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Arts, Karsten; Deijkers, J. H.; Faraz, T.; Puurunen, Riikka; Kessels, Wilhelmus M.M. (Erwin); Knoops, Harm C. M.

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Published in:
Applied Physics Letters

DOI:
10.1063/5.0015379

Published: 22/07/2020

Document Version
Peer-reviewed accepted author manuscript, also known as Final accepted manuscript or Post-print

Please cite the original version:
Arts, K., Deijkers, J. H., Faraz, T., Puurunen, R., Kessels, W. M. M., & Knoops, H. C. M. (2020). Evidence for low-energy ions influencing plasma-assisted atomic layer deposition of SiO2: Impact on the growth per cycle and wet etch rate. *Applied Physics Letters*, *117*(3), Article 031602. https://doi.org/10.1063/5.0015379

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Evidence for low-energy ions influencing plasma-assisted atomic layer deposition of SiO_2: impact on the growth per cycle and wet etch rate

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This work provides evidence that plasma-assisted atomic layer deposition (ALD) of SiO_2, a widely applied process and a cornerstone in self-aligned multiple patterning, is strongly influenced by ions even under mild plasma conditions with low-energy ions. In two complementary experimental approaches, plasma ALD of SiO_2 is investigated with and without the contribution of ions. The first set of experiments is based on microscopic cavity structures, where part of the growth surface is shielded from ions by a suspended membrane. It is observed that a lower growth per cycle (GPC) and a better material quality are obtained when an ion contribution is present. Without any ion contribution, a GPC of 1.45±0.15 Å/cycle and wet etch rate of 4±1 nm/s (in 30:1 buffered HF) are obtained for a deposition temperature of 200 °C. With an ion contribution these values decrease, where the magnitude of the decrease appears to be determined by the supplied ion energy dose. For extended ion doses, the GPC decreases to 0.85±0.05 Å/cycle and the wet etch rate to 0.44±0.09 nm/s, approaching the value for a thermal oxide. The important role of ions is confirmed by the second experimental approach, which is based on ion-selective quartz crystal microbalance measurements. By these results, it is demonstrated that ions have a stronger impact on plasma ALD of SiO_2 than usually considered, providing essential insights for tailoring the film growth.

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Silicon oxide is an ubiquitous material that has many applications in nanoelectronics[1,2] as well as in many other fields such as photovoltaics[3] and photonics[4]. Due to the ongoing downscaling of device features, atomic-scale processing techniques such as (plasma-assisted) atomic layer deposition (ALD)[5,6] are becoming increasingly important, also for the synthesis of nm-thin SiO_2 films.[1,7] Among others,[1] plasma ALD has become vital for the growth of SiO_2 sidewall spacers in self-aligned multiple patterning,[8,9] which now represents one of the largest segments of the global ALD market.[7] A key benefit here is that plasma ALD of SiO_2 is relatively facile compared to thermally-driven ALD and can provide high quality SiO_2 even at low temperatures such as 50 ℃.[10,11]

As shown for several plasma ALD processes, energetic ions impinging on the surface during the plasma steps can play an important role.[12] For example, Profijt *et al.*[13] demonstrated that significantly increasing the kinetic energy of the ions through substrate biasing can induce a change in the growth per cycle (GPC) and material properties for Al_2O_3, Co_3O_4 and TiO_2. In more comprehensive studies, Faraz *et al.*[14] and Karwal *et al.*[15,16] reported a large and often beneficial impact of substrate biasing and high ion energies (e.g., 100-200 eV) on plasma ALD of titanium-, hafnium- and silicon-based oxides and nitrides.

In this work, we provide conclusive evidence that even ions with low energies of <20 eV can significantly influence plasma ALD of SiO_2. This influence is seen for instance in the GPC and film quality, even under mild plasma conditions and when using a grounded substrate. Here, the film quality is assessed by the wet etch rate (WER) of the SiO_2 film in a buffered hydrofluoric acid (BHF) solution. Moreover, the work demonstrates that the supplied ion energy dose[17] (eV nm^{-2} $cycle^{-1}$) is a key parameter, which can be used to tailor the film growth. These insights are valuable for current and future applications of plasma ALD of SiO_2 and expectedly also other materials.

The impact of ion exposure has been investigated by two independent experimental methods. In the first method, lateral-high-aspect-ratio (LHAR) trench structures were used,[18,19] where only part of the growth area was exposed to ions. In the second method, film growth was monitored by a sensor with a quartz crystal microbalance (QCM), where the flux of ions to the quartz crystal could be controlled by varying the

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voltage applied to a grid embedded in the sensor.[20] The main focus of this work is on the experiments using LHAR samples. In these experiments it should be noted that ultraviolet (UV) and vacuum ultraviolet (VUV) radiation, which was present only at the ion-exposed surface, might also have affected the growth to some extent. Still, the experiments using the ion-selective QCM sensor, which has the same transmission of (V)UV radiation in ion-blocking and ion-transmission mode, confirm that the observed trends were caused by ion exposure rather than by (V)UV.

