Combinatorial synthesis of BaClF-ReF₃ (Re=La, Pr, Er, Sm) layers with graded-index as antireflection coatings in the thermal infrared

Bin Li^{1*}, Ping Xie¹, Weitao Su², Xiaofeng Ma¹, Haihan Luo¹, Dingquan Liu^{1,3}

¹*Shanghai Institute of Technical Physics, Chinese Academy of Sciences,
Shanghai, 200083, China*

²*Institute of Materials Physics, Hangzhou Dianzi University, Hangzhou,
Zhejiang Province, 310018, China*

³*School of Physical Science and Technology, Shanghai Tech University,
Shanghai 200031, China*

*To whom all correspondence should be addressed; e-mail: binli@mail.sitp.ac.cn

Abstract: It is a well-known fact that optical components used in the thermal infrared would be disabled without antireflection coatings due to the serious Fresnel reflections on their surfaces. The antireflection coating consisting of a single inhomogeneous layer with graded-index is an important solution. In our investigation, the combinatorial materials libraries were synthesized to explore the composition dependence of the durability and antireflection characterization of graded-index layers deposited from four rare-earth fluorides LaF₃, PrF₃, ErF₃ and SmF₃, admixed with a different amount of BaClF. It was demonstrated that the layers are robust enough to withstand normal handling and environmental conditions, furthermore, the best antireflection approach for the Ge surfaces can be achieved for the BaClF-LaF₃ layer with a BaClF concentration $x=0.51$, through the high-throughput characterization of the robustness and the spectral transmittance of the elements in the libraries. Because the optimized characteristics of a Gaussian index profile followed by a quintic-profile can be created in the layers, an average refractive index around 1.2 can be achieved, which is lower than those of infrared low-index coating materials used commonly.

Keywords: Antireflection coating; combinatorial synthesis; rare-earth fluoride; durability; graded refractive index.

1. Introduction

The lens and windows in the optical system operating in the spectral range of thermal infrared are commonly made of high-refractive-index materials, such as germanium. As a consequence, the resulting Fresnel reflections at the medium to their surface result into a lower net transmittance. For example, germanium with an index of around 4.0 will produce a reflection loss of around 36% per surface. In addition, ghosts or veiling glare appears because radiances reflected at various surfaces eventually reach the focal plane. Therefore, broadband antireflection coatings are indispensable for optical components in the thermal infrared. Depending on their structure, antireflection coatings can be classified as two types, namely, composed of homogeneous layers and inhomogeneous layers.

For the antireflection coatings with homogeneous layers, or step-index coatings, it is essential to use a low-index layer, which should be lower absorptive, mechanically and chemically stable, at the outermost to obtain the highest and broadest transmission zone [1]. Although thorium fluoride (ThF_4) is an ideal mechanically stable infrared coating material with a low refractive index of 1.35 at 10 μm , due to the detrimental property linked to its radioactivity, special handling and strict disposal are required whenever it is used [2]. Some non-radioactive substitutions for ThF_4 are the rare-earth fluorides, such as cerous fluoride (CeF_3), lanthanum fluoride (LaF_3), ytterbium fluoride (YbF_3) and yttrium fluoride (YF_3) and others. However, the layers of fluoride containing rare-earth cations are known to appear with a high intrinsic stress, generally tensile, and a low packing density [3, 4]. For example, reported stress values for CeF_3 thin films with a thickness of 100 nm deposited at two temperatures are 1.5×10^8 Pa at 230 °C and 2.3×10^8 Pa at 20 °C [5]. A high intrinsic stress can induce a variety of undesirable consequences, including distortion of substrate, cracks and delamination in films, peeling-off from the substrate, even the failure of the durability and optical performance [3, 6].

Since Rayleigh, in 1880, mathematically demonstrated that graded-refractive-index layers have broadband antireflection characteristics, another type of antireflection coatings with a single inhomogeneous layer are shown advantageous over step-index coatings with respect to omnidirectionality and broad-band behavior [7, 8]. In recent years, investigations into the approaches for a graded-index layer are focused intensively

on the special nanostructures on the substrate surfaces [9-13]. Such a nanostructured surface leads to a density gradient and a refractive index gradient to suppress reflectance exponentially with the increase of the index-graded thickness. However, these nanostructures are generally fabricated by complicated processes, such as electron-beam lithography, etching, glancing angle or oblique-angle electron-beam deposition and nano-imprint techniques. It is highly desirable to realize the graded-index in a mechanically reliable, single inhomogeneous layer by controlling the volumetric composition of two different optical materials along its thickness direction.

