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Citation: Wang, Zhengwei, Chen, Guodong, Wen, Ming, Hu, Xutao, Liu, Xing, Wei, Jingsong, Wu, Qingsheng and Fu, Yong Qing (2022) Electrochemical Strategy for High-Resolution Nanostructures in Laser-Heat-Mode Resist Toward Next Generation Diffractive Optical Elements. *Small*, 18 (17). p. 2200249. ISSN 1613-6810

Published by: Wiley-Blackwell

URL: <https://doi.org/10.1002/smll.202200249> <<https://doi.org/10.1002/smll.202200249>>

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1 Electrochemical strategy for high-resolution nanostructures in laser-heat-mode resist toward
2 next generation diffractive optical elements
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22 **Abstract:** For achieving high-resolution nanostructures for next generation diffractive optical
23 elements (DOEs) using an environmentally friendly process, we propose and develop an
24 electrochemical development strategy using AgInSbTe based laser heat-mode resist (AIST-
25 LHR). Based on electrical resistivity difference of amorphous and crystalline phases for this
26 resist, an etching selectivity ratio of ~30:1 (i.e., the etch ratio between the amorphous and

1 crystalline ones) is achieved through the oxidation of Fe^{3+} ions with the assisted pitting
2 activation etching using Cl^- ions in an acid medium. Nanostructures with a minimum feature
3 size down to 41 nm have successfully been generated, including grating patterns, meta-
4 surface optical structures, gears and language characters. Using a post-plasma etching process,
5 the nanostructures are successfully transferred from the AIST-HLR onto silica substrate, and
6 X-ray grating patterns with line space of 80 nm have been created as a demonstration for its
7 potential applications in DOEs.

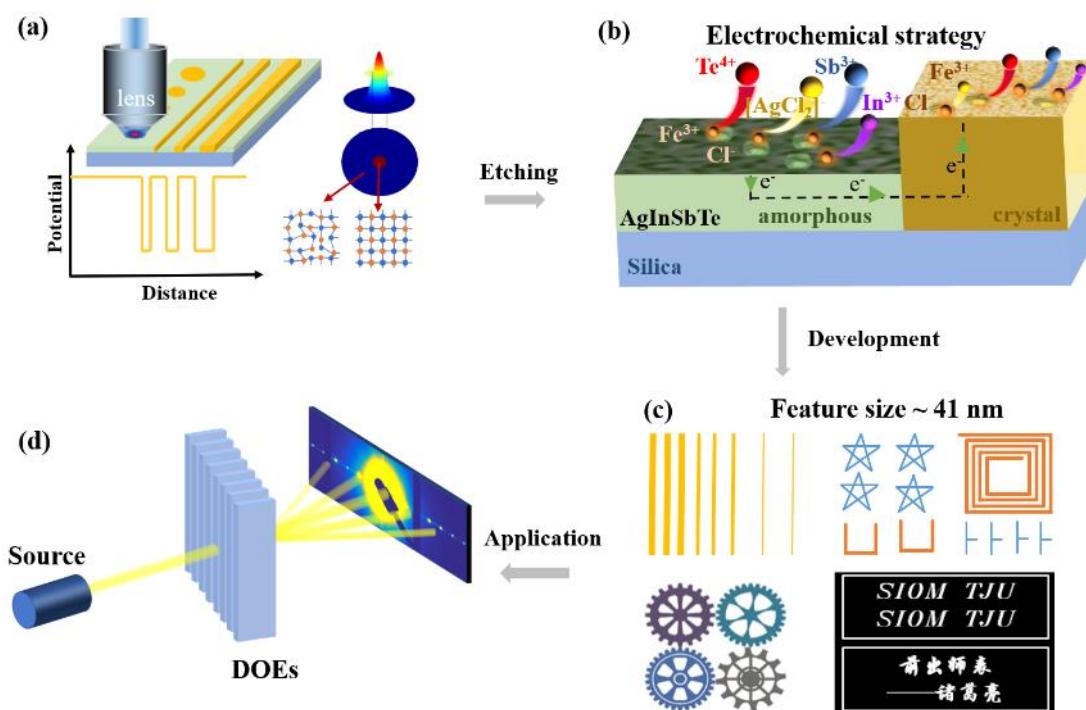
8 **Keywords:** Electrochemical development, high-resolution lithography, AgInSbTe laser heat-
9 mode resist, ~~optical diffraction device~~-diffractive optical elements

10 1. Introduction

11 Diffractive optical elements (DOEs) are applied in various fields such as holographic
12 recording media,^[1-3] diffractive surface gratings,^[4,5] photonic crystal color pixels of
13 sensors,^[6,7] spatial light modulators,^[8,9] and meta-surfaces.^[10-11] For these applications, high-
14 resolution feature sizes and low-cost but highly precision processes are critically demanded.
15 Laser heat-mode lithography, a non-diffraction-limited and maskless direct laser writing
16 (DLW) technique, can be used to fabricate large-area micro/nanostructures.^[12-16] Various
17 inorganic laser heat-mode resists (LHRs), such as AgInSbTe (AIST), SbTe, and GeSbTe, are
18 commonly used in the lithography process.^[14-19] Among them, AIST is preferred due to its
19 rapid and stable phase transformation.^[20-22] In a standard process of laser heat-mode
20 lithography, a laser spot is focused onto the AIST resist. Its phase is changed from an
21 amorphous phase to a crystalline one, which can be used to generate various micro-/nanoscale
22 patterns. The development of the AIST resist is generally carried out in a solution of 17%
23 ammonium sulfide.^[23,24] However, hydrolysis of the ammonium sulfide releases toxic and
24 corrosive hydrogen sulfide gas, which causes serious air pollution and potential dangers to
25 operators. Furthermore, this photoresist development process not only has a low etching rate,

but also generates inhomogeneous structures. Therefore, it is critically required to develop a new solution which is not only environment-friendly, but also efficiently develops arbitrary and high-resolution micro/nanostructures.

The AIST contains four metal elements (i.e., Ag, In, Sb, and Te), and thus it is an arduous task to find a desirable developer which can effectively etch all these elements in the AIST. Owing to the high oxidation potentials of $\text{Fe}^{3+}/\text{Fe}^{2+}$ ($\phi_{\text{Fe}^{3+}/\text{Fe}^{2+}}$, +0.771V), Fe^{3+} ions can oxidize many metals in an acid medium,^[25] and thus can be applied to etch the AIST-LHR. In an acid medium with the excessive ions of Cl^- , these Cl^- ions can act as a promotor for pitting activation, thus effectively removing the passivation layers.^[26] On another matter, the amorphous AIST has a short-range order and a low electrical resistivity. After its crystallization, the AIST exhibits a long-range order and a significantly increased electrical resistivity.^[27] The differences of its electrical resistivities at different phases cause the different etching rates in the solution. Hence, modifying the electrochemical reactions during the development could be applied as a new strategy to achieve high-resolution arbitrary nanostructures using the AIST-LHR in the FeCl_3 solution.



1 **Figure 1.** Design and fabrication of high-resolution arbitrary micro/nano-structures: (a)
2 exposure of arbitrary patterns with three-dimensional temperature distribution on the surface
3 of AIST film and corresponding potential distribution; (b) electrochemical development
4 process; (c) various arbitrary structures of AIST-LHR; (d) fabrication of DOEs via plasma
5 etching.

