Microwave plasma assisted process for cleaning and deposition in future semiconductor technology

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Abstract. The epitaxial growth of silicon layers is an important step in the fabrication of semiconductor devices. For conventional silicon epitaxy, high temperatures, up to 900 °C are necessary. However, in future, semiconductor technology epitaxy processes at lower temperatures are required to increase the integration density. The goal of this study was to investigate microwave plasma assisted processes for the selective removing of thin silicon oxide, the cleaning of silicon surfaces and the depositing of high quality silicon films. The main focus was to apply these processes for low temperature epitaxy. All processes, such as oxide removal, cleaning and deposition, were done in one chamber and with microwave plasma assistance. In order to remove silicon dioxide, the etching behavior of hydrogen, fluorine, and hydrogen/fluorine plasma was studied. It was shown, that with hydrogen/fluorine plasma, the best selectivity of oxide to silicon was reached. The deposition process of silicon was studied by growing μc-Si films. The process was characterized and optimized by spectral ellipsometry. After a successful characterization of all process steps, silicon epitaxy layers have been grown with in-situ removal of native oxide and in-situ surface cleaning. The temperature for all process steps was reduced below 450 °C.

1. Introduction
Silicon based epitaxy is a key process in semiconductor technology. Modern devices such as SiGe heterojunction bipolar transistors (HBTs) [1] or strained silicon MOS transistors [2] are based on epitaxy processes. Conventional chemical vapor deposition (CVD), which is used in industry, needs temperatures higher than 700°C. However, lower deposition temperatures are required due to the reduction of the structures’ size, sharp doping profiles, and increased thickness of strained layers.

Presently, high temperatures are still required not only for the epitaxial deposition, but also for the preceding cleaning State-of-the-art for pre-epitaxial cleaning is a high temperature annealing in hydrogen atmosphere, the so call “hydrogen bake” [3]. Therefore in order to realize a low temperature epitaxy, both the cleaning as well as the deposition must be conducted at low temperatures.

For low-temperature pre-epitaxial cleans, different hydrogen plasmas were investigated [4]. Usually, an additional ex-situ removal of the native oxide with HF-acid is required [5]. Nishino et al. [6] describe the selective etching of silicon dioxide to silicon in a NH3/NF3 plasma. This process is not widely investigated and until now not used for pre-epitaxial cleaning.

Plasma enhanced chemical vapor deposition (PECVD), which is used to grow amorphous [7] or microcrystalline (μc) silicon films [8], was also investigated for epitaxial applications [8]. However, an in-situ simultaneous surface cleaning and epitaxial growth at low-temperature, without any additional wet-clean step, not yet, to our knowledge, is published.
In this paper, we describe a microwave-plasma enhanced chemical vapor deposition (MECVD) system for silicon epitaxy with in-situ cleaning steps. For the removal of the native oxide, the etching behavior of hydrogen, fluorine and hydrogen/flourine plasma was systematically studied. Especially the influence of the plasma on the etching behavior was investigated. For the deposition process, the growth of µc-Si is studied to find out ideal process conditions for high crystallinity films. Finally, we will report in-situ surface cleaning followed by growing a silicon epitaxial layer, without any additional wet-cleaning steps.

2. Experimental
The plasma system is a prototype, built by Muegge GmbH. The 2.45 GHz microwave plasma source is attached on top of an aluminum reactor (Figure 1). The source is designed for power from 600 W up to 3000 W and the typical process pressure is between 150 mTorr and 1000 mTorr. The system is suited for 200 mm wafers. The distance between the floating substrate heater and the plasma source can be varied from 20 mm to 170 mm. This is an extremely important feature because it allows investigating the influence of different plasma species, i.e. ions, electrons and radicals. If the substrate is next to the plasma, radicals, ions and electrons reach the surface. However, if the substrate is far away from the plasma source, only the radicals reach the substrate surface. A detailed description of the system is given in [9].

For all experiments, p-type (100) Si wafers were used. For the etching experiments, 15 nm thermal oxide was grown and patterned by lithography followed by a wet-chemical etching. This allowed measuring both, the silicon and silicon dioxide etching rate at the same time. The silicon dioxide thickness was measured by spectral ellipsometry and the silicon thickness by atomic force microscopy (AFM) step measurements. The µc-Si films have been deposited on samples having a 100 nm thermal oxide. The characterization was done by spectral ellipsometry. For the epitaxial deposition standard (100) Si wafer without any pre-treatment were used. The crystalline quality was determined using Raman spectroscopy and electron channeling pattern (ECP).

3. Results and discussion

3.1. Hydrogen plasma etching of silicon and silicon dioxide
At first, the etching behavior of silicon as well as of silicon dioxide in the microwave plasma was investigated. For stable plasma conditions, the hydrogen was diluted in argon. The hydrogen to argon
flow ratio was 1 to 6. The substrate was heated up to 400 °C and a microwave power of 1.5 kW was applied.