Although it has been a long history to deposit a layer with a tailored refractive index and to modify their crystallographic structure, density, and stress by evaporating simultaneously two substances with different indices from two sources, unfortunately, there exists no general solution for this problem, and one has to use more or less trial-and-error methods for the design process. To the best of our knowledge, there has not been a thorough and systematic investigation into the properties of a single inhomogeneous layer consisting of the volumetric composition of two different, in particular, fluorides (chlorides). The result is that, typically, only a relatively small number of materials systems can be examined, and, often characterization integrated into the materials development loop cannot be carried out directly.

Combinatorial methods, which have been applied to the discovery and optimization of a number of functional materials [14-18], might be expected to accelerate the searching for an inhomogeneous layer consisting of two infrared low-index materials, which possess an extraordinarily lower reflection due to an appropriate refractive index gradient; in addition, which is robust enough to withstand the rigors from their applications and environments. This approach requires synthesizing materials libraries of layers with high accurate stoichiometry and easiness of measuring optical properties, such as spectral transmittance, etc. In this paper, the combinatorial synthesis of infrared low-index layers with continuously varying indices was described for the first time. Combinatorial materials libraries, which were designed to investigate directly the composition dependence of durability and antireflection characteristics of single graded-index layers, were created by sequentially depositing thin-film precursors at different sites on a substrate using a series of precisely positioned shadow masks. Four rare-earth fluorides, LaF_3 , praseodymium fluoride (PrF_3), erbium fluoride (ErF_3), and samarium

fluoride (SmF_3) admixed with different amounts of barium chloridefluoride (BaClF) were discussed as a test case.

2. Experimental

2.1 Synthesis of combinatorial materials libraries

A double-polished single-crystal Ge (111) wafer with a diameter of 25 mm and a thickness of 2.5 mm, was used as the substrate, because germanium is a common material used for the optical components in the thermal infrared. Deposition was carried out using thermal evaporation in the chamber of a KD500 box coater in a background vacuum 2.0×10^{-3} Pa. The substrate was heated by radiation heaters, and its temperature was sensed by a platinum resistance transducer pressed directly against its upper surface. The signals from the transducer were transferred out through a set of electric-brush and slip-ring to operate a temperature controller and a constant temperature of 200°C is maintained.

(a)

(b)

(c)

(d)

Fig. 1 The masking scheme (a) and the masks used practically in the deposition of precursors (b), the procedure to deposit the layers of precursors (c), the designed stoichiometry map for the quadrant of BaClF-ErF_3 (d)

A set of quaternary combinatorial masks was used to generate the material libraries in 12 steps. The masking scheme is presented in Fig. 1 (a), and the picture of masks used practically is also shown in Fig. 1 (b). Firstly, a layer of precursor LaF_3 with a thickness of 80 nm was deposited to generate an array of 16 elements, of which each element has a size of 1 mm×1 mm and spaced 1 mm apart, on the substrate using A_1 mask. This was followed by deposition of layers of precursors, PrF_3 , ErF_3 , and SmF_3 , with a thickness of 80 nm using A_2 , A_3 and A_4 masks respectively. Then layers of precursor BaClF with different thickness were deposited in the following sequence: 20 nm, 40 nm, 60 nm using B_2 , B_3 and B_4 masks respectively; 5 nm, 10 nm and 15 nm using C_2 , C_3 and C_4 masks respectively, where A , B and C are the quaternary masks used in the deposition steps, the subscript $i=1, 2, 3$ and 4 indicates an $(i-1) \times 90^\circ$ clockwise rotation of the mask relative to the orientation of the mask. The procedure to deposit the layers of precursors was illustrated in details in Fig. 1 (c). As a consequence, an 8×8 array was generated on the substrate; of which each element consists of a layer of rare-earth fluorides with a thickness of 80 nm and a layer of BaClF with different thickness. The stoichiometry map is designed and demonstrated in Fig. 1 (d) for the quadrant of BaClF-ErF_3 and corresponding percentage for BaClF in the sum of BaClF and ErF_3 is presented in Table 1. The same map applies to the other quadrants containing the different host rare-earth fluoride materials.

