

Research paper

Characterization of $\text{Ru}_{4-x}\text{Ta}_x$ ($x = 1,2,3$) alloy as material candidate for EUV low-n mask

Meiyi Wu^{a,b}, Jean-François de Marneffe^a, Karl Opsomer^{a,d}, Christophe Detavernier^d, Annelies Delabie^{a,b}, Philipp Naujok^c, Özge Caner^{a,b}, Andy Goodyear^f, Mike Cooke^f, Qais Saadeh^e, Victor Soltwisch^e, Frank Scholze^e, Vicky Philipsen^{a,*}

^a IMEC, Kapeldreef 75, B-3001 Leuven, Belgium

^b KU Leuven, Department of Chemistry, Leuven, Belgium

^c optiX fab GmbH, Hans-Knoell-Strasse 6, 07745 Jena, Germany

^d Ghent University, Department of Solid State Sciences, Krijgslaan 281 (S1), 9000 Ghent, Belgium

^e Physikalisch-Technische Bundesanstalt, Abbestr. 2-12, 10587 Berlin, Germany

^f Oxford Instruments Plasma Technology, North End, Yatton, Bristol, United Kingdom



ARTICLE INFO

Keywords:

EUV lithography

EUV mask absorber

Alloy absorber for EUV mask

RuTa alloy

Material optical properties refractive index

Mask absorber etching

Mask absorber characterization

ABSTRACT

$\text{Ru}_{4-x}\text{Ta}_x$ ($x = 1,2,3$) alloys are studied as absorber candidates for EUV low-n mask. We report the morphology, surface roughness as well as the chemical composition of the as-deposited alloy films for better theoretical model building of the EUVL absorber stack. Their refractive indices are reconstructed by optimizing measured EUV reflectivity data for the purpose of enabling rigorous EUVL imaging calculations in the future work. The stabilities (both physical and chemical) of these absorber candidates are verified which contribute to a long lifetime of the mask in its working environment. This includes the resistance assessments of the thin films against high temperature up to 500 °C, different mask cleaning solutions and hydrogen environment which is present in EUV scanners. Etching of RuTa is explored using halogen-based reactive ion etch technique. A low etch rate is obtained with a moderate etch selectivity to Ru, which is the capping layer of multilayer mirror on a EUVL mask.

1. Introduction

The development of extreme ultraviolet lithography (EUVL) is pushing EUV imaging to enable high-volume manufacturing of integrated circuits beyond 14 nm half-pitch ($\sim\text{N}2$ node) at scaled dimensions. The so-called mask 3D (M3D) effect [1–3] is caused by the oblique incidence (6° chief-ray angle from normal) of the EUV light beam on the mask, the angular dependent EUV reflectance of the mask multilayer mirror and the thickness, as well as the optical response of the mask absorber. The current state-of-art TaBN mask absorbers have a thickness of 60–70 nm, which is about 4–5 times the EUV wavelength (13.5 nm). The M3D effects can be mitigated by new mask design, particularly the selection of materials for the mask absorber [4–6]. Recently, imaging simulations efforts [7–9] proposed mask absorbers with low EUV refractive index for high contrast printing, so-called EUV low-n mask.

The material candidates must meet specific EUVL mask criteria [10].

First, they must possess good optical properties to introduce gains in EUVL imaging performance compared to the current Ta-based absorber [6]. Second, the alloy materials need to show an amorphous or nano-crystalline structure [11,12]. Third, it is crucial for the material to have good chemical and thermal stabilities, which guarantee a long lifetime of the dedicated EUVL mask. Finally, it must be etchable, to create the pattern on the mask.

In this paper, Tantalum is chosen as starting element because it is a well-known suitable EUV mask absorber material, currently used in the mask making industry. Ruthenium is selected as the complementary element in the binary alloy because of its low EUV refraction coefficient n , enabling phase shifting between photons reflected by the absorber and the mirror.

In the following sections, the $\text{Ru}_{4-x}\text{Ta}_x$ alloys are evaluated by our extensive experimental methodology flow [6]. The deposition and characterization of three different $\text{Ru}_{4-x}\text{Ta}_x$ ($x = 1,2,3$) alloys will be described. The film characterization of these materials includes

* Corresponding author.

E-mail address: vicky.philipsen@imec.be (V. Philipsen).

<https://doi.org/10.1016/j.mne.2021.100089>

Received 20 January 2021; Received in revised form 19 April 2021; Accepted 8 May 2021

Available online 12 May 2021

2590-0072/© 2021 The Authors.

Published by Elsevier B.V. This is an open access article under the CC BY-NC-ND license

(<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

morphology, surface roughness, chemical composition, optical constants, and chemical and thermal stability. Etch test is also performed, dedicated for the patterning of the absorber.

2. Sample preparation

$\text{Ru}_{4-x}\text{Ta}_x$ ($x = 1, 2, 3$) alloy film is deposited by physical vapor deposition (PVD) method as periodic nano-laminates of Ru and Ta films on 300 mm Si wafer with 0.35 nm thickness of one $\text{Ru}_{4-x}\text{Ta}_x$ ($x = 1, 2, 3$) period. The Ru:Ta ratio is tuned by adjusting relative deposition time of Ru and Ta laminates respectively to be 1:0 (pure Ru), 3:1, 1:1, 1:3, 0:1 (pure Ta). According to the Ru–Ta phase diagram, the two elements are expected to be totally mixed [13,14].

3. Characterization

3.1. Morphology and surface roughness

To investigate the morphology of the alloys, the films are measured by X-ray diffractometry (XRD) and atomic force microscopy (AFM) measurements. Fig. 1 presents the XRD result for the as-deposited films with different Ru/Ta ratios. The XRD peak at detection angle 2θ about 33° is Si (002) due to dynamical scattering of multiple replicas of the diffraction beam through the single crystal substrate. For pure Ru, three peaks are observed, indicating the Ru (100), Ru (002) and Ru (101) reflections for the hcp crystal structure. For Ta, the experimental XRD curve is a sum of intensity from multiple tabulated Ta XRD peaks. Ru_3Ta XRD peaks are like the ones of Ru with a shift towards lower angle. This is an indication that the addition of Ta stretches Ru crystalline planes. No clear peaks are observed for RuTa , indicating a nearly amorphous phase, or the size of crystallites is smaller than 1 nm according to Scherrer's formula, that was used to estimate the size of the crystallites [15]. For RuTa_3 , the peak at 39.5° represents RuTa_3 (111).

The AFM results including the root mean squared (RMS) roughness values are presented in Fig. 2 for 30 nm films. The surface roughness of the films strongly depends on the composition. RuTa and RuTa_3 have the lowest surface roughness of 0.12 nm and 0.13 nm RMS, respectively. Ru_3Ta , however, shows a high surface roughness of 0.31 nm rms. This correlates with the XRD result of Fig. 1, indicating a more amorphous phase for high Ta content and (semi-)crystalline phase at high Ru content.