Plasma ALD of SiO_2 was carried out in a FlexAL ALD system of Oxford Instruments, which was equipped with a remote inductively coupled plasma (ICP) source operated at 13.56 MHz.[21] Additionally, an external 13.56 MHz power supply could be connected to the reactor table to apply a substrate bias.[14,17] For all depositions, $SiH_2(NEt_2)_2$ was used as precursor (with doses of ~830 mTorr·s per cycle) and 100/50 sccm O_2/Ar plasma as coreactant. Unless stated otherwise, 600 W ICP power, a grounded substrate and a pressure of 50 mTorr was used during the plasma steps, providing a relatively low ion flux and energy (i.e., ~10^{13} $cm^{-2}s^{-1}$ and 9 ± 1 eV average).[22] No significant etching component (e.g., by sputtering) was present under these conditions.[22] Plasma exposure times ranging from 3.8 up to 120 s per cycle were used to demonstrate the impact of the ion dose (nm^{-2} $cycle^{-1}$). As reported in the supplementary information,[22] similar trends are obtained within shorter plasma steps when supplying a higher ion energy and flux, for example by using a lower plasma pressure.

A schematic cross-sectional side view of the used LHAR structures (PillarHall™ generation 3 and 4, developed by Puurunen and co-workers)[18,19,23–29] is provided in Figure 1A, also illustrating film growth during plasma exposure. Using a network of Si pillars, a polysilicon membrane is suspended above a Si substrate with a nominal gap height of 500 nm to form a high-aspect-ratio horizontal trench. The anisotropic ions only impinge on the surface in the plasma-exposed region that is not covered by the membrane. In contrast, the reactive plasma radicals are supplied to the exposed and shielded region, as they can diffuse into the cavity up to aspect ratios as high as ~900.[24] After deposition, the membrane can be removed using adhesive tape. Subsequently, in our experiments the SiO_2 thickness profile was measured by reflectometry

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(Filmetrics F40-UV with a StageBase-XY10-Auto-100mm mapping stage) to retrieve the local GPC in terms of thickness per cycle as plotted in Figure 1B. The local WER, as plotted in Figure 1C, was determined by measuring the thickness profile before and after a 5 s etch in 30:1 BHF at room temperature with NH_4F as the buffer agent. The noise level in the reflectometry measurements is dependent on the local thickness of the film before and after etching. In addition to reflectometry, ex-situ spectroscopic ellipsometry (SE) was performed on Si reference samples that were processed alongside the corresponding LHAR samples, to more accurately measure the GPC and WER obtained with ion exposure. To compare the impact of ions to the effect of temperature, depositions were carried out at table temperatures of 100, 200 and 300 ℃, using 250, 400 and 250 ALD cycles per sample, respectively. Further experimental details are provided in the supplementary information.[22]

The data shown in Figure 1B and C demonstrates that the GPC- and WER-values of the SiO_2 grown with exposure to ions and neutrals (shaded area) are lower than those of the SiO_2 grown by neutral species only. In the region without ion exposure, the local GPC gradually reduces with distance, while the material quality in terms of WER remains similar with distance. In the ion-exposed region, the GPC and WER significantly decrease when using longer plasma steps, which is here exemplified by showing the results when using 12 and 120 s plasma exposure. In contrast, the GPC and WER in the region without ion exposure are not significantly influenced by the plasma exposure time (aside from a deeper film penetration into the cavity for a longer plasma exposure[24]). This indicates that the radical dose itself has a negligible effect on the SiO_2 film thickness and quality when the plasma half-cycle is in saturation.

