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Characterization of silicon etching in synchronized pulsed plasma

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ABSTRACT

Pulsed plasmas have been proposed many years ago by research labs and have shown a great potential for etch process improvement. Nevertheless, they have been introduced in manufacturing only recently and the exact characteristics of pulsed plasmas in industrial scale reactors are hardly known. In this paper, we have characterized silicon etching in pulsed HBr/O₂ plasmas using advanced plasma diagnostics (mass spectrometry and ion flux probe) in a 300 mm industrial reactor. We show that pulsing the plasma at low duty cycle reduces the gas molecules dissociation and plasma temperature, as well as the flux of energetic ions to the wafer. The ions during silicon etching are mostly silicon-containing ions that are heavier at low duty cycle. Silicon patterns etched using pulsed plasmas present improved profiles, which is attributed to more uniform passivation layers at low duty cycle.

Keywords: Pulsed plasma, silicon, etching, pattern, HBr/O₂

INTRODUCTION

Plasma etching processes at 22 nm technology node and below face unprecedented challenges, to pattern nanometer-scale features in very complicated stacks of ultrathin layers and on large size wafers. Etching processes must enable the controlled patterning of sub-20 nm features with a perfect uniformity across the die, across the wafer, and from one lot to the other. In addition, ultrathin (<1 nm) layers of materials are being integrated and 3D structures are required for fin-FET fabrication, leaving no room for plasma induced damage. Equipment suppliers have recently introduced pulsed plasma reactors in manufacturing with the objective to improve plasma etching processes [1]. It is admitted that differential charging is reduced in pulsed plasmas, which minimizes pattern profile distortions [2]. Furthermore, the average ion energy is reduced in pulsed plasmas, which is expected to reduce the plasma induced damage. Finally, pulsing the plasma enables an independent control of the plasma gas molecules dissociation [3]. Even if pulsed plasmas have been widely investigated in research laboratories [2],[4], moving towards industrial scale plasmas leads to significant changes in processes that make the analysis of pulsed plasma processes in such etch reactors compulsory.

EXPERIMENTAL SETUP

1.1 Etching tool

The experiments are performed in a 300 mm G5 reactor from Applied Materials, modified to enable plasma pulsing and in-situ plasma diagnostics [3][5]. A schematic of the chamber is provided in Fig.1. The 300mm ICP reactor is equipped with the pulsyncTM system enabling synchronized pulsing of the source and bias power supplies with a duty cycle ranging from 10% to 90% at a pulsing frequency ranging between 100 Hz and 10 kHz. The source and bias power supplies can be pulsed independently (only one power supply pulsed) or synchronously with a controlled delay and controlled duty cycle for both the source and the bias power supplies. In this paper, only the synchronized pulsing mode with identical duty cycles and no delay is used. Power matching is performed using the automatic matching network as well as by using frequency tuning which consists in modulating the RF power supply frequency around the fundamental frequency (13.56 MHz) to match the plasma impedance [1].

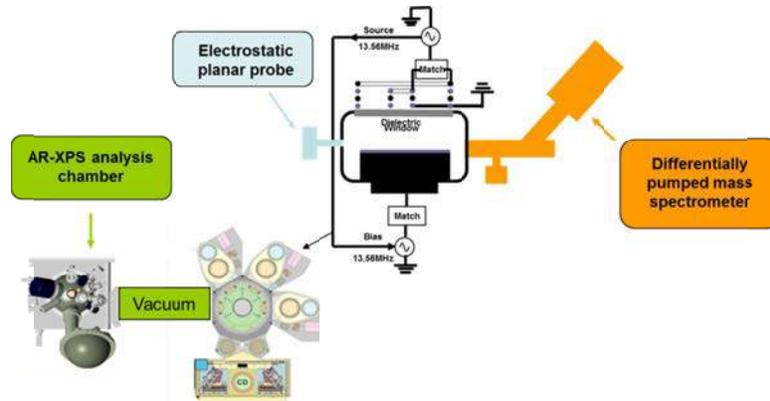


Figure 1. Schematic representation of the experimental setup, consisting in a pulsed ICP chamber equipped with differentially pumped mass spectrometry and an electrostatic planar probe. The chamber is connected under vacuum to an angle-resolved x-ray photoelectron spectroscopy system.

