Ultrasonics - Sonochemistry 40 (2018) 937–943

Contents lists available at ScienceDirect

Ultrasonics - Sonochemistry

journal homepage: www.elsevier.com/locate/ultson

The effect of ultrasonic vibration and surfactant additive on fabrication of 53.5 gr/mm silicon echelle grating with low surface roughness in alkaline KOH solution

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ARTICLE INFO

Keywords:
Surface roughness
Silicon echelle grating
Ultrasonic agitation
Surfactant additive

ABSTRACT

In the silicon echelle grating fabrication process, the “pseudo-mask” formed by the hydrogen bubbles generated during the etching process is the reason causing high surface roughness and poor surface quality of blazed plane. Based upon the ultrasonic mechanical effect and contact angle reduced by surfactant additive, ultrasonic vibration, isopropyl alcohol (IPA) and 2,4,7,9-Tetramethyl-5-decyne-4,7-diol (TMDD) were used to improve surface quality of 53.5 gr/mm echelle grating. The surface roughness R_q is smaller than 18 nm, 7 nm and 2 nm when using ultrasonic vibration, IPA and TMDD respectively. The surface roughness R_q is smaller than 5 nm and 1.5 nm respectively when combining ultrasonic vibration with IPA and TMDD. The experimental results indicated that the combination of ultrasonic agitation and surfactant additive (IPA & TMDD) could obtain a lower surface roughness of blazed plane in silicon echelle grating fabrication process.

1. Introduction

Based upon the characters including wide spectrum range, high dispersive power, high resolution ratio and full wave blazing, the 53.5 gr/mm echelle grating [1,2] has been becoming the ideal spectral component using in the optical spectrum instrument. During the fabrication of echelle grating using traditional mechanical scratching method, the trend of rebound of metal having characters including elasticity and plasticity could cause incomplete grating groove because of the deep groove depth (about 10 μm), which could cause high surface roughness of blazed plane, more groove defects and high scattering level. The anisotropy of silicon presented in alkaline solution made the silicon anisotropy wet etching technique become a new method to fabricate grating [3–7]. It is also an ideal method to fabricate 53.5 gr/mm echelle grating because of adventures including ensuring integrity of grating groove and easily obtaining lower surface roughness of blazed plane of echelle grating by strictly controlling wet etching conditions.

In the process of the chemical reaction between the silicon and KOH solution, the hydrogen bubbles generated during the etching process logged on the etched surface to form the ‘pseudo-mask’ phenomenon [8–10], which will obstruct the chemical reaction between the etchant and the silicon atoms at the surface and increase surface roughness of grating. The surface roughness of grating can cause the scattering of incident light [11,12], so how to decrease the surface roughness of grating is an important problem to the grating maker. Generally, introduction of ultrasonic vibration could improve the surface quality of etching surface of Si⟨1 0 0⟩ and Si⟨1 1 0⟩ [13–15], and in another way, the surface roughness of silicon crystal plane could be decreased by different kinds of surfactant additive [16,17]. IPA could improve the surface quality of Si ⟨1 0 0⟩ crystal plane and reduce the lateral erosion of convex corner [18], and TMDD could improve the surface quality of Si ⟨1 1 0⟩ crystal plane [19]. Jiao [20] found that both ultrasonic vibration and surfactant additive could reduce the surface roughness of Si ⟨1 1 1⟩ crystal plane, and combining the ultrasonic agitation and IPA concentration could obtain a lower surface roughness of Si ⟨1 1 1⟩ crystal plane in silicon wet etching process.

The research results mentioned above about the relationship among ultrasonic vibration, surfactant additive and silicon crystal plane including Si ⟨1 0 0⟩, Si ⟨1 1 0⟩ and Si ⟨1 1 1⟩ cannot be practiced in the fabrication of 53.5 gr/mm echelle grating whose blazed plane is Si ⟨1 1 1⟩ using silicon wet etching process. Based upon the situation, in the present paper, we discuss the relationship among ultrasonic vibration, IPA, TMDD and surface roughness of blazed plane of 53.5 gr/mm echelle grating. The purpose of this work is to achieve high quality 53.5 gr/mm echelle grating with smoother, “mirror-like” surface.

