Chemical Physics 529 (2020) 110397

Contents lists available at ScienceDirect

Chemical Physics

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

# The effects of TMDD-PA concentration on roughness of Si ⟨1 1 0⟩ and etching rate ratio of Si ⟨1 1 0⟩/⟨1 1 1⟩ in alkaline KOH solution

Chunlin Zhu[a,b], Qingbin Jiao[a], Xin Tan[a], Hao Hu[a,b], Bayanheshig[a,*]

[a] Changchun Institute of Optics, Fine Mechanics and Physics, Chinese Academy of Sciences, Changchun, Jilin 130033, China
[b] University of Chinese Academy of Sciences, Beijing 100049, China

ARTICLE INFO

*Keywords:*
Wet etching
Surface roughness
Etching rate ratio
Surfactant additive

ABSTRACT

High aspect ratio gratings (HARG) can be obtained by anisotropic etching of Si ⟨1 1 0⟩/⟨1 1 1⟩. Usually isopropyl alcohol (IPA) is added to the solution in order to smooth Si ⟨1 1 0⟩ surface. However, the addition of IPA can reduce the etching rate ratio of Si ⟨1 1 0⟩/⟨1 1 1⟩, which leads to a reduction of grating's aspect ratio. The effects of another additive TMDD-PA (TMDD: IPA = 1: 1 in wt%) were discussed. The experimental data indicates that TMDD-PA behaves better than IPA when smoothing Si ⟨1 1 0⟩ surface, and etching rate ratio of Si ⟨1 1 0⟩/⟨1 1 1⟩ increases with the increasing concentration of TMDD-PA. Mechanism of IPA and TMDD-PA in etching were analyzed. Molecules of IPA and TMDD behave differently on Si surfaces, and they have different impacts on $H_2O$ molecules.

## 1. Introduction

Compared with conventional X-ray radiographic absorption imaging, X-ray phase contrast tomography (XPCT) has higher sensitivity, thus becomes a trend in technology revolution of clinical medicine, non-destructive testing and material science [1]. Making use of Au deposited in Si HARG to absorb X-ray is the basic method of promoting sensitivity [2]. The higher aspect ratio of Au structure, the higher sensitivity XPCT has. Therefore, how to improve aspect ratio of Si grating thus improving aspect ratio of Au structure has become a key problem in researching of XPCT.

Nowadays anisotropic etching has become an ideal way to fabricate Si HARG [3]. By optimizing reaction temperature and KOH concentration, one can reach an etching rate ratio of $V_{\langle 1\,1\,0\rangle}/V_{\langle 1\,1\,1\rangle} = 300$ [4]. When Si is etched in KOH, a 'pseudo-mask' would log on the etched surface which will obstruct the chemical reaction and lower the grating uniformity and raise surface roughness [5]. Introducing additives can lift grating uniformity and smooth surface [6]. Among the additives, IPA has been widely researched and used [7], while the addition of IPA leads to a reduction of etching rate ratio of Si ⟨1 1 0⟩/⟨1 1 1⟩ [8]. Experimental data show that TMDD-PA can reduce Si ⟨1 1 0⟩ roughness, meanwhile maintain a high etching rate ratio of Si ⟨1 1 0⟩/⟨1 1 1⟩ [9]. However, the quantitative relation between TMDD-PA concentration and etching rate ratio of Si ⟨1 1 0⟩/⟨1 1 1⟩ and Si ⟨1 1 0⟩ roughness still remains unclear. Therefore, a quantitative analysis of how TMDD-PA concentration impacting on etching rate ratio of Si ⟨1 1 0⟩/⟨1 1 1⟩ and Si ⟨1 1 0⟩ roughness should be researched, which is important to the fabrication of Si HARG.

In this work, the effects of TMDD-PA and IPA of low concentration on roughness of Si ⟨1 1 0⟩ and etching rate ratio of Si ⟨1 1 0⟩/⟨1 1 1⟩ were discussed. Mechanism of IPA and TMDD-PA in etching were analyzed. The role of TMDD molecule and IPA molecule play in etching were compared. Process parameters of reaching high etching rate ratio meanwhile reducing roughness were obtained, which can provide guidance on fabricating Si HARG.