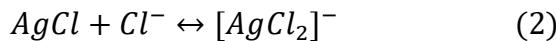
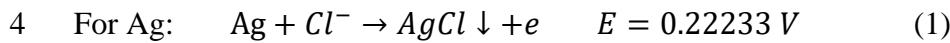
6 In this paper, we propose an environment-friendly electrochemical development strategy to
7 achieve high-resolution arbitrary patterns using the AIST-LHR. In an acid medium, Fe^{3+} ions
8 are introduced into the developer and Cl^- ions are added into the promotor. They can etch the
9 amorphous phase and crystalline phase of the AIST-LHR with different rates, and a good
10 etching selectivity ratio up to ~30:1 can be achieved between the amorphous and crystalline
11 phases. Using this new strategy, high-resolution and arbitrary structures with a minimum
12 feature size of 41 nm have been successfully obtained, including grating patterns, meta-
13 surface optical structures, various gear, language characters (both English and Chinese). For
14 demonstration of its potential applications in the diffractive optics, a subsequent plasma
15 etching process is applied to create a high-resolution DOE structures.

16 **2. Results and discussion**

17 **2.1. Fabrication strategy**

18 In the fabrication process (Figure 1), the DLW system is used to focus the laser beam onto
19 AIST-LHR surface (Figure 1a), which results in the increase of its temperature and
20 crystallization of the laser-irradiated (exposed) region (SI, Figure S1). Because the size of
21 crystallized region is mainly affected by the distribution of laser heat field, it can be much
22 smaller than the size of laser spot by controlling the time and power of laser radiation on the
23 AIST surface. In order to achieve high-resolution arbitrary micro/nano-structures, a new
24 development strategy is performed in the FeCl_3 acid solution to selectively etch the
25 amorphous phase and crystalline phases. The mechanism for this process is illustrated in
26 Figure 1b.

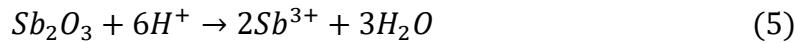
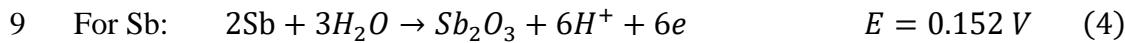
Because the electrode potential of $E(Fe^{3+}/Fe^{2+})$ (0.771V) is higher than those of $E(Ag^+/Ag)$, $E(In^{3+}/In)$, $E(Sb_2O_3/Sb)$, or $E(TeO_2/Te)$, the four metal elements in the AIST-LHR can be gradually dissolved according to the following reactions.



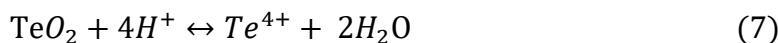
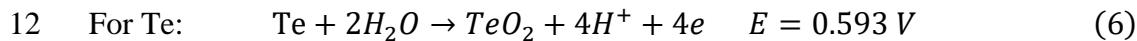
$AgCl$ precipitates can be converted into soluble product of $[AgCl_2]^-$ with the excess Cl^- ions.



Elements of In can be oxidized into In^{3+} ions which are stable in the In solution.



Sb can be oxidized into Sb_2O_3 , and then dissolved in the acidic condition which is rich in Cl^- .



Te is eventually oxidized and dissolved in the acidic and Cl^- environment.

Additionally, different electrical resistivities between its laser beam-exposed (crystalline) and unexposed (amorphous) regions cause large differences in their electrode potentials. To verify this, a Kelvin probe force microscope (KPFM) was used to characterize the surface potential changes on the AIST-LHR after laser beam exposure (SI, Figure S2). There is a clear difference in the work functions of amorphous and crystalline phases, which are linked to their differences in charge transfer properties. During the development process, the amorphous and crystalline phases can be considered as two metallic electrodes, which are immersed in an electrolyte solution containing the depolarizer (Fe^{2+}/Fe^{3+}) to form a short-circuit primary battery (Figure 1b). When the amorphous and crystalline phases are in contact, current density of anodic dissolution for the amorphous phase of the AIST-LHR is increased significantly. Therefore, electrode potential of the amorphous phase is increased, thus increasing its dissolution rate. In contrast, the electrode potential of crystalline phases is

1 decreased. Therefore, the overpotential of anodic dissolution reaction of crystalline phases is
2 decreased after contacting with the amorphous phase, thus reducing anodic corrosion rate of
3 the crystalline phases. Clearly using this new electrochemical development strategy; the
4 differences of electrode potentials cause a significantly enhanced etching selectivity between
5 amorphous and crystalline phases of the AIST-HLR, thus achieving high-resolution
6 nanostructures (Figure 1c).

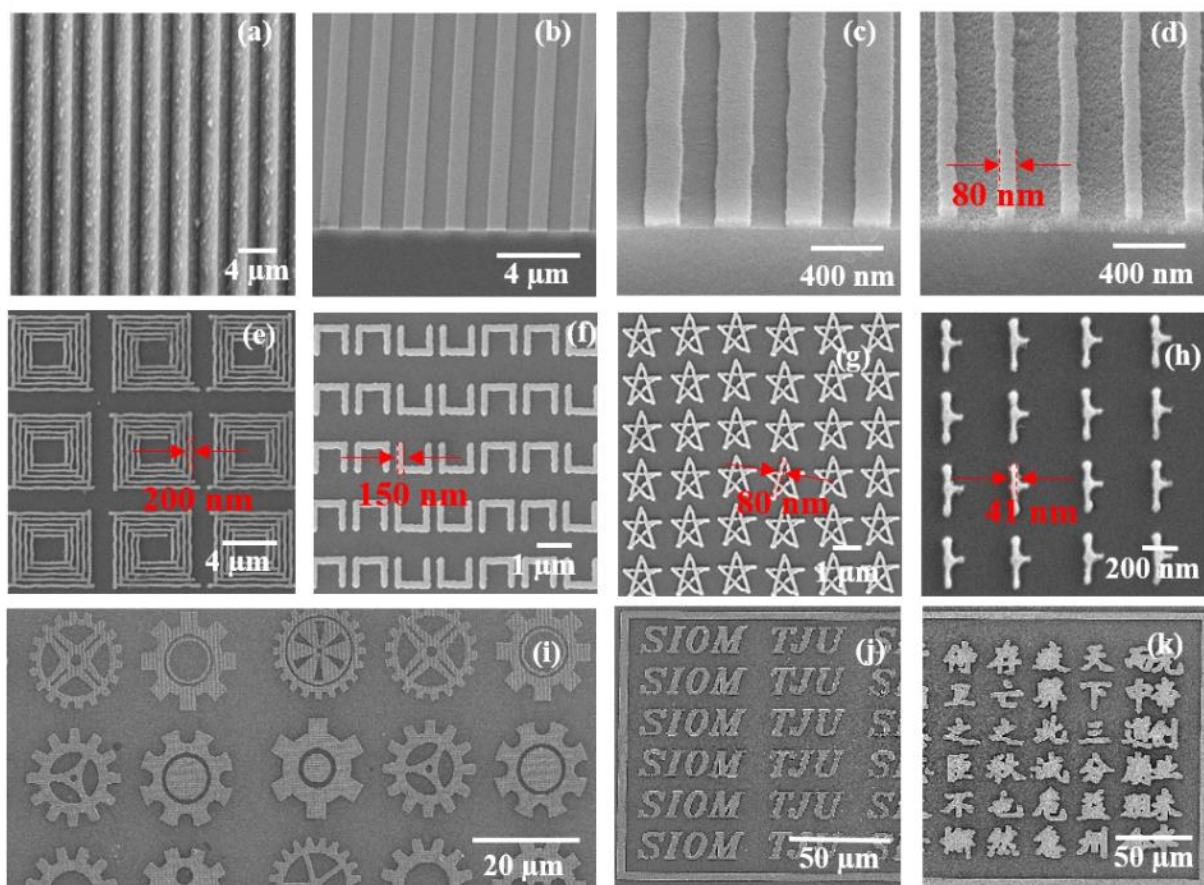
7 Furthermore, the developed AIST-HLR can be effectively used as a mask for post-dry etch
8 process. Based on the proposed electrochemical development strategy using the AIST-LHR
9 and a standard plasma etching process, a high-resolution silica ~~diffraction grating device~~ DOE
10 (Figure 1d) is fabricated, and its quality is comparable to those made using the focused ions
11 beam lithography.