Element number ^a	Thickness of BaClF layer (nm)	Percentage
5-5	0	0
5-6	5	0.03
6-6	10	0.06
6-5	15	0.09
5-7	20	0.12
5-8	25	0.14
6-8	30	0.17
6-7	35	0.19
7-7	40	0.21
7-8	45	0.23
8-8	50	0.25
8-7	55	0.27
7-5	60	0.29

7-6	65	0.30
8-6	70	0.32
8-5	75	0.33

^a first number designates line and second number designates column in the array.

Table 1. The concentration of BaClF was designed for the elements in the BaClF-ErF₃ system

(a)

(b)

Fig. 2. The combinatorial materials libraries (a), and subjected to the adhesion test (b)

After the deposition of double layer of fluorides (chlorides) as precursors, their interdiffusion at elevated temperatures is needed. However, it is necessary for the precursors to interdiffuse at a relatively low temperature to approach thermodynamically

stable phases close in stoichiometry in order to prevent from Ge element diffusing into the layers of fluorides (chlorides), because Ge has a lower melt temperature (937.4 °C). An extended period (160 hours) of low-temperature (400°C) annealing was carried out in a quartz ampoule evacuated to 5×10^{-5} Pa for proper interdiffusion, which was followed by a series of high temperature annealing steps, at 500 °C for 24 h, 550 °C for 12 h, 600 °C for 8 h, sequentially in vacuum. The combinatorial materials libraries are demonstrated in Fig. 2 (a).

2.2 Characterization of combinatorial materials libraries

Since it is possible that the cracks appear in the surfaces of the layers (elements) in combinatorial materials libraries either spontaneously or application of an environmental condition due to high intrinsic stress existing in fluoride layers, the layer surfaces were inspected using an Olympus DSX500 opto-digital microscope with a new observation method called MIX, which combines both of bright-field and dark-field observation to enhance hard-to-see microscopic cracks. When removal of the libraries from the quartz ampoule, inspections were done immediately at a magnification of 555×. After 1 day of exposure to the normal environment, inspections were taken again.

The libraries were then subjected to the durability tests, including water solubility, adhesion and moderate abrasion, in accordance with the military specification MIL-C-4847A in the United States. After these tests, inspections were done and photographs were taken from layer surface in order to exam whether or not the deterioration occurs, such as delaminations, peeling-off, cracks or scratches. In Fig. 2 (b), the combinatorial materials libraries were illustrated being subjected to the adhesion test.

In order to explore the crystallographic structure and trace phases existing in the layers, micro-area X-ray diffraction (μ -XRD) was carried out using a Rigaku D/Max-Rapid II X-ray diffractometer, which is equipped with a large curved imaging plate detector and a rotating anode X-ray generator designed specifically for micro-area and trace phase analyses. Characterization was performed with Cu K_{α} radiation operating at 40 kV and 250 mA. Diffraction data recorded on the 2D image plate were integrated between 20 and 80° with a step of 0.045°. Exposure time for each element was more than 30 minutes in order to realize the detection of trace phase. The XRD pattern of an uncoated area of the Ge substrate was demonstrated in Fig. 3.

Fig. 3 The XRD pattern of an uncoated area on the Ge substrate

The stoichiometry of all elements was determined using the energy dispersive X-ray analysis (EDX) from a Horiba EX-220 energy dispersive X-ray microanalyzer (model 6853-H), which is attached to a Hitachi S-4300 cold field emission scanning electron microscope (FE-SEM) without coating the surfaces. Prior to the analysis, a calibration was carried out.

The in-depth chemical composition analyses were investigated throughout the complete inhomogeneous layers for selected element in the libraries by secondary ions mass spectroscopy (SIMS) using a Cameca IMS-7f (Gennevilliers, France) equipment. Typical analysis conditions were 5 keV Cs^+ at 35 nA into a $150 \times 150 \mu\text{m}^2$ raster with detected area of 30 μm diameter at the center of the raster. Sensibility factors were determined with reference sample whose chemical composition was determined by energy dispersive spectroscopy.

In order to evaluate directly antireflection characteristics of every layers on germanium surface, the transmission spectra of all elements were collected in the spectral range of $2.5 \sim 15 \mu\text{m}$ at 4 cm^{-1} spectral resolution under a Bruker's Hyperion 2000 microscope with a $50 \mu\text{m}^2$ aperture using a Bruker Vertex-70 Fourier-transform infrared spectrometer, which is equipped with a standard ceramic glow bar as light source and a liquid-nitrogen-cooled mercury cadmium telluride detector. The Hyperion microscope was set to transmission mode to record the transmission spectra through each layer. The incident angle of the beam on the surfaces is 23.58° to the normal, as set by the Schwarzschild objective.