## 2. Experimental

The silicon wafer used in our experiment is 4 inch in diameter and 500 ± 10 µm in thickness with a resistivity of 1–10 Ω cm, and a $SiO_2$ layer with a thickness of 300 nm is deposed on silicon wafer using the thermal growth method. A BP212-7CP photoresist layer is spread on the $SiO_2$ layer, and exposed under a 40 µm period silica mask. After development, the $SiO_2$ layer is etched using the BHF method. The wafers were then etched in different solutions.

The solutions were 50 wt% KOH added TMDD-PA and IPA with different concentrations. The temperature was 21 ± 0.2 °C. To make convenience for calculating etching rate of Si ⟨1 1 0⟩ and Si ⟨1 1 1⟩, the etching time was set to 15 h & 45 min. Since the saturation concentration of TMDD-PA was 1 wt%, for the convenience of discussing

* Corresponding author.
*E-mail address:* bayin888@sina.com (Bayanheshig).

https://doi.org/10.1016/j.chemphys.2019.110397
Received 23 February 2019; Received in revised form 11 May 2019; Accepted 4 June 2019
Available online 05 June 2019

relationship between TMDD-PA and IPA, the additive concentrations were set to 0.2 wt% IPA, 0.4 wt% IPA, 0.6 wt% IPA, 0.8 wt% IPA, 1.0 wt % IPA, 0.2 wt% TMDD-PA, 0.4 wt% TMDD-PA, 0.6 wt% TMDD-PA, 0.8 wt% TMDD-PA, 1.0 wt% TMDD-PA. The etching depth of Si ⟨1 1 0⟩ and Si ⟨1 1 1⟩ was measured using SEM, which would be divided by etching time to calculate etching rate $V_{\langle 1 1 0\rangle}$ and $V_{\langle 1 1 1\rangle}$. The ratio of $V_{\langle 1 1 0\rangle}$ and $V_{\langle 1 1 1\rangle}$ is the etching rate ratio of Si ⟨1 1 0⟩/⟨1 1 1⟩. The roughness of Si ⟨1 1 0⟩ was measure using AFM.

## 3. Results and discussion

### *3.1. The effect of TMDD-PA on Si ⟨1 1 0⟩ surface roughness*

Fig. 1 shows the Si ⟨1 1 0⟩ roughness under different additive concentrations. When additive concentration increases, Si ⟨1 1 0⟩ roughness decreases gradually. Si ⟨1 1 0⟩ roughness added IPA decreases slower than TMDD-PA, which means the effect of IPA concentration on Si ⟨1 1 0⟩ roughness is weaker. Fig. 1 also shows that TMDD-PA behaves better than IPA under all concentrations studied.

The decrease of Si ⟨1 1 0⟩ roughness is due to the absorption of additive molecules on reaction surface, which slows down the etching rate [10]. Different Si surfaces and different additives have different effects on the decreasing of roughness [11 8]. On Si ⟨1 1 0⟩ surfaces, when additive molecules have longer C-chains, fewer hydroxyl groups and higher non-polarity effect of alkyl groups, the etching rate is slower [12]. TMDD has one more hydroxyl group than IPA, while its C-chain is longer than IPA. When an additive molecule is absorbed on the surface, its C-chains are toward Si surface and hydroxyl groups toward water [12], which means C-chain has a main effect in absorption. Thus the