12 **2.2. Lithographed nanostructures**

13 Using the conventional photolithography with a light wavelength λ of 405 nm and a
14 numerical aperture of NA=0.8, it is difficult to achieve a structure with a feature size D
15 smaller than 618 nm based on the equation of $D=(1.22\times\lambda)/NA$. Figure 2(a) shows scanning
16 electron microscope (SEM) images of various high-resolution structures, which were obtained
17 using the conventional photolithography method. Using a conventional positive-photoresist
18 such as S1805, widely used in h-line or g-line lithography, can hardly achieve the
19 nanostructures with a minimum feature size about $0.5 \mu\text{m}$ ^[28]. Whereas the feature size of
20 AIST-LHR is mainly determined by the distribution of temperature field during the laser
21 beam exposure process, but not by the Abbe diffraction limit for the photolithography^[22].

22 Using the AIST-LHR, we can precisely control the temperature fields using the laser beam,
23 and thus nanoscale crystallized patterns can be easily realized. Using our newly proposed
24 electrochemical development strategy, it is possible to achieve large-scale and high-resolution
25 nanostructures with feature sizes ranging from nanoscale to microscale, e.g., with

1 periods/linewidths from microscale ($2 \mu\text{m}/1 \mu\text{m}$), down to nanoscale (400 nm/200 nm and
 2 300 nm/80 nm) as demonstrated in Figures 2b-d. High-resolution meta-surface optical
 3 structures have also been successfully fabricated, including helically chiral structure, split-
 4 ring structure, hollow star-like structure, and three rotationally symmetrical structure (Figures
 5 2e-h). The minimum line-width we have achieved in this study is ~ 41 nm. Furthermore,
 6 various arbitrary nanostructures, e.g., various gear patterns and different language characters
 7 (including English and Chinese) have been successfully created (Figures 2i-k).



8
 9 **Figure 2.** SEM images of various micro/nanostructures (9 mm^2 on the silica substrates). (a)
 10 produced from a conventional photoresist (S1805) with the developed gratings
 11 period/linewidth of $3 \mu\text{m}/1 \mu\text{m}$; (b) AIST-LHR patterns after electrochemical developing with
 12 gratings having period/linewidth of $2 \mu\text{m}/1 \mu\text{m}$; (c) 400 nm/200 nm features; and (d) 300
 13 nm/80 nm features; multi-functional meta-surfaces for optical structures including helical
 14 chiral (e), split-ring(f), hollow star-like(g), and three rotational symmetry(h) structures with
 15 the feature size of 41 nm ; arbitrary cross micro-/nanoscale various gear patterns (i), English (j)
 16 and Chinese characters (k).

17

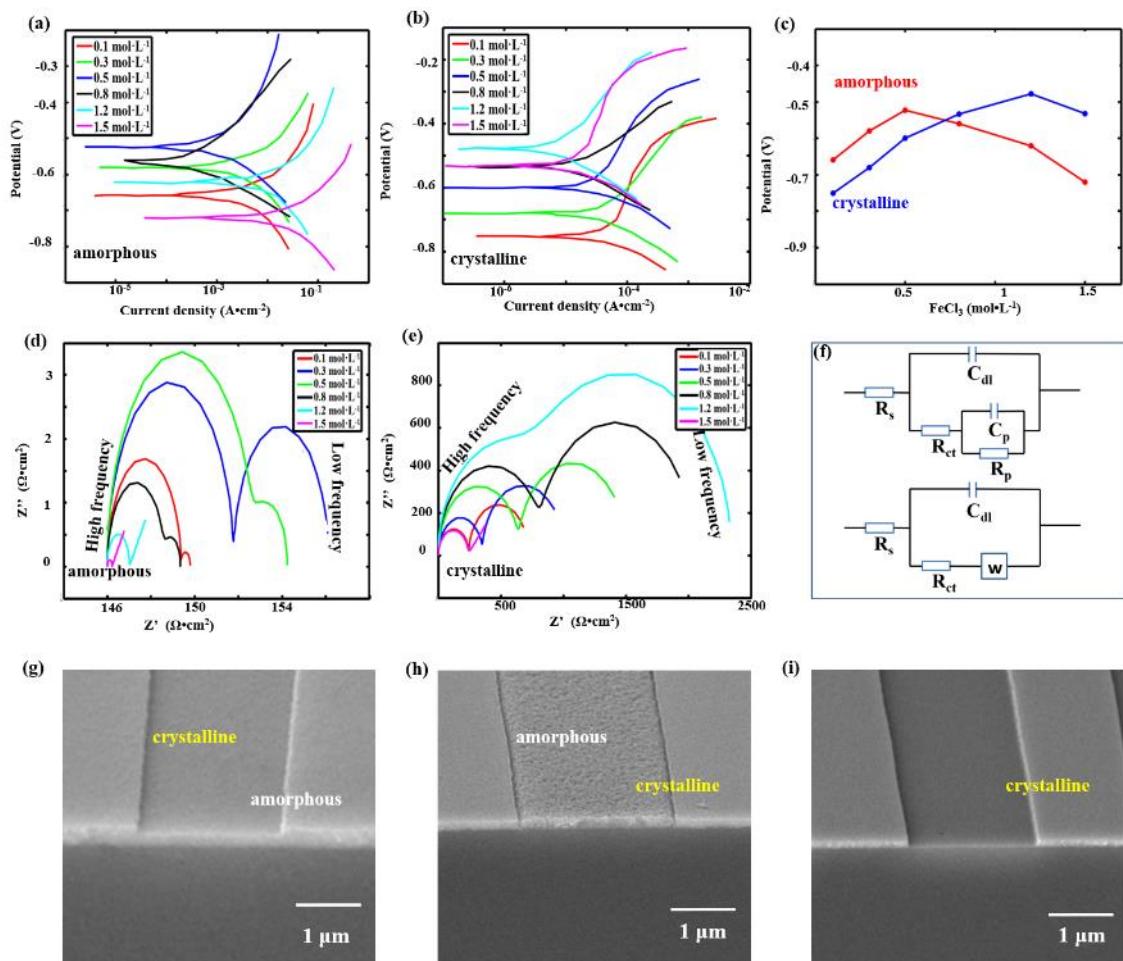
18 2.3. Mechanism of electrochemical development