For a more direct observation of the structure of the three alloys, transmission electron microscopy (TEM) technique is applied. The cross-sectional view TEM images for each alloy film are presented in Fig. 3, for 50 nm thick films. The upper bright layer on top of the $\text{Ru}_{4-x}\text{Ta}_x$ ($x = 1, 2, 3$) films represents spin-on carbon which is deposited during the sample preparation for TEM measurement. It is then followed by a 2–3

nm surface oxide of the alloy. The Ru_3Ta top surface shows higher roughness compared to RuTa and RuTa_3 , in agreement with the AFM measurements. The three alloys can be distinguished by their bulk morphology. The presence of Moiré fringes with a columnar structure in the Ru_3Ta film is caused by overlapping nano-crystal grains, which is a direct evidence of crystallinity. The RuTa layer shows an amorphous structure through its entire thickness. RuTa_3 does not show Moiré fringes, but presents dark zones in the layer, which indicate an inhomogeneous density caused by nano-crystal grains. The TEM result agrees with the XRD data in Fig. 1 where only RuTa is found amorphous. A bright layer at the alloy/Si substrate interface is observed for all three alloys. This is due to the natural oxidation of the Si wafer surface.

The XRD, AFM and TEM morphological inspections described in this paragraph therefore allow to conclude that for $\text{Ru}_{4-x}\text{Ta}_x$ ($x = 1, 2, 3$) alloys, $x = 2$ leads to an amorphous thin film, while $x = 1$ and 3 show crystallinity of the thin films to different extent.

3.2. Chemical composition

The compositions of the deposited films are characterized by Ruthenium backscattering spectrometry (RBS) and X-ray photoelectron spectroscopy (XPS). The Ru:Ta ratios of the three alloys determined by these two techniques are presented in Table 1. Ru:Ta ratios determined by RBS, which probes the films through their entire thickness (50 nm), are close to the nominal ones. The probing depth of XPS, is limited to a few nanometres in the vicinity of the top surface. The XPS analysis shows a Ta rich surface for all three alloys compared to the bulk compositions. Particularly for RuTa_3 , the Ru:Ta ratio on the surface is 1:8, which indicates some Ta segregation at the surface and near-surface areas. At 284.2 eV, the Ru 3d photoemission peak overlaps with the C 1 s peak [16], leading to entangled carbon and ruthenium contributions. It is known that surfaces exposed to ambient are contaminated with carbon; therefore, the Ru content indicated in Table 1 is overestimated. Table 2 shows the atomic percentages of the measured alloy thin films. Elements such as oxygen and carbon are removed from the table as they may suffer from the influence of the surface contamination. The surface of Ta-rich materials is mostly covered by oxide, while the Ru-rich materials show much less oxidation. This is in line with the chemical activity of Ta and is later confirmed by EDS-STEM.

For more detail of the bulk chemical composition, energy dispersive X-ray spectroscopy (EDS) in scanning transmission electron microscopy (STEM) is applied to the three alloys. An example of the acquired data is given in Fig. 4 for Ru_3Ta . Ruthenium and Tantalum suffer from EDS spectral peak overlap with carbon and silicon signals, respectively, leading to significant background Si and C contributions. The O detection in the bulk of Ru_3Ta layer is attributed to the oxidation of the TEM specimen during sample preparation. A stronger O EDS emission signal is detected at the top surface of Ru_3Ta , as well as at the bottom interface with Si, representing oxide of Ru/Ta and Si, respectively.

The elemental profiling is obtained by performing a signal intensity scan along the arrow presented in the high-angle annular dark-field image (HAADF) in the left part of Fig. 5. To increase signal/noise ratio, the scan is averaged over the shaded area instead of a single line. A depth profile (from the bottom of the film to the top) of atomic concentration is then obtained for each element by normalizing each EDS intensity by its emission yield, as presented in the right part of Fig. 5. The Ru:Ta ratio remains constant through the bulk part of the film (position approximately from 10 to 58 nm). Oxidation at the Ru_3Ta top surface is clearly observed from the O peak at position = 60 nm, as well as the native SiO_x layer at the Ru_3Ta /Si bottom interface (O peak at position = 7 nm).

Atomic concentration depth profiles of RuTa and RuTa_3 are shown in Fig. 6. It can be observed that, close to the top surface, the Ru signal drop to zero while the Ta signal remain finite, corresponding to top Ta segregation thicknesses of approximately 2 nm and 3 nm, respectively. The surface oxidation is observed from the depth profile of O; therefore,

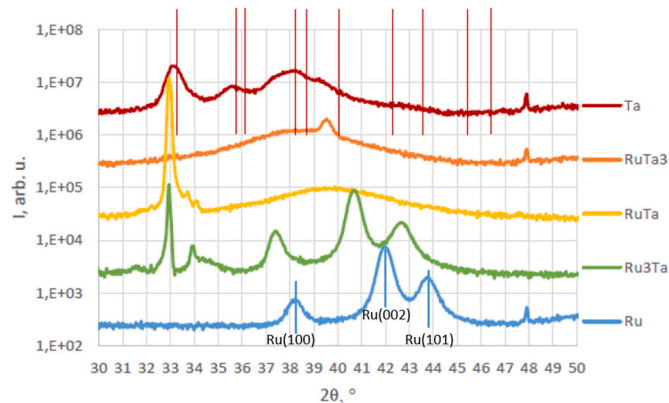


Fig. 1. XRD measured as deposited for 30 nm films of Ru, Ru_3Ta , RuTa , RuTa_3 and Ta. Vertical solid lines in the figure indicate tabulated Ta peaks.

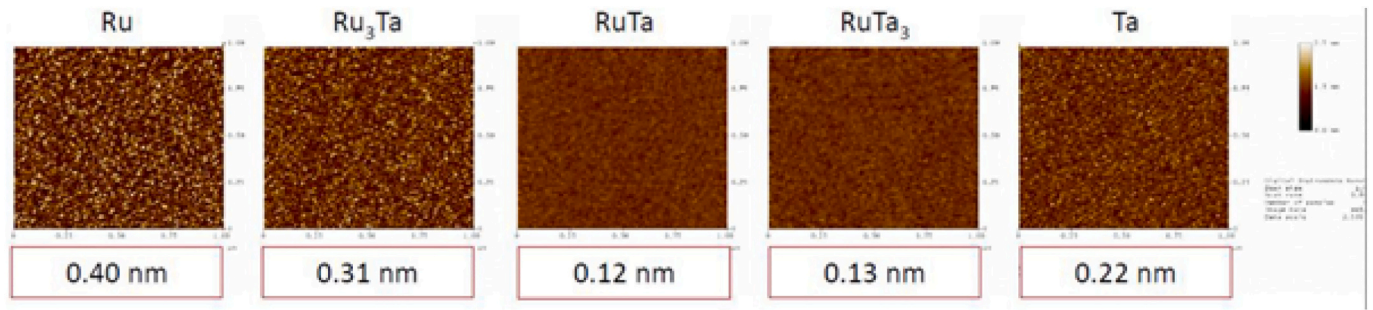


Fig. 2. AFM images and RMS values measured as deposited for 30 nm films of Ru, Ru₃Ta, RuTa, RuTa₃ and Ta.