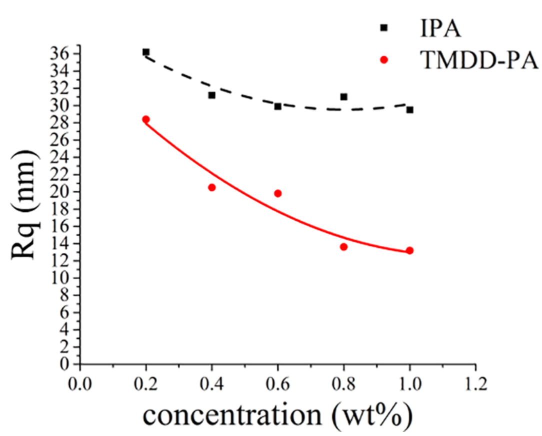


**Fig. 1.** Roughness(Rq) of Si ⟨1 1 0⟩ in 50 wt% KOH with different concentrations of IPA and TMDD-PA.

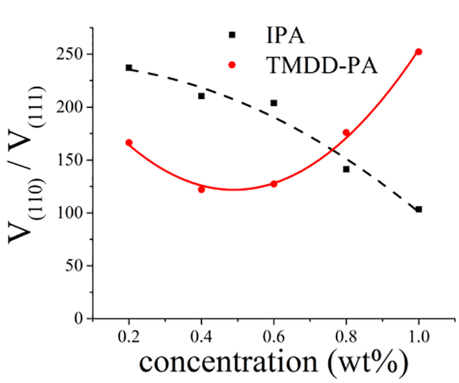


**Fig. 2.** Etching rate ratios of Si ⟨1 1 0⟩/⟨1 1 1⟩ in 50 wt% KOH with different concentrations of IPA and TMDD-PA.

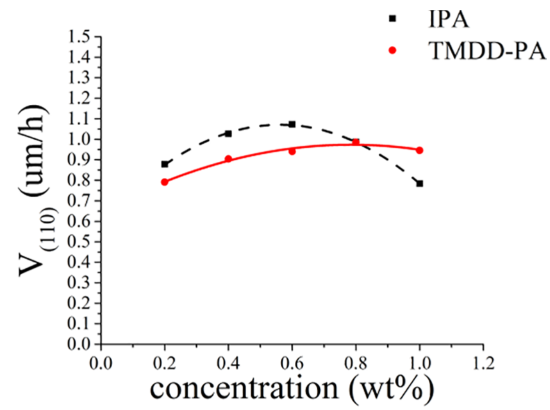


**Fig. 3.** Etching rates of Si ⟨1 1 0⟩ in 50 wt% KOH with different concentrations of IPA and TMDD-PA.

absorption of TMDD is stronger than IPA, which leads to its better performance of smoothing Si ⟨1 1 0⟩ surface.

### *3.2. The effect of TMDD-PA on etching rate ratio*

Fig. 2 shows the etching rate ratio under different additive concentrations. The etching rate ratio of IPA climbs firstly, reaches its peak and then reduces. The etching rate ratio of TMDD-PA firstly decreases, and then increases gradually, finally surpasses IPA at a concentration of 0.72 wt% approximately.

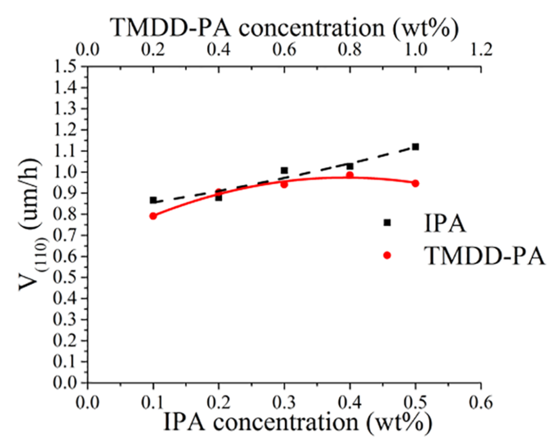


**Fig. 4.** Etching rates of Si ⟨1 1 0⟩ in 50 wt% KOH with IPA and TMDD-PA which contains the same quantity of IPA respectively.