1 To understand the wet-etching (or developing) mechanisms for using FeCl_3 to etch the
2 AIST-LHR, we investigate the characteristics of the electrochemical development. Electrode
3 potential, etching current and impedance of the AIST-HLR during its development process
4 have been studied in detail. Figures 3a-b show the obtained electro-potential polarization
5 curves of the amorphous and crystalline AIST-LHR in different concentrations of FeCl_3
6 solutions. Their corresponding fitting parameters are listed in Table S1. As shown in Figure
7 3c, when the concentration of FeCl_3 solution is lower than 0.5 and 1.2 $\text{mol}\cdot\text{L}^{-1}$, their etching
8 potentials are increased with the increase of FeCl_3 concentration, whereas their etching
9 current densities are decreased due to the formation of a surface passivation layer. Further
10 increase of the FeCl_3 concentration leads to a downward trend of etching potentials, whereas
11 the etching current density is increased sharply. This is mainly because the increase of Cl^-
12 concentration enhances the pitting reactions, thus removing the passivated layer.^[29]

13 Spectra of electrochemical impedance spectroscopy (EIS) show two capacitive arcs in
14 different solution concentrations for the amorphous and crystalline phases, respectively
15 (Figures 3d-e). The high-frequency band of capacitive arcs is related to the double-layer
16 capacitance (C_{dl}) and charge-transfer resistance (R_{ct}), and the low-frequency band one is
17 related to resistance (R_p) of the corrosion product layer formed on the surface of AIST-LHR.
18 The capacitance resistance increases with an increase in the FeCl_3 concentration because of
19 the formation of a passivation layer on the surface. As the concentration of FeCl_3 is
20 continually increased to 0.5 or 1.2 $\text{mol}\cdot\text{L}^{-1}$ for the amorphous or crystalline phases,
21 respectively, the passivation layer disappears. The reaction is changed from a dynamic control
22 mode to a substance diffusion control mode, which causes the increased diffusion resistance
23 (W).^[30]

24 The equivalent circuit diagrams (Figure 3f) are proposed and used to fit the electrochemical
25 impedance data, where R_s is the solution resistance and C_p is the corrosion product layer
26 capacitance. The corresponding impedance-fitting parameters are listed in Table S2. Results

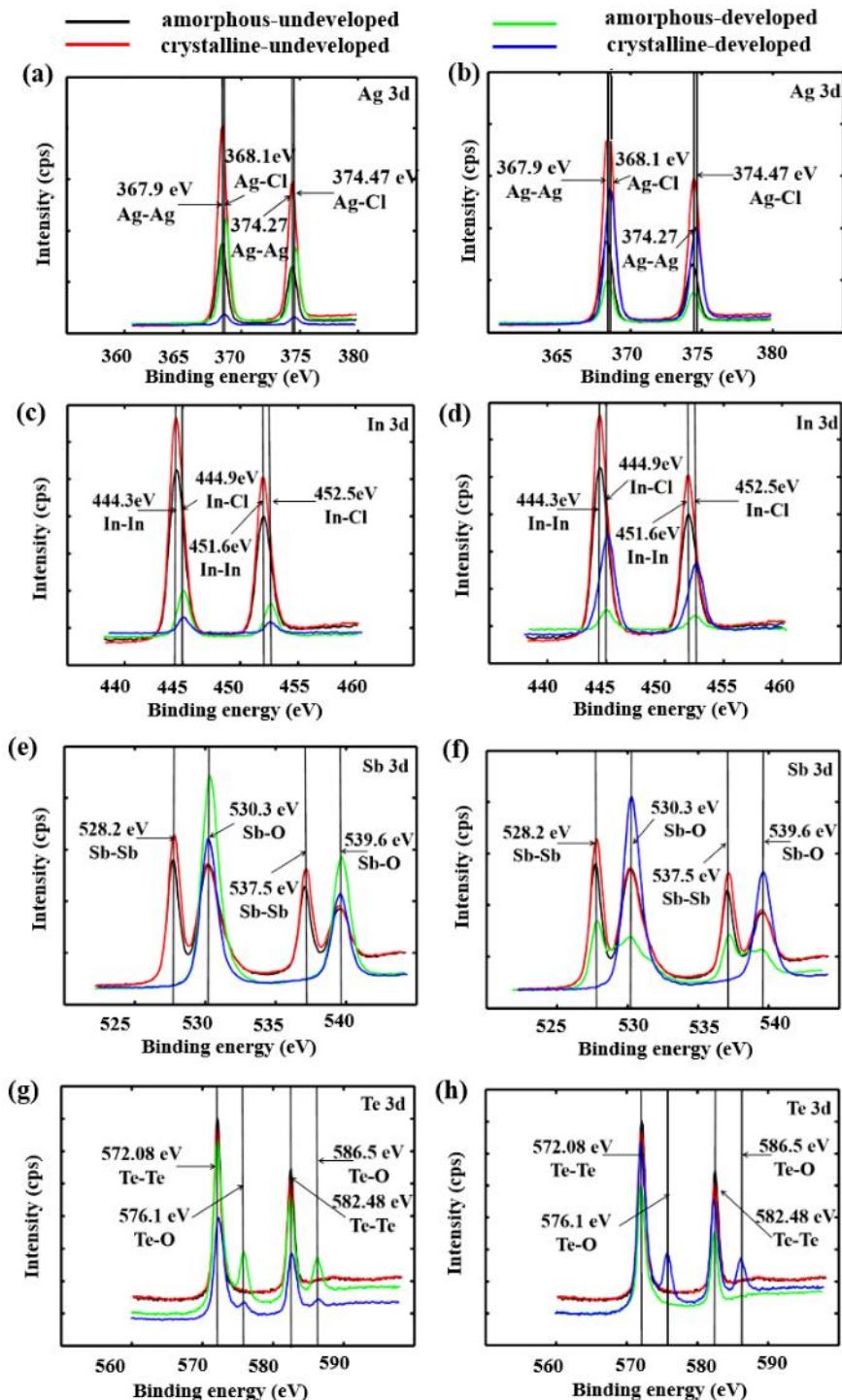
1 confirm that the impedance values of the crystallized phase are larger than those of the
 2 amorphous phase, thus more etching products are adhered to surface of amorphous phase.
 3 Using a FeCl_3 solution of $0.5 \text{ mol}\cdot\text{L}^{-1}$ for about 60 s, the increase of etching current density
 4 results in the increase of the height of amorphous area compared with the crystalline area
 5 (Figure 3g), and the etching products are adhered to surface to form a passivation layer.
 6 Whereas using a higher FeCl_3 concentration, this passivation layer is dissolved. The
 7 development morphologies obtained at durations of 10 and 30 s (Figure 3h-i) with a solution
 8 concentration of $1.2 \text{ mol}\cdot\text{L}^{-1}$ show that the height of crystalline region is larger than that of the
 9 amorphous region. A pitting morphology caused by Cl^- ions can be clearly seen in Figure 3i.



