, silicon films also play an important role in the production of transistor, photoelectric detector, photoelectric coupler. Silicon dioxide is a kind of low refractive material (n=1.45~1.47) that has good performance. Silicon dioxide is the lowest refractive material which is required for multilayer thin film. Silicon dioxide has good chemical stability and excellent mechanical properties. Due to the low refractive index and good light penetration, silicon is used in the surface of optical devices as protective layer, passivation layer and anti-reflection coating.

Normally for the OVD applied in the

anti-counterfeiting field, the metal–dielectric film stack was chosen over the all dielectric stack because equivalent performance requires fewer layers and is therefore easier to manufacture in PVD and also with lower cost [9]. The structure of the OVD is composed of an internal reflective metal, a dielectric spacer layer of low-index material, and an absorber layer. A symmetrical structure that exhibits the same color on both sides is necessary for the print requirement.

The based color stack is made up with three layers, silicon reflect layer, dielectric space layer and absorbing layer. Its structure is Air/(M'L)$_x$/M/Glass, the role that number of cycles x plays periodic repetition. Fig. 1 shows the reflection spectra of this structure with 0° observation angle. Increasing x can achieve the purpose of compression reflection bandwidth and the saturation is improved as well as the color brightness of reflected light. Regarding the structure Air/(Si'SiO_2)$_x$/Si/Glass as an example, Fig. 2 shows the reflection spectra of this structure with 0° observation angle and the color variation path from 0° to 90°. As show in the figure, when x is 4, 5 and 6, these color variation of reflected light is almost same. In practical application, the higher x, means the more film layers, so the normal x is 1 and 2.

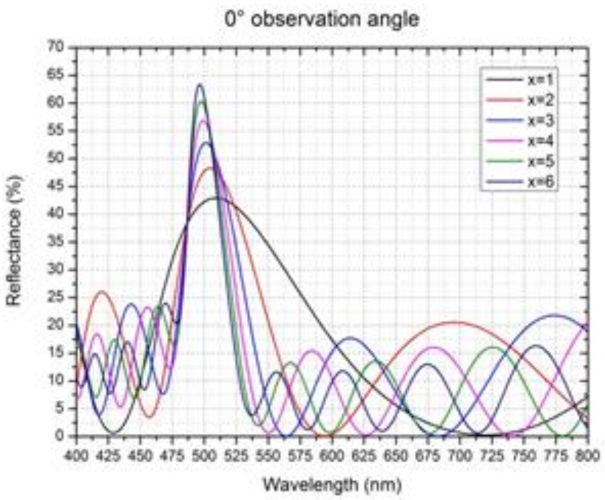

Fig. 1. The reflection spectra (with 0° observation angle) of films based on Si and SiO_2 with different x

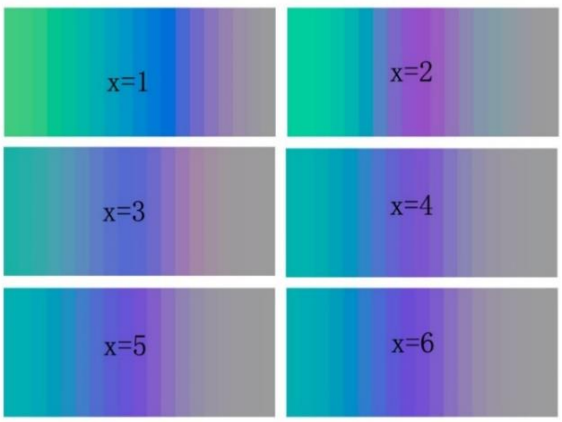

Fig. 2. The color variation path (0° to 90°) of films based on Si and SiO_2 with different x

In general, the structures of optically variable thin film designed only with silicon and silicon dioxide are simpler than other structures. What's more, because of the easy access to the raw material, the working gas is easy to control in the fabrication process, this film structure which is based on a single silicon coating material will be the most common structure and the simplest way for fabrication. Therefore, a symmetric five-layer structure, as a specific instance, will show optically variable thin film based on a single silicon coating material.