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http://dx.doi.org/10.1016/j.ultsonch.2017.09.011
Received 14 July 2017; Received in revised form 6 September 2017; Accepted 6 September 2017
Available online 07 September 2017
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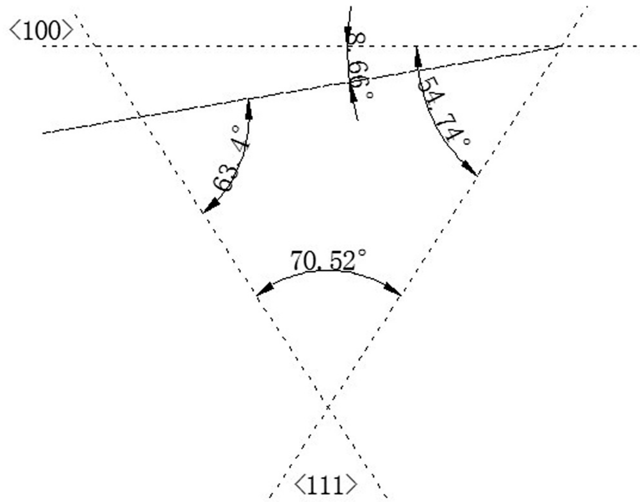

Fig. 1. Relationship between silicon crystal planes and blazed angle.

2. Experimental procedure

The line density of echelle grating fabricated in experiment is 53.5 gr/mm. According to the design result of grating perimeter, the diffractive efficiency of grating in blazed wavelength of 532 nm meets the practical requirement under the condition of Littrow incidence when the blazed angle of grating is 63.4°. The relationship between silicon crystal planes and blaze angle is shown in Fig. 1. The dotted line part in figure shows the relative position between Si⟨1 1 1⟩ crystal plane and Si⟨1 0 0⟩ crystal plane. According to the theoretical design, the blazed angle is 63.4° when the silicon wafer was cut by the angle of 8.66° routed around the Si⟨1 0 0⟩ crystal plane. The relative position between cut surface and Si⟨1 0 0⟩ crystal plane is shown as the solid line part.

The sketch showing process flow diagram of silicon echelle grating fabrication is shown in Fig. 2. The ⟨1 0 0⟩ silicon wafer made by China Electronics Technology Group Corporation No.46 Research Institute was high-purity float zone silicon whose diameter, thickness and resistivity were 76.2 mm, 500 μm and 2000 Ω cm respectively, which is shown as process (a). As shown in process (b), after fabricating silicon wafer, a SiO_2 layer with thickness of 150 nm was deposed on silicon wafer using thermal growth. Silicon with SiO_2 layer was cleaned in accordance with the order of the toluene, acetone, alcohol and water, and then photoresist whose model was BP212-7S was coated with spin coating. The spin speed, coating time and photoresist thickness was 3000 rpm, 30 s and 600 nm respectively. The silicon wafer was harden into the oven after coating with hardening temperature of 90 °C and hardening time of 20 min, which is shown as process (c). Through fan-shaped mask exposing, developing and SiO_2 wet etching, the Fan-shaped SiO_2 mask was obtained on the silicon wafer during process (d) and (e). In order to improve the alignment accuracy, rectangles on the mask have been distributed in the range of ± 1.95° separated by 0.05° [21]. In the process (f), the silicon with the Fan-shaped SiO_2 mask was etched in KOH solution to fix the crystal orientation. When the etching finished, the grooves were measured by SEM to find out the rectangle which is the closest to the crystal orientation. After fixing crystal orientation during process (f), the silicon was cleaned and the photoresist was spin again, which were shown in process (g). After spinning photoresist, we fabricated the echelle grating SiO_2 mask according to the order of “exposure-development- SiO2 etching [22,23]”, which were shown from process (h) to (i). After fabricating the echelle grating SiO_2 mask, echelle grating was fabricated in KOH solution (with ultrasonic vibration or/and surfactant additive) during process (j).