10

11 **Figure 3.** (a, b) Polarization curves of amorphous and crystalline AIST-LHR with the size of
 12 9 mm^2 ; (c) Etching potential trends of amorphous and crystalline AIST-LHR with the sample
 13 size of 9 mm^2 ; (d, e) Impedance spectrum curves of amorphous and crystalline AIST-LHR
 14 with the sample size of 9 mm^2 ; (f) Fitted circuit diagram; SEM images with the sample size of
 15 9 mm^2 obtained at $0.5 \text{ mol}\cdot\text{L}^{-1}$ FeCl_3 for 60 s (g), of $1.2 \text{ mol}\cdot\text{L}^{-1}$ FeCl_3 for 10 s (h) and 30 s (i),
 16 respectively.

1 In summary, due to the difference of potentials between the crystalline and amorphous
2 electrodes, they exhibit different etching rates in the development prcoess. At a lower
3 concentration of FeCl_3 , the etching current density of the amorphous region is greater than
4 that of the crystalline region, and the etching products are adhered to the film surface to form
5 a passive layer. At this moment, the height of amorphous region is higher than that of
6 crystalline region, but it cannot be used as a good photoresist (or it can not form a good
7 window-like structure). As the concentration of FeCl_3 is increased, the passive film layer
8 disappears, and the corrosion rate of the amorphous region is higher than that of the
9 crystalline region, which makes the height of crystalline region much higher than that of
10 amorphous region, thus completing the electrochemical development.



1

2 **Figure 4.** XPS analysis of amorphous developed, amorphous undeveloped, crystalline
 3 developed and crystalline undeveloped samples with the size of 9 mm². The results of Ag 3d
 4 (a, b), In 3d (c, d), Sb 3d (e, f), and Te 3d (g, h) are obtained at 0.5(left) and 1.2 mol·L⁻¹
 5 (right), respectively.

6 To verify the changes of surface etching chemistry, analysis using an X-ray photoelectron
 7 spectroscope (XPS) was performed, and the obtained results are shown in Figure 4. In Figure
 8 4a, Ag 3d peaks of AIST-LHR are identified at 367.9 and 374.27 eV, respectively,

1 corresponding to $3d^{5/2}$ and $3d^{3/2}$ Ag-Ag bonds.^[31] However, these peaks are disappeared after
2 the resist is etched in $0.5 \text{ mol}\cdot\text{L}^{-1}$ FeCl_3 solution, whereas new peaks are identified at 368.1
3 and 374.47 eV, which are corresponding to those of Ag-Cl bonds. These peaks are
4 significantly higher for the amorphous phase than that for the crystalline phase.^[32] The Ag-Cl
5 bonds are identified in the crystalline phase even at a high concentration ($1.2 \text{ mol}\cdot\text{L}^{-1}$) of the
6 FeCl_3 solution. The AgCl was further converted into soluble product of $[\text{AgCl}_2]^-$ when the Cl^-
7 ions are excessive in the solution (Figure 4b). Meanwhile, the Ag-Ag bonds are detected in
8 the amorphous phase due to the disappearance of passivation layer. For the In 3d, the peaks at
9 444.3 and 451.6 eV are corresponding to the $3d^{5/2}$ and $3d^{3/2}$ peaks of In-In bonds (Figures 4c-
10 d) for both the crystalline and amorphous ones, respectively,^[33] indicating that they are mainly
11 existed as In-In bonds before etching.^[34] Whereas after etching, a weak In-Cl bond appears. In
12 Figures 4e-f, the Sb 3d $^{5/2}$ and Sb 3d $^{3/2}$ peaks of the Sb-Sb bonds are at 528.2 and 537.5 eV,
13 respectively.^[35] Their oxidation bond energies are 530.3 and 539.6 eV,^[36] both of which are
14 corresponding to those of Sb-O bonds. The Sb-Sb bonds disappear when the etching occurs at
15 $0.5 \text{ mol}\cdot\text{L}^{-1}$ FeCl_3 solution, because Sb is oxidized into Sb_2O_3 . While at $1.2 \text{ mol}\cdot\text{L}^{-1}$ solution,
16 the Sb-Sb bonds can still be detected in the amorphous phase, owing to the disappearance of
17 the passivation layer. Figures 4g-h show the peaks of Te 3d at 572.08 and 582.48 eV,
18 corresponding to the homopolar bonds of Te-Te.^[37] The Te-O bond appears after wet etching
19 in a $0.5 \text{ mol}\cdot\text{L}^{-1}$ FeCl_3 solution due to the oxidation of Fe^{3+} .^[38] However, this bond disappears
20 in a $1.2 \text{ mol}\cdot\text{L}^{-1}$ FeCl_3 solution, which indicates the disappearance of the passivation layer.

21 Comparatively, etching in the $0.5 \text{ mol}\cdot\text{L}^{-1}$ FeCl_3 solution results in the larger height of
22 amorphous area than that of crystalline area, which shows the characteristics of a positive
23 resist. Whereas etching in the $1.2 \text{ mol}\cdot\text{L}^{-1}$ FeCl_3 solution shows the characteristics of a
24 negative resist, i.e., obtaining a lower height of amorphous area than that of crystalline area
25 (SI, Figure S4-S5).

1 In brief, the etching rate of the amorphous phase is much higher than that of the crystalline
 2 phase, which can be explained by the reaction kinetics. The rate constant k_c of a chemical
 3 reaction can be expressed as:

$$4 \quad k_c = \frac{kT}{\hbar} \exp\left(-\frac{-\Delta G_{A \rightarrow C}^*}{RT}\right) \quad (8)$$

5 where k is the Boltzmann constant, \hbar is the Planck constant, R is the Avogadro constant, T is
 6 the temperature, and $\Delta G_{A \rightarrow C}^*$ is the activation energy of amorphous to crystalline phases. The
 7 amorphous phase has a short-range ordered lattice structure.^[39] There are more unbounded
 8 electrons in the amorphous phase, which makes it easier to lose electrons during the
 9 electrochemical reactions. Therefore, the amorphous phase only needs a lower activation
 10 energy to generate active particles and trigger the electrochemical reactions. When the film is
 11 crystallized, the system is in a much more stable stage, without many unpaired electrons.
 12 Therefore, a much higher activation energy is required to initiate the reaction, thus the etching
 13 rate of the crystalline phase is much lower than that of the amorphous phase.