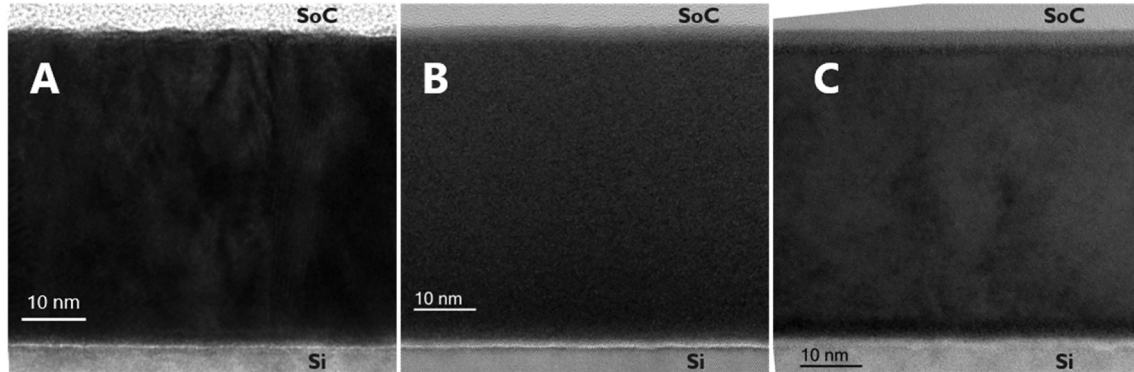


Fig. 3. TEM result of 50 nm thick films of the alloys. A: Ru₃Ta, B: RuTa and C: RuTa₃.

Table 1

Ru:Ta ratio comparison among designed value, RBS analysis and XPS analysis for 50 nm thick films.

Sample	Ru:Ta ratio		
	Designed	RBS analysis	XPS analysis
Ru ₃ Ta	3:1	3.6:1	2.9:1
RuTa	1:1	1:1.1	1:1.8
RuTa ₃	1:3	1:2.7	1:8

Table 2

Atomic concentrations (at.%) as calculated from the fits on the XPS spectra.

Sample	Ta (at.%)		Ru (at.%)	
	Ta metal	Ta oxide	Ru metal	Ru oxide
Ru	/	/	15.20	7.48
Ru ₃ Ta	3.36	2.36	8.21	8.11
RuTa	4.17	11.54	5.50	2.88
RuTa ₃	6.11	15.86	2.10	0.71
Ta	9.25	16.33	/	/

we can conclude that the surface layer is oxidized Ta. Because of Ta diffusion towards the surface, the Ru shows an increased density just underneath the Ta-enriched top layer (see the marked “Ru rich zone” in Fig. 6). Looking back at the Fig. 5 for Ru₃Ta, tantalum segregation is not visible due to the high Ru content, making Ta oxidation less likely.

3.3. Optical constants reconstruction

The reconstruction of the alloys' optical constants was realized by optimizing an inverse problem aiming at the minimization of an objective function which compares the measured EUV reflectivity (EUVR) data against a simulation based on an assumed model, with the residual weighted by the measurements' error. The acquisition of the

EUVR data was conducted at the soft X-ray radiometry beamline (SX700) in the radiometry laboratory of PTB in the electron storage ring facility BESSY II [17]. The reflectivity was measured for the angular range 3.5° - 85.5° regarding the sub-EUV spectral range 10 nm – 20 nm. For the data optimization, a four-layer model (on a Si-substrate) was assumed to initialize the forward calculation. The model's stratification is composed (by ascending order) of the substrate's native oxide, the sputtered alloy, its oxide layer followed by a carbonaceous contamination layer to compensate the presence of sticking volatiles since the samples were handled in ambient atmosphere prior to the measurements [18,19]. Fig. 7 presents the comparison between measured and the reconstructed reflectivity curves at a wavelength of 13.5 nm for the three binary alloys.

As a result of the EUVR data optimization, optical constants (n and k , or $1-\delta$ and β) of the alloys are reconstructed for each measured at-wavelength. At 13.5 nm, the reconstructed values are close to the tabulated values [20]. The optical constants of all three compositions are summarized in Table 3.

3.4. Stability test

The thermal stability is characterized by in-situ XRD. The sample is heated from room temperature up to 500 °C at a constant increasing rate of 0.2 °C per second. Diffraction spectra are measured using Cu K X-ray at every 1 °C to verify if change of crystallinity occurs including phase and intensity [11]. The result is presented in Fig. 8 for RuTa and RuTa₃.

For RuTa, at 50 °C, the peak at detection angle 2θ about 33° is the contribution from Si substrate, which is explained in the as-deposited XRD result in Fig. 1. Other weak peaks, related to Ru (FCC), Ta (BCC) or RuTa (tetr), are barely visible. The film is amorphous or nanocrystalline with small grain size as deposited. This confirms the TEM observation presented in section 2.2. By increasing the temperature, there is no change in the XRD spectrum as shown in Fig. 9, the alloy remains mainly amorphous up to 500 °C. This indicates good thermal