The characterization of optical constants of inhomogeneous layers with continuously varying index was carried out for some selected elements in the libraries by fitting the transmittance measurement data. The average indices of refraction n and extinction coefficient k was derived by using Lorentz oscillator as a dispersion model, as described in details in our previous studies [19, 20]. The profile of refractive index was also investigated using OptiChar (version 8.85), which is one of the modules of OptiLayer thin film software (OptiLayer GmbH, Russia) [21]. In the analysis of the spectral transmittance, a five order Schroeder's approximation was used to determine the degree of inhomogeneity of layers.

3. Results and discussions

Fig. 4 The concentration percentage of BaClF in the BaClF-LaF₃ system

From the measurement of stoichiometry for all elements in the libraries using the EDX, it was possible to calculate the percentage of element concentration of Ba, designated as $x=[\text{Ba}]/[\text{Ba}]+[\text{Re}]$ (Re=La, Pr, Er, Sm) across the entire inhomogeneous layers. A comparison of x detected for all elements with one calculated from the thickness of precursor layers of BaClF, for example, in the system of BaClF-LaF₃ was illustrated in Fig. 4. A green line as a guideline for the eye is also included within the figure to represent the calculated amounts. It can be shown that the detected amounts of BaClF in the layers increases linearly with the increasing of thickness of precursor layers of BaClF. It is assumed that the difference to the element concentration of Ba can be

ascribed to the difference of vapor pressures of BaClF and rare-earth fluorides. A similar tendency exists in the layers in other quadrants containing the host rare-earth fluorides, PrF_3 , ErF_3 and SmF_3 . Therefore, it can be easier to control the stoichiometry in layers in libraries by depositing different thickness of precursor layers of BaClF, which established the basic of investigating the composition dependence of robustness and spectral transmittance of the graded-index layers as antireflection coatings in the thermal infrared.

Fig. 5 A panoramic photograph of the surface of the synthesized libraries after the durability tests were performed

A panoramic photograph of the layer surfaces in libraries after the durability tests was presented in Fig. 5, which was taken employing image stitching and Extended-Focal-

Imaging (EFI) capabilities. The layer surfaces in the libraries show no initial or final indications of delaminations, peeling-off and cracks, which can be caused by the high intrinsic stress in fluoride layers. It can be concluded that the BaClF-ReF₃ (Re=La, Pr, Er, Sm) layers are robust enough to withstand durably normal handling and environmental conditions.

A discussion about the investigations into antireflection characteristics of the layers on germanium substrates, their average indices of refraction n and extinction coefficients k , and normalized refractive index profile along thickness direction, as well as, their crystallographic structure and trace phase constitutions, was presented in more details as following:

3.1 BaClF-PrF₃

The elements included in the first quadrant in the libraries belong to this system.

Fig. 6. SIMS depth profiles of elements of Ba and Pr in the element 4-5 in libraries

In Fig. 6, the secondary ion mass spectrometry (SIMS) depth profiles was illustrated of elements of Ba and Pr in the element 4-5 in the combinatorial materials libraries. It can be demonstrated that the interdiffusion between PrF₃ and BaClF combines two layers of precursors together to an inhomogeneous layer, through which BaClF and PrF₃ can penetrate entirely each other. Due to the difference of vapor pressures between BaClF and rare-earth fluorides, the ion intensity of Ba element is much greater than that of Pr element. It is in a good agreement with the measurement of stoichiometry using the EDX, since a percentage of element concentration of Ba, $x=0.72$, can be detected across the

entire layers.

The transmission spectra of five elements with representative concentrations of BaClF were shown in Fig. 7 (a). A spectrum measured on the uncoated area of Ge substrate is also presented in order to make a comparison. It is demonstrated that the water absorption bands will become deeper with the increasing of concentrations of BaClF in the layers. In addition, it can be seen that the transmittance of layers will increase with the increasing of concentrations of BaClF. In the spectral range from 2.5 to 7.5 μm , the optimized antireflection characteristics can be obtained for the layer with a value of $x=0.72$; meanwhile, the optimized characteristics can also be obtained for the layer with a value of $x=0.42$ for the spectral range beyond 7.5 μm .

