

# Lithography and reactive ion etching optimization towards low-loss TiO<sub>2</sub> waveguides

I. Hegeman, S.M. Garcia-Blanco

University of Twente, Optical Sciences, 7522NH Enschede, Netherlands

*TiO<sub>2</sub> is emerging as material platform for integrated photonics [1–3]. However, the propagation losses remain too high for industrial applications. In order to reduce the waveguide losses, effort is put on the optimization of the lithography and etching process. The sidewall roughness induced by etching is critical for the waveguide performance. To reduce sidewall roughness, negative E-beam lithography is used. A negative E-beam resist (ARN 7520.18) followed by the conductive coating (AR-PC 5091) are applied by spin-coating. An HMDS layer underneath the resist is utilized to improve adhesion to the substrate and therefore allow structures with high aspect ratio. Reactive ion etching with pure SF<sub>6</sub>, CHF<sub>3</sub>, HBr, Cl<sub>2</sub> and BCl<sub>3</sub> are compared. BCl<sub>3</sub> chemistry showed to be most beneficial. The influence of additional Ar and O<sub>2</sub> flow and varying the HF power and pressure to etching in BCl<sub>3</sub> are reported.*

## Introduction

TiO<sub>2</sub> is an emerging material for integrated photonics [1–3]. The high refractive index of around 2.3 allows to scale down integrated photonic circuits and the bandgap of higher than 3 eV [4] results in a large transparency window. Because of the high non-linearity, four-wave mixing [2], supercontinuum generation [3] and third harmonic generation [5] have been demonstrated. Furthermore the negative thermo-optic coefficient [6] (TOC) can be used to design athermal devices by combining TiO<sub>2</sub> with a material with a positive TOC such as Si<sub>3</sub>N<sub>4</sub> [7] or Si [8]. The optical propagation losses remain however relatively high and go down to 9.7 dB/cm at a wavelength of 633 nm [9] and 4 dB/cm at 1550 nm [10], when using conventional fabrication techniques, i.e. deposition, lithography and etching. By using a lift-off process, lower losses of 7.5 and 1.2 dB/cm at 633 nm and 1550 nm respectively can be obtained [1].

In most cases, etching of TiO<sub>2</sub> is performed using reactive ion etching (RIE) with fluorine as chemical component [2,9–11], often with addition of O<sub>2</sub> and Ar. These processes are however all performed by using a Cr or Al hard mask, made by E-beam lithography (EBL) using positive resist, followed by lift-off. Using only negative resist would result in a much simpler process.

Several studies have been performed to compare the RIE characteristics of TiO<sub>2</sub> in different chemicals. These studies include etching with SF<sub>6</sub>, CH<sub>3</sub> and Cl<sub>2</sub> [12], HBr and Cl<sub>2</sub> mixtures [13], CF<sub>4</sub>/Ar/N<sub>2</sub> [14], CF<sub>4</sub>/Ar/O<sub>2</sub> [15], SF<sub>6</sub>/Ar, CF<sub>4</sub>/O<sub>2</sub> and CF<sub>4</sub>/Ar [16] and BCl<sub>3</sub>/Ar [17]. These studies however do not show the selectivity of TiO<sub>2</sub> towards resist, which is a crucial factor for waveguide fabrication. Furthermore, many studies are performed by different groups, which makes it hard to compare different chemistries quantitatively.

In this work, we show the development of a process recipe for negative EBL resist. The etch rates of the EBL resist, SiO<sub>2</sub> and TiO<sub>2</sub> are compared for different RIE chemistries. For BCl<sub>3</sub> the influence of assisting gasses and different etching parameters are compared to optimize the etching recipe.