1.2 Mass spectrometry

The etch reactor is equipped with an EQP 500 mass spectrometer from Hiden Analytical with a beam chopper and two differential pumping stages [6]. The entrance orifice is positioned in plane with the reactor sidewall at a height approximately 5 cm above the wafer holder. Two diagnostic modes of the mass spectrometer are used for the analysis of neutrals and ions. The full experimental procedure for neutrals and ions analysis is described in details in another paper [7]. Basically, the spectrometer is tuned with argon gases. The chopper is not used and the ionization energy is set to 70 eV to determine full neutral mass spectra. The residual signal is measured under vacuum and removed from the plasma mass spectrum. For single neutral species density measurement, we use ionization at threshold energies in combination with the beam chopper. The same procedure is used to record the ion mass spectra (without ionization in the spectrometer). For single ion species, the IEDF at the sidewall is measured and integrated to determine the contribution of each ion in the ion flux.

1.3 Planar electrostatic probe

A planar electrostatic probe [8] is also mounted on the etch reactor at the same position as the mass spectrometer. The electrostatic planar probe consists of a stainless steel disc surrounded by a guard ring. The probe is polarized by a pulsed power supply through a blocking capacitor. The ion flux is measured by the discharge current of the capacitor. This system is adapted to determine the ion flux in pulsed plasmas [9].

1.4 Angle resolved x-ray Photoelectron Spectroscopy

The etching platform is connected to an angle resolved x-ray photoelectron spectrometer through a robotized vacuum chamber. The XPS system is equipped with a high resolution monochromatic Al $K\alpha$ source at 1486.6 eV. For all our experiments we used 8 different nominal detection angles ranging from 23.5° to 72.5° referred to the normal of the wafer. In addition, the spectrometer is equipped with an electron beam system for charge neutralization or for mask discrimination in the chemical topography analysis mode. The technique used to analyze the sidewall passivation layer thickness and composition is described in another paper [10]. Arrays of line/space patterns are analyzed perpendicularly to the analyzer plane. Photoelectrons originating from the sidewalls of the patterns are shaded by the neighboring pattern, depending on the analysis angle (from 23.5° to 72.5°). The mask contribution is removed by charging using the electron beam. Thus, the angular response of the sidewall can be obtained, and the thickness and composition of the passivation layer along the sidewalls can be calculated.

1.5 Etching process

In this paper, we focus on an HBr/O₂ plasma process dedicated to silicon etching. The gas flux is set to 200 sccm and 5 sccm for HBr and O₂, respectively. The pressure is set to 20 mT, the source power to 750 W and the bias at 200 W (when used). Mass spectrometry measurements are performed at 10 mT. The etched stack consists of a SiO₂ hard mask on silicon with line equal space patterns defined by 193 nm or e-beam lithography and transferred into the SiO₂ hard

mask by plasma etching using a tri-layer scheme. Before silicon etching, a 3 s breakthrough step is performed to remove any stripping-induced silicon oxide from the open areas. The chamber operates in seasoned conditions: the chamber is cleaned first, then coated with SiO₂ by a SiCl₄/O₂ plasma followed by a O₂ plasma, then a dummy silicon wafer is processed with the process of interest before processing the real wafer. For diagnostics without silicon etching, the process is performed in a clean chamber mode. Silicon pattern profiles are observed by secondary electron microscopy using a JEOL 7500F SEM.

RESULTS

1.6 Plasma diagnostic without silicon etching

In a first set of experiments, the plasma composition is analyzed without wafer in the reactor and without rf bias power. Fig. 2 shows the neutral mass spectra in the HBr/O₂ plasma. We can see in that the plasma is composed of Br, HBr, Br₂, H_xO and O_x with x between 1 and 2. CO₂, HCl and HF come from the background that is not perfectly subtracted in spectral mode (the chopper is not used). Note that the spectra correspond to the fractionated pattern of the plasma neutrals and that the mass spectrometer transmission function is not corrected here. As a consequence, no direct comparison of the species intensity can be done but we can compare the change of relative composition between the experiments.