The average indices of refraction n and extinction coefficient k , derived by fitting the transmittance measurement data, of layer with a BaClF concentration x of 0.42 were presented in Fig. 7 (b). It can be found that the layer possess an extraordinarily lower average refractive index, for example, an index of 1.222 at 10 μm can be achieved, which is obviously lower than those of infrared low-index coating materials used commonly.

Since the advantage of antireflection coatings with a single inhomogeneous layer is that they do not suffer from limited bandwidth and angular dependence, which are typical of solid thin-film stacks; moreover, the graded index of refraction is not as critically dependent on the precise phase relations typical of interference coatings; the normalized profile of refractive index was also illustrated in Fig. 7 (c). The symbol d in the abscissa corresponds to the thickness of layer. It can be shown that near the interface to the medium (air), a Gaussian index profile is presented; then, a transition zone appears, which has a quintic-index profile characteristics. The gradually increasing of refractive index near the interface to the germanium substrate can be ascribed to the diffusion of the element of Ge into the layer. The profile of refractive index is in good agreement with the result for depth profiles of Ba and Pr presented in Fig. 6, since BaClF has a greater refractive than that of rare-earth fluorides [20, 22]. It has been reported that the Gaussian index profile and quintic-index profile are near the optimum profile to minimize the Fresnel reflections [23], therefore, in our investigation, an extraordinarily lower reflection and average refractive index can be attributed to an appropriate refractive index gradient existing in the layer. In the graphical abstract, the color contour of refractive index profile

is illustrated in the inhomogeneous layer on Ge substrate.

In order to make a clear elucidation about trace phases in the layers in BaClF-PrF₃ system, an enlargement of XRD pattern of the element 4-5 obtained using the micro-area X-ray diffraction was presented in Fig. 7 (d). It can be shown that the peaks corresponding to trace phases can be ascribed to BaClF, PrF₃ and praseodymium chloride (PrCl₃). The position and intensity of reflections given on the JCPDS cards for BaClF, PrF₃ and PrCl₃ were also added in figure, respectively. The emergence of PrCl₃ implied that precursor used in the synthesis is not pure enough.

(a)

(b)

(c)

(d)

Fig. 7. The transmission spectra of inhomogeneous layers with different concentrations of BaClF in the BaClF-PrF₃ system (a), average refractive index n and extinction coefficient k (b) and normalized profile of refractive index (c) of the layer with a BaClF concentration x of 0.42, phase analysis for a representative element, 4-5 (d).

3.2 BaClF-ErF₃

The elements included in the fourth quadrant in the libraries belong to this system.

The transmission spectra of five elements with representative concentrations of BaClF were shown in Fig. 8 (a). It can be seen that the spectral transmittance of the layers decreases with the increasing of the concentrations of BaClF. In addition, the transmittance of the layers in the entire spectral range, of which the concentrations of BaClF is greater than 0.1, is lower than that of Ge substrate; furthermore, these spectra have an almost same characteristics, regardless the concentrations of BaClF.

The average indices of refraction n and extinction coefficient k of layer with a BaClF concentration x of 0.08 were presented in Fig. 8 (b). It can be found that the layer has an index 1.224 at 10 μm . The normalized profile of refractive index of layer was also illustrated in Fig. 8 (c). A Gaussian index profile followed by approximate quintic-index profile characteristics can be shown. The gradually increasing of refractive index near the interface to the germanium substrate can be ascribed to the diffusion of the element of Ge into the layer.

The XRD pattern of the element 8-5 was presented in Fig. 8 (d). It was shown that the peaks of trace phases can be ascribed to BaClF and ErF_3 only. The position and intensity of reflections given on the JCPDS cards for BaClF and ErF_3 were also added in figure, respectively.

(a)

(b)

(c)

(d)

Fig. 8. The transmission spectra of inhomogeneous layers with different concentrations of BaClF in the BaClF-ErF₃ system (a), average refractive index n and extinction coefficient k (b) and normalized profile of refractive index (c) of the layer with a BaClF concentration x of 0.08, phase analysis for a representative element, 8-5 (d).

3.3 BaClF-SmF₃

The elements included in the third quadrant in the libraries belong to this system.

The transmission spectra of five elements with representative concentrations of BaClF were shown in Fig. 9 (a). It can be seen that the spectral transmittance decreases with the increasing of the concentrations of BaClF. The transmittance of the layers, of which the concentrations of BaClF are greater than 0.14, is lower than that of Ge substrate; furthermore, these spectra have an almost same characteristics, regardless the concentrations of BaClF.