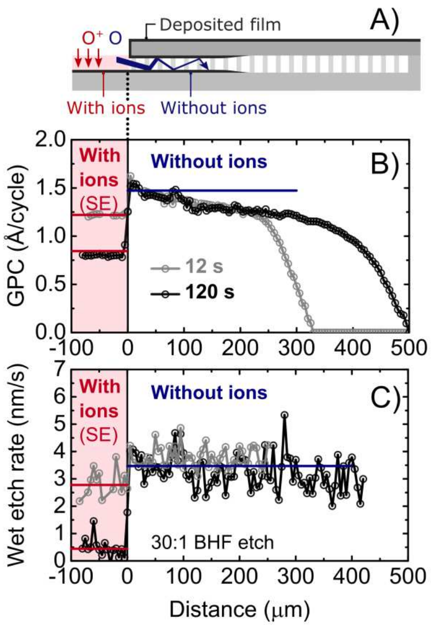

Figure 1: LHAR cavity structures[18,19,23–29] *(A) with which the GPC (B) and wet etch rate (C) of* SiO_2 *films grown with and without ion contribution were investigated. The horizontal bars indicate the values obtained with (left) and without (right) ion exposure, which are based on the thickness profiles measured by reflectometry after removal of the membrane. The values obtained with ions (left) have been confirmed by SE. These results, obtained at a table temperature of 200 ℃ using plasma steps of 12 and 120 s, demonstrate that the GPC and WER decrease by the contribution of ions.*

This experiment using LHAR samples has been repeated for a series of plasma exposure times, at various table temperatures. The results shown in Figure 2 confirm that the plasma exposure time has a limited effect on the GPC and WER when the SiO_2 is grown by neutral species only. In contrast, the GPC and WER are reduced with ion contribution, where the reduction in GPC and WER is larger for longer plasma steps. The refractive index (at 633 nm) remains approximately constant at $n \approx 1.45$ (see supplementary information),[22] indicating that the film density is relatively unaffected. As reference values, Figure 2 also provides the WERs measured for SiO_2 grown by plasma-enhanced chemical vapor deposition (PECVD)[22] and for a thermal oxide film. These values, obtained in this work under identical conditions, are similar to values reported in the literature (e.g., 1.4 nm/s for PECVD SiO_2 and 0.28 nm/s for a thermal oxide, extrapolated for 30:1 BHF from Williams *et al*.[30]). This comparison indicates that the film quality in terms of WER is similar to PECVD SiO_2 for moderate ion doses and approaches the high quality of a thermal oxide for extended ion doses. Here it should be noted that the ion energy also plays a role, as exemplified by the deposition using 60 W biasing (giving high ion energies of ~120 eV average).

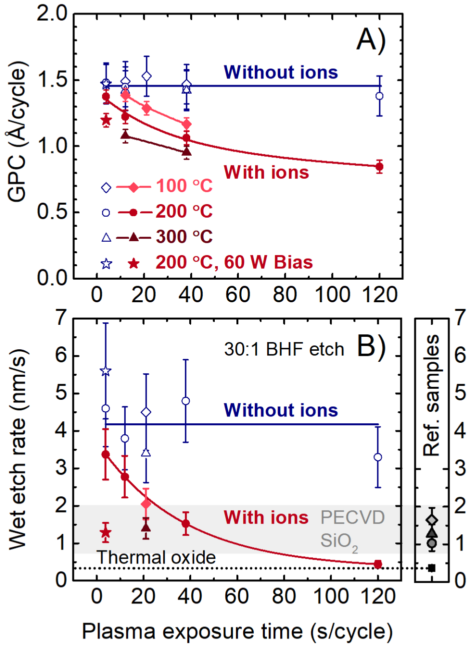

Figure 2: GPC (A) and wet etch rate (B) of SiO_2 films grown with and without ion contribution at table temperatures of 100, 200 and 300 °C, determined as shown in Figure 1. With ion contribution, the GPC and WER decrease when using longer plasma exposures or by substrate biasing (here using 60 W bias power). For the deposition using plasma steps of 120 s, the WER approached the value measured in this work for a thermal oxide (dotted line). The column at the right also provides WER values measured in this work for PECVD SiO_2 grown at 100, 200 and 300 °C.

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Note that the GPC and WER are two very different parameters, where the GPC is influenced by the surface chemistry during film growth (e.g., OH surface coverage[10]), while the WER reflects the properties of the deposited film (e.g., impurity content[31]). Nevertheless, a high similarity between the impact of ions on the GPC and on the WER is observed. Both effects could be caused by surface dehydroxylation induced by the kinetic energy delivered by the impinging ions. A lower OH surface coverage can limit the amount of precursor adsorption per cycle and thereby lower the GPC,[10] while dehydroxylation could also lower the OH impurity content in the film and reduce the WER.[31] Similarly, a higher deposition temperature can also induce dehydroxylation[32] and lower the GPC[10] and WER. These factors make the effects of ion exposure and temperature somewhat interchangeable, as also observed in Figure 2.

