

Etch profile engineering of TiN thin films by dry reactive ion etching in fluorine- and chlorine-based gas chemistries

Tibor Izsák^{1*}, Sergei Krylov¹, Tomáš Ščepka¹, Oleksandr Romanyuk², Igor Píš¹, Ján Fedor¹, Boris Hudec¹

¹ Institute of Electrical Engineering, Slovak Academy of Sciences, Dúbravská cesta 9, 841 04 Bratislava, Slovak Republic

² FZÚ - Institute of Physics, Czech Academy of Sciences, Cukrovarnická 10, 162 00 Prague 6, Czech Republic

e-mail: tibor.izsak@savba.sk

Abstract *The dry reactive ion etching of 100 nm thick TiN films grown on SiO₂/Si substrates was studied using an inductively coupled plasma (ICP) system in different gas chemistries (CF₄/Ar, Cl₂/Ar, BCl₃/Ar). The influence of the gas mixture, ICP and RF power, and process pressure on the etch rate, etch profile, homogeneity, and selectivity against the photoresist mask was investigated. Inclined sidewall profiles with a tilted angle of 17°–54° were observed for samples etched in CF₄/Ar and BCl₃/Ar. In contrast, etching in Cl₂/Ar resulted in an anisotropic etch profile of >85°, with sharp, vertical walls, independent of the etching conditions. The chemical composition of the etched TiN surfaces was characterised using ex-situ X-ray photoelectron spectroscopy (XPS). XPS results demonstrated no contamination from non-volatile by-products of plasma etching in F- or Cl-based chemistries, and preserving the stoichiometric ratio of Ti:N. This result was supported by resistivity measurements. The etch rates typically range from 10 to 30 nm/min. Such low etch rates enabled controllable etching of TiN thin films, avoiding trenching and the redeposition of the SiO₂ underlayer on the TiN sidewalls. The etching mechanisms of TiN in different gas chemistries are also discussed.*

Keywords TiN; RIE; ICP; XPS; fluorine; chlorine

1. Introduction

Titanium nitride (TiN) is a key material in the semiconductor industry thanks to its compatibility with CMOS devices. It is characterised by many interesting properties, such as high thermal stability and good electrical conductivity. It also has a matching lattice structure and exhibits good adhesion with high-k materials (e.g., HfO₂, ZrO₂, Al₂O₃) [1,2]. TiN has many applications, including tunable work-function metal gates in field-effect transistors (FETs) [3], diffusion barriers [4], metal hard masks [5], anti-reflective [6] or neural electrode coatings [7], extreme ultraviolet patterning [8], Schottky photodetectors [9], and in solar energy applications [10,11] or in plasmonics for photothermal-chemodynamic cancer therapy [12]. TiN shows great potential as a key material for the development of scalable, integrated biomedical sensors [13], implantable devices, and micro/nanoelectronic systems [14].

The TiN film is also used as the bottom electrode in metal–insulator–metal (MIM) structures for resistive switching [15]. Resistive switching has recently attracted lots of interest because it can be used in non-volatile memory devices. Resistive random-access memories (RRAMs) have emerged as a promising alternative to conventional charge-based flash memories due to their notable features, including high speed, ultra-low power consumption, and a small footprint [16,17]. Therefore, RRAMs are expected to revolutionize the existing data storage hierarchy in future high-speed information systems. However, to fabricate RRAMs (i.e., MIM structures), several steps are needed, including the structuring of the TiN film.

Various etching processes have been developed for TiN, including wet etching processes [18,19], conventional dry reactive ion etching (RIE) processes using chlorine- or fluorine-based chemistries (Cl- or F-based chemistries) [20–22], or plasma atomic layer etching [23], and thermal gas-phase etching [24]. Wet etching processes typically result in high surface roughness, which makes

controlling the etch rate at the nanometre scale difficult. Although RIE can control the etch rate and produce anisotropic patterns, many studies do contradict in explanation of etching mechanism of TiN thin films. For example, Chiu et al. reported that the etch rate of TiN was high, due to the easy formation of highly volatile etch by-products [25]. On the other hand, Abraham et al. reported that the etch rate of TiN was slow, and it was difficult to obtain anisotropic etch profiles [6]. Another issue in TiN etching in Cl- and F-based plasmas relates to the formation of non-volatile by-products that can degrade the properties of the final etched structures. Therefore, a thorough study is needed to optimise the etching process for each application, achieving the required etch rate, etch profile and selectivity to the mask material.

This study investigates the dry reactive ion etching of 100 nm thick TiN films using an inductively coupled plasma (ICP) system with different gas chemistries (CF_4/Ar , Cl_2/Ar , and BCl_3/Ar). The influence of the gas mixture ratio, the effect of the ICP and RF power, and the process pressure were investigated in terms of the etch rate, etch profile, homogeneity, and etching selectivity against the lithography-patterned photoresist mask (PR).

2. Experimental part

TiN films with a nominal thickness of 100 nm were deposited on the SiO_2/Si substrates (300 nm/525 μm in thickness) by a DC magnetron sputtering using a Ti target under the following conditions: DC power 350 W, a gas mixture of 30/1.8 sccm of Ar/N_2 , a working pressure of 1.75 mTorr and a process temperature of 200 $^\circ\text{C}$ on an AJA Orion 8E deposition system.

AZ5214E photoresist (MicroChemicals GmbH) was used as an etching mask. This was deposited on the samples using a spin-coater at 4000 rpm for 40 s, followed by a soft-bake at 90 $^\circ\text{C}$ for 5 min. UV exposure was performed using a KARL SUSS MJB 3 mask aligner with an exposure time of 4.5 s, after which AZ400K developer was applied for 45 s. In addition to the photoresist (PR) mask, a small piece of silicon (Si) wafer was also placed on the sample during the reactive ion etching (RIE) process, acting as a mechanical mask to evaluate the etch rate of the photoresist itself (see Fig. 1). In this work, we define the etching selectivity as the ratio of the PR etch rate against the TiN etch rate ($S = \text{ER}_{\text{PR}}/\text{ER}_{\text{TiN}}$). A lower S is preferable to maintain the integrity of the much thicker PR mask during the TiN patterning.

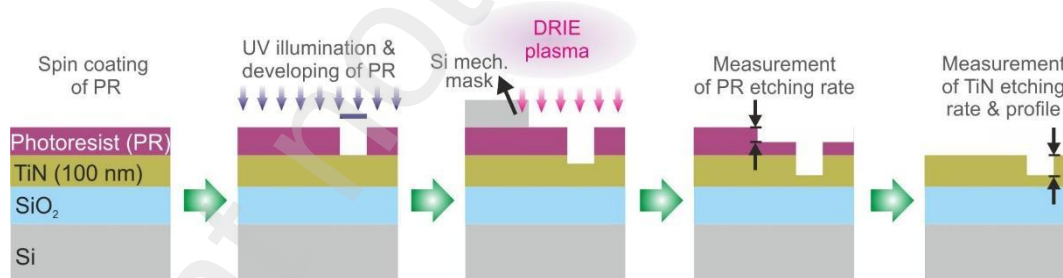


Fig.1. Schematic representation of the dry reactive ion etching process and evaluation of the etch rates of the photoresist mask and TiN layer.

The RIE of TiN films was performed in an Oxford Plasmalab 100 ICP system. This system is equipped with both RF and ICP sources. The first set of experiments studied the effect of fluorine-based plasma chemistry by varying the ratio of CF_4 to Ar in an RF plasma (80 W), with the ICP power set to zero. Further studies involved varying additional parameters, such as the ICP power (in the range of 0–200 W) and the process pressure (in the range of 8–22 mTorr). The second set of experiments examined chlorine-based plasma chemistry by replacing the CF_4/Ar gas mixture with Cl_2/Ar or BCl_3/Ar .

The etch depth and the etch profile were evaluated from surface contact profilometer (Bruker Dektak XT) measurements and from the cross-sectional scanning electron microscopy (SEM) images taken with a FEI FEG250 SEM.

X-ray photoelectron spectroscopy (XPS) was used to characterise the chemical composition of the etched surfaces of the TiN thin films. XPS measurements were performed using an AXIS-Supra photoelectron spectrometer (Kratos Analytical Ltd., UK). Survey and high-resolution core-level spectra were measured using a monochromated Al K α (1486.6 eV) X-ray source with a 0.7×0.3 mm² spot size. Photoelectrons were collected in a constant analyzer energy mode with a pass energy of 10 eV, giving an overall energy resolution of 0.45 eV as measured on the Ag 3d_{5/2} line width. The X-ray incidence angle was 54.4°, and the photoelectron emission angle was 0° with respect to the surface normal. To remove surface hydrocarbon contamination and the native oxide layer while minimizing sputter-induced changes to the chemical state and composition, the samples were cleaned using an argon gas cluster ion beam (Ar-GCIB). The Ar ion beam energy was set to 5 keV, and the mean Ar cluster size was set to 1000 atoms. Atomic concentrations were determined from the corresponding photoelectron peak areas after Shirley background subtraction, taking into account the relative sensitivity factors of the elements, as implemented in the ESCApe software (Kratos Analytical). High-resolution spectra were fitted using KolXPD software [26], employing the Voigt functions for all components except of the TiN Ti 2p peaks, which were modelled with asymmetric Gaussian broadened Donjiac-Sunjic functions.

3. Results and discussion

3.1. Etching of TiN in fluorine-based chemistry

3.1.1. Etch rate and etch profile

The first set of experiments was performed in an RF plasma only with a variable CF₄-Ar gas mixture ratio (Fig. 2a). The reason for this was to minimize the etch rate of the photoresist mask (ER_{PR}) by setting the ICP power to zero. As it was measured, the ER_{PR} was less than 30 nm/min at the expense of the etch rate of TiN (ER_{TiN}). The ER_{TiN} varied from 2 nm/min to 6.4 nm/min, corresponding to the lowest (3.8%) and the highest (95.2%) fluorine content in the CF₄-Ar gas mixture, respectively (Fig. 2a). The selectivity against the PR (defined as $S = ER_{PR}/ER_{TiN}$) was approximately 4 in all cases. This means that the PR was etched 4× faster than the TiN layer. Adding 100 W of ICP power caused a twofold decrease in selectivity for a fluorine content of 95.2%, while at low fluorine content of 3.8% the selectivity was almost identical to that observed without ICP power (see Fig. 2b). Increasing the ICP power further to 200 W decreased the selectivity to 1.6 and increased the ER_{TiN} to ~41 nm/min at a fluorine content of 95.2% (Fig. 2c). This also proves that the chemical etching mechanism is dominant.