During process (j), the samples were etched in an ultrasonic bath, and the temperature was 30 °C and was controlled with an accuracy of ± 0.2 °C. The concentration of KOH solution is 50 wt%. In order to keep solution concentration uniform, the condenser pipe is added during the wet etching process. Ultrasonic with different frequency and power, IPA and TMDD with different concentration were introduced in the experiment process. For the convenience of discussion, a parameter named ultrasound intensity is defined, which is the ratio of ultrasound intensity divided by volume of the liquid. The range of ultrasonic frequency and ultrasound intensity is 20 kHz-100 kHz and 10 W/L-100 W/L respectively, the concentrations of IPA are 5 vt%, 10 vt%, 15 vt% and 20 vt%, and the concentrations of TMDD are 0.2 wt%, 0.4 wt%, 0.6 wt %, 0.8 wt% and 1.0 wt%. Firstly, the effect of ultrasonic vibration, IPA

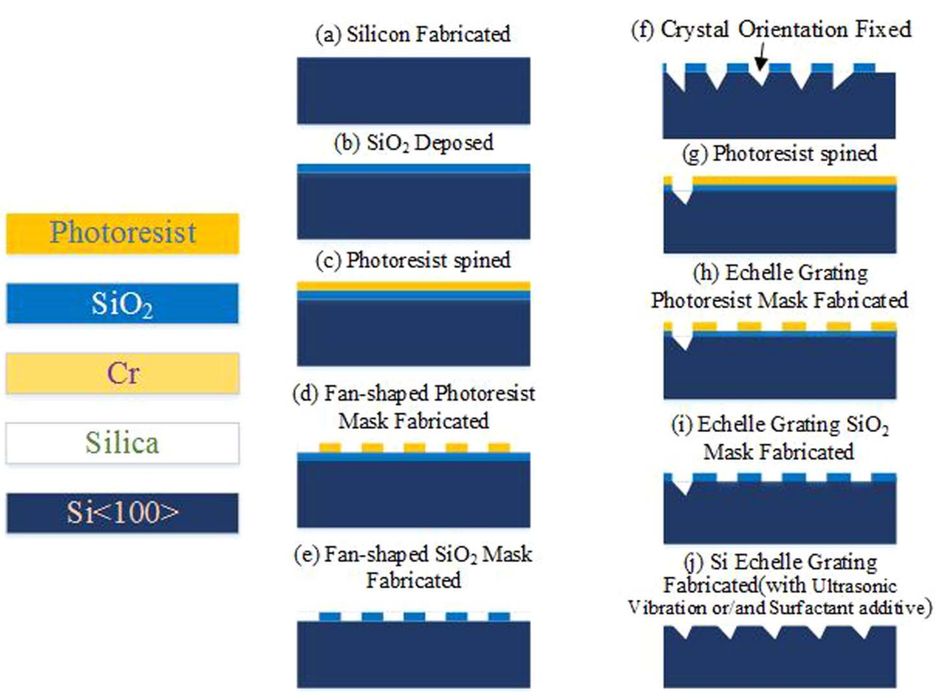

Fig. 2. The sketch showing process flow diagram of silicon echelle grating fabrication.