To confirm that ions are the species responsible for the observed effect, an additional experiment has been performed in the same reactor using a special ion-selective QCM sensor (Quantum probe of Impedans Ltd.). In this sensor the QCM was embedded in a retarding field energy analyzer (RFEA).[20] An RFEA is normally used to measure the energy distribution and flux of ions impinging on the substrate.[17,20,33,34] Here, as illustrated in Figure 3A, the RFEA grids were used to completely block ($eV_D > E_{ion}$) or partly[22] transmit ($V_D = 0$) the flux of ions to the quartz crystal, where V_D is the potential of the discriminator grid and E_{ion} the maximum ion energy.[20] A representative result is shown in Figure 3B, where the absolute change in resonance frequency (which is proportional to the deposited mass)[20,35] is plotted for 9 ALD cycles of SiO_2 with and without ion transmission. The slope of this signal represents the GPC in terms of mass per cycle, which here also reflects the thickness per cycle since the mass density is approximately unaffected.[22] Under the used plasma conditions (100 ℃, ~19 mTorr, 100/50 sccm Ar/O_2, 600W ICP power, 10 W bias power and 5 s plasma steps), the GPC with ion exposure was reduced to 78±7 % of the value obtained without ion transmission. This is comparable to the reduction in GPC observed using the LHAR samples when using 38 s plasma exposure.

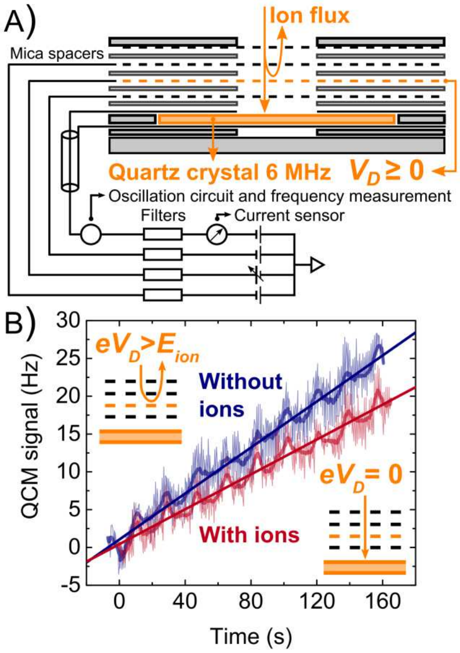
A)
Ion flux
Mica spacers
1.5 mm
Quartz crystal 6 MHz
$V_D \geq 0$
Oscillation circuit and frequency measurement
Filters
Current sensor
B)
$eV_D > E_{ion}$
Without ions
$eV_D = 0$
With ions
QCM signal (Hz)
30
25
20
15
10
5
0
-5
0
40
80
120
160
Time (s)

Figure 3: Cross-sectional side view of the ion-selective quartz crystal microbalance sensor used in this work (A). The quartz crystal is embedded in an RFEA which can be used to measure the energy distribution of ions and to block (voltage $V_D > E_{ion}/e$) or transmit ($V_D = 0$) the flux of ions to the quartz crystal. Panel (B) shows results obtained for plasma ALD of SiO_2, which confirm that the GPC is reduced upon exposure to ions. Here, the raw data of three sets of measurements (light background signal), smoothened signals and linear fits are overlaid. Schematic (A) has been reproduced from Sharma et al., Rev. Sci. Instrum. 87, 043511 (2016),[20] *with the permission of AIP Publishing.*

Both experimental approaches thus indicate a significant impact of ions on plasma ALD of SiO_2, yet the magnitude of this impact will depend on the reactor and plasma conditions used, i.e., on the flux and energy of the impinging ions, making it difficult to predict the growth behavior in general. A multitude of data corresponding to various experimental conditions is given in Figure 4, which reveals that the magnitude of the influence of ions appears to be determined by the delivered ion energy dose. This parameter, calculated as ion flux × plasma exposure time × mean ion energy,[17] was here estimated by RFEA measurements (see supplementary information).[22] The data is benchmarked against values obtained by Faraz *et al*.[14] and by the ion-selective QCM data (the ratio $\frac{\mathrm{GPC}_{With\ ions}}{\mathrm{GPC}_{Without\ ions}}$ scaled assuming 1.45 Å/cycle in ion-blocking mode).[22] Figure 4 can serve as a map to compare very different reactors and processing conditions. It also shows that the influence of ions on plasma ALD of SiO_2 is negligible when supplying an ion energy dose lower than ~3 eV nm^{-2} per cycle. On the other side, the growth is significantly influenced when dosing for instance 100 eV nm^{-2} per cycle or higher. This effect will only be obtained at the surfaces undergoing ion impingement, e.g., the planar top and bottom surfaces of a 3D trench structure and not its vertical sidewalls.[14]