## E-beam lithography

For the EBL process a negative resist (ARN 7520.18) is spin coated on top of a 4 inch Si wafer with an 8 μm thermal oxide layer. The spin coating is performed for 3 minutes at 1500 rpm, followed by a baking step of 1 minute at 85 °C. The E-beam exposure is performed using the Raith EBPG5150 with an acceleration voltage of 100 kV. Comparing the structures written with

different doses, showed an optimum dose of  $1000 \mu\text{C}/\text{cm}^2$ . After exposure, the patterns are developed in undiluted AR 300-47 developer for 1 minute. The resist patterns contain lines with a width varying between 300 and 1000 nm and gaps between 100 and 1000 nm. The resist showed bad adhesion to the substrate, causing the resist patterns to release or stick together. An example is shown in figure 1(a). The electrically insulating substrate causes charge build up during the exposure. As a result, stitching errors occur between write fields, causing shifts of up to several micrometers in the patterns, shown in figure 1(b).

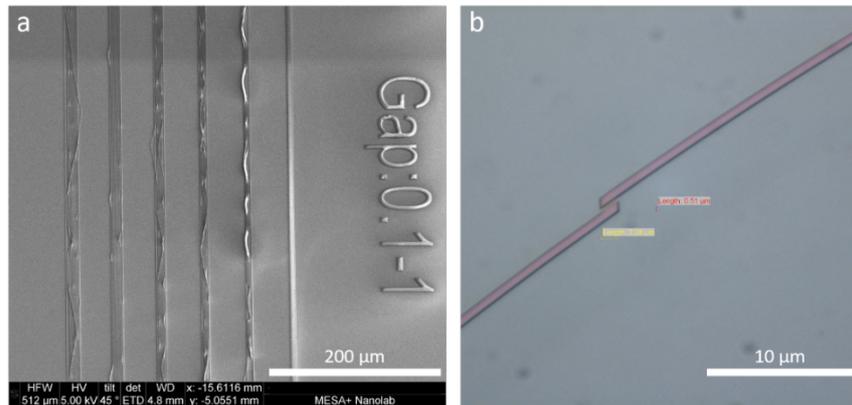


Fig. 1. (a) SEM of negative E-beam resist lines showing bad adhesion to the substrate. (b) Microscope image showing typical stitching errors between write fields during E-beam lithography, as a result of charging of the substrate.

To improve the adhesion of the resist to the substrate, an HMDS layer is spin coated for 45 seconds at 4000 rpm, prior to the spin coating of the resist. In order to prevent charge build up, a conductive coating (AR-PC 5091) is applied on top of the resist. This is also performed by spin coating for 45 seconds at 2000 rpm. The resulting patterns are shown in figure 2. The height of the resist is around 670 nm, with small variations per process. Stitching errors do not occur and good adhesion of the resist to the substrate is obtained. Patterns show to be 50 nm narrower than designed, causing gap sizes to be 50 nm wider. As shown in figure 2b, gaps of 150 nm are well defined and opened during development. Smaller gaps might be possible, but these are not tested, since 150 nm is sufficient for waveguide design.

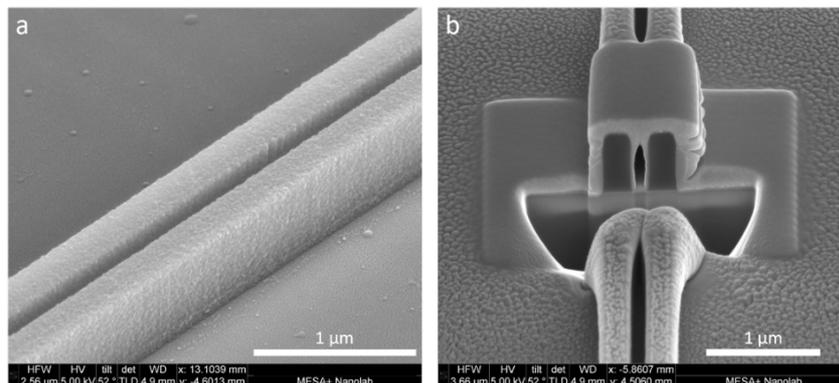


Fig. 2. SEM image of 650 nm thick and 250 nm wide negative E-beam resist lines with a gap of 150 nm on top of a  $\text{SiO}_2$  substrate, (a) sideview (b) cross section.

