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Investigation of sub-nm ALD aluminum oxide films by plasma assisted etch-through

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Abstract

A new technique, called "plasma defect etching" (PDE), is proposed for studying the continuity of ultra-thin layers. The PDE technique utilizes the extremely high selectivity in the deep reactive ion etching (DRIE) process, thus achieving visualization of the defects in the layer, because etching of substrate happens only through voids and microholes of the layer. The etch profile generally reproduces the non-continuous structure of the layer. This PDE technique was applied for the investigation of thin, sub-nm aluminum oxide films grown on silicon wafers by atomic layer deposition (ALD) technique. Silicon substrate was etched by SF_6 at cryogenic temperatures in an inductively coupled plasma (ICP) reactor, exploiting the extremely high ratio of silicon/aluminum oxide etch rates in fluorine plasmas. The surface morphology was characterized by scanning electron microscopy (SEM) and atomic force microscopy (AFM). The PDE method shows that in the case of water as an oxidation precursor, separate islands of aluminum oxide form during the five first ALD cycles. On the other hand, the use of ozone precursor helps to oxidize silicon surface and facilitates growth of a uniform layer.

Keywords: Ultra-thin layer; Atomic layer deposition; Plasma etching; Aluminum oxide; Scanning electron microscopy; Atomic force microscopy

1. Introduction

Atomic layer deposition (ALD) provides excellent uniformity, conformality and thickness control of the deposited thin film in the nanometer range [1–3]. This is based on the self-terminating reactions during the each growth cycle [2]. Areas of application of ALD are rapidly extending, and several main reasons for this can be mentioned: dimensional scaling down in microelectronic devices, requirements for lower film growth temperatures, requirements for very good film uniformity for 300 mm Si wafers, search for new materials as thin adhesion layers or diffusion barriers for Cu as an interconnect material [3]. ALD is also becoming a very important nanofabrication technique.

The formation of sub-nm layers is more complicated than that of thicker films because during the initial cycles, or the so-called incubation period, reactions are affected first of all by the original surface of the substrate [4]. Determination of the growth mode and investigation of layer growth during the incubation period is a challenging task because of the generally small analysis area of available direct measurement techniques, such as atomic force microscopy (AFM) and transmission electron microscopy (TEM) [5–7] and because of the non-trivial interpretation of indirect ones, such as secondary ion mass spectroscopy (SIMS) or X-ray photoelectron spectroscopy (XPS) [8,9].

Aluminum oxide Al_2O_3 is one of the most attractive ALD materials particularly because of its thermal and chemical stability, excellent dielectric properties, and good adhesion to many surfaces. It makes a promising candidate for replacing SiO_2 for gate dielectrics. Aluminum oxide growth is one of the most widely investigated and developed ALD processes, nevertheless, its initial growth phase on hydrogen terminated silicon surface is not completely clear [2].

Aluminum oxide, because of its hardness and chemical inertness, can also be used as a mask in deep etching of silicon by reactive ion etching (RIE). Recently, Dekker [10] evaluated mask properties in an ICP reactive ion etcher using the Bosch process. Exceptional selectivity for silicon over Al_2O_3 was obtained, reaching 100 000:1. Tegen and Moll [11] investigated

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aluminum oxide mask properties for magnetically enhanced RIE and ICP-RIE, mainly at room temperatures. Their result was about 50:1 or lower selectivity for silicon over Al_2O_3. Our previous tests showed that extremely high silicon to Al_2O_3 selectivity (reaching 70 000:1) can be obtained by etching silicon in ICP reactor at cryogenic temperatures [12].

We are proposing a new technique for studying of ultra-thin layer which can be described as "plasma defect etching". Very short plasma etching (of few seconds duration) pulse is applied in order to "texturize" silicon surface through the mask formed by the discontinuous sub-nanometer thick layer of aluminum oxide grown by ALD. The silicon substrate is etched only through voids and microholes of the mask, and the etch profile generally reveals the non-uniform and non- continuous structure of the ALD grown aluminum oxide layer. Deep reactive etching at cryogenic temperature was applied in this work, exploiting the extremely high ratio between the etch rates for silicon and aluminum oxide. The etch profile was characterized by scanning electron microscopy (SEM) and atomic force microscopy (AFM) techniques. Hydrogen-terminated silicon substrates were used and both water and ozone were applied as oxidants, in order to understand the initial steps of aluminum oxide growth.

2. Layer formation

All the processing was done in a cleanroom (ISO class 4–5). Silicon wafers of 100 and 200 mm diameter were used as substrates. In order to perform the layer growth process at the same initial conditions, the substrates were rinsed for 1 min in buffered hydrofluoric acid solution (Sioetch solution, Merck, Germany) containing about 2% of hydrofluoric acid. This native-oxide removing step was done just before transferring of the wafers into the ALD reactor. Therefore, ALD process was performed on hydrogen-terminated silicon surface.