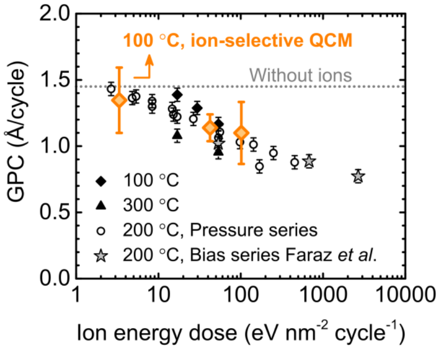

Figure 4: GPC of SiO_2 grown with ion exposure, showing a clear trend with the supplied ion energy dose as measured by an RFEA. The ion energy dose was varied by using different plasma pressures and exposure times (this work) and by substrate biasing (Faraz et al.)[14]. The trend is confirmed by the ion-selective QCM measurements, for which the data is scaled assuming a GPC of 1.45 Å/cycle in ion-blocking mode (dotted line, see Figure 2).

In conclusion, we have demonstrated that ions have a stronger impact on plasma ALD of SiO_2 than usually considered. Even low-energy ions (<20 eV) can significantly influence the GPC and material quality, where the magnitude of this influence can be predicted by the supplied ion energy dose. Aside from a deeper fundamental understanding, these insights provide very practical opportunities as well. For instance, a low plasma pressure, substrate biasing or extended plasma exposure time can be used to increase the ion energy

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dose and optimize material quality. In contrast, a low ion energy dose allows for a more uniform and conformal film in terms of thickness and material properties. Finally, the difference in WER with and without ion exposure can be exploited for topographic selective processing on 3D substrates.[12,14] This work thus provides valuable insights for tailoring SiO_2 film growth by ALD in state-of-the-art and next-generation device applications.

Supplementary material

See supplementary material for the RFEA data and conditions, plasma etch test, refractive indices and for further experimental details on the LHAR structures, SE measurements, PECVD conditions and ion-selective QCM measurements.

Acknowledgments

This work is part of the research program HTSM with Project No. 15352, which is (partly) financed by the Netherlands Organization for Scientific Research (NWO). VTT Technical Research Centre of Finland Ltd. and Dr. M. Utriainen are acknowledged for supplying the PillarHall™ LHAR3 and LHAR4 conformality test structures. Impedans Ltd. and Dr. D. Gahan are acknowledged for providing the Quantum Single Sensor gridded quartz crystal microbalance and for technical consultation. Furthermore, C. van Helvoirt, T. de Vries, P. Bax and W.J.H. Berghuis are thanked for their technical support.

Data availability statement

The data that supports the findings of this study are available within the article and its supplementary material at http://doi.org/[doi].

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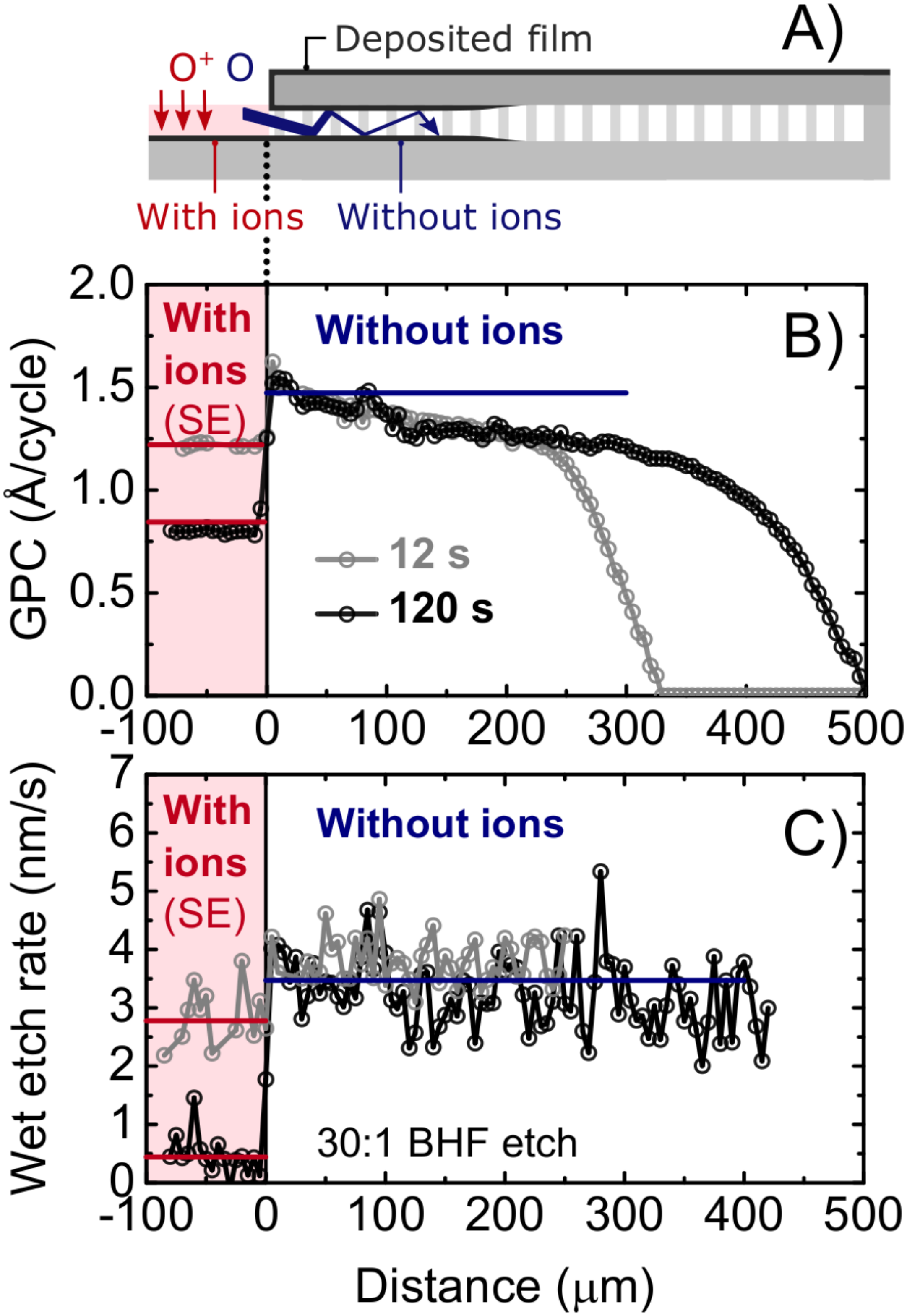