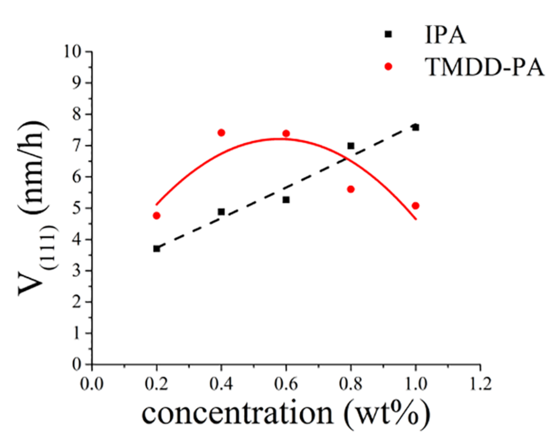


**Fig. 5.** Etching rates of Si ⟨1 1 1⟩ in 50 wt% KOH with different concentrations of IPA and TMDD-PA.

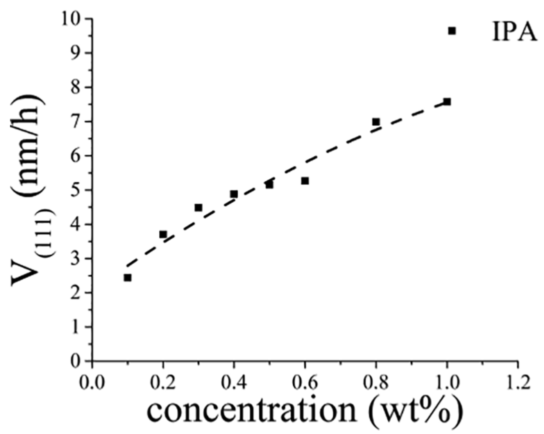


**Fig. 6.** Etching rates of Si ⟨1 1 1⟩ in 50 wt% KOH with different concentrations of IPA.

Etching rate ratio depends on the etching rate of Si ⟨1 1 0⟩ and Si ⟨1 1 1⟩. Additives impact etching rate ratio by modulating etching rate of different Si surfaces. The relationship between etching rate of different Si surfaces and additive concentration should be analyzed respectively.

Fig. 3 shows the etching rate of Si ⟨1 1 0⟩ under different additive concentrations. The etching rate increases firstly and then decreases with the increasing of IPA concentration. The etching rate maintains increasing with the increasing of TMDD-PA concentration, and surpasses IPA at 0.8 wt%. The absorption of additive molecules slows down the etching rate, while in high concentration KOH solutions, a few IPA adding into solution can pace up the etching rate. In high concentration KOH solutions, the hydration of $K^+$ and $OH^-$ consume much $H_2O$ molecules. IPA can hinder the hydration, in other words dehydrating $K^+$ and $OH^-$, and liberate the water molecules [10]. Since the etching rate depends on the product of hydroxide ions and free water concentration ($R \approx [H_2O]^a \times [OH^-]^b$) [13], the addition of IPA increases etching rate. The absorption of additive molecules can reduce reaction rate. Absorption, together with dehydration, impacts on the etching rate. When dehydration is stronger than absorption, the etching rate increases. With the increasing of IPA concentration, absorption surpasses dehydration, and the etching rate reduces. Fig. 4 shows Si ⟨1 1 0⟩ etching rete under 0.1 wt%–0.5 wt% IPA and 0.2 wt%–1.0 wt% TMDD-PA (the quantity of IPA is equal in two kinds of additives, since TMDD-PA is made up of TMDD: IPA = 1: 1). The trend of etching rate increasing is alike between IPA and TMDD-PA, and among the 5 contrast groups, etching rate of TMDD-PA is always a little slower than IPA, which indicates that only IPA can dehydrate while TMDD cannot. When IPA concentration is lower than 0.5 wt%, more $H_2O$ molecules are released with the increasing of IPA concentration, thus the etching rate under 0.1 wt%–0.5 wt% IPA and 0.2 wt%–0.4 wt% TMDD-PA increase gradually. When IPA concentration is higher than 0.5 wt%, no more $H_2O$ were released. However, the absorption of IPA is still increasing, thus the etching rate starts to decrease.

Fig. 5 shows the etching rate of Si ⟨1 1 1⟩ under different additive concentrations. The etching rate of solutions added TMDD-PA increases firstly, and then decreases. The etching rate of solutions added IPA increases gradually and surpasses TMDD-PA. The increasing of etching rate at low concentrations indicates that the pacing up of rate induced by IPA's dehydration also exists on Si ⟨1 1 1⟩. However, as Fig. 6 shows, differently with Si ⟨1 1 0⟩, the rate remains increasing on Si ⟨1 1 1⟩ with the increasing of IPA concentration. In other words, dehydration of IPA remains stronger than absorption on Si ⟨1 1 1⟩. This indicates that the absorption of IPA on Si ⟨1 1 1⟩ is weaker than that on Si ⟨1 1 0⟩. On Si ⟨1 1 1⟩, the absorption of TMDD-PA surpasses dehydration, and produce a yielding point on relationship between Si ⟨1 1 1⟩