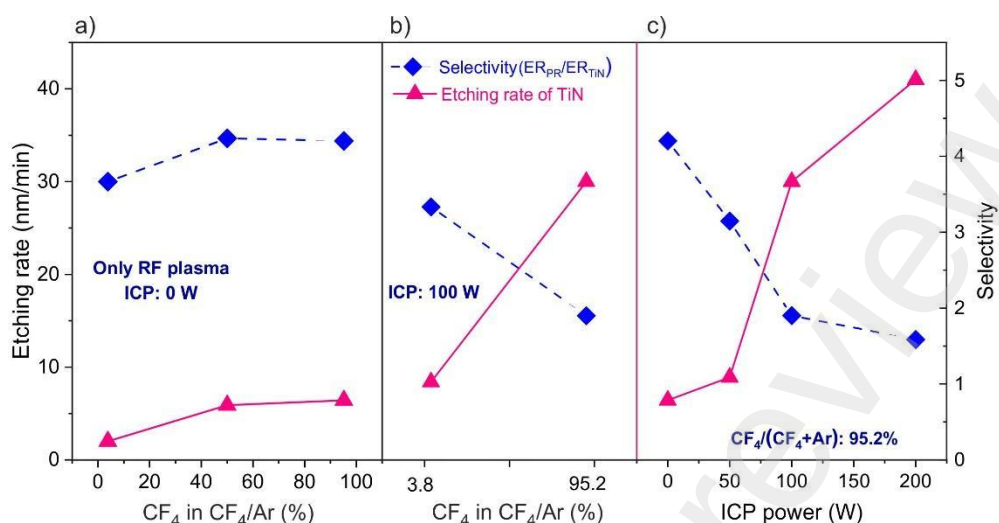


Fig. 2. a,b) Etch rate of the TiN layer as a function of the CF₄-Ar gas mixture for ICP = 0 W (only RF plasma) (a), and for ICP = 100 W (b), respectively. The corresponding selectivity (dashed blue line, right y-axis) is calculated as $S = ER_{PR}/ER_{TiN}$, where ER_{PR} and ER_{TiN} are the etch rates of the photoresist and the etch rate of the TiN, respectively. c) The etch rate of the TiN films as a function of the ICP power (0, 100, and 200 W) with the corresponding selectivity at a constant CF₄/Ar gas mixture of 50/2.5 sccm. Other parameters were kept constant: RF power 80 W, pressure 15 mTorr, substrate holder temperature 20°C.

The obtained etch rates are shown in Fig. 2a for a 95.2% Ar-rich gas mixture with an ER_{TiN} of 2 nm/min. Increasing the CF₄ content increased the ER_{TiN} by a factor of three. Etching in pure Ar plasma is therefore limited as there is no chemical contribution, and under these experimental conditions (i.e. 80 W of RF power and a corresponding DC voltage of approximately -300 V), the sample is only exposed to weak ion bombardment. In CF₄/Ar-based chemistry, the etching of the TiN film is generally achieved by radicals such as F and CF_x. F radicals react with Ti and N to produce TiF_x and NF_x as reaction products, respectively. The NF_x reaction products are considered to evaporate very easily due to the low boiling point of NF₃ (128.8 °C) [27]. TiF₄ also evaporates easily, as its sublimation temperature is 284 °C. However, TiF₃ is a non-volatile compound with a very high boiling point (1400 °C), resulting in a low etch rate of TiN in F-based chemistry and low taper angle etch profiles [27].

On the other hand, the addition of ICP to RF power increases the etch rate by accelerating chemical reaction with ion-stimulated desorption of the reaction products: ICP increases both dissociation and ionization rates, and thus densities and fluxes of F atoms and positive ions. This results in increased sputtering yields due to higher ion bombardment of the surface. This effect is also evident in Figs. 2b and 2c, where higher ICP powers result in higher etch rates of TiN and in lower selectivity against the PR mask.

The ICP power also had a strong influence on the etch profile of the samples. Without the ICP and with RF plasma only, the sidewall showed a ~17° tilted etch profile (Fig. 3). By increasing the ICP power, the angle of the etch profile also increased to ~33° and ~51° for 100 W and 200 W, respectively (Fig. 3). This effect could be related to the significant lateral etching of the photoresist mask at lower ICP and the increased ion bombardment towards the TiN surface at higher ICP power.

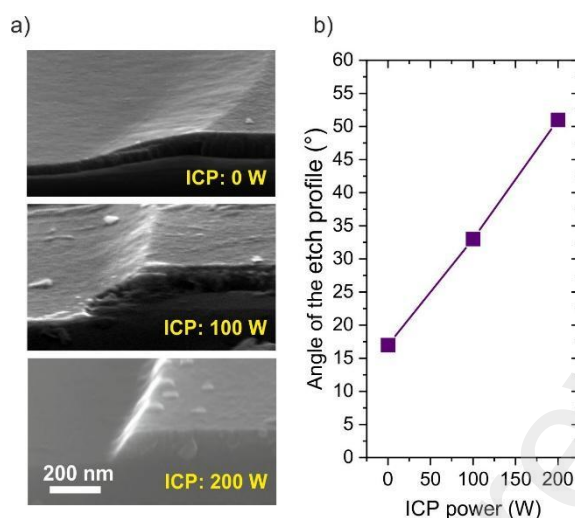


Fig. 3. a) SEM images of the etch profile of TiN films etched at different ICP powers (0, 100, and 200 W) and the corresponding etch angle (b). The other etching parameters were kept constant (RF power 80 W (DC voltage approx. -300 V), gas mixture $\text{CF}_4/\text{Ar}=50/2.5$ sccm, pressure 15 mTorr, substrate holder temperature 20 °C).

3.1.2. Chemical composition analysis

Figure 4 compares the XPS spectra of four selected TiN samples. Two samples were etched using only RF plasma with different CF_4/Ar ratios, one sample was etched with the addition of ICP power (i.e., both RF and ICP sources were switched on), and one as-grown sample without RIE treatment was used as a reference (see Tab. 1).

Table 1. Description of the TiN samples used for the XPS measurements

Sample	Gas mixture in the RIE process	RF power (W)	ICP power (W)	Note
#1a	-	-	-	as-grown (reference)
#2a	CF_4/Ar : 25/25 sccm	80	-	50% CF_4 in CF_4 -Ar gas mixture
#3a	CF_4/Ar : 50/2.5 sccm	80	-	95.2% CF_4 in CF_4 -Ar gas mixture
#4a	CF_4/Ar : 50/2.5 sccm	80	100	95.2% CF_4 in CF_4 -Ar gas mixture

XPS measurements revealed the presence of fluorinated titanium on the etched TiN surfaces. As shown in Fig. 4a, the F 1s peak (~685 eV) was present in all samples etched using fluorine-based chemistry; however, its intensity diminished upon the addition of ICP to RF. This reduction is associated with the aforementioned effects, such as an increased ionization rate and ion bombardment, which inhibit the redeposition of non-volatile TiF_x by-products.

The Ti 2p peak (Fig. 4c) exhibited a complex profile, as the signal from TiN (455.0 eV) overlaps with native surface oxides [28,29]. In the as-grown sample, a slightly higher TiO_2 content was observed, indicated by the Ti(IV) peak at 458.5 eV, along with sub-oxides at ~456.7 eV. Following RIE, the oxide content decreased across all samples. A representative XPS spectrum with highlighting the satellite and shake-up peaks of the TiN sample after RIE can be found in the supplementary file (Fig. S1).

The N 1s spectra (Fig. 4d) revealed no significant differences between the samples. The sharp peak at 397.2 eV corresponds to TiN, and a less intense feature at ~396.3 eV is assigned to titanium

oxynitrides. The O 1s spectra (Fig. 4b) were dominated by a component of TiO₂ at 530.2 eV. A broader feature at higher binding energies (531–532 eV) is attributed to overlapping signals from titanium oxynitrides and C-O groups associated with a surface contamination layer formed through exposure to air (Fig. 4e). The O 1s signal at the highest binding energies is assigned to surface C-OH or Ti-OH groups. Notably, after etching, the signals from the C-O and -OH groups in the O 1s peak decreased significantly.

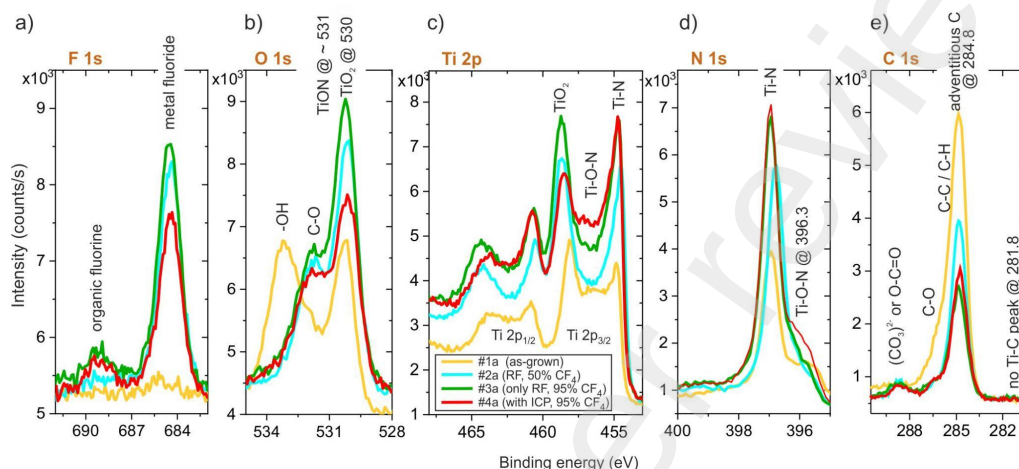


Fig. 4 Comparison of the XPS spectra of four selected samples: as-grown TiN (sample #1a), TiN etched in RF plasma only in 50% (sample #2a) and 95.2% (sample #3a) of CF₄ in CF₄-Ar gas mixture, and TiN sample etched with addition of ICP power (100 W) in 95.2% of CF₄ in CF₄-Ar gas mixture (sample #4a). The other etching parameters were as follows: RF power 80 W, pressure 15 mTorr, substrate holder temperature 20°C.

3.1.3. Etch uniformity

The aforementioned experiments were carried out on small samples with a size of 1x1 cm². However, to produce devices on a larger scale, the homogeneity of the etching process needs to be optimized. Therefore, in the next set of experiments, the pressure was varied, while other parameters were kept constant (i.e., gas mixture 95.2% of CF₄ in CF₄/Ar, RF power = 80 W, ICP power = 100 W). To simulate a large substrate, two small samples (in size of 1x1 cm²) were placed inside the chamber on the 4" substrate holder, as shown in Fig. 5a. One sample was placed in the centre of the 4" Si substrate holder and the second sample was placed 1 cm away from the first. This arrangement enabled the simulation of the etch homogeneity of a 5x5 cm² (~2") substrate.

Figure 5b shows the etch rate of TiN as a function of the distance from the centre of the substrate holder. The etch rate of TiN ranged from 25 to 29.5 nm/min. The highest ER_{TiN} was measured at an 8 mTorr pressure (29.5 nm/min), which is consistent with theory. Reducing the gas pressure at a fixed CF₄/Ar ratio results in a decrease in both density and flux of fluorine atoms on the etched surface, but causes an increase in ion flux and mean ion energy. Consequently, as the gas pressure decreases, the conditions for ion-stimulated desorption of reactive products from the surface improve, resulting in an increasing fraction of the acceptable free surface for chemical reactions [22,30,31].