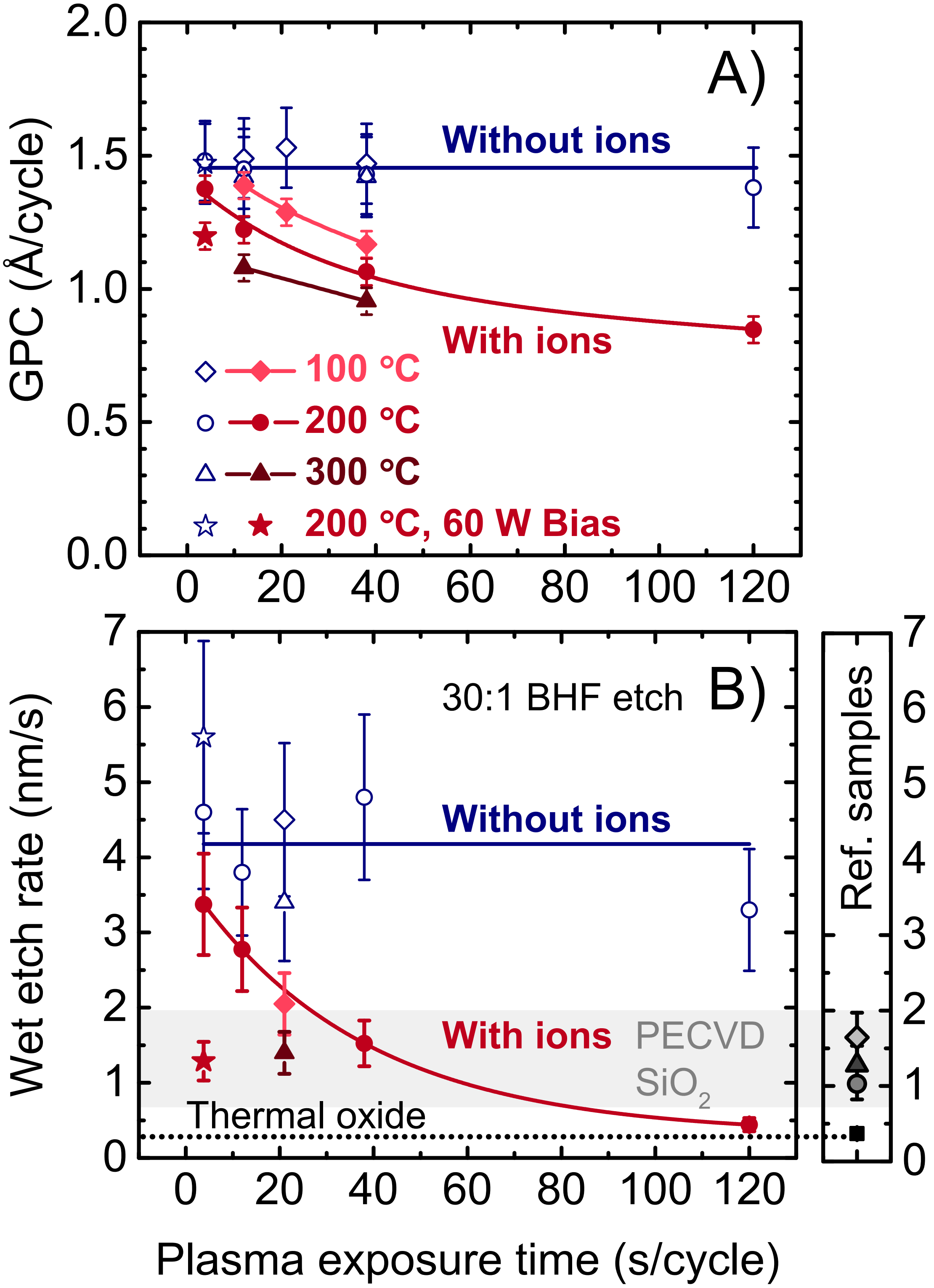
A)
Without ions
With ions
100 °C
200 °C
300 °C
200 °C, 60 W Bias
GPC (Å/cycle)
2.0
1.5
1.0
0.5
0.0
0
20
40
60
80
100
120
B)
30:1 BHF etch
Without ions
With ions
PECVD
SiO$_2$
Thermal oxide
Wet etch rate (nm/s)
Ref. samples
7
6
5
4
3
2
1
0
Plasma exposure time (s/cycle)