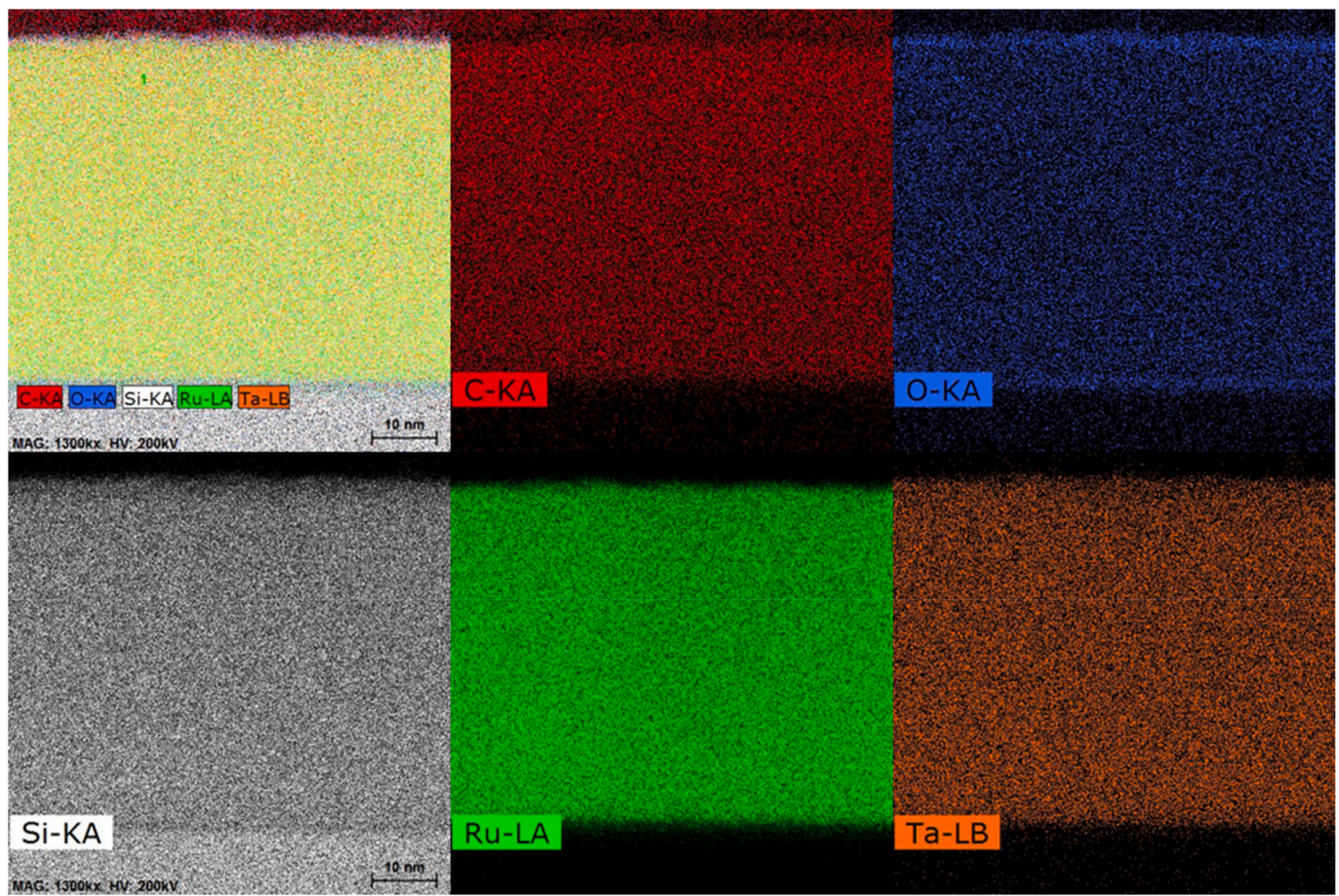


Fig. 4. EDS-STEM of a 50 nm film of Ru_3Ta , different characteristic X-ray emissions, namely C $\text{K}\alpha$, O $\text{K}\alpha$, Si $\text{K}\alpha$, Ru $\text{L}\alpha$ and Ta $\text{L}\beta$, are distinguished by color.

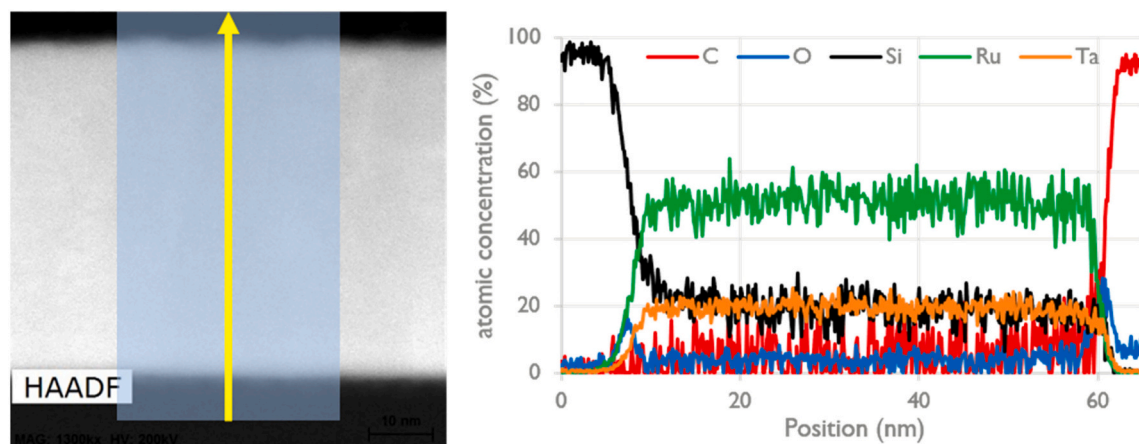


Fig. 5. Ru_3Ta HAADF and EDS-STEM. In EDS-STEM, the position goes from bottom to the surface of the film. Left: averaged scan area. Right: calculated atomic concentration for C, O, Si, Ru and Ta; the position 0 nm correspond to the Si substrate and the position 65 nm correspond to the top of the absorber.

stability of RuTa .

For as-deposited RuTa_3 , an intense peak is found at about 40° representing BCC- RuTa_3 (110), confirming the crystallinity observed by TEM. The high intensity of this diffraction peak and the lack of other diffraction peaks related to RuTa_3 suggests strong texturing of RuTa_3 grains with (110) aligning with the film surface. In addition, the contribution of Ru (110) and beta-Ta (100) can be observed as rather flattened peaks in the range $34^\circ < 2\theta < 38^\circ$. These observations indicate that although RuTa_3 may have formed during co-deposition, elemental

Ru and Ta remain present in the film. As the temperature increases, recrystallization happens starting from 130°C where the RuTa_3 (BCC) peak intensity starts to increase as shown in Fig. 9. This is probably due to the grain size growth of the as-deposited RuTa_3 grains. At 200°C , the RuTa_3 (BCC) peak intensity is tripled compared to the one measured at 50°C . Consequently, Ru and Ta contributions in the spectra entirely disappear, indicating a complete crystallization. A “shadow” peak remains at 35.5° which is a mirror peak of the main RuTa_3 (BCC) peak (due to the energy separation of Cu $\text{K}\alpha$ and $\text{K}\beta$ emitted simultaneously from

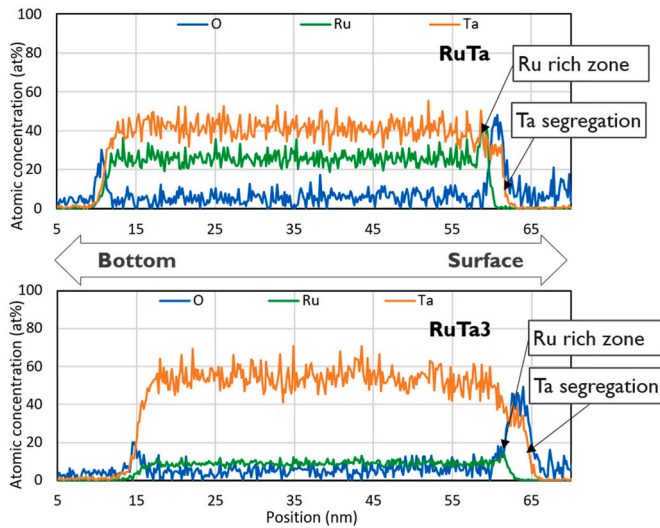


Fig. 6. Depth profile of atomic concentration of Ru, Ta and O in 50 nm films of (A) RuTa and (B) RuTa₃ obtained by EDS-STEM. The signals of C and Si are removed from the figure to highlight the comparison between Ru and Ta.

the X-ray tube). The thermal stability of Ru₃Ta is not measured, as we know already from Fig. 1, that the crystallinity is much severe compared to the other two alloys.

Chemical endurance tests of Ru_{4-x}Ta_x ($x = 1, 2, 3$) alloys were performed, against several standard mask cleaning solutions, namely deionized water (DIW, pH 6), 1% ammonia hydroxide (NH₄OH, pH 12) and 0.2–0.5% tetramethylammonium hydroxide (TMAH, pH 12). Although the standard mask cleaning process takes around 30 min, a 24-h immersion time was used to simulate multiple cleaning. An additional sample for each alloy composition was kept in atmosphere as a reference. X-ray reflectometry (XRR) using 8048 eV X-ray is applied to check whether the structure of the film changes, including total thickness and density. The results are presented in Fig. 10 for all three alloy compositions. The shape of the curves remains consistent before and after the tests. The critical angle remains at the same location, indicating that there is no change of density of the material. The frequency of the oscillation of the curve also remains constant, indicating that the total thickness of the film also does not change. Some minor structural variation can be observed, particularly for RuTa₃. A shift of secondary oscillation can be observed around a grazing incident angle of $\sim 1^\circ$. This secondary oscillation is related to the oxidation or contamination of the surface, which changes very slightly after the beaker test.

To mimic the working environment of a EUVL mask in a scanner [21], the alloys are then exposed in a hydrogen plasma environment for

24 h. The H₂ pressure is set to be 0.15 mbar with filament voltage 19 V to generate the plasma [22]. The pre- and post-exposure samples are compared using RBS and XRR. Fig. 11 presents the RBS analysis which indicates that no atomic concentration change occurs during the exposure. The variation of Ru and Ta content of RuTa₃ is within the uncertainty of RBS measurement. The XRR measurement in Fig. 12 confirms such stability as the reflectivity curves remain unchanged for all three alloys.