## Etching

The RIE is performed using the Oxford Plasma Pro 100 Cobra. The relevant etch parameters are shown in table 1. In each case, 25 sccm is used for the reactive gas flow. The etch rates in the 5 different available chemistries are compared and summarized in table 2. Etch rates of  $\text{TiO}_2$  are measured by ellipsometry before and after etching using the Woollam M-2000UI. Etch rates

of the negative resist and SiO<sub>2</sub> are measured by measuring the step height before etching, after etching and after stripping the resist. This is done with the Veeco Dektak 8.

Pressure (mTorr)	Time (mm:ss)	HF power (W)	ICP power (W)	Temperature (°C)
10	01:00	20	1500	10

Table 1. Etch parameters

	SF <sub>6</sub>	CHF <sub>3</sub>	HBr	Cl <sub>2</sub>	BCl <sub>3</sub>
Resist	175	36	20	77	34
SiO <sub>2</sub>	71	73	10	~0*	15
TiO <sub>2</sub>	55	15	~0*	4	45

Table 2. Etch rates for different reactive gasses with a flow of 25 sccm

\*no etching measured within measurement limit

RIE with BCl<sub>3</sub> shows the second highest etching speed of TiO<sub>2</sub>, and the best selectivity of 1.29 towards resist and 3 towards SiO<sub>2</sub>. The characteristics of BCl<sub>3</sub> etching are determined as a function of Ar and O<sub>2</sub> flow, HF Power and pressure. The etching rates are shown in figure 3. The BCl<sub>3</sub> flow is kept at 25 sccm and the other parameters are given in table 1, except for figure 3(c-d) where the HF power and pressure are increased.