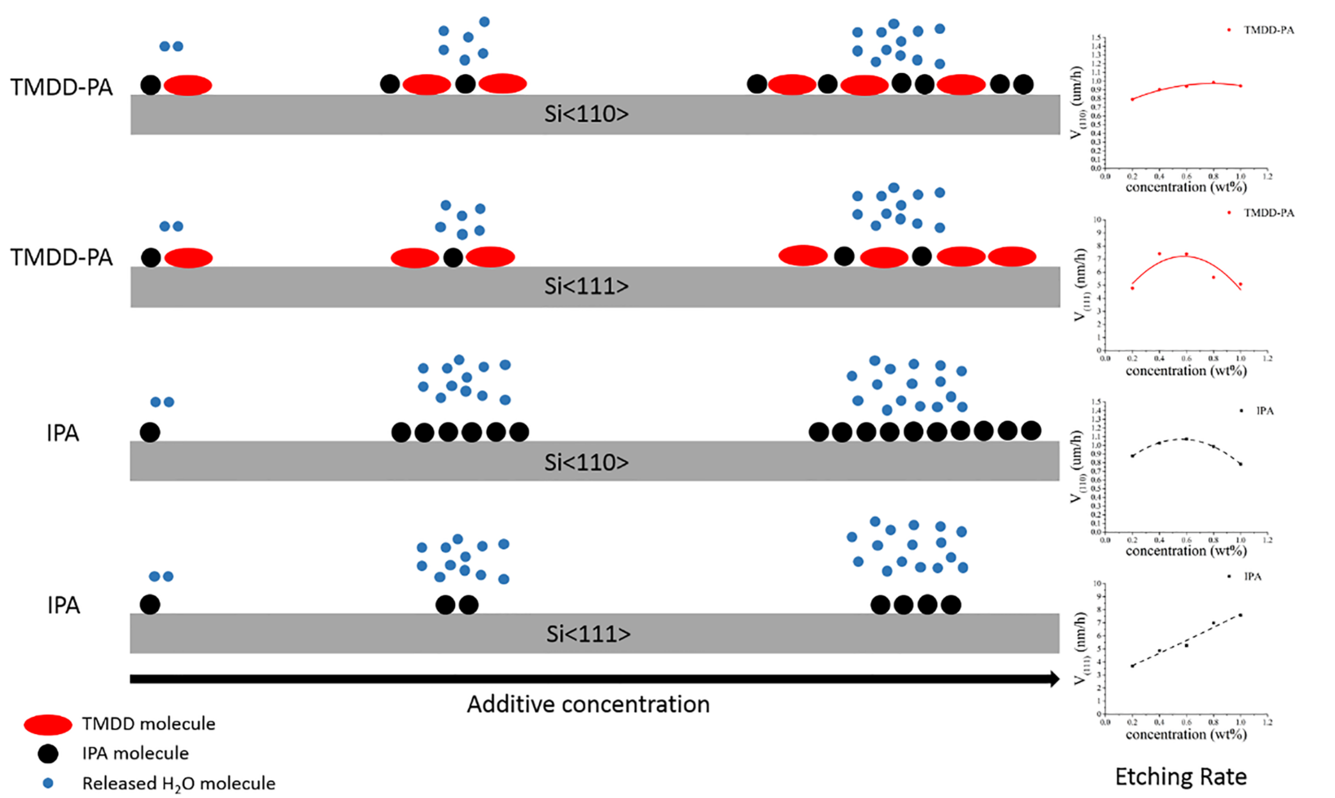


**Fig. 7.** Additives behave differently on Si ⟨1 1 0⟩ & Si ⟨1 1 1⟩. Molecular size, dehydrate ability and surface bonds' angle lead to different etching rate.

etching rate and TMDD-PA concentration. This indicates that on Si ⟨1 1 1⟩, the absorption of TMDD is much stronger than IPA. Since different surfaces have different types of bonds, when molecule is absorbed on Si surface, it behaves differently on different surfaces as seen in Fig. 7. Si ⟨1 1 1⟩ surface is full of B-type bonds, which have larger distance between each other than distance of bonds on Si ⟨1 1 0⟩. The size of TMDD is bigger than IPA, hence TMDD is easier to be absorbed on Si ⟨1 1 1⟩ than IPA.