In the design of optically variable thin film, to achieve a good high color saturation, the ultra-thin silicon film as absorbing layer was chosen, the silicon layer that is less than 10 nm. However, for the silicon film as reflecting layer, because of the demand of high reflection, based on the single-layer reflectance analysis, the internal reflective silicon thickness is chosen from 40-100nm. The Fig. 3 shows the reflectance change with the different silicon thickness. The reflectance of single-layer silicon first increases with the increase of silicon layer thickness, then as the thickness increase to a certain level, the reflectance begins to drop down instead due to the effect of absorption.

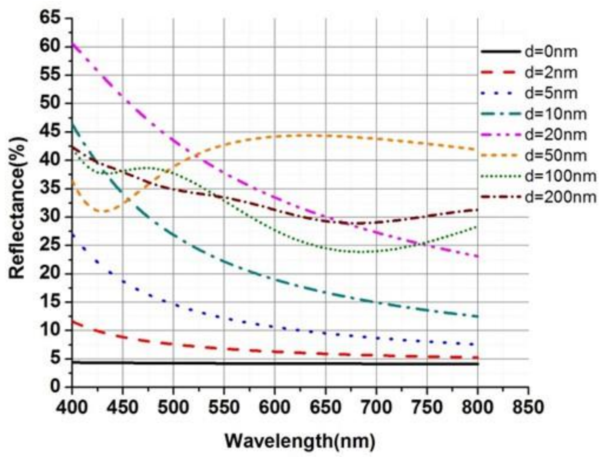

Fig. 3. The reflectance of different silicon thickness

In this specific example, we design a five-layer thin-film stack which is composed of symmetrical silicon and silicon dioxide, the structure of film system is air/M'LMLM'/glass. In this structure, the M' represents the silicon layer which is designed as absorption layer and the physical thickness is 2.65 nm. The M represents the silicon layer which is designed as reflector and the physical thickness is 50 nm. The dielectric spacer layer L adopts silicon dioxide material and the physical thickness of L is 372.4 nm. The reference wavelength was set at 510 nm. The incident medium for light is air and its refractive index is Na=1. The substrate is K9 glass and the refractive index is Ng=1.52. Fig. 4 shows the reflection spectra of theory design when the observation angles are 0° and 60°, and red solid line and blue dotted line represent the two curves respectively. Based on the reflection spectra, it can be seen the yellow green color will be display in the observation angle 0° because of the reflection main peak wavelength is about 520 nm, and when the observation angle is changed into 60°, the reflection spectra of interference stack shifts towards shorter wavelengths with the angle of incidence increased. The reflection main peak wavelength is about 430 nm. Therefore the blue color is displayed. Fig. 5 shows the variation of color with 5° intervals from 0° to 90°. The change of color is shown in this figure, and there also are obvious changes for the color from 0° to 60°. From Fig. 5, it is obvious that the color of reflected light is yellow green with 0° observation angle, and then change blue with 60° observation angle.

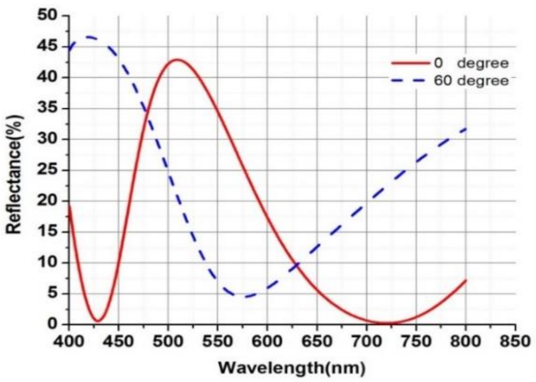

Fig. 4. The reflectance curves of theoretical film system with 0° and 60° observation angle