Although the highest ER_{TiN} was measured for the sample etched at 8 mTorr, it had the worst homogeneity. The most homogeneous distribution was observed at a pressure of 15 mTorr. Here, the difference between the maximum and the minimum etch rates (Δ_{ER}) was only 1.2 nm/min. For 8 and 22 mTorr, the Δ_{ER} was estimated to be 4.3 and 3.6 nm/min, respectively. Therefore, in all experiments, the pressure was set to 15 mTorr and only the other parameters were varied.

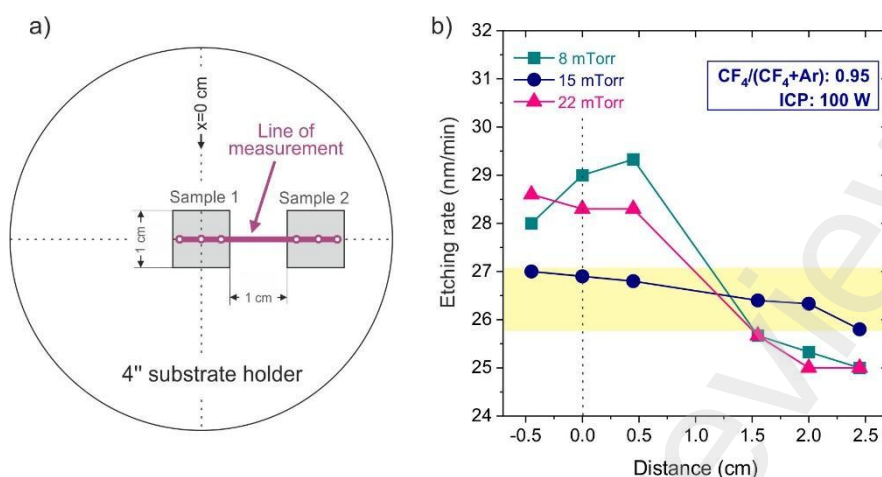


Fig. 5 a) The experimental setup for studying the etch uniformity with two $1 \times 1 \text{ cm}^2$ samples placed on the 4" substrate holder in the ICP chamber. b) The etch rate of TiN as a function of pressure (8, 15, and 22 mTorr) and distance from the centre ($x = 0 \text{ cm}$) of the substrate holder. The other etching parameters were kept constant (RF power 80 W, ICP power 100 W, gas mixture $\text{CF}_4/\text{Ar} = 50/2.5 \text{ sccm}$, substrate holder temperature 20°C).

3.2. Etching of TiN in chlorine-based chemistry

In some cases, when the 100 nm thick TiN film was overetched, a redeposition of the SiO_2 underlayer on the TiN sidewalls and trenching was observed after the RIE in CF_4 -Ar gas chemistry (see Fig. 6). This could also be due to the fact that the etch rate of the SiO_2 in F-based chemistry is approximately 2-3 times higher than the etch rate of TiN. To avoid redeposition of SiO_2 and the trenching effect, the fluorine-based chemistry was replaced with chlorine-based chemistry, and several dry reactive ion etching experiments were performed.

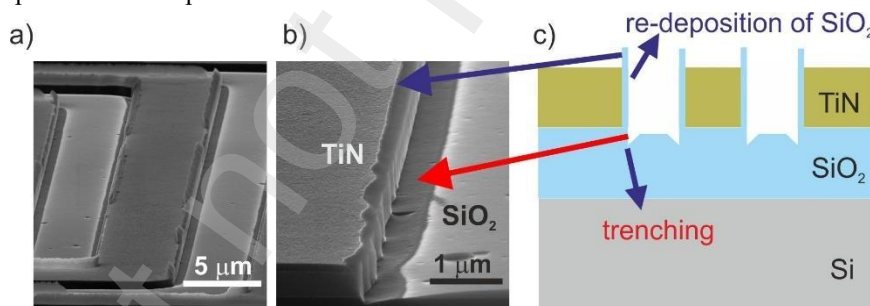


Fig. 6. a,b) SEM images of the TiN samples after long-term RIE in CF_4 -Ar gas chemistry and c) schematic drawing of the SiO_2 redeposition and trenching mechanism.

Figure 7 summarises the etch rates of TiN and the corresponding selectivity against a photoresist mask etched in Cl-based chemistry at different ratios of Cl_2 :Ar or BCl_3 :Ar, as well as at different ICP and RF powers. The pressure was kept at 15 mTorr because the best homogeneity was observed in F-based chemistry under these conditions. Compared to F-based chemistry, etching in Cl_2 -Ar chemistry only resulted in an anisotropic etch profile ($>85^\circ$) with sharp, vertical walls (see Fig. 8a-d), independent of the etching conditions, and 3-4 times higher etch rates of TiN. For example, at a Cl_2 :Ar ratio of 1:1, the ER_{TiN} was $\sim 98 \text{ nm/min}$, whereas at the same etching conditions for CF_4 :Ar, the ER_{TiN} was $\sim 30 \text{ nm/min}$. In our case (a 100 nm thick TiN on SiO_2), the etch rate of $\sim 98 \text{ nm/min}$ was too fast; therefore, we reduced the Cl_2 :Ar ratio to 1:10 or 1:20 (see Fig. 7a). Although the ER_{TiN} decreased to $\sim 28 \text{ nm/min}$ at the 1:20 Cl_2 :Ar ratio, the selectivity against the PR mask increased to 2. This could be

due to the higher efficiency of the physical sputtering of the PR mask resulting from the increased number of Ar ions in the gas mixture.

Next experiments were focused on the effect of lowering RF power from 80 to 30 W (see Fig. 7b and 7c, respectively) while varying the ICP power at a constant Cl_2 :Ar ratio of 1:10. Interestingly, the highest selectivity (~ 2.5) was observed at 50/80 W ICP/RF power. The etch profile did not change significantly; anisotropic etching ($>85^\circ$) was observed even at very low ICP/RF power (0 W/30 W) (Fig. 8d).

Replacing Cl_2 with BCl_3 resulted in an 8-10 times lower ER_{TiN} (~ 8 nm/min) and an increased selectivity against the PR (see Fig. 7d). Nevertheless, the etch profile exhibited a tilted angle of approximately 54° (Fig. 8e). In certain cases, inclined edges of TiN structures are desired, for instance, to enhance the adhesion of metallization during the fabrication process of crossbar arrays.

Compared to CF_4 /Ar-based plasma, for the Cl_2 /Ar-based plasma etching, the NCl_x and TiCl_x have high vapour pressures (or low boiling points, e.g. 136.5°C for TiCl_4), resulting in easy etching of the TiN layer and in the highest etch rate with an anisotropic etch profile (vertical walls) compared with CF_4 /Ar and BCl_3 /Ar chemistry. The high etch rate in Cl_2 /Ar-plasmas is also due to the lower chemical bond strength of the Ti-Cl_4 compared to TiN. Therefore, Cl atoms formed in the plasma can spontaneously react with TiN, and the ion bombardment (controlled by RF and ICP sources; see Figs. 7b,c) supports the physical reaction by breaking the chemical bonds on the surface. This is why the etching process in Cl-based plasmas is referred to as ion-enhanced chemical etching [25,27,32].

In Cl-based chemistry, neither SiO_2 redeposition nor trenching was observed. Moreover, etching of SiO_2 was also suppressed compared to F-based chemistry. For example, under RIE conditions of 200 W ICP power, 80 W RF power (approx. -300 V DC Voltage), 1:1 of Cl_2 /Ar, 15 mTorr pressure, the etch rate of the SiO_2 was only ~ 9 nm/min, while the ER_{TiN} was ~ 98 nm/min, which means that the TiN is etched 10 times faster than SiO_2 .

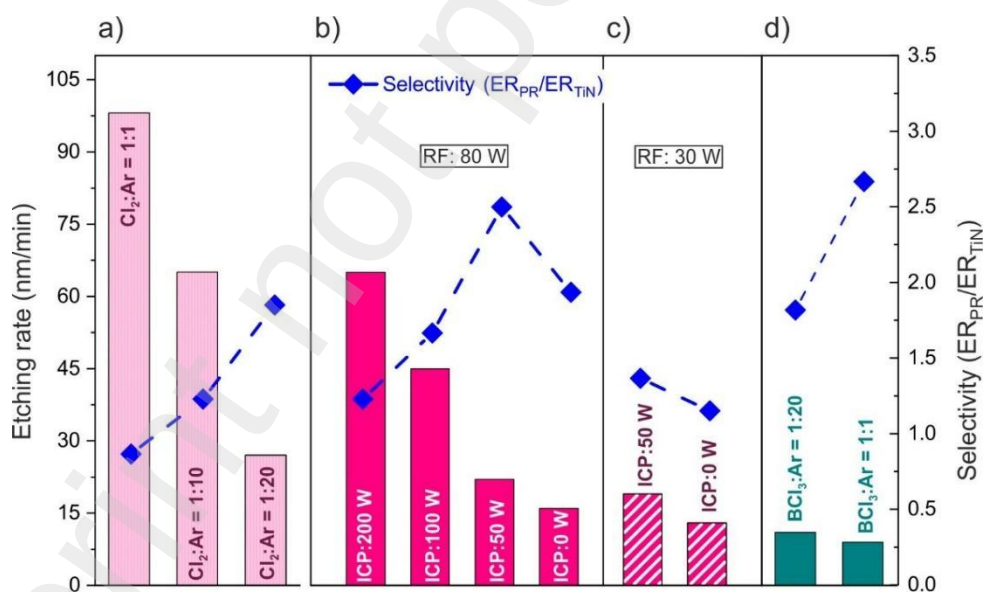


Fig. 7. Etch rate of TiN films (columns) and corresponding selectivity (dotted lines) of the samples etched in Cl_2 -Ar (a,b,c) and BCl_3 -Ar (d) gas chemistry with varied parameters; a) the variable parameter was the ratio of Cl_2 :Ar; the other parameters were constant (ICP 200 W, RF 80 W, pressure 15 mTorr); b,c) the variable parameter was the ICP power. The other parameters were Cl_2 :Ar=1:10, pressure 15 mTorr, RF power 80 W and 30 W for b) and c), respectively. d) The variable was the ratio of BCl_3 :Ar gas mixture. The other parameters were kept constant: ICP 200 W, RF 80 W, pressure 15 mTorr.

