Fabrication of antireflective hydrophobic periodic micro-hole structures on ZnS surface by femtosecond laser direct writing

Kun Zhou\textsuperscript{1,2,3,4}, Yanping Yuan\textsuperscript{1,2,3,4,*}, Jimin Chen\textsuperscript{1,2,3,4}, Chunlian Wang\textsuperscript{1,2,3,4}, Shibo Xiang\textsuperscript{1,2,3,4}

1 Institute of Laser Engineering, Faculty of Materials and Manufacturing, Beijing University of Technology, Beijing 100124 China
2 Key Laboratory of Trans-scale Laser Manufacturing Technology (Beijing University of Technology), Ministry of Education, Beijing 100124 China
3 Beijing Engineering Research Center of Laser Technology, Beijing University of Technology, Beijing 100124 China
4 Beijing Engineering Research Center of 3D Printing for Digital Medical Health, Beijing University of Technology, Beijing, 100124, China
* Corresponding author: ypyuan@bjut.edu.cn

Abstract. ZnS has a promising wide range of applications in optical and optoelectronic areas. But the Fresnel reflection on ZnS surface reduces the transmittance of light and causes an obstacle in its applications. Thus, it is crucial to minimize the Fresnel reflection to promote the antireflection property. This paper demonstrates an effective way to fabricate antireflective periodic micro-hole structures on ZnS surface by femtosecond laser direct writing. The effects of laser power, scanning speed on the morphology of the holes are investigated. The fabricated structures exhibit an excellent antireflection property, and achieve more than 30% decrease in reflectance in the near-ultraviolet spectral wavelength range and near-infrared spectral region (200-800 nm), reducing 35% in 280 nm, especially. Besides, the prepared surface demonstrates effective performance concerning hydrophobicity with a contact angle of 107.4°, and the contact angle of unprocessed ZnS is 96.2°. These results show that the femtosecond laser can induce the antireflection and hydrophobic properties on the surface of ZnS, which has a potential application in outdoor optical and optoelectronic devices.

1. Introduction
ZnS is one of important semiconductors [1], and also a promising optical window material, has been widely researched. Due to its large bandgap (3.72 eV), anti-corrosion ability, excellent mechanical property, low cost and suitable for large scale fabrication, ZnS has many crucial applications in light-emitting diodes (LEDs), flat panel displays and optical windows, etc [2-3]. However, the Fresnel reflection loss emerges during the transmission of light, due to the high refractive index (n=2.2) of ZnS. Hence, it is important to fabricate antireflective structures on ZnS to increase the transmittance of incident light and promote optical property [4-5].

The traditional method is to fabricate multi-layer thin film [4, 6], but it has many disadvantages like narrow bandwidths, easy peeling off and refractive index mismatch between layers [7]. Inspired by the excellent antireflection property of ‘month-eye’, people are dedicated to fabricate sub-
wavelength structures (SWS) with gradient refractive index to enlarge the transmission of light and improve optical imaging quality [5, 8, 9]. However, current fabrication methods of SWS like reactive ion etching, nano-imprint lithography and e-beam lithography are limited to particular material, complicated step and time-consuming manufacturing [10-13].

Femtosecond laser direct writing is a promising method to fabricate SWS due to its high machining precision, good controllability and low cost [14-16]. Li fabricated antireflective microstructures on superhydrophobic titanium alloy surface, and obtained good antireflection property [17]. Li fabricated a planar convex spherical micro-lens with fully conformal broadband antireflective SWS based on three-dimensional laser direct writing, and obtained the minimum reflectance near 1.55 \( \mu \)m wavelength [18]. Zhao Lei fabricated hexagonal periodic micro-nano pore structures, with low reflectance in the wavelength range of 300-780nm, and large water contact angle (140 °) [19].

In this paper, we demonstrate an effective way to fabricate antireflective hydrophobic periodic micro-hole structures on ZnS surface by femtosecond laser direct writing (FLDW). The effects of laser power, scanning speed on the morphology of the holes are investigated. The fabricated periodic structure under the optimal machining parameters achieves more than 30% decrease in reflectance in 200-800 nm, reducing 35% in 280 nm, especially. Besides, the prepared surface demonstrates effective performance concerning hydrophobicity with a contact angle of 107.4° without the treatment of siliconization. The results show that the femtosecond laser can induce the antireflection and hydrophobic properties on the surface of ZnS, which has a potential application in outdoor optical and optoelectronic devices.