14 **2.4. Key influencing factors for development**

15 We have further studied the variations in reaction speeds and selective etching ratios with
 16 the concentration of FeCl_3 solution, based on the measured structure's heights after
 17 development. The obtained results are shown in Figure 4a. In these cases, an etching ratio less
 18 than 1 indicates that the height of amorphous region is larger than that of crystalline region,
 19 which links to the characteristics of a positive resist. Whereas if the etching ratio is larger than
 20 1, it indicates that the height of crystalline region is larger than that of the amorphous region,
 21 showing the characteristics of a negative resist. In this study, when the concentration of FeCl_3
 22 solution is lower than $1.2 \text{ mol}\cdot\text{L}^{-1}$, the etching selectivity ratio is increased from ~ 1 to ~ 30
 23 with an increase of FeCl_3 concentration from $0.1 \text{ mol}\cdot\text{L}^{-1}$ to $1.2 \text{ mol}\cdot\text{L}^{-1}$. With a concentration
 24 of $1.2 \text{ mol}\cdot\text{L}^{-1}$, the etching rates of the amorphous and crystallization phases are 3.0 and 0.1

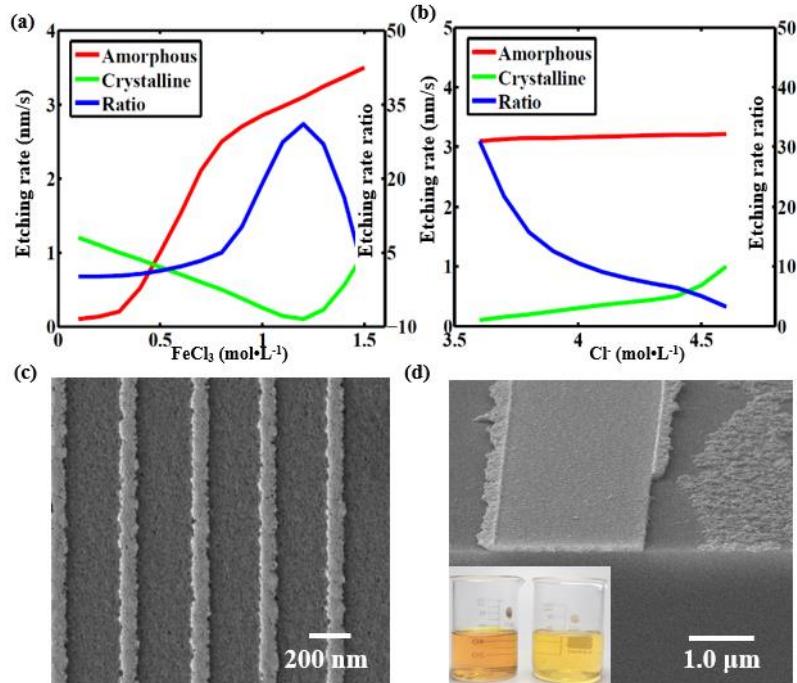
1 nm/s, respectively, which is corresponding to an etching selection ratio of ~30:1. This shows
2 that the AIST-LHR has an excellent etching selectivity.

3 During the developing process, it is critical to understand the effect of Cl⁻ ions on the
4 etching selectivity at different Fe³⁺ concentrations. The NaCl was selected to add into the
5 solution in order to adjust the concentration of Cl⁻ in the developer. Figure 4b shows the
6 obtained relationships among Cl⁻ concentration, etching selectivity ratio, and reaction rate at a
7 Fe³⁺ concentration of 1.2 mol·L⁻¹. Results show that with the increase of Cl⁻ concentration, the
8 etching selectivity ratio is gradually decreased, and the reaction rate is increased accordingly.

9 Whereas when the Cl⁻ concentration is further increased to 4.6 mol·L⁻¹, the selective corrosion
10 ratio is decreased to ~3:1. This is mainly because the further increase of Cl⁻ concentration
11 accelerates the pitting activation etching and depassivation of the crystalline region, along
12 with the increase of surface roughness (Figure 4c). Owing to the enhanced pitting effect of Cl⁻
13 ions on the film, excessive edge roughness of the obtained patterns can be observed.
14 Therefore, the concentration of Cl⁻ ions should be controlled as low as possible, in order to
15 minimize the edge roughness during the developing process.

16 Additionally, because of the existence of hydrolysis reactions of Fe³⁺, with the increase of
17 etching time, a large amount of Fe(OH)₃ precipitates are produced in the developing solution,
18 which affects the diffusion of Fe³⁺, thus causing a large amount of development defects
19 (Figure 5d). The color change (inset of Figure 5d) of FeCl₃ solutions (1.2 mol·L⁻¹) before and
20 after adding 0.1 mol·L⁻¹ HCl reveals that the solution is transformed from a turbid phase into
21 a clear one, which can effectively reduce the hydrolysis of Fe³⁺. Therefore, to improve the
22 stability of the development process, a mixed solution of 1.2 mol·L⁻¹ FeCl₃ and 0.1 mol·L⁻¹
23 HCl should be used to prevent the formation of impurity ions in this study. Besides the above
24 two key influencing factors (i.e., the concentration of FeCl₃ solution and the concentration of
25 Cl⁻), uniformity of development structure obtained at different duty cycles was also
26 investigated. The detailed results are shown in the SI (Figure S6-S9). The uniformity of

1 linewidth and depth can be well controlled by adding appropriate etching additives (e.g., di-
 2 hydroxyethyl water-solubility imidazoline) and surfactants (e.g., sodium dodecyl sulfate)
 3 during the electrochemical development.



4
 5 **Figure 5.** (a, b) The variation trend of etching rate amorphous and crystalline phases and
 6 selection ratio of with the concentration of Fe^{3+} and Cl^- , respectively; (c) SEM image with a
 7 sample size of 9 mm^2 of one obtained at Cl^- concentration of $4 \text{ mol} \cdot \text{L}^{-1}$ for understanding the
 8 effect of Cl^- on the roughness of line edges; (d) Effect of pH on surface morphology.

9 2.5. Demonstration for fabrication of an optical diffraction gratinga DOE

10 In this section, we will apply the electrochemical development strategy to demonstrate
 11 the fabrication of a ~~X-ray grating~~ DOE on the silica substrate, for diffractive optics
 12 applications. As shown in Figure 2d, the obtained feature size of the fabricated AIST-LHR on
 13 the silica is 80 nm and the pitch is 300 nm. Through the following etching process with SF_6
 14 and O_2 plasma, the structures are successfully transferred onto the silica. Figure 6a shows an
 15 image of the fabricated grating with a functional area of $\sim 120 \text{ mm} \times 100 \text{ mm}$. As
 16 demonstrated in Figure 6b, the grating lines have been etched with a depth of $\sim 500 \text{ nm}$.

17 The fabricated grating using the newly proposed electrochemical development strategy is
 18 characterized using X-rays. When the X-ray beam passes through this diffraction grating, it is

1 split up into a central bright beam plus a number of side beams. A detector was employed to
2 measure the beams intensity. With a beam energy of 10 keV and a record time of 0.1 s, we
3 randomly measured the intensity of the +1_{st} order beam and selected 6×6 points in the whole
4 device, in order to check the uniformity of the whole grating pattern. The obtained results are
5 shown in Figure 6c. The average +1_{st} order beam intensity distribution in each region is
6 ~4500, and the intensity of each region is quite consistent, revealing that the grating has a
7 good uniformity. Figures 6d-e show the diffraction results of one of the points and the
8 corresponding intensity distributions of -6_{th} to +6_{th} order beams (with a recording time of 1s
9 and sheltered 0th-order and part of 1st-order beams). The appearance of split beams with
10 different diffraction orders clearly demonstrates that the fabricated grating is effective in light
11 splitting.