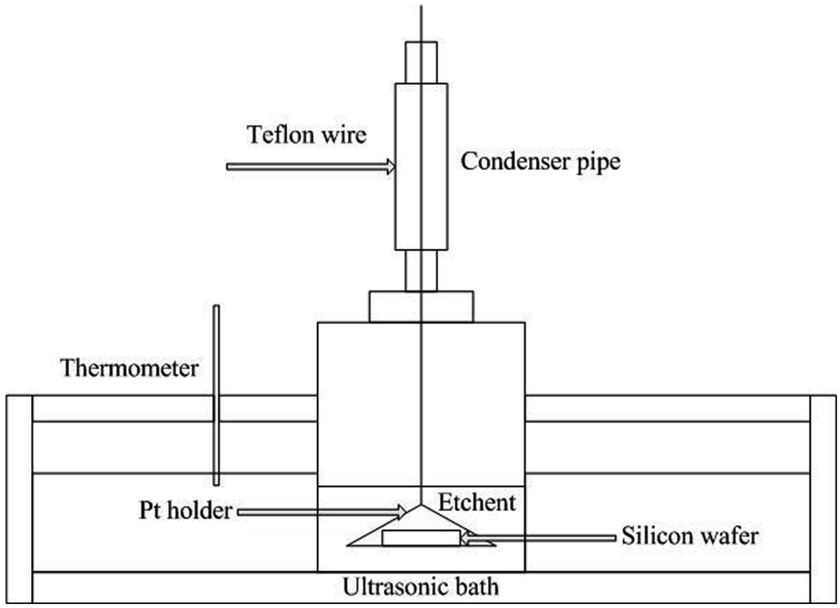

Fig. 3. The sketch showing experimental equipment in silicon echelle grating fabrication process.

Table 1
Measurement results of surface roughness on blazed plane of 53.5 gr/mm echelle grating under conditions with ultrasonic vibration and without ultrasonic vibration.

Ultrasonic frequency (kHz)	Ultrasound intensity (W/L)	Measured Surface roughness R_q(nm)(x_i)	$\bar{x}$	v_i	$\sigma_{\bar{x}}$	σ	$3\sigma_{\bar{x}}$	Surface roughness R_q(nm)
20	50	15.33 15.32 15.28 15.26 15.35	15.31	0.02 0.01 -0.03 -0.05 0.04	± 0.037	± 0.017	± 0.05	15.30 ± 0.05
40	50	13.10 13.12 13.08 13.16 13.09	13.11	-0.01 0.01 -0.03 0.05 -0.02	± 0.032	± 0.014	± 0.04	13.11 ± 0.04
60	50	11.22 11.19 11.21 11.18 11.23	11.21	0.01 -0.02 0 -0.03 0.02	± 0.021	± 0.009	± 0.03	11.21 ± 0.03
80	50	9.22 9.26 9.19 9.24 9.20	9.22	0 0.04 -0.03 0.02 -0.02	± 0.029	± 0.013	± 0.04	9.22 ± 0.04
100	50	7.13 7.11 7.14 7.10 7.09	7.11	0.02 0 0.03 -0.01 -0.02	± 0.020	± 0.009	± 0.03	7.11 ± 0.03
0	0	41.51 41.46 41.52 41.48 41.45	41.48	0.03 -0.02 0.04 0 -0.03	± 0.031	± 0.014	± 0.04	41.48 ± 0.04

and TMDD on the surface roughness of blazed grating was discussed respectively, which means that the ultrasound was not used during discussing the effect of concentration of IPA and TMDD on surface roughness of blazed plane of echelle grating. And then, the effect of IPA and TMDD (with ultrasonic vibration) was also discussed respectively. The roughness of blazed plane of silicon echelle grating was inspected with the AFM whose model is “Dimension Icon”. The morphology of grating was inspected with the SEM whose model is “JFM-6700F”. The surface tension γ and contact angle θ of 50 wt% KOH solution with different concentrations of surfactant additive was measured using

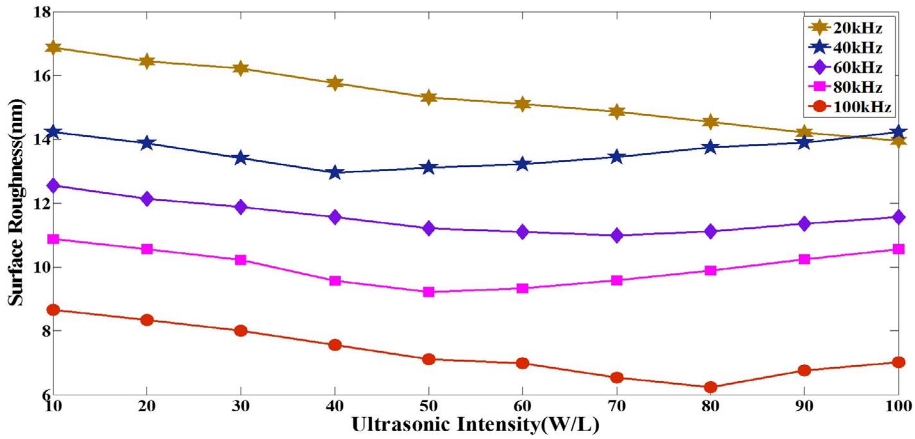

Fig. 4. The sketch showing relationship between surface roughness and ultrasound intensity.