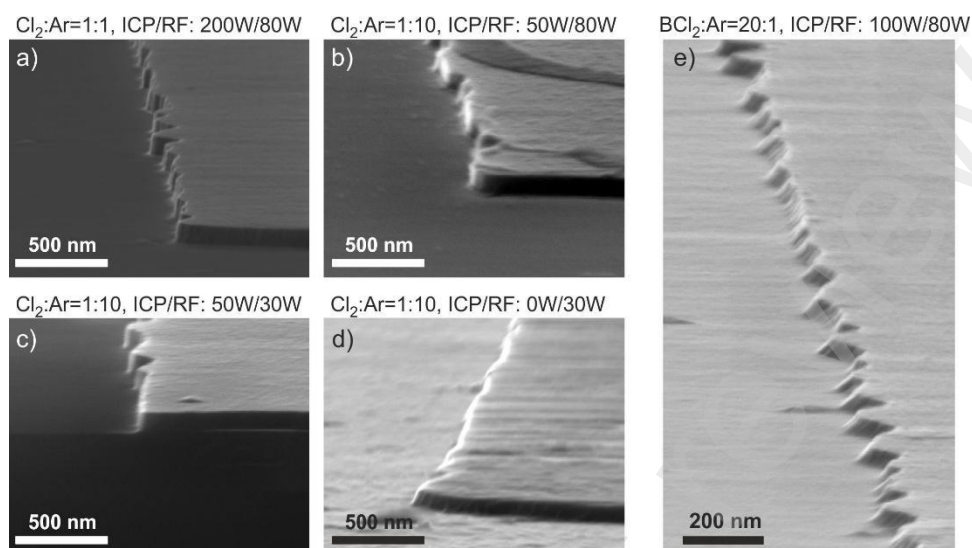


Fig. 8. Tilted-angle SEM images of the selected TiN samples etched in Cl_2 -Ar (a-d) or BCl_3 -Ar (e) gas chemistry.

3.3. Concentration depth profiles

To evaluate whether TiN surface regions contain fluoride, chloride, or carbon after RIE with different gas chemistries, the surface chemical compositions of the samples listed in Table 2 were analysed by XPS in combination with Ar-GCIB sputtering. Figure 9a displays the measured atomic concentration depth profile of the as-grown sample. The carbon signal decreased after 80 s of sputtering, indicating the removal of the adventitious carbon overlayer. A substantially longer sputtering time was required to remove the native oxide layer, as TiO_xN_y residues were still detected after more than 3000 s of sputtering. Consequently, the XPS spectra of the other samples were acquired using a sputtering time step of 920 s. The XPS depth profiles of the other samples are shown in Figure S2 in the supplementary file.

Table 2. Summary of the TiN samples used for XPS analysis, their corresponding resistivity, and the Ti:N stoichiometric ratios determined from XPS spectra before and after 920 s of sputtering with a 5 keV Ar_{1000}^+ cluster ion beam.

Sample	Gas mixture in RIE (sccm)	Etching time (s)	Note*	Resistivity ($\mu\Omega\cdot\text{cm}$)	Ti:N ratio**	
					at 0 s	at 920 s
#1b	-	-	as-grown (reference)	71	0.9	1.0
#2b	CF_4/Ar : 25/25	60	F-based chemistry (CF_4)	65	0.9	1.0
#3b	Cl_2/Ar : 25/25	15	Cl-based chemistry (Cl_2)	63	0.9	1.2
#4b	BCl_3/Ar : 25/25	60	Cl-based chemistry (BCl_3)	53	1.1	1.1
#5b	Ar: 50	40	physical sputtering by Ar	51	1.0	1.2

* The other etching parameters were the same for each set of experiments (ICP power 200 W, RF power 80 W, DC voltage -290 V), pressure 15 mTorr.

** The error bar of Ti:N ratio is generally 20%, i.e. in our case ± 0.2 .

After 920 s of Ar-GCIB sputtering, the carbon signal disappeared completely, confirming that the carbon was present only at the very top of the surface in the form of adventitious carbon. This is

illustrated in Fig. 9b, which shows the C 1s spectra before and after sputtering for sample #2b, etched using the F-based chemistry. The same decrease in the carbon signal was observed for all samples. A similar trend was observed in the F 1s and Cl 2p spectra of the samples etched using F- or Cl-based chemistry, respectively (see Figs. 9c–d). For samples etched in CF_4/Ar or BCl_3/Ar gas mixtures (samples #2b and #4b), F 1s or Cl 2p peaks were detected before sputtering, but disappeared after a short Ar-GCIB sputtering. Compared with samples #2a–4a (see Fig. 4a), the intensity of F 1s peak recorded on sample #2b was lower due to the higher ICP power (200 W) used, resulting in more intense ion bombardment than in the samples discussed in Section 3.1, for which either no ICP power (only RF power) or 100 W of ICP power was applied. Nevertheless, the XPS data demonstrate that no contamination from non-volatile by-products of plasma etching in F- or Cl-based chemistries was present. This conclusion is further supported by the resistivity measurements. The resistivity ranged from $71 \mu\Omega\cdot\text{cm}$ to $51 \mu\Omega\cdot\text{cm}$ (Table 2). The highest resistivity ($71 \mu\Omega\cdot\text{cm}$) was measured for the as-grown sample. After etching in CF_4 - or Cl_2 -based chemistry, it slightly decreased to $\sim 65 \mu\Omega\cdot\text{cm}$. The lowest resistivities were observed for Ar- and BCl_3 -etched samples ($51 \mu\Omega\cdot\text{cm}$ and $53 \mu\Omega\cdot\text{cm}$, respectively), which is in good agreement with the increased ratio of the Ti:N to 1.1 from the initial 0.9 for the as-grown sample (Table 2.). Typical resistivity for TiN thin films ranges from 100 to $300 \mu\Omega\cdot\text{cm}$, with high-quality, dense films achieving values $<100 \mu\Omega\cdot\text{cm}$ range [33,34].

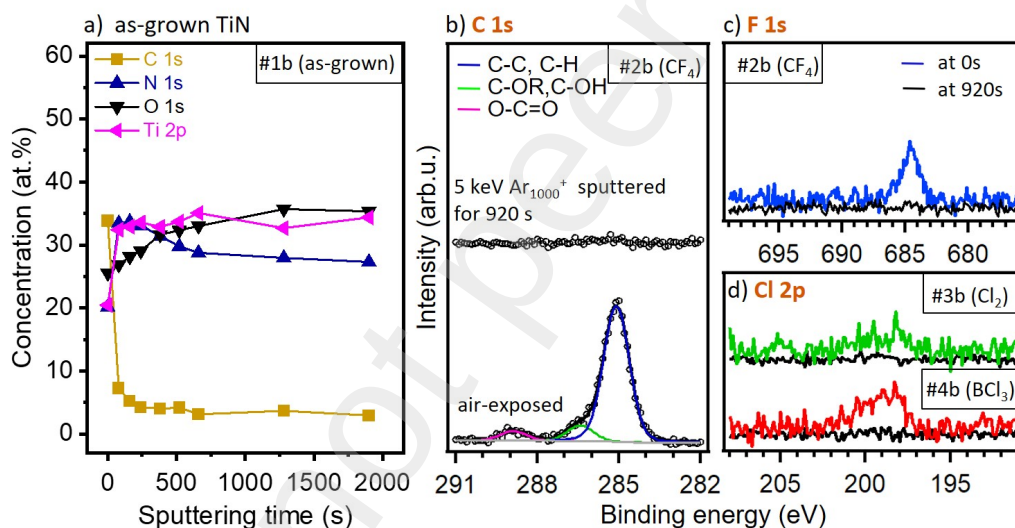


Fig. 9. a) XPS depth profile of as-grown sample #1b obtained by Ar-GCIB sputtering. b) C 1s spectra of sample #2b (etched in the F-based chemistry) before and after 920 s of sputtering with a 5 keV Ar_{1000}^{+} cluster ion beam; c) -d) F 1s and Cl 2p spectra of samples #2b, #3b, and #4b (etched in F- or Cl-based chemistries) acquired before and after 920 s of sputtering.

Figure 10a shows a comparison of the high-resolution O 1s, Ti 2p, and N 1s XPS spectra of sample #2b before (i.e., air-exposed samples after the RIE treatments) and after Ar-GCIB sputtering. The Ti 2p peak can be deconvoluted into three components: TiN, TiO_2 , and titanium oxynitride, the latter overlapping with the TiN shake-up satellite [28,29]. After sputtering, the signal from TiN increased in both the Ti 2p and N 1s spectra as the carbon was removed and the surface TiO_2 layer thickness decreased. The reduction of the surface oxide layer is also evident in the O 1s spectra, which additionally reveal that the sputtering induced partial mixing between TiO_2 and TiN, resulting in the formation of a thin titanium oxynitride interface.

Figure 10b shows the XPS spectra of all samples after Ar-GCIB sputtering. The primary differences are observed in the amount of remaining TiO_2 and TiO_xN_y components, which we attribute to variations in the thickness of the native oxide layer. The Ti:N stoichiometric ratios derived from

the Ti-N components in the Ti 2p and N 1s peaks are summarised in Table 2. Due to overlapping signals from the TiN shake-up features, titanium oxynitrides, and residual titanium suboxides, the Ti 2p peak fitting introduces a non-negligible uncertainty in the stoichiometry estimates. By varying the peak-constraint parameters used in the Ti 2p fitting process, this error was estimated to be approximately 20%. Within this measurement uncertainty, the RIE-treated samples exhibit Ti:N ratios equivalent to that of the as-grown, untreated sample, indicating that the chemical composition of the TiN remained unchanged by the RIE processes.

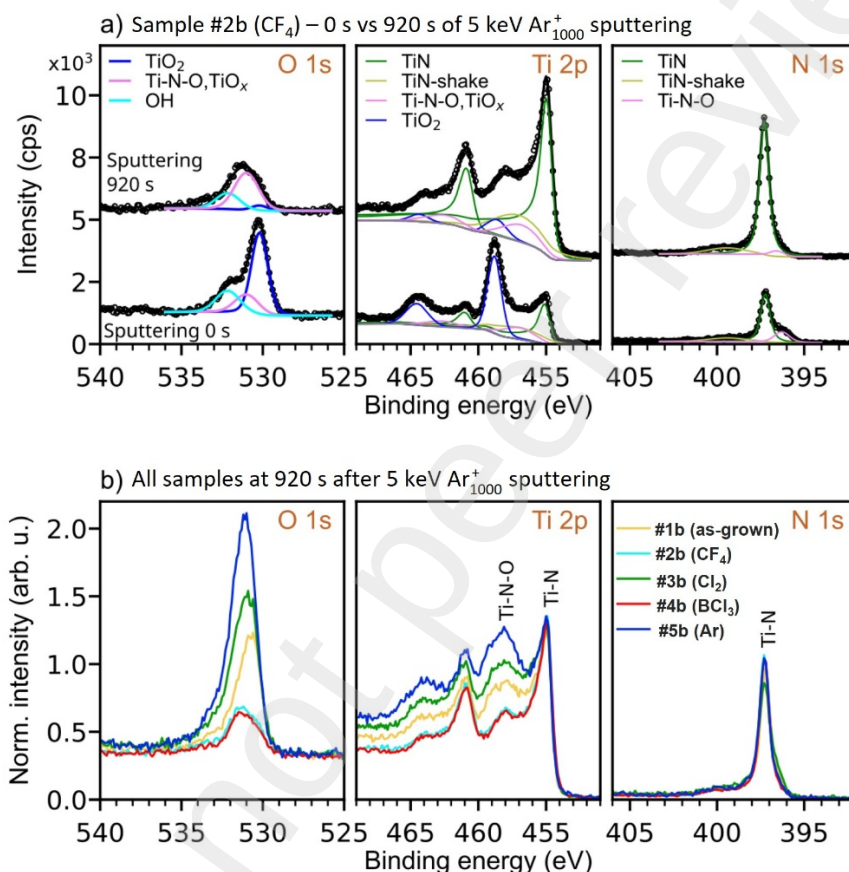


Fig. 10. a) Narrow-range XPS spectra of O 1s, Ti 2p, and N 1s for sample #2b before sputtering and after 920 s of Ar-GCIB sputtering. b) XPS spectra of samples #1b–#5b after 920 s of Ar-GCIB sputtering. The intensities are normalized to Ti 2p (TiN) peak height.