The dependency of the etching rate on the distance, between the surface and the plasma source was investigated in order to understand the influence of ions, electrons, and radicals on the reaction kinetics. For these experiments, the pressure was kept at 200 mTorr. The results are shown in Figure 2. Etching is only observed at a distance less than 70 mm, and quite a different etching behavior for silicon dioxide and silicon can be observed. The silicon dioxide etching rate is almost constant in the range between 15 mm and 70 mm. The silicon etching rates are much higher between 15 mm and 40 mm and drop drastically beyond this distance. An explanation for this behavior can be given by the different influence of plasma species depending on the distance to the microwave source. In the region directly in the vicinity of the plasma, ions, electrons and radicals are available. Impinging ions break up the chemical bonds at the surface and a chemical etching with hydrogen radicals is possible. Because the Si-Si bond is much weaker than the Si-O bond, the difference in etching rate can be explained. If the distance increases the density of ions decreases rapidly while the high energy electrons are still present. Therefore at a distance between 40 mm and 70 mm mostly electrons reach the substrate surface. While electrons hitting the semiconducting silicon surface are neutralized by recombination processes, the isolating silicon dioxide will be negatively charged by them. This in turn leads to an increased ion bombardment of the silicon oxide compared to silicon. This explains why the etching rate of silicon dioxide does not drop as much as that of the silicon. Beyond 70 mm no charged particle reach the surface, and only hydrogen radicals are remaining, which are not able to initiate etching process [10]. This proves that between 20 mm and 70 mm a physical impact of charged particle dominates.

![Figure 2](image-url)

**Figure 2.** Etching rate of silicon dioxide (left axis, red) and silicon (right axis, blue) as a function of distance to the plasma source.

After these basic investigations the etching rate of Si and SiO2 as a function of the working pressure for a minimum distance of 20 mm has been investigated (Figure 3). It can be seen, that both etching rates decrease by increasing pressure. At pressures above 400 mTorr no etching rate can be determined. Normally, if the pressure increases, the radical density increases. This should lead to an increasing etching rate. However, it was shown above, that hydrogen radicals on their own do not etch silicon or silicon dioxide. If the pressure increases, the ion energy decreases because of the decrease of the mean free path. Therefore it can be concluded, that the limiting factor for hydrogen plasma etching is the ion energy, and not the radical density.

In conclusion it can be stated that the etching of silicon and silicon dioxide by hydrogen radicals is only successful, if an addition physical impact exists. The limiting factor for the chemical etching is the energy of ions, which are able to crack the chemical bond at the surface.
Figure 3. Etching rate of silicon dioxide (left axis, red) and silicon (right axis, blue) as a function of working pressure.

3.2. Fluorine plasma etching of silicon dioxide

Fluorine radicals are known to etch silicon as well as silicon dioxide [11]. Typical precursors usually are CF₄ [12] or NF₃ [13], but molecular F₂ can also be used [14]. The fluorine etching is a typical dry chemical etching, which should only be limited by the radical density. The etching behavior of silicon dioxide in a F₂/He and a NF₃/Ar microwave plasma was investigated. The explored parameters were working pressure and distance between the substrate and plasma source. The total gas flow was fixed at 840 sccm, the power was kept at 1.5 kW and a temperature of 400 °C had been chosen.

The results are shown in Figure 4 and 5. In contrast to hydrogen etching for both gas chemistry the etching rate increases with increasing working pressure. This proves, the radical density and not the physical impact is the limiting factor for the chemical reaction.

Figure 4. Etching rate of silicon dioxide in a NF₃ and F₂ microwave plasma as a function of working pressure.

For the investigation of the effect of distance, the pressure was fixed at 200 mTorr. As can be seen from Figure 5 two different etching regions are found. In both regions, the etching rates decrease linearly, but with different slopes. For a distance between 20 mm and 70 mm the etching rates decrease rapidly. Apparently the impact of ions and electrons enhances the etching rate. However, it can be clearly seen that even at a distance beyond 70 mm, where only radicals are present a significant etching rate exists, i.e. pure chemical etching takes place. In this region, the decrease of the etching rate can be explained by the reduced radical density. The etching behavior of NF₃ compared to F₂ is very similar. This suggests that in both cases F-radicals are the main etching species. The results show that the physical impact can enhance the etching, but the limiting factor is the radical density.
Figure 5. Etching rate of silicon dioxide as a function of distance between the substrate and the plasma source using NF₃ and F₂ microwave plasmas.

3.3. Hydrogen/Fluorine plasma etching
As shown above, hydrogen, as well as fluorine plasma, can be used to etch silicon dioxide. However, the selectivity to silicon is not very good. The main reason is that the Si-O binding energy is significantly higher as compared to the Si-Si bond. It was shown that in a NH₃/NF₃ plasma, a selective etching of silicon dioxide over silicon can be realized [6]. The microwave plasma system was investigated to realize the selective remove of oxide with a H₂/NF₃-discharge. These experiments were done at a distance of 70 mm. This means that the hydrogen radicals do not etch. The power and the working pressure were 1.5 kW and 200 mTorr, respectively.