3.5. RuTa patterning using reactive ion etching

Plasma-based pattern transfer is explored for RuTa (best of the three considered alloys, concerning morphology and surface roughness, as presented in section 2.1). Reactive ion etching (RIE) [23] is studied on blanket films using chlorine- and fluorine-based plasmas. The etch of RuTa need to be selective to Ru, in order to preserve the Ru capping of the multilayer mirror during patterning. This Ru capping layer is only 2–3.5 nm thick, while the RuTa film is about 50 nm thick; a maximum recess of ~ 0.5 nm is acceptable without degrading the passivation properties of the Ru cap. Non-uniformities of the etched layer, as well as of the plasma etch process itself, imposes to apply some over-etch, to make sure that the RuTa mask is removed everywhere on the EUV mirror. Deposition steps used in EUV mask manufacturing target highly uniform film deposition, $\sim 0.5\%$ 3σ ; while associated etch process do target uniformity below 2% 3σ . As a consequence, in order to compensate for a total non-uniformity of $\sim 2.5\%$ 3σ , a minimum over-etch of around $\sim 3\%$ should be applied during the plasma etch process. Applied to a RuTa film thickness of 50 nm, with a tolerance of 0.5 nm recess into the Ru cap, a minimum selectivity $S = \text{RuTa}:\text{Ru} \sim 3$ need to be achieved to meet process specifications. Besides, a hardmask is required as photoresist is etched fast. We therefore included in this study two commonly used hardmask materials: SiO₂ and Si₃N₄. Two recipes are applied for this process, one with low voltage (LV) and the other with high voltage (HV). The film thickness is evaluated by spectroscopic ellipsometry with the tool Woollam M-2000 for RuTa film before and after the etch process. Plasma etch tests were carried out in an Oxford Instruments Plasma Technology ICP system: PlasmaPro 100 Cobra,

Table 3

Optical constants of the three Ru_{4-x}Ta_x alloys at wavelength of 13.5 nm reconstructed from measured EUVR data.

Alloy	Reconstructed optical constants	
	$n(1-\delta)$	$k(\beta)$
Ru ₃ Ta	0.907	0.021
RuTa	0.927	0.025
RuTa ₃	0.944	0.030

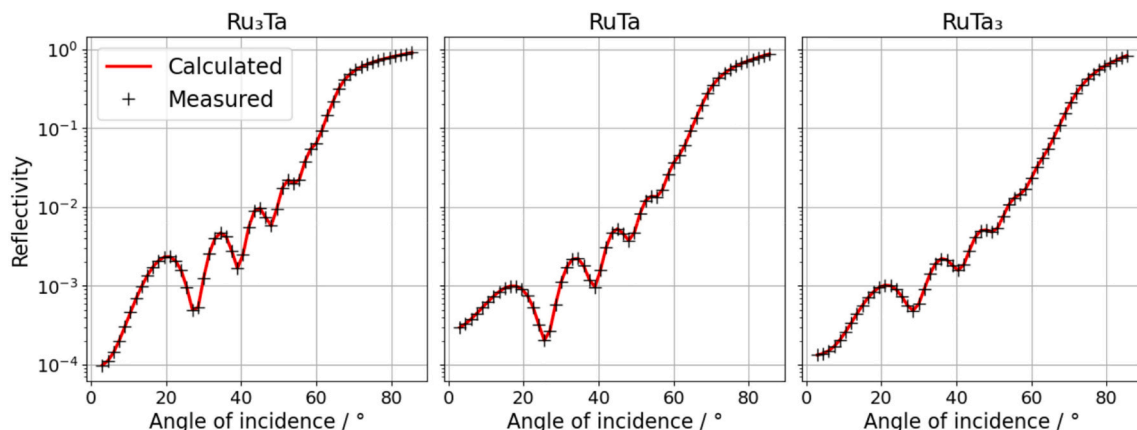


Fig. 7. Plots comparing the measured and the reconstructed reflectivity curves at a wavelength of 13.5 nm for the three binary alloys.

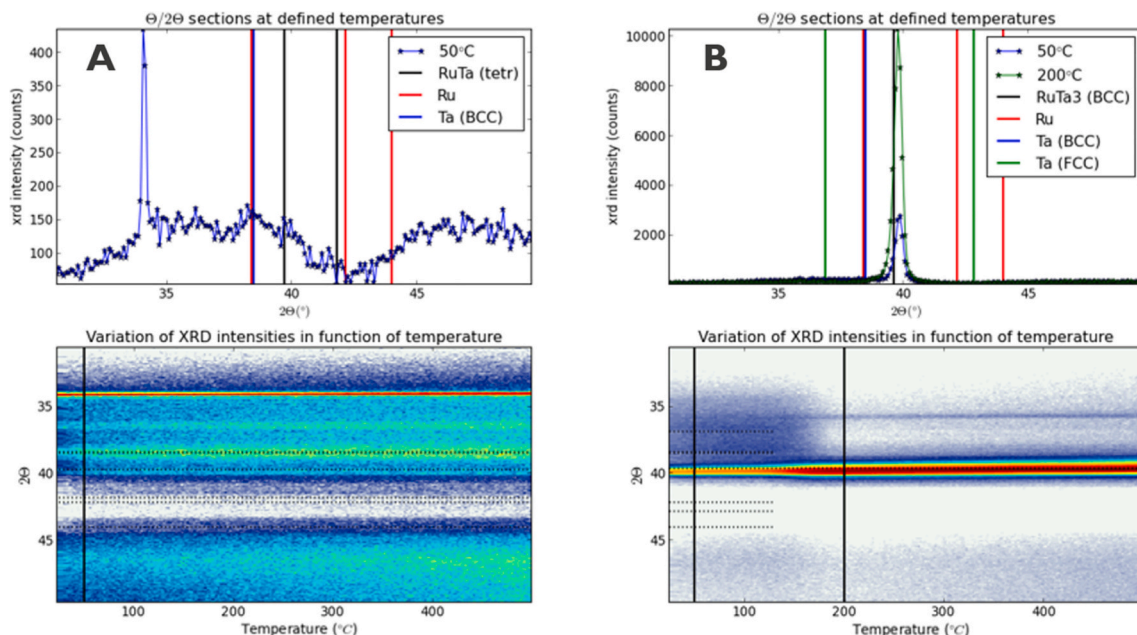


Fig. 8. IS-XRD for 50 nm films of (A) RuTa and (B) RuTa₃. Upper part presents the spectra of certain temperature(s) shown by vertical line(s) in lower part, which is the spectra variation as function of the rising temperature.