The average indices of refraction n and extinction coefficient k of layer with a BaClF concentration x of 0.14 were presented in Fig. 9 (b). It can be shown that an index of 1.213 at 10 μm can be achieved for this layer. The normalized profile of refractive index of layer was also illustrated in Fig. 9 (c), which is a Gaussian index profile followed by approximate quintic-profile. The gradually increasing of refractive index near the interface to the germanium substrate can be ascribed to the diffusion of the element of Ge into the layer.

The XRD pattern for the element 8-4 was presented in Fig. 9 (d). It was shown that the peaks of trace phases can be ascribed to BaClF, SmF_3 and barium oxide (BaO). The position and intensity of reflections given on the JCPDS cards for BaClF, SmF_3 and BaO were also added in figure, respectively. The emergence of trace phase of BaO implied that precursor used for the synthesis is not pure enough.

(a)

(b)

(c)

(d)

Fig. 9. The transmission spectra of inhomogeneous layers with different concentrations of BaClF in the BaClF-SmF₃ system (a), average refractive index n and extinction coefficient k (b) and normalized profile of refractive index (c) of the layer with a BaClF concentration x of 0.14, phase analysis for a representative element, 8-4 (d).

3.4 BaClF-LaF₃

The elements included in the second quadrant in the libraries belong to this system.

The transmission spectra of five elements with representative concentrations of BaClF were illustrated in Figure 10 (a). The spectral transmittance of the layers decreases with the concentration increase until $x=0.33$. The spectral transmittance in the layers will increase with the further increasing of concentrations of BaClF. The best antireflection approach for the Ge surfaces can be achieved for the BaClF-LaF₃ layer with a BaClF concentration x of 0.51.

The average indices of refraction n and extinction coefficient k of layer with a BaClF concentration x of 0.51 were presented in Fig. 10 (b). It can be shown that an average index of 1.195 at 10 μm can be achieved. Its normalized profile of refractive index of layer was also illustrated in Fig. 10 (c), which is a Gaussian index profile followed by approximate quintic-profile.

The XRD pattern for the element 4-4 was presented in Fig. 10 (d). The peaks corresponding to trace phases can be ascribed to BaClF, LaF₂ and LaF₃. The position and intensity of reflections given on the JCPDS cards for BaClF, LaF₂ and LaF₃ were also added in figure, respectively.

(a)

(b)

(c)

(d)

Fig. 10. The transmission spectra of inhomogeneous layers with different concentrations of BaClF in the BaClF-LaF₃ system (a), average refractive index n and extinction coefficient k (b) and normalized profile of refractive index (c) of the layer with a BaClF concentration x of 0.50, phase analysis for a representative element, 4-4 (d).

4. Conclusion

An improvement to the method of combinatorial synthesis reported by X. D. Xiang and colleagues is carried out. This rapid and efficient method is used to accelerate the investigation into the composition dependence of the durability and antireflection characterization of inhomogeneous infrared low-index layers with an appropriate refractive index gradient consisting of host rare-earth fluorides, such as LaF₃, PrF₃, ErF₃ and SmF₃, admixed with the different amount of BaClF. Although the primitive aim of our investigation is to search for a lower absorptive, robust, infrared low-index layer to reduce Fresnel reflection on the surface of infrared optical components, this improvement

also can be used in the discovery and optimization of a number of other optical materials.

It was demonstrated in our investigation, that the layers are robust enough to withstand normal handling and environmental conditions. In addition, the best antireflection characteristics can be carried out for the BaClF-LaF₃ layer with a BaClF concentration $x=0.51$, through the high-throughput characterization of the durability and the spectral transmittance of the elements in the libraries. Because the optimized characteristics of Gaussian index profile followed by a quintic-profile can be generated in the layers, an average refractive index around 1.2 can be achieved, which is lower than those of infrared low-index coating materials used commonly.

Acknowledgments

This work is supported by the National Science Foundation of China (NSFC) under Grant No. 61178039 and Grant No. 61306115. Authors are grateful to Prof. X. M. Meng in Technical Institute of Physics and Chemistry (IPC), Chinese Academy of Sciences, for his helps in performing the EDXA analyzes, to Prof. X. P. Gu in the School of Geosciences and Info-Physics, Central North University for his helps in performing the micro-area X-ray diffraction analyzes, and to Dr. S. Pan in Institute of materials science, Nanchang University for his helps in performing the secondary ions mass spectroscopy analyzes.

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