12 Furthermore, the diffraction efficiencies of the fabricated grating were tested and the
13 obtained results are shown in Figure 6f. We calculated the theoretical diffraction efficiency
14 using the publicly available data from the Berkeley Laboratory Centre for X-ray optics
15 (<http://henke.lbl.gov/>). The calculated and measured results match well. All these results
16 clearly prove that the electrochemical development strategy is effective for preparation of
17 high-resolution optical device. However, we should address that the efficiency is still
18 relatively low, mainly due to the high absorption of X-rays by silica.

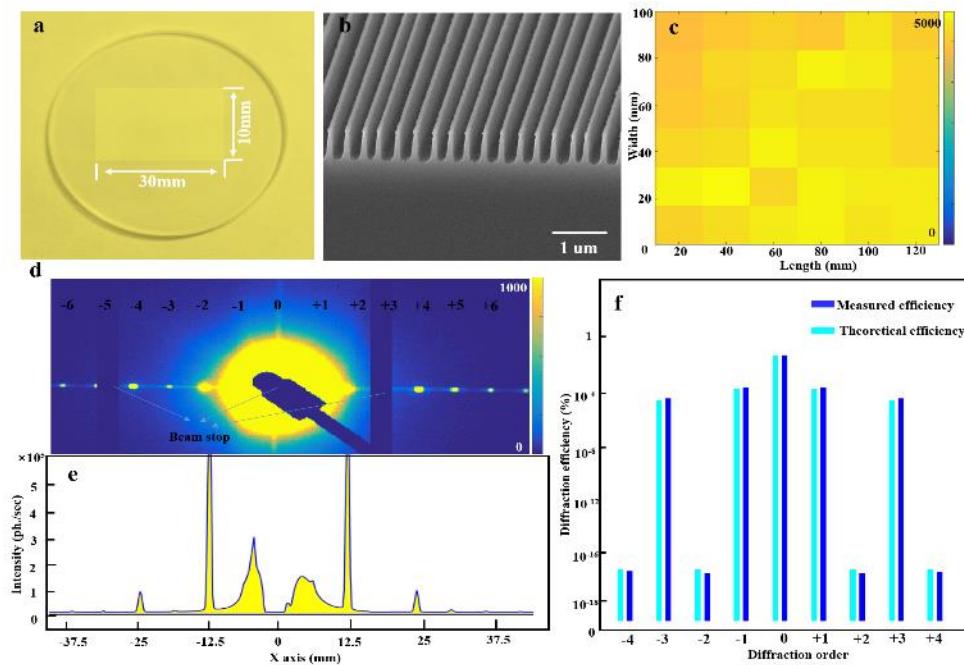


Figure 6. Results of fabricated grating DOE through electrochemical developed AIST-LHR. (a) Photograph of the fabricated grating on the silica substrate, (b) cross sectional SEM image of fabricated grating with the sample size of 30 mm×10mm, (c) 1st order beam intensity map of the grating measured with 10 keV X-rays, (d) detector spatial data showing the grating diffraction at a distance of 21 m downstream of the grating, (e) intensity line profile from the detector image across the grating diffraction orders up to the 6th, (f) Measured and theoretical diffraction efficiency of different diffraction order (-4th to +4th).

3. Conclusions

In summary, this work research a new electrochemical methodology to realize high-resolution and arbitrary patterns of AIST-LHR through the oxidation of Fe³⁺ ions with the assisted pitting activation etching using Cl⁻ ions in an acid medium. Using the optimized concentration of Fe³⁺ and Cl⁻ ions, an etching ratio of amorphous vs. crystalline regions up to ~30:1 can be achieved with a minimized feature size of ~41 nm. The inhomogeneity of development process, which is mainly caused by galvanic etching and surface hydrophilicity, can be effectively minimized by applying the additives and surfactants. An optical diffraction device A DOE of an X-ray grating is fabricated using the AIST-LHR, and show good uniformity and diffraction properties. Electrochemical development based on laser heat-mode lithography is an environment friendly method which produces large scale, uniform, high-resolution and arbitrary micro and nanostructures.

1 **4. Experimental procedures**

2 *Preparation of amorphous AIST-LHR:* An 80 nm thick AIST was deposited using a
3 magnetron sputtering system (JPG 560) on quartz glass (SiO_2 , 99.0%, Φ 30 mm, thickness: 1
4 mm) with an area of 9 cm^2 and a thickness of 1.3 mm. The obtained film was amorphous. The
5 background pressure of the deposition chamber was less than $6.0 \times 10^4 \text{ Pa}$, the sputtering
6 power was 40 W, and the working pressure was 0.8 Pa under an Ar atmosphere.

7 *Exposure and development:* A lithography system, using a laser beam to induce thermal
8 exposure in both vector and scalar modes, was used for patterning AIST-LHR. The
9 wavelength was 405 nm and the numerical aperture of the objective lens was 0.8. The
10 corresponding theoretical spot size was 0.62 μm . At room temperature and under the
11 atmospheric environment, the patterned sample was immersed in the developer solution for
12 development, after which the samples were washed with deionized water and dried with N_2 .

13 *Characterization:* Surface morphology of the structures was characterized using an atomic
14 force microscope (AFM, Veeco, Multi-mode V, America), SEM (Carl Zeiss, Zeiss Auriga,
15 Germany), TEM and high-resolution TEM (HRTEM, JEM-2100EX microscopy, Japan), and
16 an optical microscope (OM, Olympus, BX51, Japan). Crystalline structures of the materials
17 were evaluated using an XRD (PANalytical, Empyrean, Netherlands) with a $\text{Cu K}\alpha$ radiation
18 source ($\gamma=0.154056 \text{ nm}$). Element analysis was carried out using an energy disperse X-ray
19 spectroscopy (EDS, Oxford, TN5400, Britain) conducted at 15 keV. Elemental and chemical
20 binding structures were obtained using an XPS (Thermo Fisher Scientific, K-ALPHA,
21 America) with $\text{Al K}\alpha$ radiation with an energy of 1486.6 eV. Binding energies were calibrated
22 using the peak of the contaminate carbon ($\text{C } 1\text{s}=284.6 \text{ eV}$).

23 *Electrochemical experiment:* Electrochemical behavior of the AIST in the FeCl_3 solution was
24 studied using an electrical potentiometric polarization method with a CH1760E
25 electrochemical workstation. The reference electrode was a saturated calomel. The auxiliary
26 electrode was a platinum electrode. The experimental temperature was maintained at 25°C.

1 The sample was immersed in the FeCl_3 solution until the potential was stabilized. The
2 potential was scanned from the cathodic to the anodic with a scanning range of -0.2 to 0.2 V
3 and a scanning speed of 0.5 mV/s. The corrosion potential, E_{corr} , and the corrosion current
4 density, I_{corr} , were obtained by fitting the measured polarization curves using the Cview
5 software package. Under the applied potential of the electrode, the EIS data were obtained by
6 scanning from a high frequency of 10000 Hz to a low frequency (0.1 Hz) with a sinusoidal
7 voltage amplitude of 5 mV. The impedance spectrum data were fitted using the ZSimpWin
8 software package, and the electrode property was analyzed according to the equivalent circuit.

9 *Plasma Etching:* The pattern transfer from the AIST-HLR to the silica substrate was
10 performed using an RIE equipment (Plasma-Therm, Vision 322, America). The etching
11 parameters were 70 sccm SF_6 flow, 6 sccm O_2 flow, 250 W source power, 20 mTorr chamber
12 pressure, and 20 °C cooling temperature. It was etched for 10 min. After etching, the
13 proposed FeCl_3 developer was used to remove the residual AIST-HLR.