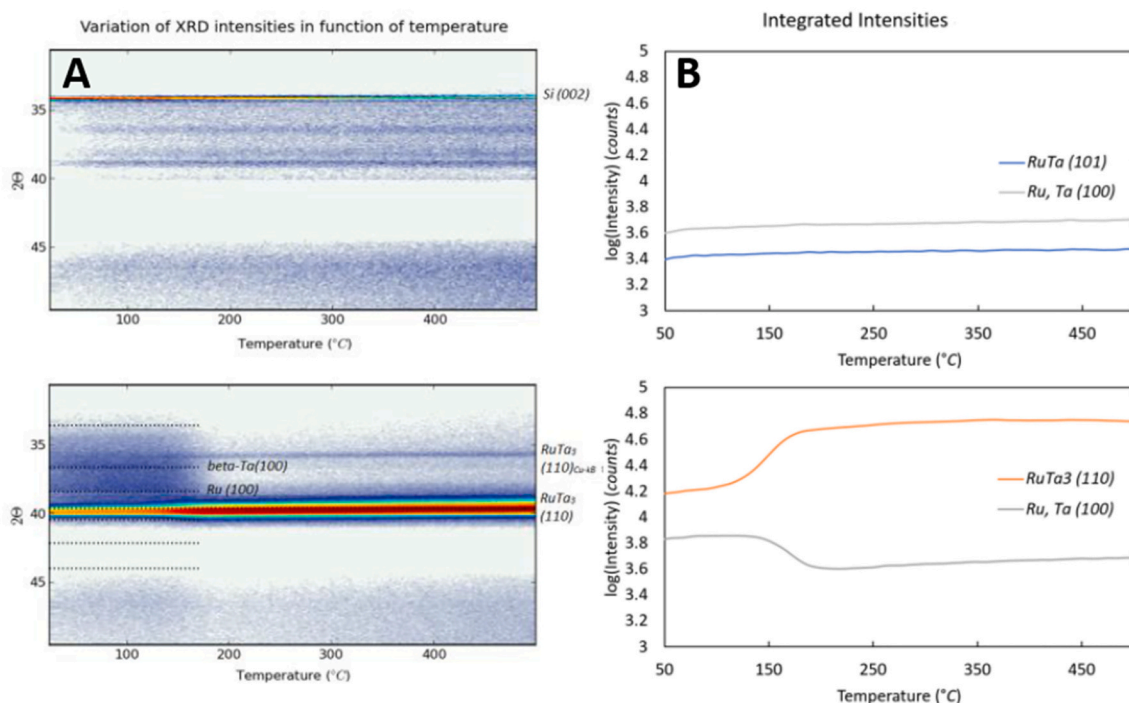


Fig. 9. (A) IS-XRD spectra showing the variation as function of the rising temperature for 50 nm films of RuTa (top) and RuTa₃ (bottom). (B) representing integrated intensities of diffraction peaks in RuTa (top) and RuTa₃ (bottom).

using small samples pasted on carrier wafers (Al₂O₃ coated Si wafer for fluorine-based plasmas, Si₃N₄-coated Si wafer for chlorine-based plasma). For each plasma chemistry, two RIE conditions are studied: the first one at high bias voltage (67 V) or power (20 W), corresponding to a high ion bombarding mode, where the etch process involve a significant sputtering component. The second RIE condition uses low bias voltage (0 V) or low bias power (10 W), corresponding to a low ion bombardment mode, called ‘soft landing’, where the etch is more chemically driven.

The results are presented in Fig. 13, where the etch rates of blanket films of these materials are compared all together. Fig. 13 (a) shows the etch rates for chlorine-based processes (Cl₂, BCl₃), while Fig. 13 (b) focuses on fluorine-based processes (SF₆, CF₄) – Si₃N₄ was not screened as it is known to etch faster than SiO₂ using F-containing chemistry. For both chlorine and fluorine plasma chemistries, the removal rates of RuTa are moderate as compared with SiO₂ and Si₃N₄, indicating that both these masking materials are unsuitable. As expected, using higher bias increases the etch rates, due to the catalytic effect of ion

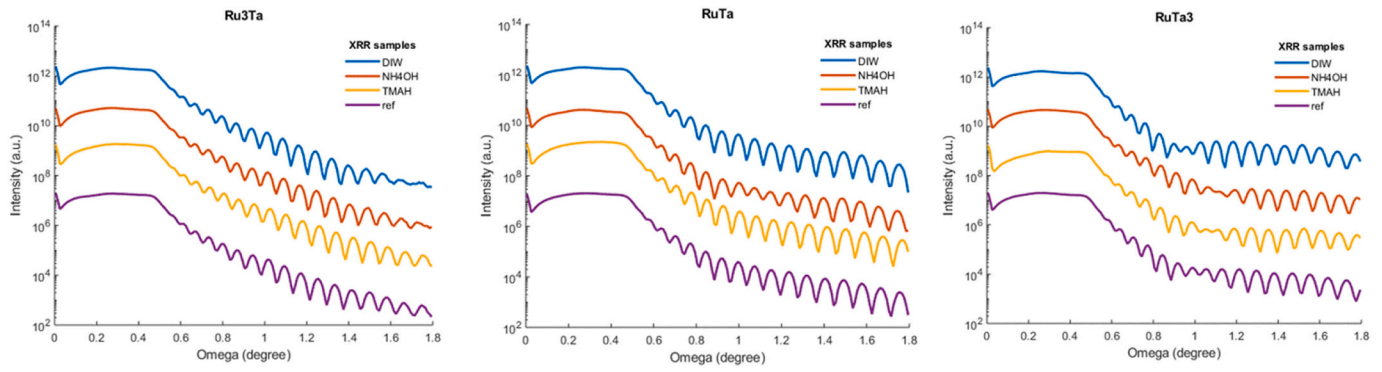


Fig. 10. XRR curves of 50 nm films of the three $\text{Ru}_{4-x}\text{Ta}_x$ alloys before and after 24-h beaker test in different cleaning solutions. For readability and clarity of the curves, the intensities are shifted along the Y-axis on purpose.

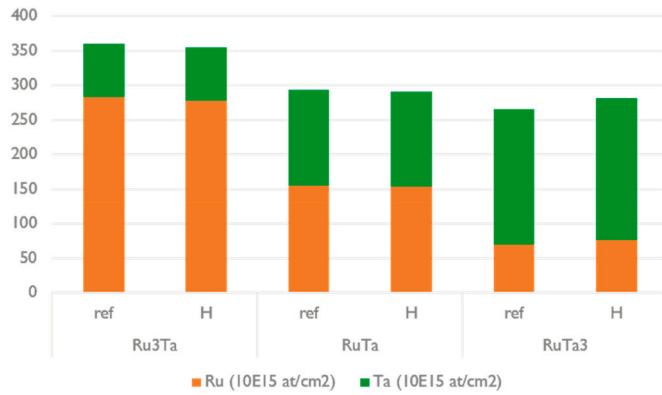


Fig. 11. Atomic content of 50 nm films of the three $\text{Ru}_{4-x}\text{Ta}_x$ alloys before (ref) and after 24-h exposure in hydrogen plasma (H) obtained from RBS analysis.

bombardment on the surface chemical reactions. The Fig. 13 (c) shows the RuTa:Ru selectivity numbers S , calculated based on the data from Figs. 13 (a,b). As can be observed from that graph, the achieved selectivity barely reaches the target for the CF_4/Ar , Cl_2/Ar and BCl_3/Ar mixtures, however the SF_6/Ar processes do reach $S \sim 5$ (high bias) and 22 (low bias). In order to reduce further the sputtering character of the process, pure SF_6 plasma has been tested, however it produced bubbling and cracking of the RuTa film. The etch rate was also non-linear, slowing significantly as the etch proceeded. These problems appeared to be related to preferential rapid chemical etching of Ta, while the etching of Ru was mostly physical. Diluting the SF_6 with Ar minimise bubbling and improves etch linearity.