2. Experiment section

ZnS wafer (20 mm-diameter, 1.5 mm-thickness) are polished with acetone and absolute ethanol in ultrasonic cleaner for 5 minutes, respectively, then dried naturally. Figure 1 shows the machining process. The femtosecond laser with wavelength of 800 nm is generated by Ti: sapphire laser system (Spitfire Ace PA-100, Spectra-Physics, USA) at a repetition rate of 200 Hz with a pulse duration of 50 fs. The periodic micro-hole structures are fabricated on the surface of washed ZnS wafer on a 3D high precision platform. The precision of the platform is micro level. The laser beam is focused on the surface of ZnS sample with a focusing system that consisted of a PBS and a mirror and a 10 X objective lens (Nikon). The light source is used for providing brightness, and the CCD system is used for monitoring the processing progress constantly. The scanning direction is perpendicular to the laser incident direction. The laser power can be adjusted by HWP (half wave plate) and attenuator. The scanning speed can be adjusted by the connected computer software. By adjusting the laser power, scanning speed and interval, different types of periodic micro-hole structures are obtained.

The surface morphology of periodic micro-hole structures is observed by a scanning electron microscope (SEM, SU4800). In order to determine the composition and structure of the crystal, the X-ray diffraction spectral of samples are measured by diffractometer (D8 Advance) in the range of 10°-80°. Three-dimensional morphology of the sample and depth of holes is measured by an atomic force microscope (AFM, BRUKER Dimension Icon). The reflectance of sample in the wavelength range of 200-800 nm is measured by a ultraviolet visible near infrared spectrophotometer (UV-3600) capable of efficiently collecting stray light generated by diffuse reflection. The wettability is measured by a contact angle goniometer (Kruss DSA 10).
3. Results and discussions

3.1. morphology characterization

SEM images of periodic micro-hole structures on the surface of ZnS wafer at different laser power and scanning speed is shown in Fig. 2. The laser power is fixed at 0.05 mW, 0.075 mW and 0.1 mW. The laser parameters given in the experiments are as follows: repetition rate of 200 Hz, pulse width of 50 fs, scanning speed of 0.8 mm/s, 1.0 mm/s and 1.2 mm/s, respectively. A line-by-line array processing method is used in this experiment. By controlling the scanning speed and repetition rate, we can adjust the interval between adjacent holes in X direction, and the interval in Y direction is controlled by parameters in the line array processing method. The single hole is produced by single pulse processing by controlling the scanning speed and repetition rate. The interval between holes is 4 μm, 5 μm and 6 μm, respectively.

Fig. 2 SEM images of periodic micro-hole structures on the surface of ZnS wafer at different laser power and scanning speed. (a, b) 0.05 mW, 0.8 mm/s; (c, d) 0.075 mW, 1.0 mm/s; (e, f) 0.1 mW, 1.2 mm/s.

Compared with SEM images, (laser power of 0.05 mW, scanning speed of 0.8 mm/s) is the most suitable parameter for fabricating periodic and regular distributed micro-hole structures, as shown in Fig. 2(a, b).

When the laser power is 0.05 mW, the shape of holes is very regular (like a circle) and the remelted zone is small (less than 0.1 μm). When the laser power is 0.075 mW and 0.1 mW, the shapes of holes are not so round, it may result from the fluctuation of laser source. Besides, the width of melted zone gets larger with the increase of laser power (0.3 μm for 0.075 mW, 0.34 μm for 0.1 mW), which makes the quality of holes not so good.

When the scanning speed is 0.08 mm/s, the holes are closely arranged and the distance between central of holes is 4 μm without overlapping. When the scanning speed increase, the distance between
holes gets larger, and the proportion of holes area becomes smaller, which will reduce the antireflection performance.

Fig. 3 AFM images of periodic micro-hole structures on the surface of ZnS wafer at different laser power and scanning speed. (a) 0.05 mW, 0.8 mm/s; (b) 0.075 mW, 0.8 mm/s.

The 3D morphology of periodic micro-hole structures at 0.05 mW laser power, 0.8 mm/s scanning speed, and 0.075 mW laser power, 0.8 mm/s scanning speed are shown in Fig. 3. The depth of holes at 0.05 mW is about 120 nm, and the depth of holes at 0.075 mW is about 150 nm. The micro scale hole and nano-meter scale hole depth can effectively increase the light capture.

3.2. XRD characterization
To investigate the change of crystal structure of periodic micro-hole structures on the surface of ZnS, the X-ray diffraction spectral is measured by D8 Advance diffractometer in the range of 10°-80°, as shown in Fig. 4.

Fig. 4 XRD spectra of periodic micro-hole structures with different processing parameters. (black) 0.05 mW, 0.8 mm/s; (red) 0.075 mW, 1.0 mm/s; (blue) 0.1 mW, 1.2 mm/s.