Conclusion

The dry reactive ion etching (RIE) of TiN film on SiO_2/Si substrate was studied using an inductively coupled plasma (ICP) system in different gas chemistries (CF_4/Ar , Cl_2/Ar , BCl_3/Ar). The aim was to find an appropriate etch rate that still maintains sufficient selectivity against the photoresist mask, while achieving an engineered etch profile (i.e., a perpendicular etch profile or inclined edges) and preserving the stoichiometric ratio of Ti:N.

In our selected etching conditions, the etch rates (ER) typically range from 10 to 30 nm/min. Such low etch rates enabled more controllable etching of TiN thin films, avoiding trenching and the redeposition of the SiO_2 underlayer on the TiN sidewalls.

In the case of the F-based chemistry, the ICP power strongly influenced the etch profile. Without the ICP with RF plasma only, the sidewall showed a tilted etch profile of $\sim 17^\circ$, while by increasing the ICP power, the angle of the etch profile also increased to $\sim 33^\circ$ and $\sim 51^\circ$ for 100 W and 200 W, respectively. XPS measurements revealed the presence of fluorinated titanium on the etched TiN surfaces, however, its intensity diminished upon the addition of ICP to RF. This reduction is associated with increased ionization rate and ion bombardment, which inhibit the redeposition of non-volatile TiF_x by-products at higher ICP power. The optimal etch uniformity over an area of $5 \times 5 \text{ cm}^2$ was achieved for a process pressure of 15 mTorr. In this case, the difference between the maximum and the minimum etch rates (Δ_{ER}) was only 1.2 nm/min.

Compared to F-based chemistry, etching in Cl_2 -Ar chemistry only resulted in an anisotropic etch profile ($>85^\circ$) with sharp, vertical walls, independent of the etching conditions, and 3-4 times higher etch rates of TiN. Replacing Cl_2 by BCl_3 resulted in an 8-10 times lower ER_{TiN} ($\sim 8 \text{ nm/min}$). Nevertheless, the etch profile in BCl_3 -Ar chemistry exhibited a tilted angle of approximately 54° , which is a favourable result for certain applications, such as bottom electrodes for crossbar structures.

The XPS results demonstrate that there is no contamination from non-volatile by-products of plasma etching in F- or Cl-based chemistries. This conclusion is further supported by the resistivity measurements, which showed no significant differences among the samples. Based on the results, we determined the optimal condition for the perpendicular or inclined etch profile etching of 100 nm thick TiN on a SiO_2/Si substrate as follows: a) for perpendicular profiles: ICP/RF power 200/80 W, Cl_2/Ar 15/15 sccm, pressure 15 mTorr, process time 2 min; b) for inclined etches: ICP/RF power 100/20 W, CF_4/Ar 50/2.5 sccm, pressure 15 mTorr, process time 3.5 min.

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Table 1. Description of the TiN samples used for the XPS measurements

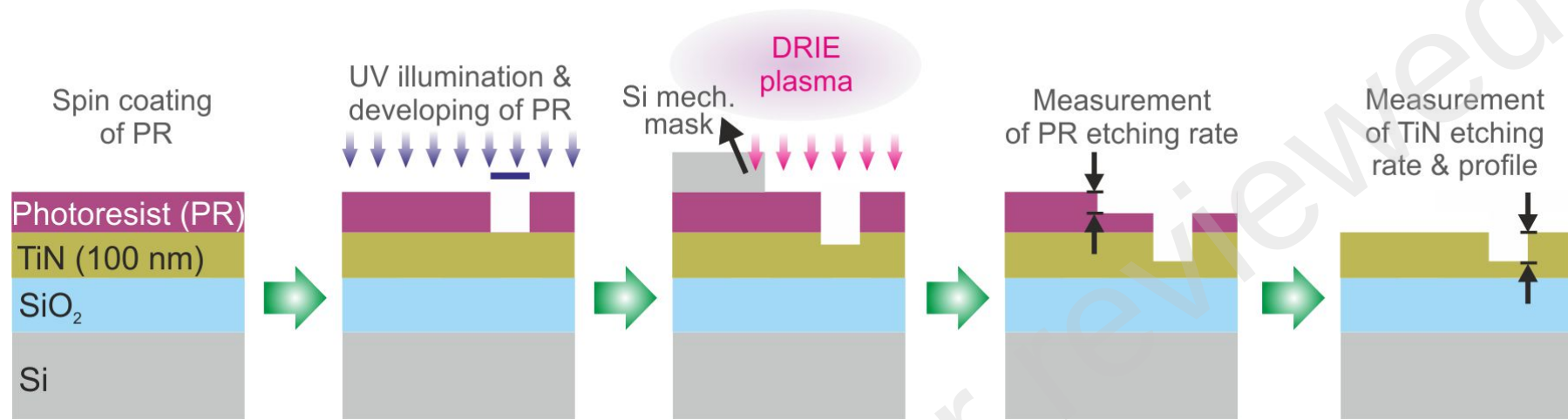
Sample	Gas mixture in the RIE process	RF power (W)	ICP power (W)	Note
#1a	-	-	-	as-grown (reference)
#2a	CF ₄ /Ar: 25/25 sccm	80	-	50% CF ₄ in CF ₄ -Ar gas mixture
#3a	CF ₄ /Ar: 50/2.5 sccm	80	-	95.2% CF ₄ in CF ₄ -Ar gas mixture
#4a	CF ₄ /Ar: 50/2.5 sccm	80	100	95.2% CF ₄ in CF ₄ -Ar gas mixture

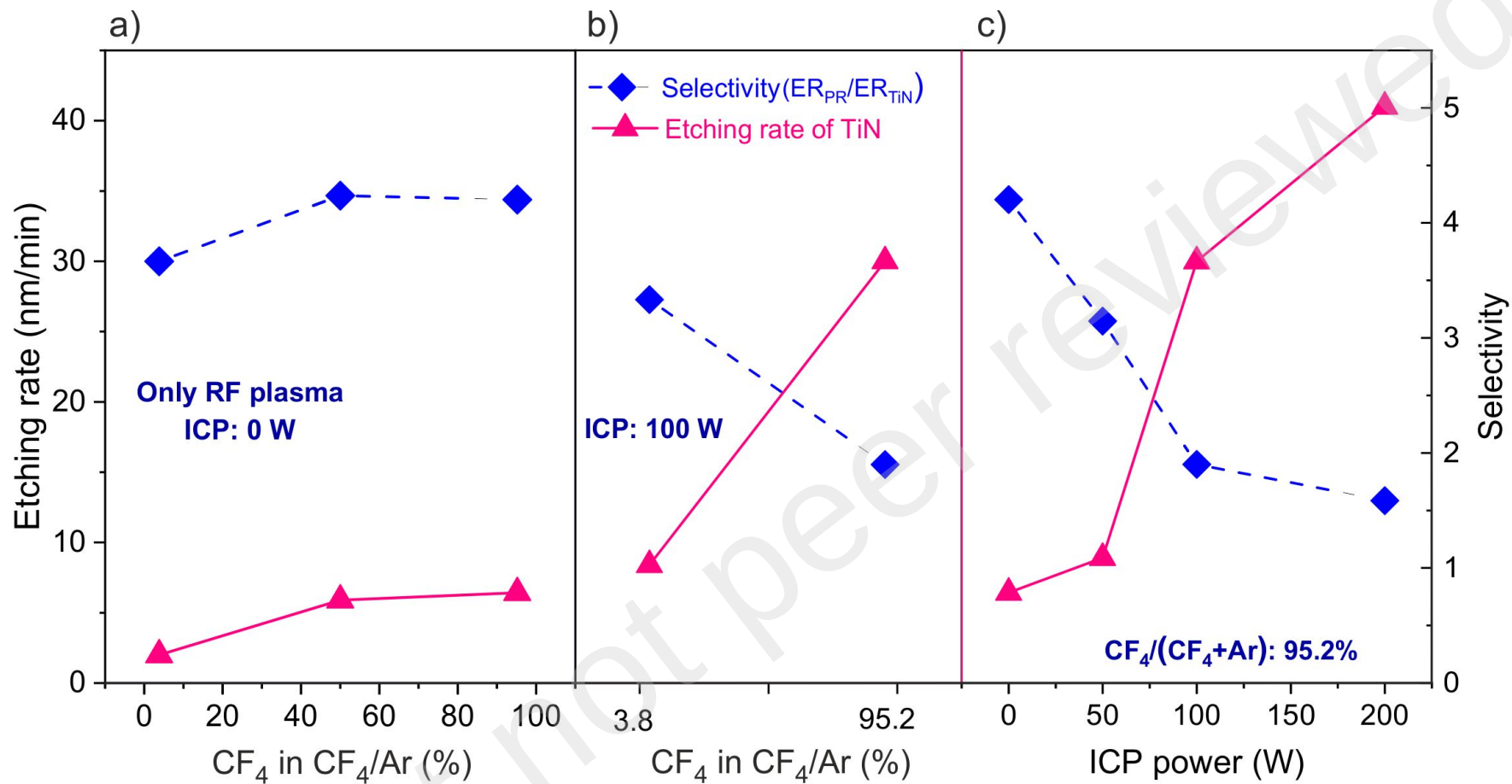
Table 2. Summary of the TiN samples used for XPS analysis, their corresponding resistivity, and the Ti:N stoichiometric ratios determined from XPS spectra before and after 920 s of sputtering with a 5 keV Ar₁₀₀₀⁺ cluster ion beam.