The CF_4/Ar etch resulted in no bubbling/cracking and gave a linear

RuTa etch rate but produced lower selectivities. Cl_2/Ar and BCl_3/Ar gave similar results, with low to moderate RuTa:Ru selectivity and insufficient selectivity to SiO_2 or Si_3N_4 mask layers.

As the SF_6/Ar is known to be rather isotropic when applied to patterned structures, i.e. the present data indicate the interest of a multi-step etch recipe triggered by sophisticated endpoint detection methods, i.e. a main etch with high bias and fast etch rate, offering sidewall passivation (CF_4/Ar) but marginal RuTa:Ru selectivity, associated with a soft-landing step (SF_6 -based) showing higher selectivity but lower rate. As thick Si-based hardmasks will introduce aspect ratio challenge of the patterned feature, further exploration of alternative hardmask candidates and their removal process after patterning is required. For the future, more etch test with patterned samples are required to validate these statements.

4. Conclusion

$\text{Ru}_{4-x}\text{Ta}_x$ ($x = 1, 2, 3$) alloys are proved to be promising candidates as EUVL absorber. In this paper we focus on the characterization of these materials. An overview is presented in Table 4. The three proposed alloys, namely Ru_3Ta , RuTa and RuTa_3 , exhibit excellent resistance against cleaning solutions and H plasma exposure. The bulk part of the films has homogenous elemental distribution. On the top surface, Ta segregation towards top and surface oxidation is observed for all three compositions. Therefore, the surface is expected to be native Ta oxide, except for Ru_3Ta which still has Ru content on top despite the Ta segregation. The experimentally determined optical constants at wavelength of 13.5 nm are reported, which is important for the precision and reliability of the EUV imaging simulations [24]. Particularly for RuTa , a good thermal stability up to 500 °C is observed, with a 50 nm thin film remaining amorphous through the heating process.

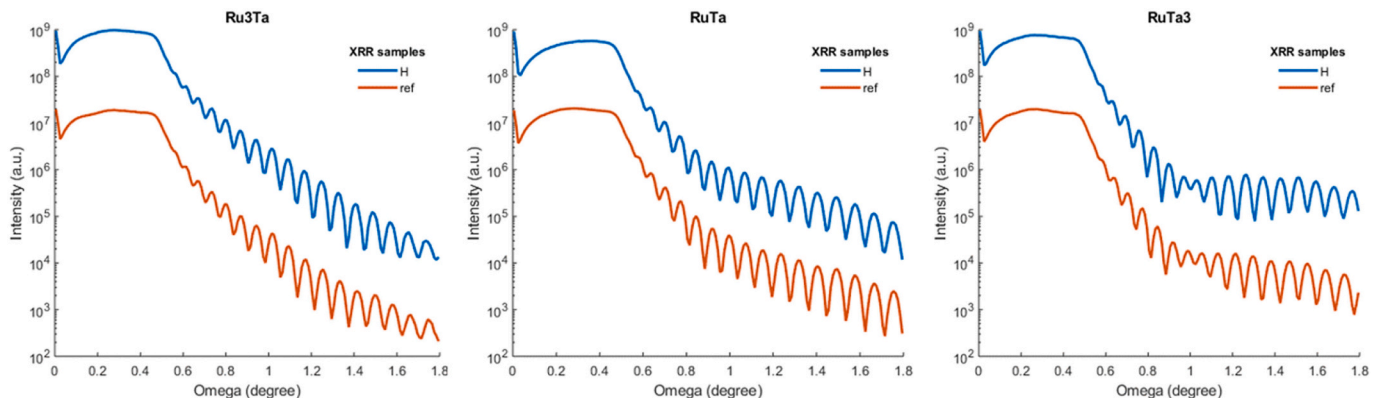


Fig. 12. XRR curves of pre/post hydrogen plasma exposure samples of 50 nm films of the three $\text{Ru}_{4-x}\text{Ta}_x$ alloys.

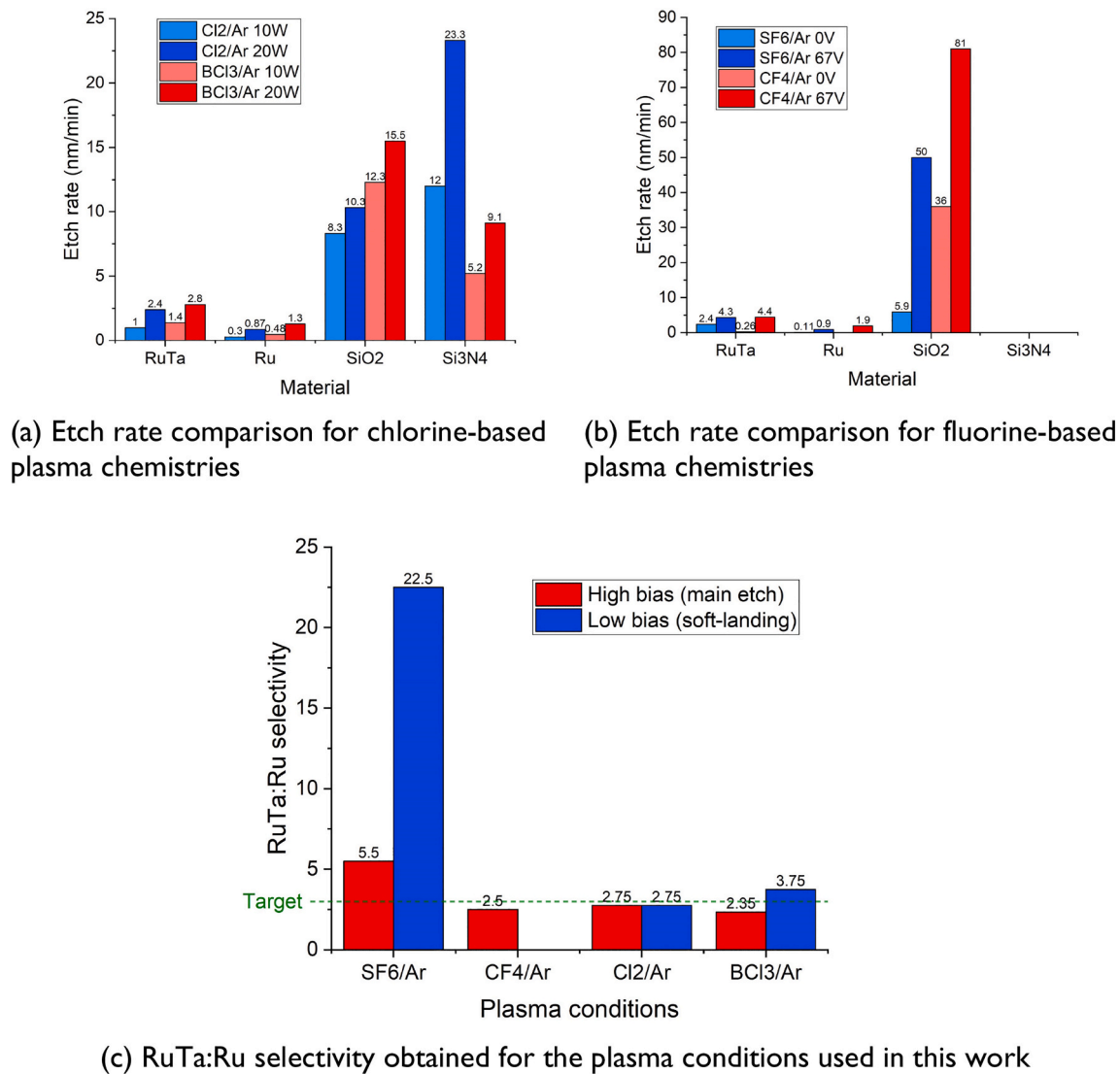


Fig. 13. Etch comparison among RuTa, Ru and two hardmask materials using chlorine- and fluorine-based plasma RIE.