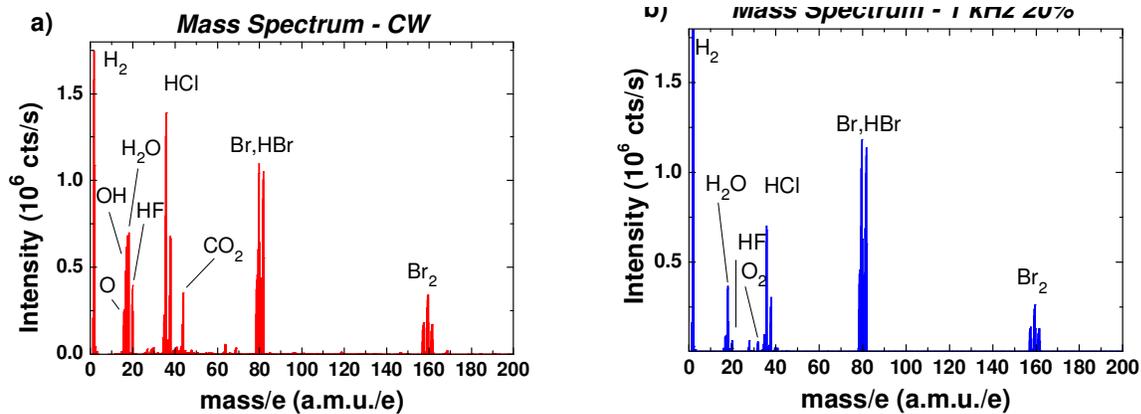


Figure 2. Mass spectra of neutral species present in the HBr/O₂ plasma at 0W bias power in a) continuous wave mode b) pulsed at 1kHz 20% DC

To compare the plasma composition in CW and in pulsed mode, we quantified the density of Br, HBr, Br₂ and O₂ using the beam chopper and threshold ionization. The other species (H_x, H_xO, O) are not quantified due to a too small signal to noise ratio. Figure 3 shows the variation of the O₂, Br, Br₂ and HBr densities as a function of the duty cycle in the HBr/O₂ plasma pulsed at 1kHz. Two important trends can be observed. First, it is clear that the total density of species increases when the duty cycle decreases. We must keep in mind that H_x, O and H_xO are not taken into account here.

The species density increase is attributed to a decrease of the time average gas temperature when the plasma is pulsed at lower duty cycle. Gas heating is basically reduced due to a lower average source power in pulsed mode. Assuming that H and H₂ have a similar density to Br and Br₂, respectively, and neglecting O-containing species, we can estimate the plasma temperature around 650 K in CW mode, consistent with the literature [11]. The temperature decreases and is expected to tend towards 330 K at very small duty cycle. Secondly, we can see that the relative amount of atomic species (reactive radicals) decreases when the duty cycle decreases. This indicates that the plasma gas molecules dissociation is reduced when the duty cycle decreases. As a consequence, the density of reactive radicals decreases when the plasma is pulsed at low duty cycle. Both phenomena are particularly significant at duty cycles below 35%.

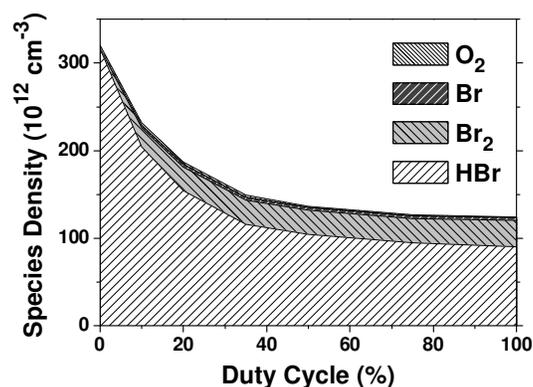


Figure 3. Species density measured by molecular beam mass spectrometry in a HBr/O₂ plasma pulsed at 1kHz. A duty cycle of 0% corresponds to the gas (no plasma struck) while a duty cycle of 100% correspond to a CW plasma