Sample	Gas mixture in RIE (sccm)	Etching time (s)	Note*	Resistivity ($\mu\Omega\cdot\text{cm}$)	Ti:N ratio**	
					at 0 s	at 920 s
#1b	-	-	as-grown (reference)	71	0.9	1.0
#2b	CF ₄ /Ar: 25/25	60	F-based chemistry (CF ₄)	65	0.9	1.0
#3b	Cl ₂ /Ar: 25/25	15	Cl-based chemistry (Cl ₂)	63	0.9	1.2
#4b	BCl ₃ /Ar: 25/25	60	Cl-based chemistry (BCl ₃)	53	1.1	1.1
#5b	Ar: 50	40	physical sputtering by Ar	51	1.0	1.2

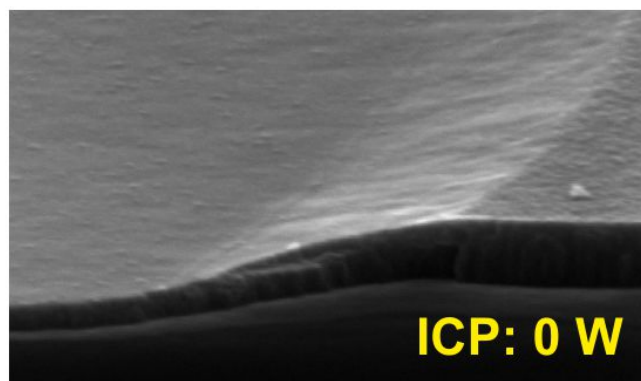
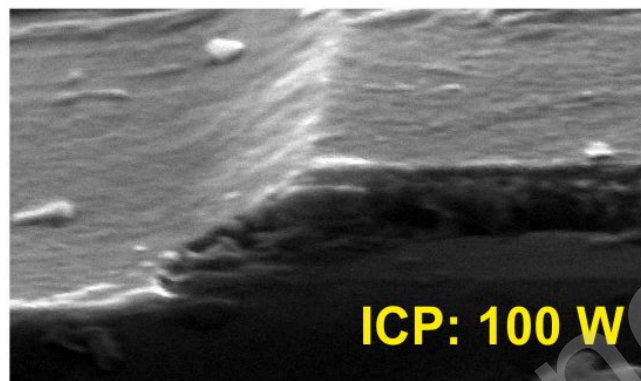
* The other etching parameters were the same for each set of experiments (ICP power 200 W, RF power 80 W, DC voltage - 290 V), pressure 15 mTorr.

** The error bar of Ti:N ratio is generally 20%, i.e. in our case ± 0.2 .

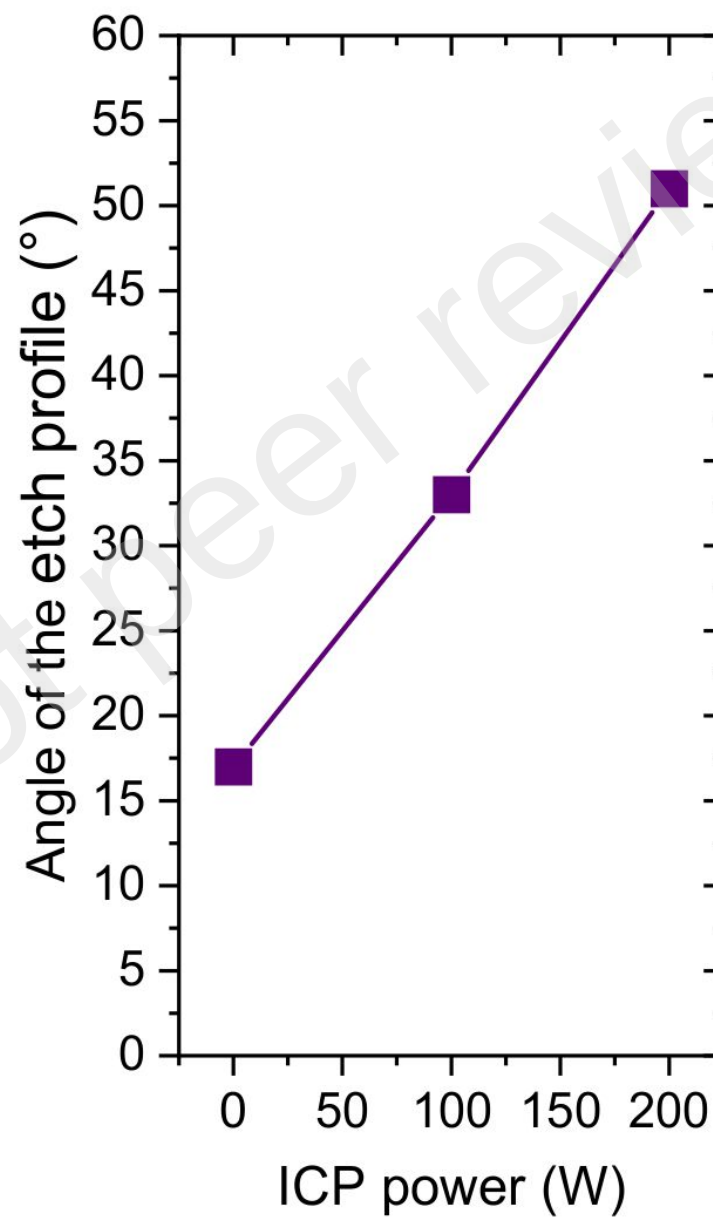


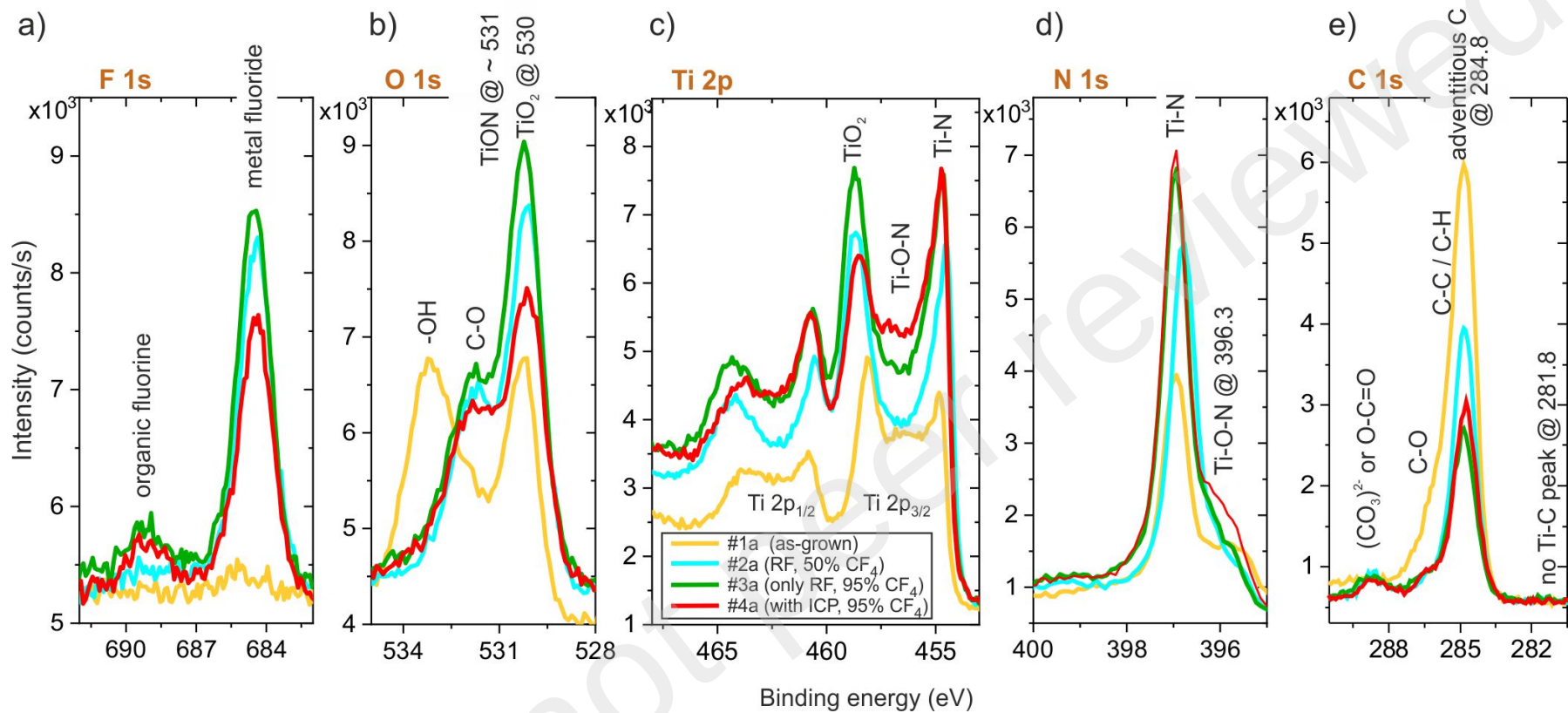


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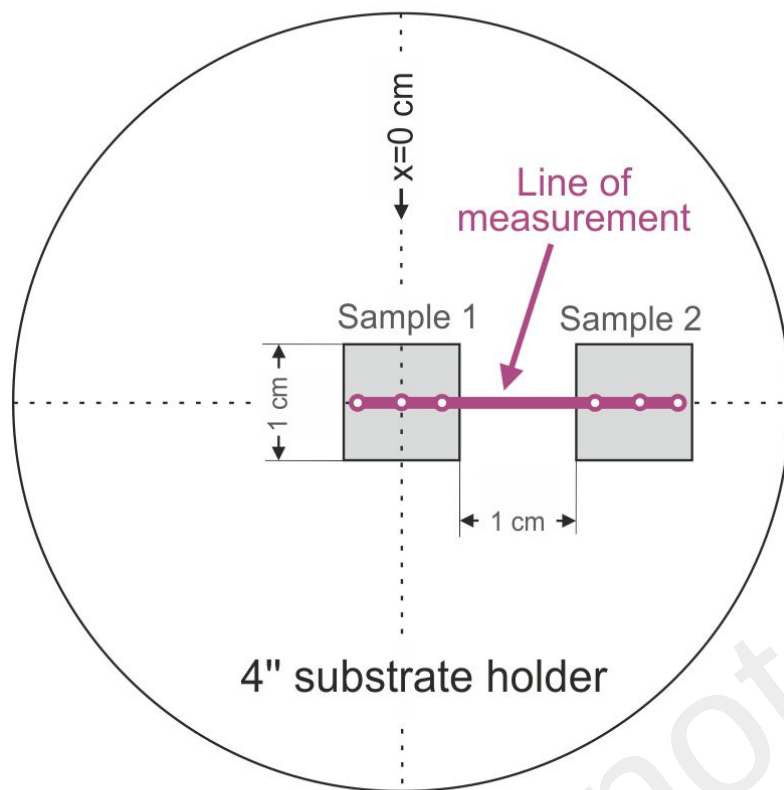