Table 2
Measurement results of surface roughness on blazed plane of 53.5 gr/mm echelle grating under conditions with different concentrations of IPA and TMDD (without ultrasonic vibration).

Concentration of surfactant additive	Measured Surface roughness R_q(nm)			Surface roughness R_q(nm)
	1	2	3	
5 vt%IPA	6.38	6.32	6.34	6.35 ± 0.05
10 vt%IPA	6.09	6.04	6.06	6.05 ± 0.05
15 vt%IPA	5.74	5.79	5.72	5.74 ± 0.07
20 vt%IPA	5.56	5.49	5.54	5.53 ± 0.06
0.2 wt%TMDD	1.64	1.61	1.62	1.62 ± 0.03
0.4 wt%TMDD	1.23	1.25	1.19	1.22 ± 0.05
0.6 wt%TMDD	1.06	1.05	0.99	1.03 ± 0.06
0.8 wt%TMDD	0.89	0.91	0.84	0.86 ± 0.08
1.0 wt%TMDD	0.52	0.49	0.51	0.51 ± 0.03

surface tensiometer modeled by BZY-201 and the optical contact angle measurement instrument modeled by DSA 20. Fig. 3 is the sketch showing experimental equipment in silicon wet etching process.

3. Result and discussion

3.1. The effect of ultrasonic frequency on surface roughness of blazed plane of echelle grating

The surface roughness of five gratings under conditions with ultrasonic agitation and without ultrasonic agitation were measured by using AFM, where the ultrasound intensity is equal to 50 W/L, and the measurement range is about 5 μm × 5 μm and the ultrasonic frequency is 20 kHz, 40 kHz, 60 kHz, 80 kHz, and 100 kHz respectively. It can be seen from the measured results shown in Table 1 that the surface roughness of blazed plane of echelle grating decreases with the increasing of ultrasonic frequency and the surface roughness of blazed plane with different ultrasonic frequencies are all less than that without ultrasonic agitation. During the reaction process between silicon wafer and KOH solution, the hydrogen bubbles generated will log on the etched surface to form the 'pseudo-mask' phenomenon, which will obstruct the chemical reaction between the etchant and the silicon atoms at the surface and increase surface roughness of blazed plane of grating. The aim of introducing ultrasound is to shock the hydrogen bubbles on the basis of the mechanical effects of it, which will decrease the duration for which the hydrogen bubbles are attached to the etched surface, and then improve the roughness quality. It can be seen that the decreasing ability of surface roughness increases with the increasing mechanical effect of ultrasound.

3.2. The effect of ultrasound intensity on surface roughness of Si (1 1 1) crystal plane

The relationship between ultrasonic intensity and surface roughness of blazed plane of 53.5 gr/mm echelle grating on the basis of different ultrasonic frequencies is shown in Fig. 4. The surface roughness of blazed plane decreases with the increasing ultrasonic intensity when the frequency is 20 kHz, and the surface roughness of blazed plane decreases with the increasing ultrasonic intensity firstly and then increases with the increasing ultrasonic intensity when ultrasonic frequency range is 40 kHz–100 kHz. There was no maximum ultrasonic intensity observed when operating at 20 kHz, which was similar with the phenomena found by Hagenson [24], and the maximum ultrasonic intensity all existed in the curves when ultrasonic frequency range is 40 kHz–100 kHz. A possible explanation for the observed decrease at high powers is the formation of a dense cloud of cavitation bubbles near