We also investigated the average ion flux in pulsed HBr/O₂ plasma. Figure 4. shows the composition of the ion flux measured by mass spectrometry at the chamber walls for different duty cycles in the HBr/O₂ plasma pulsed at 1kHz. The light ions H⁺ and H₂⁺ cannot be detected accurately with our system. As shown in this figure, the total ion flux decreases when the duty cycle decreases. The ion flux is mostly composed of Br₂⁺ and to a lower extent of H₃O⁺. The other ions represent less than 10% of the ion flux and consist of Br₃⁺, HBr₂⁺, H₂Br⁺, HBr⁺ and Br⁺. The relative contribution of Br₂⁺ increases when the duty cycle decreases. This is simply indicating that the balance between dissociation and recombination tends toward recombination when the duty cycle decreases.

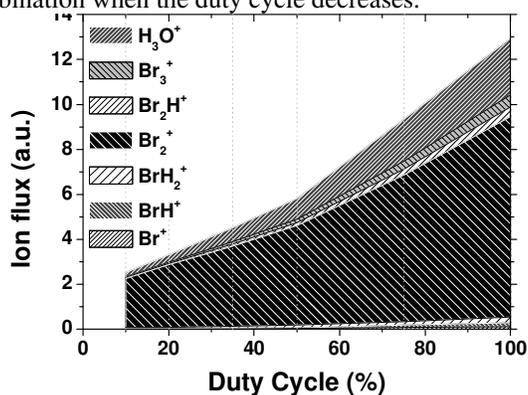


Figure 4. Ion flux composition determined by mass spectrometry in HBr/O₂ plasma pulsed at 1kHz. A duty cycle of 100% corresponds to the CW mode.

The whole results in the HBr/O₂ plasma indicate that pulsing the plasma leads to a decrease of the plasma temperature and of the ion flux. The balance between dissociation and recombination tends towards more recombined and less dissociated species when the duty cycle decreases. This is impacting both the neutral flux and the ion flux composition.

1.7 Plasma diagnostic during silicon etching

In a second set of experiments, the plasma composition is analyzed during silicon etching. As shown in figure 5, the plasma composition is strongly modified compared to the plasma without bias. Many silicon-containing species are now observed. When the plasma is pulsed at low duty cycle, we can see that the intensity of the Si-containing species decreases compared to the CW plasma. This can be explained by the formation of more volatile etch by-products in pulsed mode (less direct sputtering of low volatility species and less dissociation of etch by-products in the plasma) and by the decrease of the flux of etch by-products due to a decrease of the etch rate at lower duty cycle.

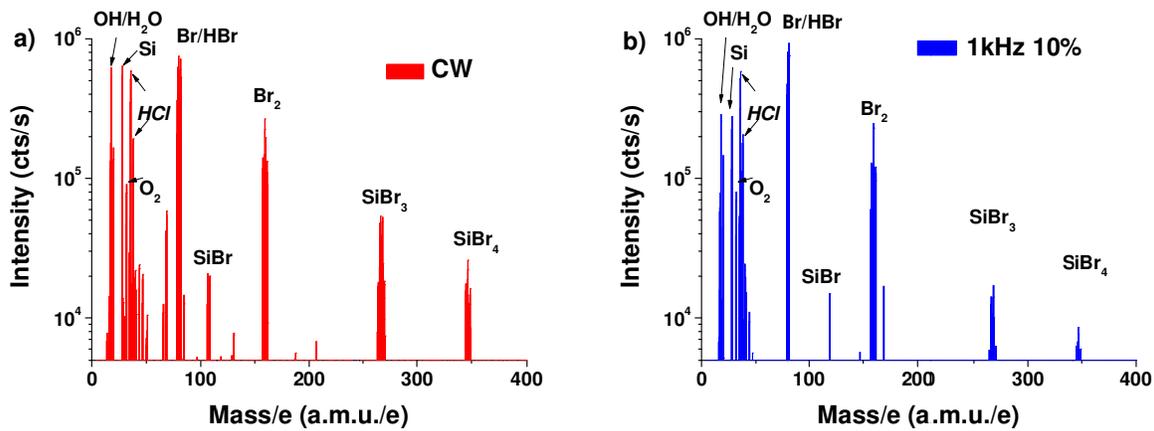


Figure 5. Mass spectra of neutrals during silicon etching in HBr/O₂ plasma a) in CW mode b) pulsed at 1kHz 10%