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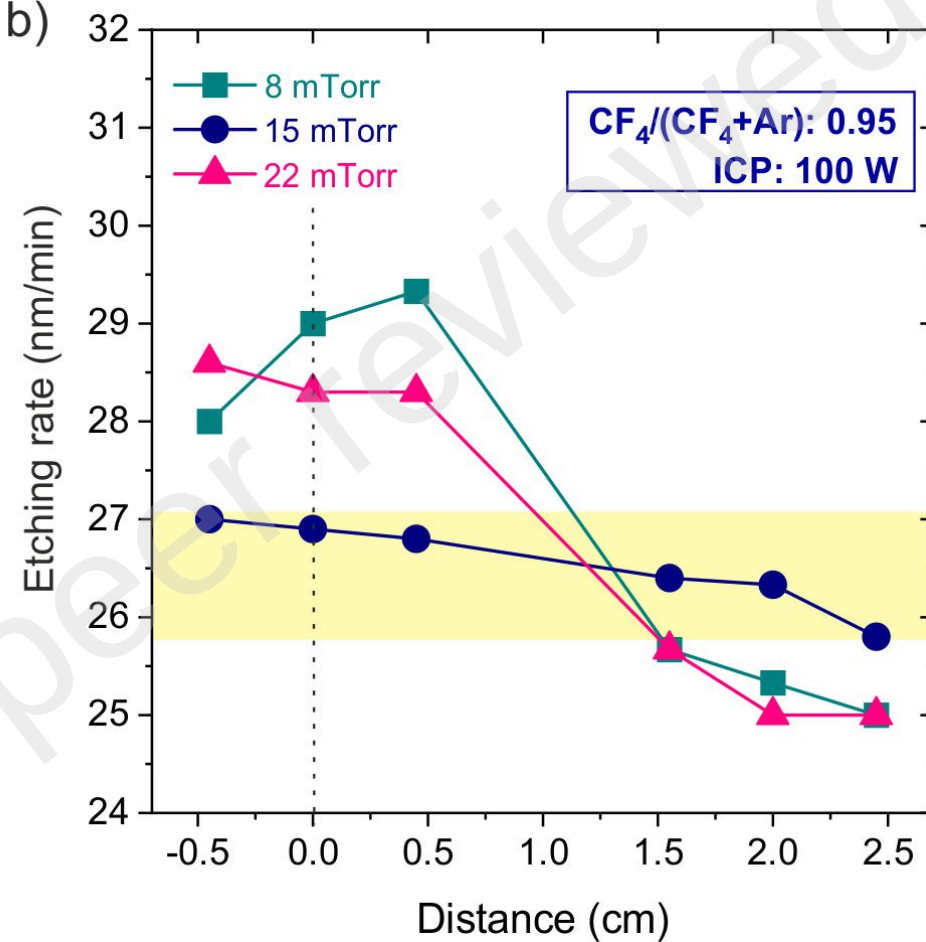




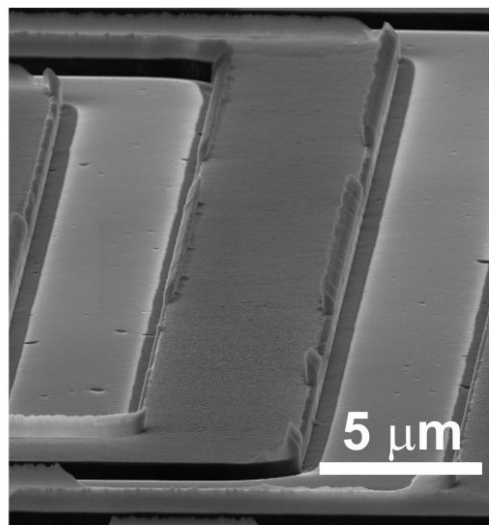
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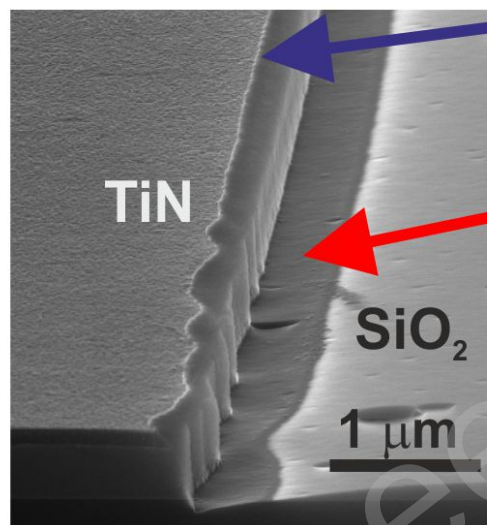
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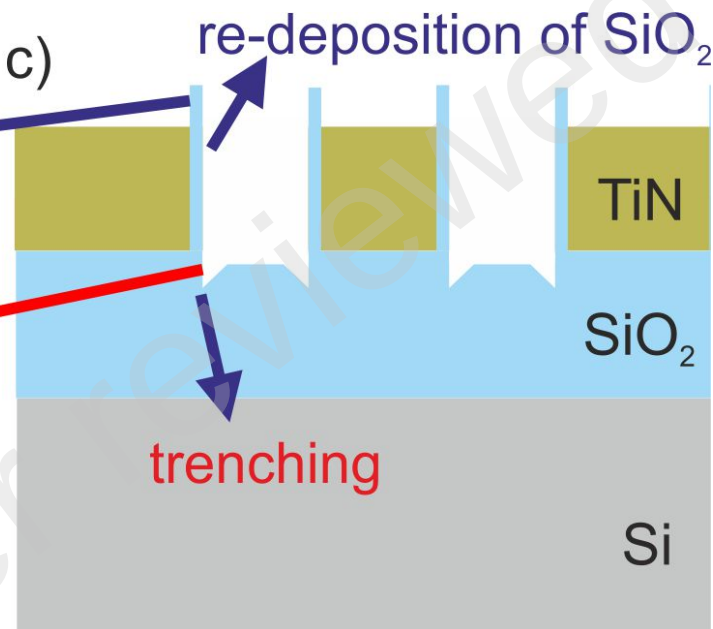
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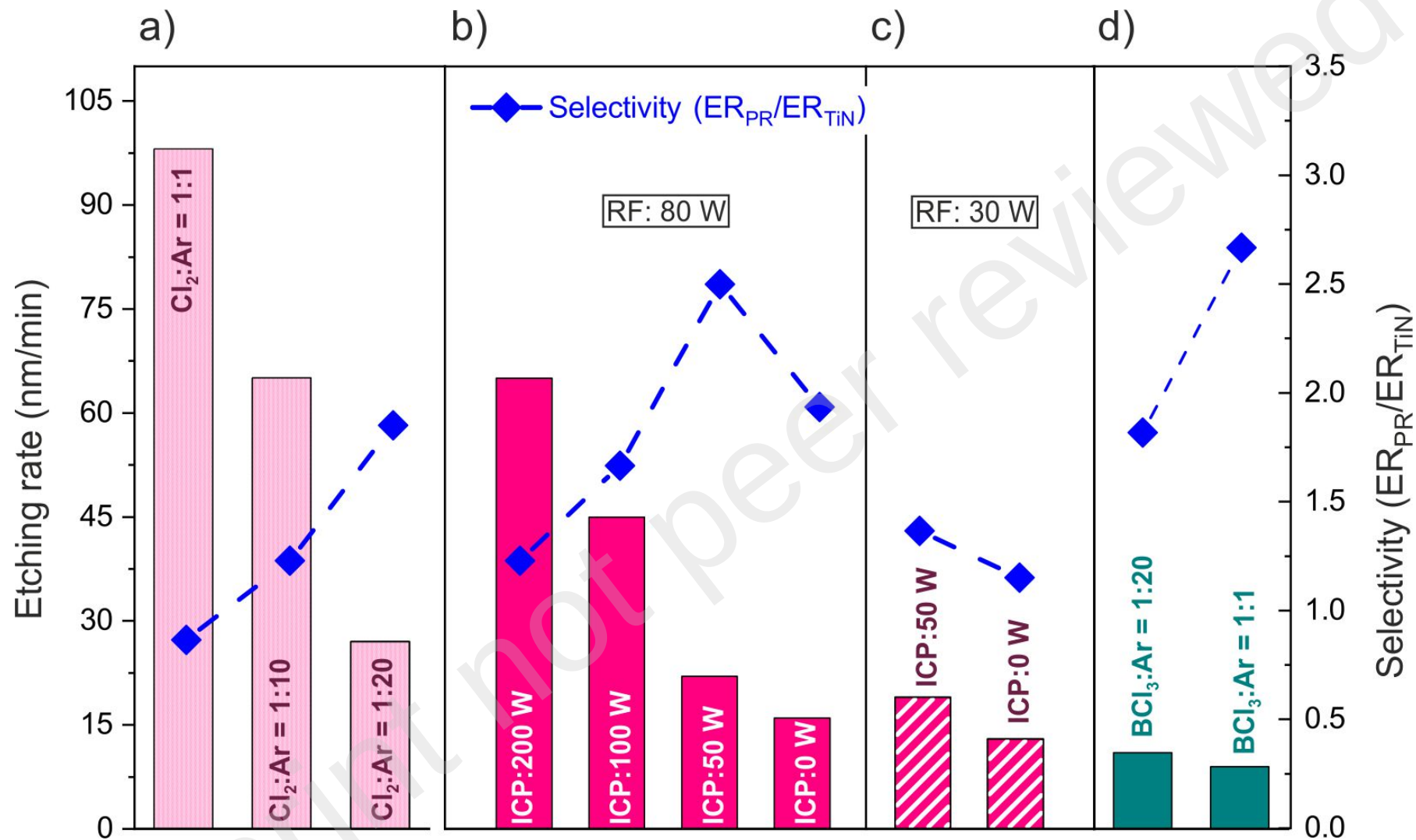


b)

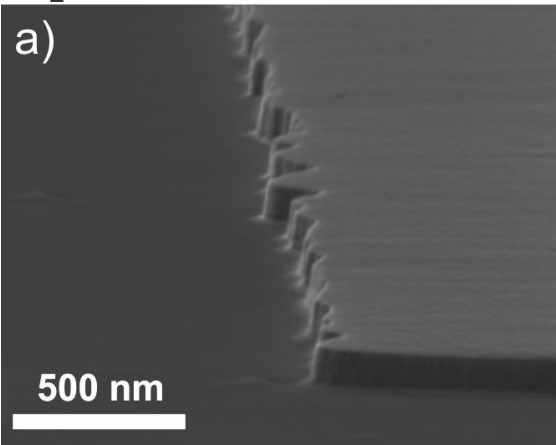


c)