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Applied Physics Letters

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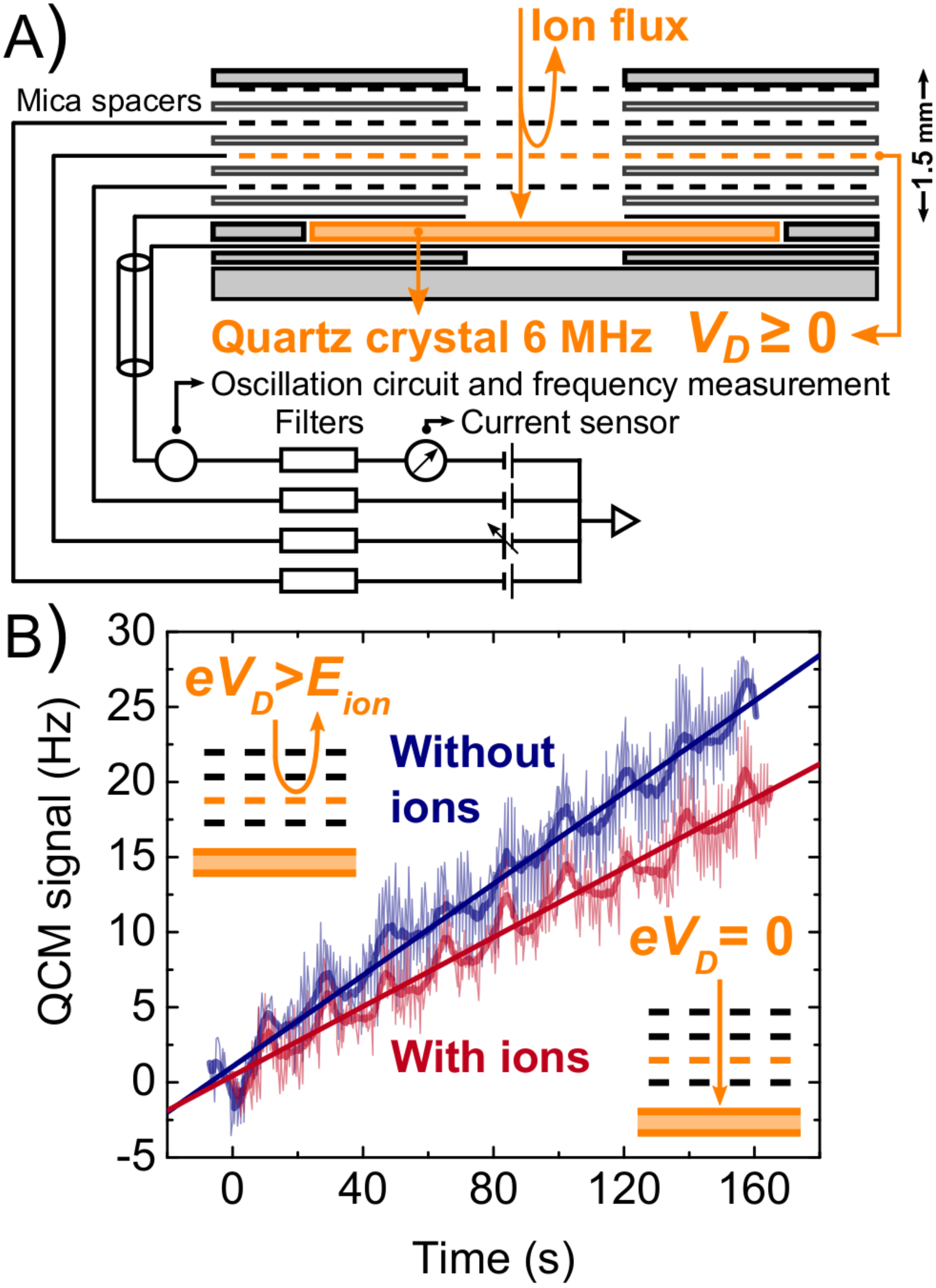