Similarly, the ion flux composition is strongly modified by silicon etching. As we can see in fig. 6, the ion flux is mostly composed of silicon-containing ions in the CW plasma, which is due to a lower ionization threshold energy of these species compared to HBr molecules [12]. This means that most of the ions involved in silicon etching are silicon-containing ions. When the plasma is pulsed at low duty cycle, the proportion of silicon-containing species decreases as observed for the neutral species. Furthermore, the proportion of light Si-containing elements (e.g. Si⁺) decreases more than the proportion of heavier Si-containing species (e.g. SiBr₃⁺), which indicates a lower fragmentation of etch by-products and the formation of more volatile etch by-products when the plasma is pulsed at low duty cycle.

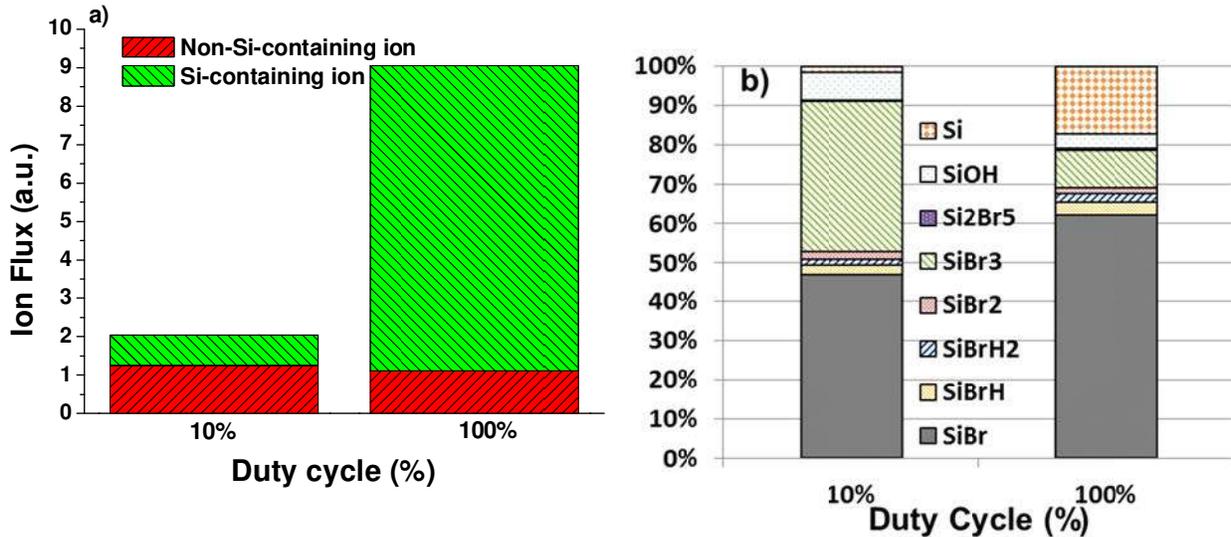


Figure 6. Ion flux composition during silicon etching in HBr/O₂ plasma pulsed at 1kHz. A duty cycle of 100% corresponds to the CW mode. a) Repartition between Si-containing ions and non-Si containing ions b) repartition of Si-containing ions