It can be seen that all the characteristic peaks (1 11, 200, 220, 311, 400) are reduced after laser processing compared with the standard JCPDS card No. 05-0566, as shown in Fig. 4. The effect of laser processing on periodic micro-hole structures is significant. The XRD spectrum shows that the intensity of (111) diffraction peak decrease greatly with the increase of laser power, the intensity of (200, 220, 400) diffraction peak are almost vanished, and there is a slight drop in intensity of (311) diffraction peak. All these results may due to the strain free disordered blocks at high temperatures on the surface of periodic micro-hole structures produced by femtosecond laser [3].

3.3. Reflective properties
1×1 cm² periodic micro-hole structures on the surface of ZnS at optimal parameters (laser power of 0.05 mW, scanning speed of 0.8 mm/s) are with small melted zone and good surface morphology. Fig. 5 shows the surface reflectance of the laser-processed sample and unprocessed sample measured over the spectral range of 200-800 nm. The sudden change of reflectance at 370 nm and 720 nm is because the light change in the testing device (UV-3600). The periodic micro-hole structures on the surface of ZnS greatly reduce the reflectance compared with the unprocessed ZnS in the tested wavelength range, and average 30% decrease of reflectance is achieved in the wavelength range of 200-800 nm. In the
wavelength range of 250-330nm, more than 35% decrease is achieved, especially. All these results show that this kind of periodic micro-hole structures have an excellent property of antireflection.

![Image](https://via.placeholder.com/150)

**Fig. 5** Reflectance of unstructured surface of ZnS wafer and periodic micro-hole structures. (red) 0.05 mW, 0.8mm/s; (black) unprocessed ZnS.

### 3.4. Wetting properties

![Image](https://via.placeholder.com/150)

**Fig. 6** Contact angle of periodic micro-hole structures surface. (a) the unprocessed ZnS surface, (b), (c), (d), (e) the periodic micro-hole structures surface at laser power of 0.05 mW, scanning speed of 0.6 mm/s, 0.8 mm/s, 1.0 mm/s and 1.2 mm/s, (f) (g) the periodic micro-structures surface at laser power of 0.075 mW, scanning speed of 0.8 mm/s, 1.0 mm/s.

To investigate the wetting properties of periodic micro-hole structures surface, water contact angle is tested. **Fig. 6** shows the comparison of the water contact angle on the unprocessed surface and the periodic micro-hole structures surface under different laser power and scanning speed at normal temperature and pressure conditions. The contact angle of the unprocessed surface is 96.2°, as shown in **Fig. 6(a)**. The contact angles of the periodic micro-hole structures surface processed at the laser power of 0.05mW, scanning speed of 0.6 mm/s, 0.8 mm/s, 1.0 mm/s are 104.3°, 107.4°, 109.7°, respectively. There is a slight rise in CA with the increase of scanning speed. When the scanning speed is 1.2 mm/s, the contact angle dropped to 108.7°, which may be caused by the long distance between holes (6 μm). When the laser power is 0.075 mW, scanning speed of 0.8 mm/s and 1.0 mm/s, the contact angle is 106.9° and 105.9 °, respectively. It shows that the 0.05 mW is better than 0.075 mW in promoting hydrophobicity under the same scanning speed.

There is an increase (10°) in water contact angle after laser process, which means the periodic micro-hole structures surface could actually promote hydrophobicity on ZnS. There is little variation for the contact angle under the same scanning speed, different laser power. Besides, there are two ways to improve hydrophobicity, one is by siliconization to reduce surface energy, the other is by surface patterning [19]. Our samples are not implemented with siliconization. Hence, the hydrophobicity can be further improved after siliconization treatment.
4. Conclusion

ZnS has a promising wide range of applications in optical and optoelectronic areas over a broadband spectral region. But the Fresnel reflection on ZnS surface greatly reduces the transmittance of light and causes an obstacle in its applications. Thus, it is crucial to minimize the Fresnel reflection to promote the antireflection property. In this study, we demonstrate an effective way to fabricate antireflective periodic micro-hole structures on ZnS surface by femtosecond laser direct writing. The effects of laser power, scanning speed on the morphology of the holes are investigated. In the case of the optimal machining parameters (frequency repetition of 200 Hz, laser power of 0.05 mW, scanning speed of 0.8 mm/s), the radius and depth of holes is 3.4 μm and about 150 nm, respectively. The radius of holes increases with the increase of laser power, and high laser power induces large melted zone, which has a bad influence on the morphology. The fabricated periodic micro-hole structures surface has achieved more than 30% decrease in reflectance in the near-ultraviolet spectral wavelength range and near-infrared spectral region (200-800 nm), reducing 35% in 280 nm, especially, compared with the unprocessed ZnS, results show that the total reflectance in the 200-350 nm and 400-800 nm wavelength range keeps below 20% and 35%. Besides, the prepared surface demonstrates effective performance concerning hydrophobicity with a contact angle of 107.4° without the treatment of siliconization, while the contact angle of unprocessed ZnS is 96.2°. Experimental results show that the femtosecond laser can induce periodic micro-hole structures with good antireflection and hydrophobic properties on the surface of ZnS, which has a potential application in outdoor optical and optoelectronic devices.