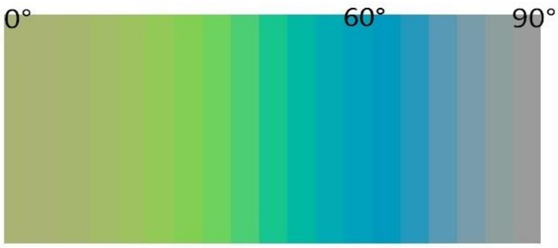

Fig. 5. The variation of color with 5°intervals from 0° to 90°

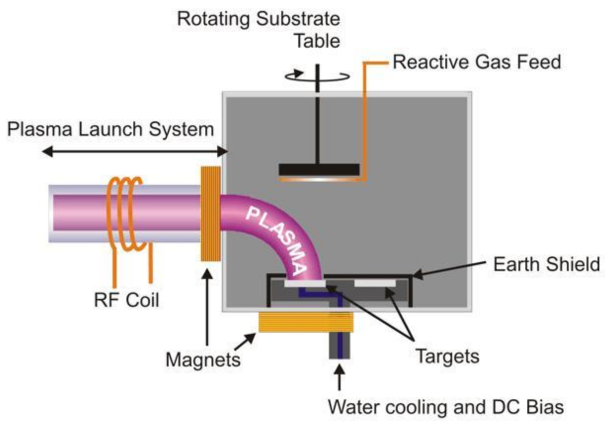

Fig. 6. The basic internal structure of deposition system

Ion beam deflection deposition technology [10] through time control thickness in Fig. 6 is adopted in the experiments and deposition parameters are presented in Table 1. The experiment sample put Schott glass (263T) as substrate whose size is 80 mm * 80 mm and thickness is 0.3 mm. Substrate is successively ultrasonically cleaned with acetone and ethanol to remove oil and wax on the surface, and then wiping the substrate with the solution which mixes alcohol and ether with ratio of 1:1. Finally, the substrate is put into vacuum chamber after drying with hot air. According to the design of film as an example, we sputtered a three-layer stack that is comprised of asymmetry silicon and silicon dioxide on the Schott glass.

Table 1. Deposition process parameters

conditions	substrate	Si	SiO_2
RF coil(A)	150	140	145
Deflection coil(A)	145	135	140
Target bias(V)	0	-600	-600
RF power(W)	1600	1600	1600
Ar flux(sccm)	75	75	75
O2 flux(sccm)	0	0	5
Vacuum pressure(torr)	1.0×10^{-5}	$1.\times10^{-5}$	8.0×10^{-6}
Deposition rate(A/s)		0.44	3.2

3. Results and discussion

Figs. 7 and 8 are respectively the real picture of film samples when under D65 illuminant irradiation with observation angles of 0° and 60°. As shown in the figures, the sample of optically variable thin film has strong metallic luster. The reflected color of film is kelly when observation angle is 0° and the color change into blue with 60° observation angle. So, the color change direction of the actual sample is basically identical with the designed thin film, and the color change is so obvious that it can be considered that the sample has good color-shifting effect.

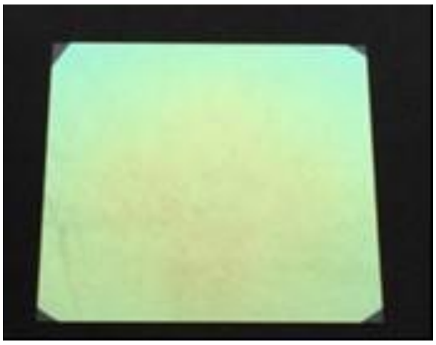

Fig. 7. The real picture of film sample with 0° observation angle

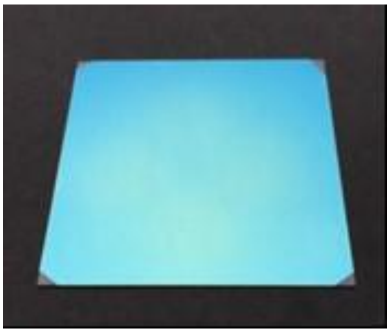

Fig. 8. The real picture of film sample with 60° observation angle

As shows in Fig. 9, the reflectance curve of actual sample in visible-band was measured and compared with theoretical design spectra. From the figure, there are some deviations in reflectance spectra between actual sample and theoretical design, to analyze the reasons for deviation, there are some possibilities such as thickness deposition system error by time-power control, especially the accuracy of the thickness of ultra-thin silicon layer. In addition, the real optical constant of silicon for the ultra-thin layer also leads to the deviations.