The time-resolved ion flux has been investigated using the planar probe during silicon etching in HBr/O₂ plasma pulsed at 1 kHz. As shown in fig 7.a, there is a strong modulation of the ion flux during the period of the plasma pulsation. The ion flux increases rapidly at the beginning of the pulse, but does not reach the value of the ion flux in the CW mode. During the OFF time, the ion flux rapidly drops but does not reach zero. We have also reported (see figure 7.b) the total average ion flux and the average ion flux from the ON time only for the HBr/O₂ plasma pulsed at 1kHz. For the duty cycles investigated here, the average ion flux is found to be always lower than the ion flux in CW multiplied by the duty cycle. This means that for identical plasma ON time, the total amount of ions reaching the probe is lower in pulsed plasma than in CW mode. The average ion flux during the ON time is always lower than the ion flux in CW mode and is the lowest at the lowest duty cycle. If we assume a perfect power coupling for the

bias power without collisional losses, we can approximate the ion energy by $E=P/I$ with E the ion energy, P the bias power, and I the ion flux [9]. For a constant bias power, the ion energy is thus strongly increased when the plasma is pulsed at low duty cycle.

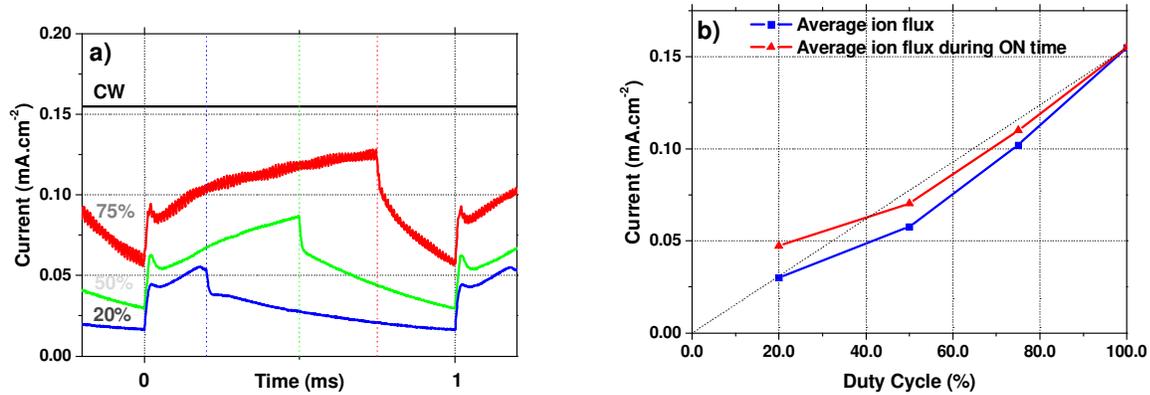


Figure 7. Ion flux measured during silicon etching in HBr/O_2 plasma pulsed at 1kHz. A duty cycle of 100% corresponds to the CW mode. a) time resolved measurement b) average ion flux and average ion flux during the plasma ON time only.

The analysis of the plasma during silicon etching shows that silicon etch by-products strongly contribute to the plasma composition and to the ion flux. When the plasma is pulsed, the presence of Si-containing species (both neutrals and ions) is reduced and Si-containing species are heavier confirming the reduced plasma dissociation under pulsed conditions. The ion flux is strongly reduced when the plasma is pulsed, which leads to an increased ion energy during the plasma ON time.

1.8 Application to silicon patterns etching

The HBr/O_2 plasma investigated above has been used to pattern trenches in silicon using a SiO_2 hard mask. For these experiments, we used time compensation, meaning that the etching time is set to have identical plasma ON time for all experiments. The time compensated etch rate is defined as the etch rate divided by the duty cycle, i.e. the etch rate considering only the plasma ON time. Figure 8 shows semi-isolated silicon patterns with equal line and space widths of 80 nm. When the duty cycle is reduced, we can observe several phenomena: 1) The etched depth increases. 2) The hard mask is less damaged. 3) The difference between open areas and dense patterns is reduced. 4) The shape of the micro trenching evolves.

The higher etched depth at low duty cycle reflects an increase in the time-compensated etch rate. This phenomenon is explained by an increased availability of etching radicals during the process. Indeed, since the density of neutrals species (and particularly reactive radicals) is hardly modulated in pulsed plasma at 1 kHz [3], a significant flux of reactive radicals impinges the surface during the OFF time and may participate to silicon etching. Even if the total reactive radicals density in the plasma decreases when the duty cycle decreases, the flux of reactive radicals during the OFF time compensates for this decrease, leading to an increased time compensated etch rate.