According to Figs. 5 and 3, the etching rate of TMDD-PA changes differently with IPA on different Si surfaces, which can be the reason why etching rate ratio of TMDD-PA surpasses IPA with the increasing of additive concentration.

## 4. Conclusion

The effects of TMDD-PA and IPA of low concentration on roughness of Si ⟨1 1 0⟩ and etching rate ratio of Si ⟨1 1 0⟩/⟨1 1 1⟩ in 50 wt% KOH solutions under 21 ± 0.2 °C were discussed. Both of two kinds of solutions can smooth Si ⟨1 1 0⟩ surface, and the roughness reduced with the increasing of additive concentrations. Better surface morphology was obtained in solutions added TMDD-PA compared with IPA. Etching rate ratio increases firstly and then decreases with the increasing of IPA concentration, while etching rate ratio decreases firstly and then increases with the increasing of TMDD-PA concentration. At about the concentration of 0.72 wt%, etching rate ratio of TMDD-PA surpasses IPA. On Si ⟨1 1 0⟩ surface, in solutions added IPA the absorption becomes stronger and surpasses the dehydration with the increasing of IPA concentration, while in solution added TMDD-PA, the absorption remains weaker than dehydration. On Si ⟨1 1 1⟩ surface, they just behave oppositely. It's concluded that IPA can dehydrate while TMDD cannot. Difference between absorption of IPA and TMDD on Si surfaces leads to different etching rate ratio changings of TMDD-PA and IPA.

## Acknowledgment

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

## References

[1] F. Pfeiffer, T. Weitkamp, O. Bunk, Phase retrieval and differential phase-contrast imaging with low-brilliance X-ray sources, Nat. Phys. 2 (2006) 258–261.
[2] J. Kenntner, V. Altapova, T. Grund, Fabrication and characterization of analyzer gratings with high aspect ratios for phase contrast imaging using a Talbot interferometer, AIP Conf. Proc. 1437 (2012) 89.
[3] A. Holke, H.T. Henderson, Ultra-deep anisotropic etching of (110) silicon, J. Micromech. Microeng. 9 (1999) 51–57.
[4] S.H. Kim, S.H. Lee, H.T. Lim, (110) Silicon Etching for High Aspect Ratio Comb Structures, 1997 6th International Conference on IEEE, 1997, pp. 248–252.
[5] Q.B. Jiao, X. Bayanheshig, Tan, The effects of ultrasound frequency and power on the activation energy in Si-KOH reaction system, Chin. Chem. Lett. 25 (2014) 617–620.
[6] M. Ahn, Fbrication of Critical-Angle Transmission gratings for high efficiency x-ray spectroscopy, Massachusetts Inst. Technol. (2009).
[7] I. Zubel, K.P. Rola, M. Kramkowska, The effect of isopropyl alcohol concentration on the etching process of Si-substrates in KOH solutions, Sens. Actuators A 171 (2011) 436–445.
[8] K.P. Rola, I. Zubel, Impact of alcohol additives concentration on etch rate and surface morphology of (100) and (110) Si substrates etched in KOH solutions, Microsyst. Technol. 19 (2013) 635–643.
[9] Y.C. Zheng, K.Q. Qiu, H.Y. Chen, Alignment method combining interference lithography with anisotropic wet etch technique for fabrication of high aspect ratio silicon gratings, Opt. Express 22 (2014) 23592–23604.
[10] I. Zubel, I. Barycka, K. Kotowska, Silicon anisotropic etching in alkaline solutions IV The effect of organic and inorganic agents on silicon anisotropic etching process, Sens. Actuators A 87 (2001) 163–171.
[11] I. Zubel, M. Kramkowska, Etch rates and morphology of silicon (hkl) surfaces etched in KOH and KOH saturated with isopropanol solutions, Sens. Actuators A 115 (2004) 549–556.
[12] W.J. Cho, W.K. Chin, C.T. Kuo, Effects of alcoholic moderators on anisotropic etching of silicon in aqueous potassium hydroxide solutions, Sens. Actuators A 116 (2004) 357–368.
[13] H. Seidel, L. Csepregi, A. Heuberger, et al., Anisotropic etching of crystalline silicon in alkaline solutions, J. Electrochem. Soc. 137 (1990) 3612–3626.