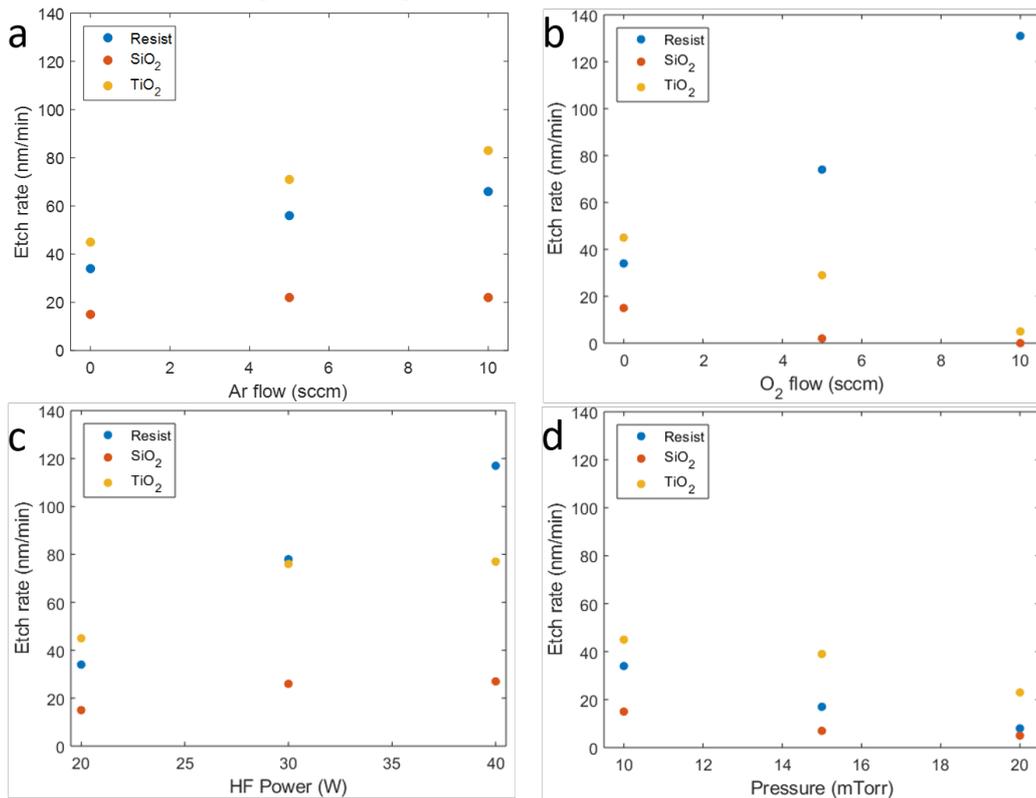


Figure 3. Etching rates of the negative E-beam resist, SiO<sub>2</sub> and TiO<sub>2</sub> for varying (a) Ar flow, (b) O<sub>2</sub> flow, (c) HF power and (d) pressure.

As shown in figure 3(a), the etching speed of TiO<sub>2</sub> and resist increase, but the selectivity stays the same. By adding some Ar into the plasma, the physical etching component increases, which increases the etching rate. Figure 3(b) shows that adding O<sub>2</sub> into the chamber decreases the SiO<sub>2</sub> and TiO<sub>2</sub> etching rate and increases the etching rate of the resist, resulting in very low selectivity of TiO<sub>2</sub> towards resist of 0.04 for 10 sccm of O<sub>2</sub>. Applying a higher HF power increases the etching speeds, but the selectivity reduces as shown in figure 3(c). Finally the

pressure is increased, which results in lower etching rates, caused by the decreased acceleration of the ions due to the increased number of ions. However the selectivity of TiO<sub>2</sub> towards resist goes up to 2.9.

## Conclusion

An EBL process has been developed to get resist patterns down to a width of 250 nm with a gap down to 150 nm by using negative E-beam resist. Stitching errors are prevented by applying a conductive coating and the adhesion to the substrate is improved with an interstitial HMDS layer. Etching with BCl<sub>3</sub> showed to be most beneficial for etching TiO<sub>2</sub>, compared to SF<sub>6</sub>, CHF<sub>3</sub>, Cl<sub>2</sub> and HBr. Selectivities towards the negative resist of 2.9 are obtained. Further optimization of the etching parameters might increase the selectivity.

## Funding

This work is part of the research programme Industrial Doctorates with project number NWA.ID.17.100, which is financed by the Dutch Research Council (NWO).