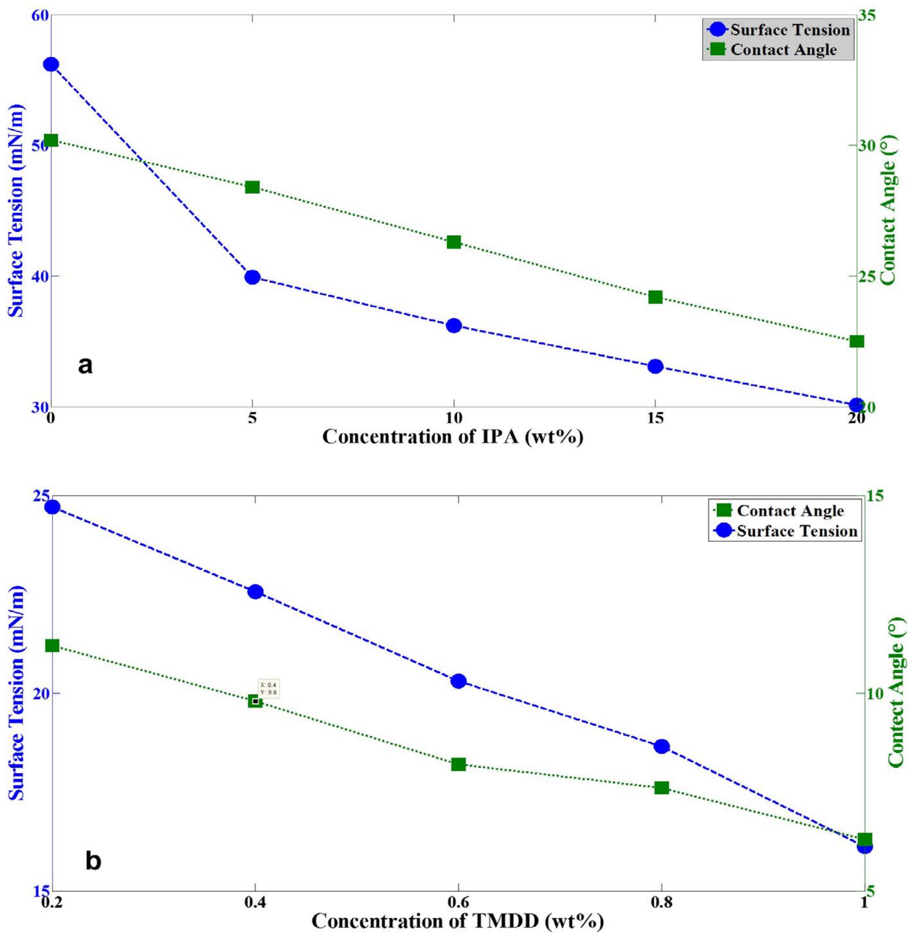

Fig. 5. The measured results of surface tension and contact angle under the conditionswith IPA and TMDD with different concentration.

the probe tip which acts to block the energy transmitted from the probe to the fluid [25], and the optimum power level is also dependent on the operating frequency[26]。

3.3. The effect of concentration of surfactant additive on surface roughness of blazed plane of echelle grating (without ultrasonic vibration)

The surface roughness of gratings under conditions with IPA (5 vt%, 10 vt%, 15 vt% and 20 vt%) and TMDD (0.2 wt%, 0.4 wt%, 0.6 wt%, 0.8 wt% and 1.0 wt%) were measured by AFM and the measurement range is 5 μm × 5 μm. It can be seen from the measured results shown in Table 2 that the surface roughness of blazed plane of echelle grating decreases with the increasing concentration of surfactant additive. During the grating fabrication process, the surface tension between gas-liquid interface is so big that it could cause big contact angle between H_2 bubble and silicon, which could make poor surface quality of grating. The introduction of surfactant additive could reduce the surface tension between gas-liquid interfaces, adhesive power of H_2 bubble to the silicon surface and contact angle between H_2 bubble and silicon, and further make grating surface quality better. The measured results of surface tension and contact angle under the conditions with IPA and TMDD with different concentration were shown in Fig. 5(a) and (b) respectively. It can be seen that the surface tension and contact angle of KOH solution with surfactant additive decrease with the increasing concentration of surfactant additive, and the surface tension and the contact angle with TMDD were smaller than that with IPA.