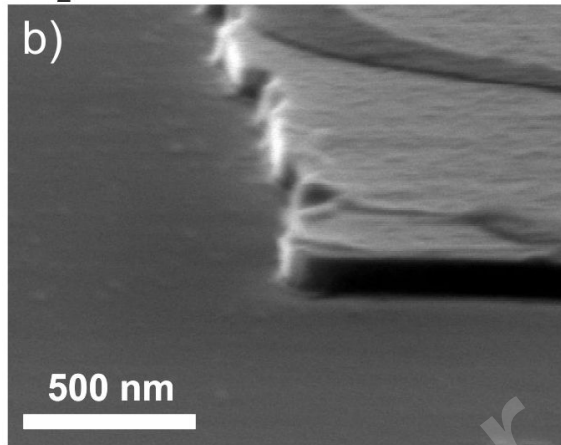




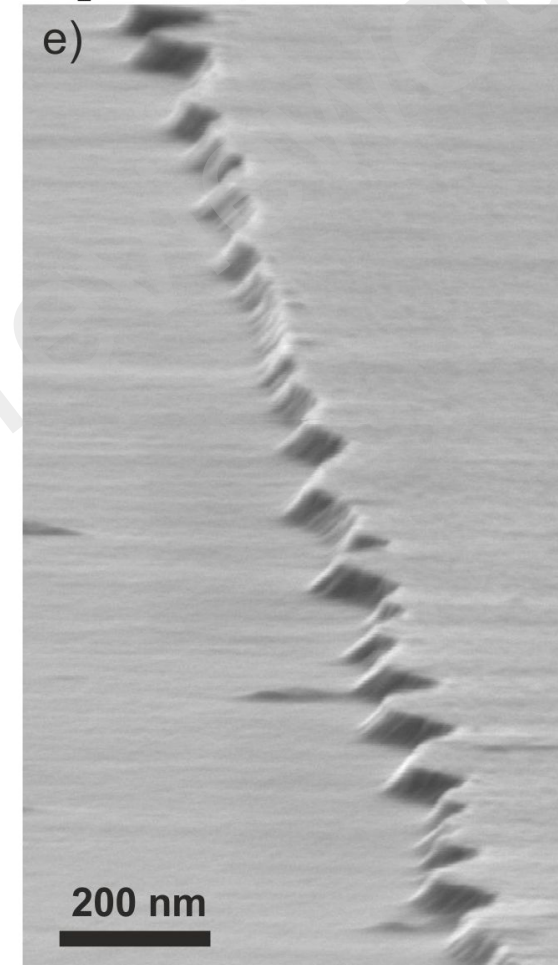
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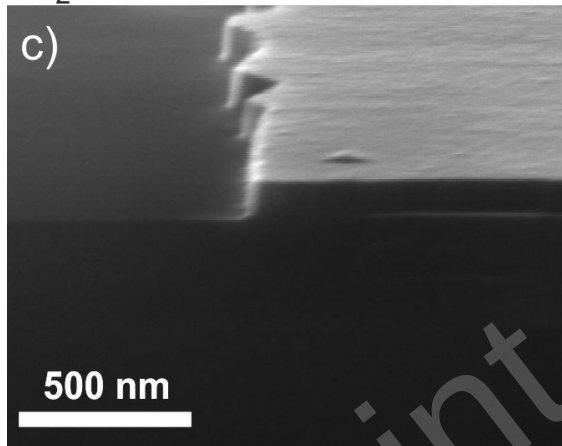
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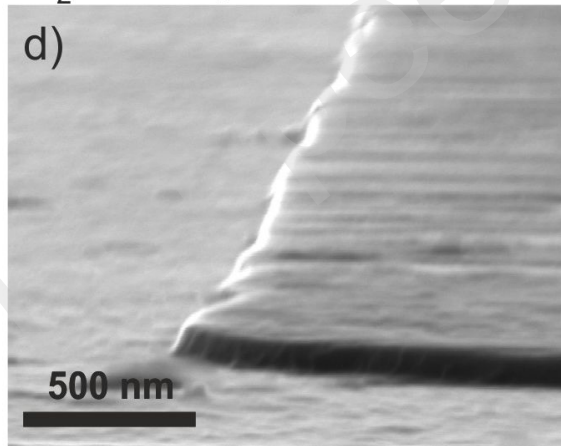
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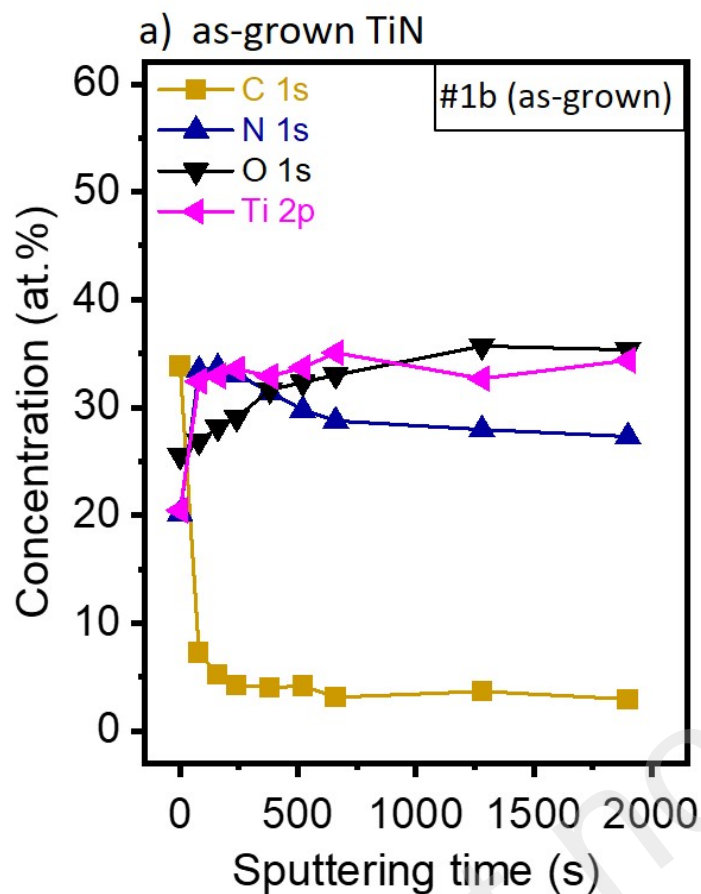
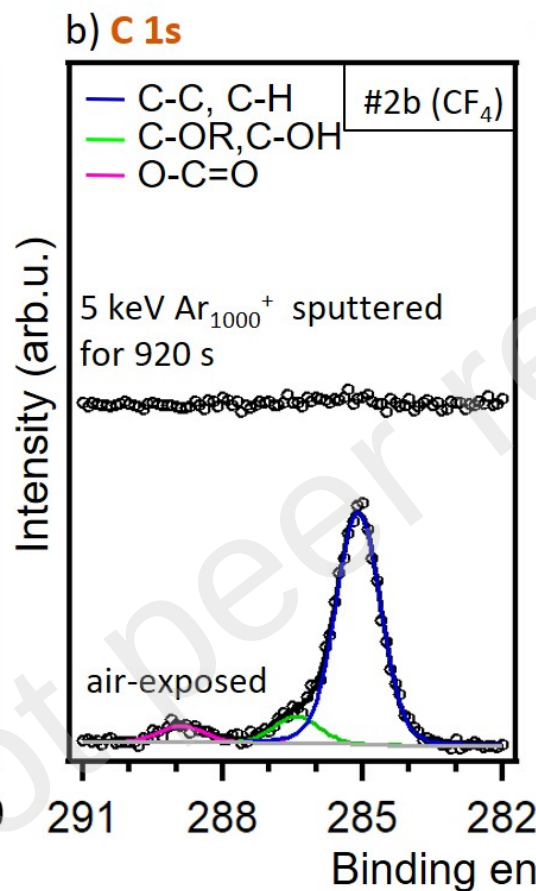
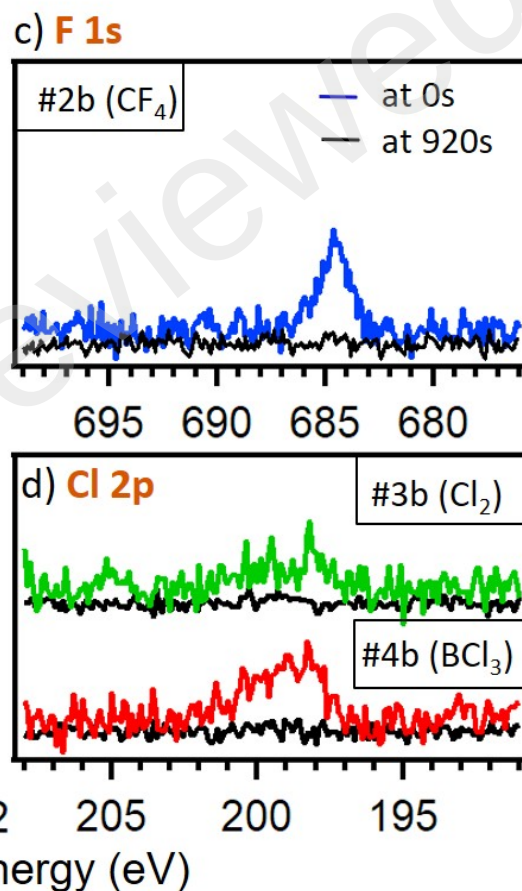


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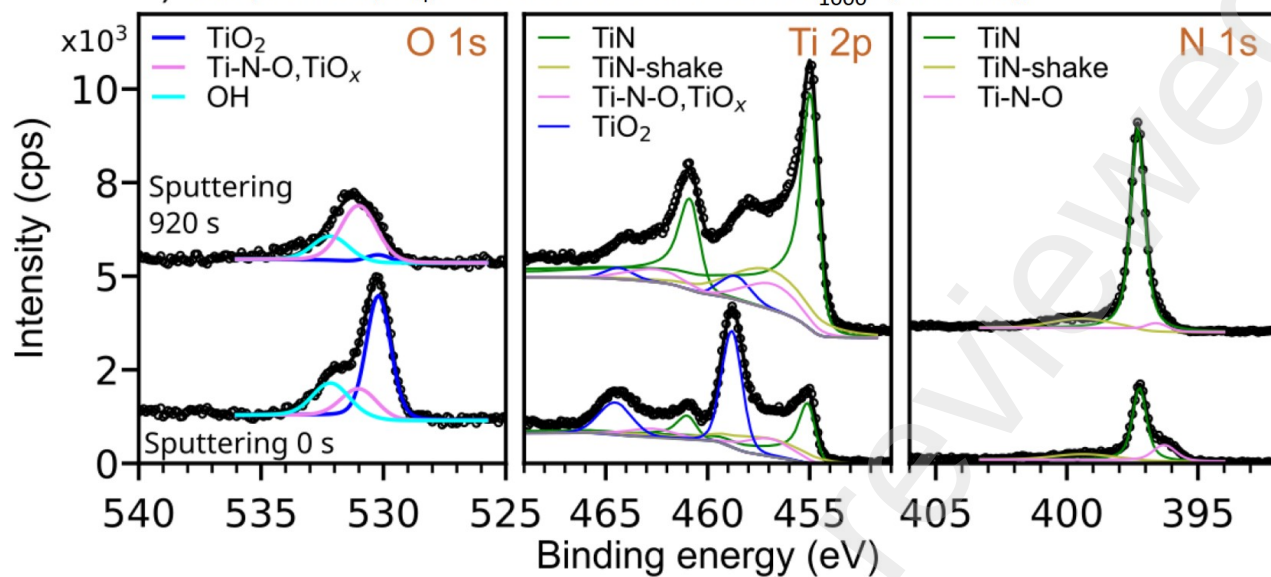


$\text{Cl}_2:\text{Ar}=1:10$, ICP/RF: 0W/30W





a) Sample #2b (CF_4) – 0 s vs 920 s of 5 keV Ar_{1000}^+ sputtering



b) All samples at 920 s after 5 keV Ar_{1000}^+ sputtering