Table 4

Summary table for characterization and patterning status of the Ru_{4-x}Ta_x alloys.

Characterization	Technique	Ru ₅ Ta	RuTa	RuTa ₃
Chemical composition	RBS	3.57:1	1:1.12	1:2.73
	XPS	2.90:1	1:1.80	1:8.00
As-deposited surface roughness (RMS)	AFM	0.31 nm	0.12 nm	0.13 nm
Morphology	XRD/TEM	Nano-crystal	Amorphous	Nano-crystal
Homogeneity	EDS-STEM	Homogeneous	Homogeneous	Homogeneous
Optical constant	EUVR	n (1-δ)	0.906	0.94
		k (β)	0.02	0.03
Thermal stability	IS-XRD	/	Stable up to 500 °C	Nano-crystal as deposited, recrystallized at ~130 °C
Cleaning resistance	XRR	DIW	Stable	Stable
		NH ₄ OH	Stable	Stable
		TMAH	Stable	Stable
H plasma resistance	RBS	Stable	Stable	Stable
Patterning	RIE	F-based	/	/
			Etch rate 4.4 nm/s Selectivity to Ru 22:1	

For patterning, the etch rate using Cl- and F-based RIE is low compared to conventional masking materials, requiring searching for alternative masking layers. The etch selectivity against Ru is marginal with CF₄-Ar, Cl₂-Ar and BCl₃-Ar, but satisfactory with SF₆-based plasma processes. For real structures, sidewall passivation concerns might require a double step etch process combining a low selectivity/

high passivation main etch step (CF₄-Ar) with a high selectivity/low passivation step (SF₆-Ar).

Declaration of Competing Interest

The authors declare that they have no known competing financial

interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

The authors acknowledge that this project has received funding from the Electronic Component Systems for European Leadership Joint Undertaking under grant agreement No 783247 - TAPES3. This Joint Undertaking receives support from the European Union's Horizon 2020 research and innovation program alongside Netherlands, France, Belgium, Germany, Czech Republic, Austria, Hungary and Israel.

Acknowledgements to

- Eric Hendrickx, Kurt Ronse on program support
- Igor A. Makhotkin on XRR support and discussions
- imec MCA team on metrology support

References

- [1] A. Erdmann, et al., Characterization and mitigation of 3D mask effects in extreme ultraviolet lithography, *Adv. Opt. Technol.* 6 (3–4) (2017), <https://doi.org/10.1515/aot-2017-0019>.
- [2] V. Philipsen, et al., Reducing extreme ultraviolet mask three-dimensional effects by alternative metal absorbers, *J. Micro Nanolithogr. MEMS MOEMS* 16 (4) (2017), 041002.
- [3] J.-H. Franke, et al., *Proc. SPIE* 11147, EUVL, 2019 (111470E).
- [4] O. Wood, et al., Alternative materials for high numerical aperture extreme ultraviolet lithography mask stacks, *Proc. SPIE* 9422 (2015) 94220I.
- [5] V. Philipsen, et al., Novel EUV mask absorber evaluation in support of next-generation EUV imaging, *Proc. SPIE* 10810 (2018) 108100C.
- [6] V. Philipsen, et al., Mask absorber development to enable next-generation EUVL, in: *Photomask Japan 2019: XXVI Symposium on Photomask and Next-Generation Lithography Mask Technology*, Yokohama, Japan, 2019, p. 24, <https://doi.org/10.1117/12.2537967>.
- [7] A. Erdmann, et al., Attenuated phase shift mask for extreme ultraviolet: can they mitigate three-dimensional mask effects? *J. Micro Nanolithogr. MEMS MOEMS* 18 (1) (2019) 011005.
- [8] C. Van Lare, et al., Mask-absorber optimization: the next phase, *J. Micro Nanolithogr. MEMS MOEMS* 19 (2) (2020) 024401.
- [9] A. Erdmann, et al., Perspectives and tradeoffs of absorber materials for high NA EUV lithography, *J. Micro Nanolithogr. MEMS MOEMS* 19 (4) (2020) 041001.
- [10] V. Luong, et al., Ni-Al alloys as alternative EUV mask absorber, *Appl. Sci.* 8 (4) (2018) 521, <https://doi.org/10.3390/app8040521>.
- [11] V. Luong, et al., Assessing stability of metal tellurides as alternative photomask materials for extreme ultraviolet lithography, *J. Vac. Sci. Technol. B* 37 (6) (Nov. 2019) 061607, <https://doi.org/10.1116/1.5125662V>.
- [12] Luong, et al., http://euvlsymposium.lbl.gov/pdf/2016/Oral/Mon_S4-3.pdf.
- [13] R.F. Zhang, et al., An informatics guided classification of miscible and immiscible binary alloy systems, *Sci. Rep.* 7 (2017) 9577, <https://doi.org/10.1038/s41598-017-09704-1>.
- [14] H. Okamoto, Phase diagram updates: section III, *J. Phase Equilibria* 12 (3) (1991) 396.
- [15] P. Scherrer, Bestimmung der Größe und der inneren Struktur von Kolloidteilchen mittels Röntgenstrahlen, *Göttinger Nachrichten* 2 (1918) 98–100.
- [16] <https://srdata.nist.gov/xps/>.
- [17] F. Scholze, et al., High-accuracy EUV metrology of PTB using synchrotron radiation, in: *Proc. SPIE* 4344, Metrology, Inspection, and Process Control for Microlithography XV, 2001.
- [18] Q. Saadeh, et al., Validation of optical constants in the EUV spectral range, in: *International Conference on Extreme Ultraviolet Lithography 2019*, Monterey, United States, 2019, p. 49, <https://doi.org/10.1117/12.2536644>.
- [19] A. Gottwald, et al., Uncertainty analysis for the determination of B4C optical constants by angle-dependent reflectance measurement for 40 nm to 80 nm wavelength, *Appl. Opt.* 56 (2017) 5768–5774.
- [20] https://henke.lbl.gov/optical_constants/getdb2.html.
- [21] S. Bajt, Optics contamination, in: V. Bakshi (Ed.), *EUV Lithography*, John Wiley & Sons, Hoboken, NJ, USA, 2009, pp. 229–230.
- [22] I. Pollentier, et al., EUV lithography imaging using novel pellicle membranes, in: *Proceedings of the SPIE* 9776, Extreme Ultraviolet (EUV) Lithography VII, San Jose, CA, USA, 2016, pp. 22–25.
- [23] S. Franssila, et al., Reactive ion etching (RIE), in: D. Li (Ed.), *Encyclopedia of Microfluidics and Nanofluidics*, Springer, Boston, MA, 2008, https://doi.org/10.1007/978-0-387-48998-8_1344.
- [24] M. Wu, et al., Study of novel EUVL mask absorber candidates, in: *J. Micro/Nanopattern. Mater. Metrol.* 20, SPIE, 2021, pp. 021002-1–021002-13.