3.4. The effect of concentration of surfactant additive on surface roughness of blazed plane of echelle grating (with ultrasonic vibration)

The surface roughness of gratings under conditions of IPA & TMDD with ultrasonic vibration (the ultrasonic frequencies, the ultrasonic intensity and concentration of IPA & TMDD were the same as Sections 3.1–3.3) were measured by AFM and the measurement range is 5 μm × 5 μm. It can be seen from the measured results shown in Fig. 6(a) and (b) that the combination ultrasonic vibration and surfactant additive (IPA & TMDD) could further reduce the surface roughness of blazed plane compared with conditions of surfactant additive (IPA & TMDD) only. Because the maximum ultrasonic intensity all existed in the curves when ultrasonic frequency range is 40 kHz–100 kHz (discussed in Section 3.2), so the maximum effect will be existed in the curves when combining ultrasound and IPA & TMDD. During the fabrication process of echelle grating, the surfactant additive (IPA & TMDD) could make the surface tension between hydrogen bubbles and etchant decreasing, reduce contact angle between hydrogen bubbles and silicon surface and further accelerate bubble detaching from silicon surface. And then, the ultrasonic field could cause acoustic streaming [27] which could redistribute the etchant velocity between

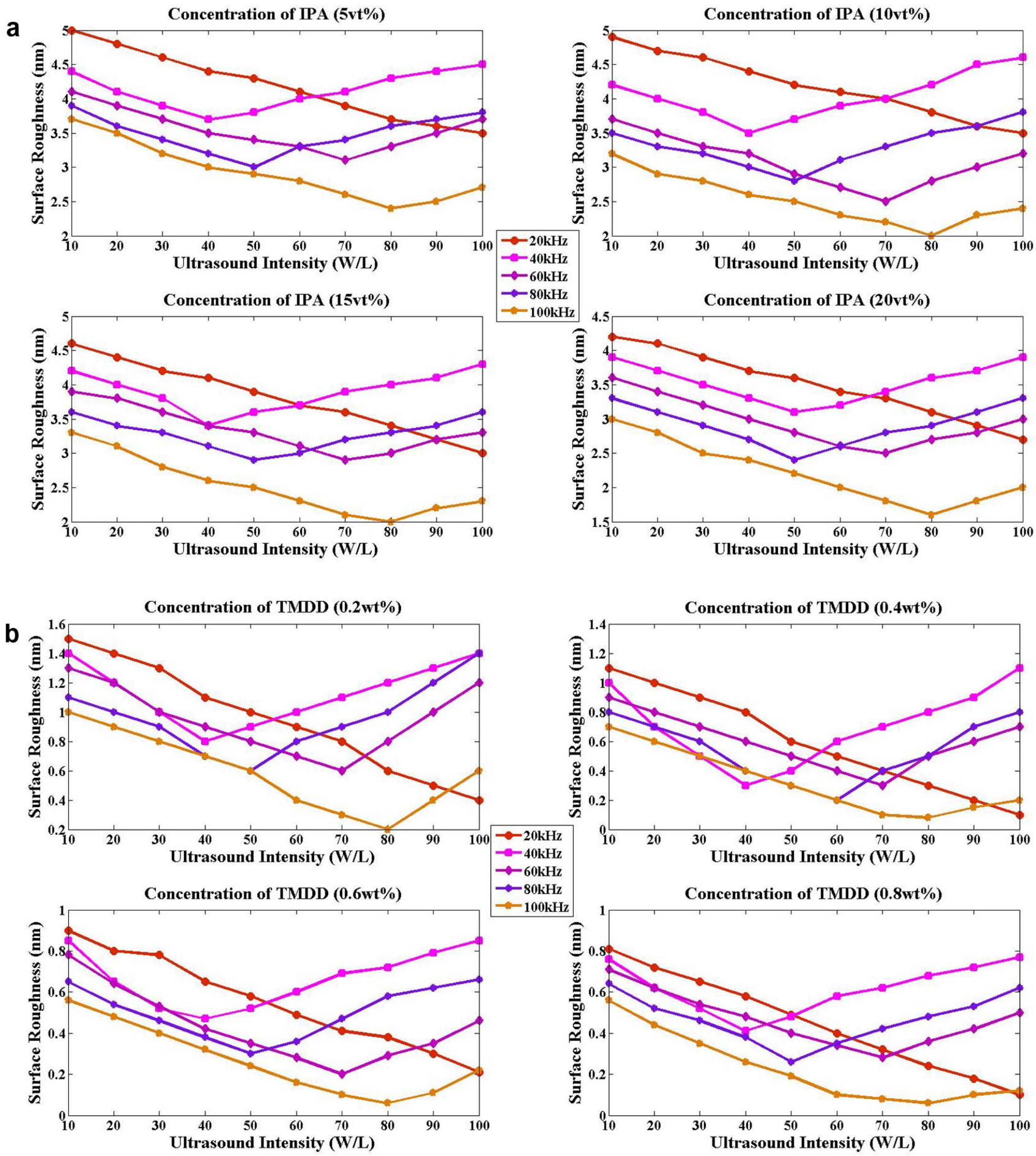

Fig. 6. The sketch showing relationship between surface roughness and concentration of surfactant additive with ultrasonic vibration.