## References

1. C. C. Evans, C. Liu, and J. Suntivich, "Low-loss titanium dioxide waveguides and resonators using a dielectric lift-off fabrication process," *Opt. Express* **23**, 11160–1169 (2015).
2. X. Guan, H. Hu, L. K. Oxenløwe, and L. H. Frandsen, "Compact titanium dioxide waveguides with high nonlinearity at telecommunication wavelengths," *Opt. Express* **26**, 1055–1063 (2018).
3. K. Hammani, L. Markey, M. Lamy, B. Kibler, J. Arocas, J. Fatome, A. Dereux, J.-C. Weeber, and C. Finot, "Octave Spanning Supercontinuum in Titanium Dioxide Waveguides," *Appl. Sci.* **8**, 543 (2018).
4. M. Landmann, E. Rauls, and W. G. Schmidt, "The electronic structure and optical response of rutile, anatase and brookite TiO<sub>2</sub>," *J. Phys. Condens. Matter* **24**, 195503 (2012).
5. C. C. Evans, K. Shtyrkova, O. Reshef, M. Moebius, J. D. B. Bradley, S. Griesse-Nascimento, E. Ippen, and E. Mazur, "Multimode phase-matched third-harmonic generation in sub-micrometer-wide anatase TiO<sub>2</sub> waveguides," *Opt. Express* **23**, 7832–7841 (2015).
6. O. Reshef, K. Shtyrkova, M. G. Moebius, S. Griesse-Nascimento, S. Spector, C. C. Evans, E. Ippen, and E. Mazur, "Polycrystalline anatase titanium dioxide microring resonators with negative thermo-optic coefficient," *J. Opt. Soc. Am. B* **32**, 2288–2293 (2015).
7. F. Qiu, A. M. Spring, and S. Yokoyama, "Athermal and high-Q hybrid TiO<sub>2</sub>-Si<sub>3</sub>N<sub>4</sub> ring resonator via an etching-free fabrication technique," *ACS Photonics* **2**, 405–409 (2015).
8. B. Guha, J. Cardenas, and M. Lipson, "Athermal silicon microring resonators with titanium oxide cladding," *Opt. Express* **21**, 26557–26563 (2013).
9. M. Furuhashi, M. Fujiwara, T. Ohshiro, M. Tsutsui, K. Matsubara, M. Taniguchi, S. Takeuchi, and T. Kawai, "Development of microfabricated TiO<sub>2</sub> channel waveguides," *AIP Adv.* **1**, 032102 (2011).
10. J. D. B. Bradley, C. C. Evans, J. T. Choy, O. Reshef, P. B. Deotare, F. Parsy, K. C. Phillips, M. Lončar, and E. Mazur, "Submicrometer-wide amorphous and polycrystalline anatase TiO<sub>2</sub> waveguides for microphotonic devices," *Opt. Express* **20**, 23821–23831 (2012).
11. M. Häyrynen, M. Roussey, A. Säynätjoki, V. Gandhi, L. Karvonen, P. Stenberg, M. Kuittinen, and S. Honkanen, "Low-loss titanium-dioxide strip waveguides by atomic layer deposition," *SPIE Photonics West 2014-OPTO Optoelectron. Devices Matter.* **8982**, 89820E (2014).
12. S. Norasetthekul, P. Y. Park, K. H. Baik, K. P. Lee, J. H. Shin, B. S. Jeong, V. Shishodia, E. S. Lambers, D. P. Norton, and S. J. Pearton, "Dry etch chemistries for TiO<sub>2</sub> thin films," *Appl. Surf. Sci.* **185**, 27–33 (2001).
13. D. Kim, A. Efremov, H. Jang, S. Kang, S. J. Yun, and K.-H. Kwon, "Etching characteristics and mechanisms of TiO<sub>2</sub> thin films in HBr/Cl<sub>2</sub>/Ar inductively coupled plasma," *Jpn. J. Appl. Phys.* **51**, (2012).
14. K. R. Choi, J. C. Woo, Y. H. Joo, Y. S. Chun, and C. Il Kim, "The dry etching characteristics of TiO<sub>2</sub> thin films in N<sub>2</sub>/CF<sub>4</sub>/Ar plasma," *Trans. Electr. Electron. Mater.* **15**, 32–36 (2014).
15. I. Hotovy, S. Hascik, M. Gregor, V. Rehacek, M. Predanocny, and A. Plecenik, "Dry etching characteristics of TiO<sub>2</sub> thin films using inductively coupled plasma for gas sensing," *Vacuum* **107**, 20–22 (2014).
16. R. Adzhri, M. K. M. Arshad, M. F. M. Fathil, U. Hashim, A. R. Ruslinda, R. M. Ayub, S. C. B. Gopinath, C. H. Voon, K. L. Foo, M. N. M. Nuzaihan, A. H. Azman, and M. Zaki, "Reactive Ion etching of TiO<sub>2</sub> thin film: The impact of different gaseous," *RSM 2015 - 2015 IEEE Reg. Symp. Micro Nano Electron. Proc.* 1–4 (2015).
17. J. C. Woo, Y. S. Chun, Y. H. Joo, and C. I. Kim, "The dry etching property of TiO<sub>2</sub> thin films using metal-insulator-metal capacitor in inductively coupled plasma system," *Vacuum* **86**, 2152–2157 (2012).