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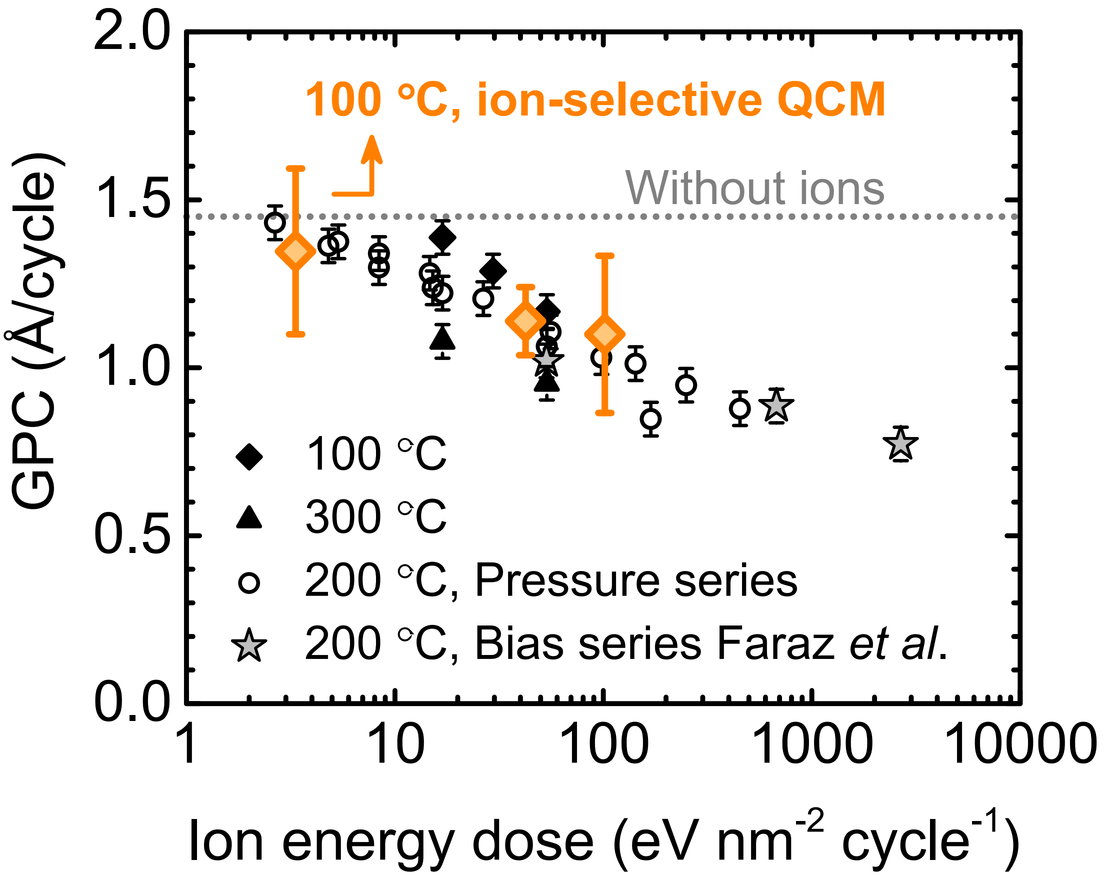
2.0
1.5
1.0
0.5
0.0
GPC (Å/cycle)
1
10
100
1000
10000
Ion energy dose (eV nm^{-2} cycle^{-1})
100 °C, ion-selective QCM
Without ions
◆ 100 °C
▲ 300 °C
○ 200 °C, Pressure series
☆ 200 °C, Bias series Faraz *et al.*