etchant and silicon surface, and offer extra volume force [28] to hydrogen bubbles. During the reaction process, the hydrogen bubbles are affected by buoyancy of etchant and volume force at the same time, which may accelerate bubble detaching speed of bubbles and further improve the surface quality of blazed plane of echelle grating. Compared with results shown in Fig. 6, the surface quality of 53.5 gr/mm echelle grating would be better with the process route using "Ultrasound + TMDD" method. The SEM chart of 53.5 gr/mm echelle grating was shown in Fig. 7.

4. Conclusion

The effect of essential factors including ultrasonic frequencies and ultrasonic intensity, different kinds of surfactant additive on the surface roughness of blazed plane of 53.5 gr/mm echelle grating have been investigated. The experimental results indicate that: (a) the surface roughness of blazed plane decreases with the increasing of ultrasonic frequencies under the same ultrasound intensity, (b) the surface roughness of blazed plane decreases with the increasing ultrasonic intensity and there was no maximum ultrasonic intensity observed when operating at 20 kHz, (c) the surface roughness of blazed plane decreases with the increasing ultrasonic intensity firstly and then increases with the increasing ultrasonic intensity and the maximum ultrasonic intensity all existed in the curves when ultrasonic frequency range is 40 kHz–100 kHz, (d) the surface roughness of blazed plane of echelle grating decreases with the increasing concentration of surfactant additive. (e) the combination ultrasonic vibration and surfactant additive (IPA & TMDD) could further reduce the surface roughness of blazed plane compared with conditions of surfactant additive (IPA & TMDD) only.

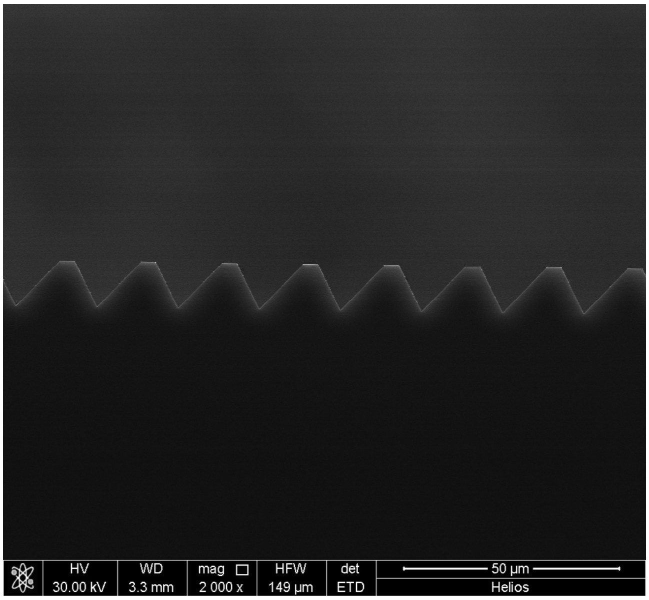

Fig. 7. The SEM chart of 53.5 gr/mm echelle grating.

Acknowledgment

This work is supported by the National Youth Science Fund of China (61605197).

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