14 *Statistical Analysis:* An 80 nm thick AIST was deposited using a magnetron sputtering system
15 and the step profile was used to measure the thickness. The substrate was a quartz glass (SiO_2 ,
16 99.0%, $\Phi 30 \pm 1$ mm, thickness: 1 ± 0.1 mm) with a writing area of 9 cm^2 for all of samples.
17 Exposed AIST-LHRs was developed in the FeCl_3 solutions of 0.1, 0.3, 0.5, 0.8, 1.2 and 1.5
18 $\text{mol} \cdot \text{L}^{-1}$ for 30 seconds for electrical potentiometric polarization examinations. The XPS tests
19 were employed on the AIST-LHR's surfaces which were developed in the 0.5 and 1.2 $\text{mol} \cdot \text{L}^{-1}$
20 FeCl_3 solution for 30 seconds. The data of impedance spectra were fitted using the ZSimpWin
21 software package, and the electrode property was analyzed according to the equivalent circuit.

22 Supporting Information

23 Supporting information is available from the Wiley Online Library or from the author.

1 Acknowledgements

2 This work was partially supported by the National Natural Science Foundation of China (Nos.
3 61627826 and 22171212), Strategic High-Tech Innovation Fund of the Chinese Academy of
4 Sciences (GQRC-19-08), International Corporation Project of Shanghai Committee of
5 Science and Technology by China (21160710300), International Exchange Grant
6 (IEC/NSFC/201078) of Royal Society UK and NSFC. Author 1 (Zhengwei Wang) and
7 Author 2 (Guodong Chen) contributed equally to this work.

8 Conflicts of interest

9 The authors declare no conflict of interest.

Received: ((will be filled in by the editorial staff))

Revised: ((will be filled in by the editorial staff))

Published online: ((will be filled in by the editorial staff))

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- 20

1 **Caption**

2 **Figure 1.** Design and fabrication of high-resolution arbitrary micro/nano-structures: (a)
 3 exposure of arbitrary patterns with three-dimensional temperature distribution on the surface
 4 of AIST film and corresponding potential distribution; (b) electrochemical development
 5 process; (c) various arbitrary structures of AIST-LHR; (d) ~~optical diffraction grating~~ DOEs
 6 fabrication via plasma etching.

7 **Figure 2.** SEM images of various micro/nanostructures (9 mm^2 on the silica substrates). (a)
 8 produced from a conventional photoresist (S1805) with the developed gratings
 9 period/linewidth of $3 \mu\text{m}/1 \mu\text{m}$; (b) AIST-LHR patterns after electrochemical developing with
 10 gratings having period/linewidth of $2 \mu\text{m}/1 \mu\text{m}$; (c) $400 \text{ nm}/200 \text{ nm}$ features; and (d) 300
 11 $\text{nm}/80 \text{ nm}$ features; multi-functional meta-surfaces for optical structures including helical
 12 chiral (e), split-ring(f), hollow star-like(g), and three rotational symmetry(h) structures with
 13 the feature size of 41 nm ; arbitrary cross micro-/nanoscale various gear patterns (i), English (j)
 14 and Chinese characters (k).

15 **Figure 3.** (a, b) Polarization curves of amorphous and crystalline AIST-LHR with the size of
 16 9 mm^2 ; (c) Etching potential trends of amorphous and crystalline AIST-LHR with the sample
 17 size of 9 mm^2 ; (d, e) Impedance spectrum curves of amorphous and crystalline AIST-LHR
 18 with the sample size of 9 mm^2 ; (f) Fitted circuit diagram; SEM images with the sample size of
 19 9 mm^2 obtained at $0.5 \text{ mol}\cdot\text{L}^{-1} \text{ FeCl}_3$ for 60 s (g), of $1.2 \text{ mol}\cdot\text{L}^{-1} \text{ FeCl}_3$ for 10 s (h) and 30 s (i),
 20 respectively.

21 **Figure 4.** XPS analysis of amorphous developed, amorphous undeveloped, crystalline
 22 developed and crystalline undeveloped samples with the size of 9 mm^2 . The results of Ag 3d
 23 (a, b), In 3d (c, d), Sb 3d (e, f), and Te 3d (g, h) are obtained at 0.5 (left) and $1.2 \text{ mol}\cdot\text{L}^{-1}$
 24 (right), respectively.

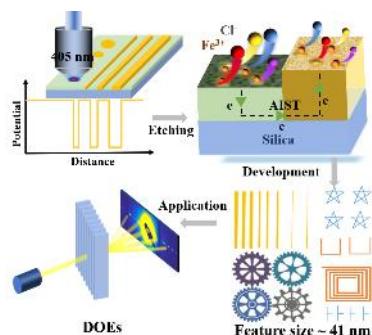
25 **Figure 5.** (a, b) The variation trend of etching rate amorphous and crystalline phases and
 26 selection ratio of with the concentration of Fe^{3+} and Cl^- , respectively; (c) SEM image with a
 27 sample size of 9 mm^2 of one obtained at Cl^- concentration of $4 \text{ mol}\cdot\text{L}^{-1}$ for understanding the
 28 effect of Cl^- on the roughness of line edges; (d) Effect of pH on surface morphology.

29 **Figure 6.** Results of fabricated ~~grating~~ DOE through electrochemical developed AIST-LHR.
 30 (a) Photograph of the fabricated grating on the silica substrate, (b) cross sectional SEM image
 31 of fabricated grating with the sample size of $30 \text{ mm}\times10\text{mm}$, (c) 1st order beam intensity map
 32 of the grating measured with 10 keV X-rays, (d) detector spatial data showing the grating
 33 diffraction at a distance of 21 m downstream of the grating, (e) intensity line profile from the

- 1 detector image across the grating diffraction orders up to the 6th, (f) Measured and theoretical
- 2 diffraction efficiency of different diffraction order (-4th to +4th).
- 3

The tables of contents entry

- 1
2
3 Electrochemical strategy for high-resolution nanostructures in laser-heat-mode resist toward
4 next generation diffractive optics-diffractive optical elements
5 *Zhengwei Wang, Guodong Chen, Ming Wen*, Xutao Hu, Xing Liu, Jingsong Wei*, Qingsheng*
6 *Wu, YongQing Fu*
7
8 Based on AgInSbTe laser heat-mode resist, an environmental friendly and homogeneous
9 electrochemical strategy has been explored for high throughput lithography of high-resolution
10 diffractive optical elements.



11

1 **Highlights:**

- 2 ● An environmental friendly electrochemical strategy performed on AgInSbTe laser heat-
- 3 mode resist for high-resolution and arbitrary pattern lithography
- 4 ● The minimum feature sizes of lithography structure can reach to 41nm.
- 5 ● Electrochemical development mechanism by the oxidization of Fe^{3+} with the assisted
- 6 pitting activation of Cl^- was systematically studied.
- 7 ● ~~Optical diffraction devices~~ Diffractive optical elements such as an X-ray grating were
- 8 fabricated using the AIST-LHR, and showed good uniformity and diffraction properties.
- 9