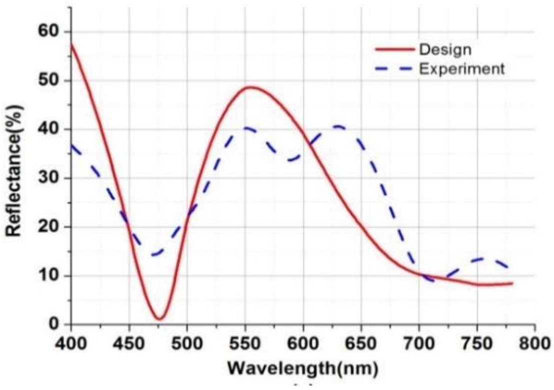

Fig. 9. The comparison of reflectance spectra between experiment and theory design

In order to obtain quantitative analysis of the color difference, we measured the chromaticity coordinates of actual sample with color measurement instrument CS-600 and listed the color difference in Table 2. From Table 2, we can see that the index between theory design and actual sample is ΔE=7.255, according to CIE1976-LAB color difference formula. Although the color difference index is consistent with the difference of reflectance spectra, the real color display is almost the same as the theoretical design. More importantly, this color difference does not affect the result of color-shifting of the thin film.

Table 2. Chromaticity coordinates and color difference

	x	y	L^*	a^*	b^*
Theoretical calculation	0.3566	0.4165	68.6466	-12.4742	30.0616
Actual measurement	0.3498	0.4063	75.71	-12.82	28.44

4. Conclusions

For the first time it is reported here on the optically variable thin film based on a single silicon coating material. It breaks the design principle that traditional optical thin films need two or more coating materials. Using single silicon as coating material has some advantages such as simple thin film stack, easily -controlled deposition process and so on. In addition, silicon is a material of wide source and it also poses no harm to the environment. Three-layer stack was described briefly and a specific instance was designed and fabricated in this research. The specific instance is Air/Si'/SiO_2/Si/Glass, a physical thicknesses of silicon are 2.56 nm and 50 nm, respectively. Under D65 illuminant, when the observation angle changes from 0° to 60°, the color observed of film sample changes from kelly to blue. The change of actual sample is consistent with theory design. So these results demonstrate that the design and fabrication of optically variable thin film based on single silicon coating material are successful and this research is of great significance.

References

[1] J. A. Dobrowolski, K. M. Baird, P. D. Carman, A. Waldorf, Journal of Modern Optics **20**, 925 (1973).
[2] J. A. Dobrowolski, F. C. Ho, A. Waldorf, Appl. Opt. **28**, 2702 (1989).
[3] B. Baloukas, L. Martinu, Appl. Opt. **47**, 1585 (2008).
[4] Y. K. Bu, R. Guo, Y. K. Li, Z. Y. Meng, N. Chen, Chin. Opt. Lett. **12**, S10604 (2014).
[5] R. Guo, N. Chen, L. J. Chen, X. Z. Wang, Z. P. Cai, K. Y. Li, Y. K. Bu, Optoelectron. Lett. **10**, 411 (2014).
[6] L. X. Xiao, N. Chen, Z. H. Deng, X. Z. Wang, R. Guo, Y. K. Bu, Opt. Commun. **359**, 250 (2016).
[7] B. Baloukas, L. Martinu, Appl. Opt. **47**(10), 1585 (2008).
[8] B. Baloukas, J. M. Lamarre, L. Martinu, Appl. Opt. **50**, C41-C49 (2011).
[9] R. W. Phillips, A. F. Bleikolm, Appl. Opt. **35**(28), 5529 (1996).
[10] Z. Liu, Y. K. Bu, Optoelectron. Lett. **9**(2), 116 (2013).

*Corresponding author: buyikun139@163.com