The etching rates of silicon and silicon dioxide were investigated in dependency on the hydrogen dilution. The results are shown in Figure 6. At a low dilution a high etching rate of silicon is observed. Besides, the selectivity is very low due to the presence of many F-radicals. With increasing hydrogen dilution the silicon etching rate decreases much faster than the etching rate of silicon dioxide and an increase of the selectivity up to around 10 is observed. This can be explained by a reaction of fluorine with hydrogen to form HF, which only etches silicon dioxide.

Figure 6. Etching rate of silicon dioxide in a NF₃ and F₂ microwave plasma as a function of distance from plasma source.

3.4. Deposition of μc-Si layers
To investigate the growth conditions of silicon films in the microwave plasma, microcrystalline silicon (μc-Si) was grown and investigated by spectral ellipsometry. For the characterization of the
crystallinity, a Bruggeman-effective-medium-approximation-model (BEMA) [15] was developed. The deposition was done from a silane/hydrogen/argon-plasma at a substrate temperature of 400 °C. It was found that high hydrogen dilution, low working pressure and high microwave power favor crystalline growth. The hydrogen flow and the silane flow were 1400 sccm and 4 sccm, respectively. To stabilize the plasma, 400 sccm Ar were added.

To investigate the effect of the plasma on the growth, the film properties in dependency on the distance were studied. Figure 7 summarizes the obtained deposition rate and the crystallinity. The deposition rate decreases exponentially with increasing distance because the number of available particles decreases. It also is obvious that the crystallinity is high and nearly constant, if the distance is below 50 mm. If the distance is further increased, the crystallinity decreases rapidly. At a distance of 70 mm and more, the film becomes mostly amorphous. These results prove that an additional physical impact of ions is necessary to achieve the growth of µc-Si with a high crystallinity.

![Graph showing deposition rate and crystallinity](image)

**Figure 7.** Deposition rate (left axis, black) and crystallinity (right axis, blue) determined by spectral ellipsometry as a function of distance from plasma source.

3.5. Silicon epitaxy at 450°C

Finally, the results of etching and µc-Si growth have been combined in order to achieve silicon homoepitaxy at low temperatures. At first the aim was to realize an in-situ removal of the native oxide followed by an epitaxial deposition of silicon layer. A NF₃/H₂ plasma etching was carried out to remove the native oxide from the silicon substrate. For this process, the substrate was positioned at a distance of 70 mm and the H₂ to NF₃ flow ratio was 100 to 1. In these conditions, a high etch selectivity of silicon dioxide to silicon was obtained. The power was 1.5 kW, the pressure 200 mTorr and the substrate temperature 450 °C. After the etching, the deposition was immediately done. During the deposition process, the distance was reduced to 40 mm, because the growth of µc-Si shows, that for high crystallinity, an additional impact of ions is required. Pressure and temperature were kept constant. The power was increased to 2.5 kW. The deposition was done with 4 sccm silane and 1400 sccm hydrogen. The film was characterized by electron channeling pattern (ECP) and Raman spectroscopy. Figure 8 shows the Raman spectra and the ECP results. The spectrum shows only the peak of the silicon crystal at 520 cm⁻¹. In the ECP picture a clear (100) pattern can be observed. This proves that epitaxial silicon was successfully grown at a low temperature with an in-situ low temperature removal of the native oxide.
Figure 8. Raman spectrum and electron channeling pattern (ECP) of an epitaxial silicon film grown at 450°C on an in-situ NF3/H2 cleaned sample.

4. Conclusion
It has been shown that “Microwave Enhanced Processes” at temperatures as low as 450°C can be used for numerous applications in semiconductor technology.

The results, obtained from the present work, can be summarized as follows:
1. In a hydrogen microwave plasma silicon and silicon dioxide can only be etched if a physical impact by ions or electrons exists.
2. In a NF3 or F2 microwave plasma, the etching of silicon dioxide is mainly limited by radicals. The physical impact plays a secondary role.
3. Both hydrogen and fluorine plasma show a higher etching rate of silicon compared to silicon dioxide.
4. In a NF3/H2 microwave discharge, a selective removal of native oxide is achieved, if the substrate is at a distance where only radicals are available and a high hydrogen dilution is used.
5. The selective etching of silicon dioxide to silicon can be explained by the formation of HF in the vapor phase.
6. μc-silicon films on silicon dioxide can only be grown, if an addition physical impact exists. Deposition with radicals leads to amorphous growth.
7. Epitaxial silicon films can be grown at 450°C with an in-situ removal of the native oxide. Additional ex-situ cleaning steps are not required.

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