By contrast, the SiO_2 etch rate is driven by the ion flux and the square root of the energy. Even if the maximum ion energy increases at low duty cycle, the flux of energetic ions strongly decreases, which leads to a decrease of the SiO_2 etch rate. This explains why the SiO_2 hard mask is better preserved when the plasma is pulsed at low duty cycle.

The difference between dense and open areas is explained by a variation of the passivation layers thicknesses. Indeed, the passivation layers are formed by the deposition of etch by-products and their subsequent oxidation at the pattern sidewalls. When the plasma is pulsed at low duty cycle, the gas fragmentation is lower. This leads to a lower flux of low-volatility etch by-products and free oxygen towards the sidewalls, which reduces the passivation layers deposition rate. As a consequence, the passivation layers are thinner, reducing the absolute difference in passivation layers thicknesses between dense and isolated structures [10]. Note that the passivation layers are strong enough to prevent lateral etching

even at 10% of duty cycle, while some lateral etching was observed in the CW mode. This may be explained by the lower density of reactive radicals in the plasma and the reduced attack of the passivation layers by ions deflected by the differential charges when the plasma is pulsed.

Finally, the shape of the microtrenching evolves when the duty cycle is reduced. In CW mode and at large duty cycle, we observe broad trenches as usually observed using HBr/O₂ plasmas [13]. They originate from the lower deposition of etch inhibitors close to the edges of the patterns due to a shading effect. At low duty cycle, much less etch inhibitors (oxygen containing species and dissociated etch by-products) are available to slow down the etching in the regions with large collection angle (far from patterns edges). This reduces the broad micro trenching at lower duty cycle. When the duty cycle is 20% or below, we can see that local micro trenching forms at the edges between patterns and the etch front. This micro trenching is explained by the shape of the pattern sidewalls that focuses the ions at the microtrenching location, locally enhancing the etching [13] and by a transition towards more ion limited etching regime at low duty cycle.

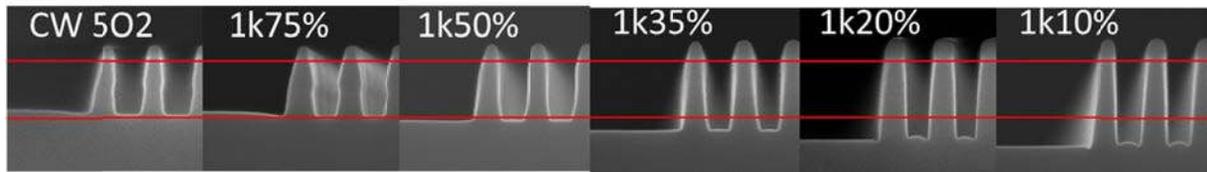


Figure 8. Semi isolated silicon patterns etched in an HBr/O₂ plasma pulsed 1 kHz and at various duty cycle with a SiO₂ hard mask. The etching time is set to have identical plasma ON time for all experiments (so-called time compensation)

CONCLUSION

In this paper, we have investigated the pulsing of an HBr/O₂ plasma for silicon etching application. When the plasma is pulsed, the neutrals density is increased and the plasma is less dissociated. Furthermore, the ion flux is reduced and the ions' chemical nature becomes more molecular. During the etching, the plasma contains many silicon-containing species, and the ion flux is mostly composed of silicon-containing ions. Pulsing the plasma at low duty cycle reduces the proportion of silicon containing species both as neutrals in the plasma and as ions in the ion flux. Contrary to neutral species, the ion flux is largely modulated when the plasma is pulsed at 1kHz. The instantaneous ion flux during the ON time is reduced compared to CW plasma, leading to an increase of the instantaneous ion energy. Pulsing the plasma strongly changes the profile of the etched silicon patterns, with an enhanced time-compensated etching of silicon and a reduced hard mask consumption at low duty cycle. The passivation layers are thinner and more uniform at low duty cycle which improves the local uniformity and the patterns profile control.

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