Acknowledgements

This research was financially supported by National Natural Science Foundation of China (NSFC) (Grant No. 51805014), National Key R&D Program of China (Grant No. 2018YFB1107401), Scientific Research Program of Beijing Municipal Education Commission (Grant No. KM201810005012).

References

[1] B X F A , B T Z , B U K G , et al. ZnS nanostructures: From synthesis to applications[J]. Progress in Materials Science, 2011, 56(2):175-287.
[2] Fu L , Fanxiu Lü, Wang X , et al. Defects in CVDZnS[J]. Rare Metals, 2011, 30(4):387.
[3] Ji-Hong, Zhao, Xian-Bin, et al. Surface modification of nanostructured ZnS by femtosecond laser pulsing[J]. Applied Surface Science A Journal Devoted to the Properties of Interfaces in Relation to the Synthesis & Behaviour of Materials, 2014.
[4] Tajik N , Ehsani M H , Moghadam R Z , et al. Effect of GLAD technique on optical properties of ZnS multilayer antireflection coatings[J]. Materials Research Bulletin, 2017:265–274.
[5] Lin Z Q , Wang G G , Li L H , et al. Preparation and protection of ZnS surface sub-wavelength structure for infrared window[J]. Applied Surface Science, 2018, 470.
[6] Joshi D N , Atchuta S R , Reddy L , et al. Super-hydrophilic broadband anti-reflective coating with high weather stability for solar and optical applications[J]. Solar Energy Materials and Solar Cells, 2019, 200.
[7] Garlisi C , Trepci E , Li X , et al. Multilayer thin film structures for multifunctional glass: Self-cleaning, antireflective and energy-saving properties[J]. Applied Energy, 2020, 264:114697-.
[8] Huang Y F , Chattopadhyay S , Jen Y J , et al. Improved broadband and quasi-omnidirectional anti-reflection properties with biomimetic silicon nanostructures[J]. Nature Nanotechnology, 2007, 2(12):770-774.
[9] Luo X , Lu L , Yin M , et al. Antireflective and Self-cleaning Glass with Robust Moth-eye Surface Nanostructures for Photovoltaic Utilization[J]. Materials Research Bulletin, 2018, 109(JAN.):183-189.
[10] Yan H , Liu T , Yang K , et al. Nanoscale etching of microporous coatings for broadband antireflection coatings[J]. Thin Solid Films, 698.
[11] Sun S , Lu P , Xu J , et al. Fabrication of Anti-reflecting Si Nano-structures with Low Aspect Ratio by Nano-sphere Lithography Technique[J]. Nano-Micro Letters, 2013, 5(1):18-25.
[12] Zhu J , Yu Z , Burkhard G F , et al. Optical Absorption Enhancement in Amorphous Silicon Nanowire and Nanocone Arrays[J]. Nano Letters, 2009, 9(1):279-282.
[13] Eto H , Hiwasa S , Taniguchi J . Tough and antifouling antireflection structures made by partial-filling ultraviolet nanoimprint lithography[J]. Microelectronic Engineering, 2018, 197(oct.):33-38.
[14] A F Z , B H W , B C W , et al. Direct femtosecond laser writing of inverted array for broadband antireflection in the far-infrared[J]. Optics and Lasers in Engineering, 129.
[15] Li Y , Zhang T , Fan S , et al. Fabrication of micro hole array on the surface of CVD ZnS by scanning ultrafast pulse laser for antireflection[J]. Optical Materials, 2017, 66:356-360.
[16] Li J , Xu J , Lian Z , et al. Fabrication of antireflection surfaces with superhydrophobic property for titanium alloy by nanosecond laser irradiation - ScienceDirect[J]. Optics & Laser Technology, 126.
[17] Li Y , Park S , Fullager D B , et al. Near-infrared transmittance enhancement using fully conformal antireflective structured surfaces on microlenses fabricated by direct laser writing[J]. Optical Engineering, 2019, 58.
[18] Zhao L , Wang Z , Zhang J , et al. Antireflection silicon structures with hydrophobic property fabricated by three-beam laser interference[J]. Applied Surface Science, 2015, 346:574-579.
[19] Ragesh P , Ganesh V A , Nair S V , et al. A review on 'self-cleaning and multifunctional materials'[J]. Journal of Materials Chemistry A, 2014, 2(36):14773-14797.