Aluminum oxide layer was grown by ALD technique in a Beneq TFS-500 reactor using trimethyl aluminum (TMA) as the precursor for aluminum, and water or ozone as the precursor for oxidation. The deposition was conducted at 220 °C temperature, and the pressure in the reactor was kept at about 5 mbar. Nitrogen was used as a carrier gas to transport precursor vapors to the wafer surface and purge reaction gases from the reactor during each reaction half-cycle. Total cycle length was 1.5 s, including 0.5 s purge pulse after each precursor pulse. Thicker layers (20–100 nm thick) were grown in order to evaluate the steady-state growth rate per cycle, which was found to be 0.90 Å/cycle and 0.84 Å/cycle for water and ozone as the oxidant precursor, respectively. These values correspond well with the aluminum oxide growth rates in ALD obtained by other authors [2,13–15].

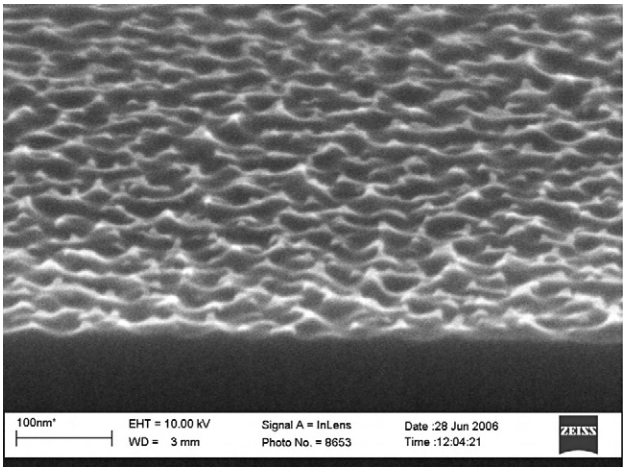

Fig. 1. SEM cross-section view of the structure grown during 2 cycles of ALD and etched for 1 s in cryo-DRIE.

Ultra-thin layers were grown for the investigation of ALD process at the initial phase: in that case, only 2, 5, 8 and 10 cycles were applied. It is inside the so called "incubation period", where the steady-state growth rate is still not established, and it is quite questionable, if there can be already a continuous layer — or only separate initial "islands" [5,16]. The obtained aluminum oxide layers were plasma etched as grown, without any annealing or other post-processing step.

3. Investigation technique

The remarkable inertness of aluminum oxide in plasma etching of silicon suggested the application of this characteristic for "amplification" or "magnification of the thickness" of a discontinuous layer. Very short plasma etching steps were applied in an Oxford Instruments Plasmalab −100 system to investigate the continuity of the layer growth in ALD reactor, starting from a few deposition cycles. The process was conducted at −110 °C, keeping 10 mTorr pressure in the chamber and using SF_6 and O_2 gas mixture (40 sccm:6 sccm) at 1000 W ICP-power. Because the layers were extremely thin, the applied DRIE step was also very short. The etch rate for silicon was about 2 μm/min (at −110 °C), therefore, longer etching could completely remove the surface structure because of the underetching. We found 1 s, 2 s, or 5 s long etching steps being optimal. Of course, the plasma itself and the etching process cannot stabilize completely during such a short time. Therefore, the silicon etch rate and anisotropy, and also aluminum oxide mask etch rate can differ from the average values.

Etched structures were characterized with a Zeiss SUPRA™ 40 field emission scanning electron microscope and NT-MDT NTEGRA atomic force microscope. In order to minimize the charging effect in SEM, caused by the nonconductive sample, the adjusting of the focus and astigmatism was done on the sample aside from the area of interest, and shifted to this area just for the final scan. For AFM a standard type cantilever with a tip radius of 10 nm was used, and the measurements were done in a non-contact mode. Those two techniques were found to complement each other nicely.

4. Results and discussion

Because ALD is based on repeated surface reactions, the initial surface of the substrate is very important for the initial stages of deposition. In the case of an unoxidized, hydrogen terminated silicon substrate also the oxidant precursor plays an important role at the initial growth stage. For this reason the behaviour of water and ozone as a precursor was compared.

4.1. TMA + water process

The ALD growth was done with TMA and water as a precursors. The PDE technique was applied then both for the substrate containing the ALD layer and for the clean silicon wafer tested as a reference. The surface of the etched reference sample was found extremely smooth, showing that etching is uniform and proving that rough surface could appear only in the presence of some masking. Fig. 1 shows SEM picture obtained after 1 s of DRIE process for the structure grown only during 2 cycles. In that case, the silicon surface is quite rough after the etching, with about 40–60 nm periodicity (Fig. 1). It can be stated from the figure, that no masking layer is left after etching. This may mean, that the aluminum oxide formed only a high

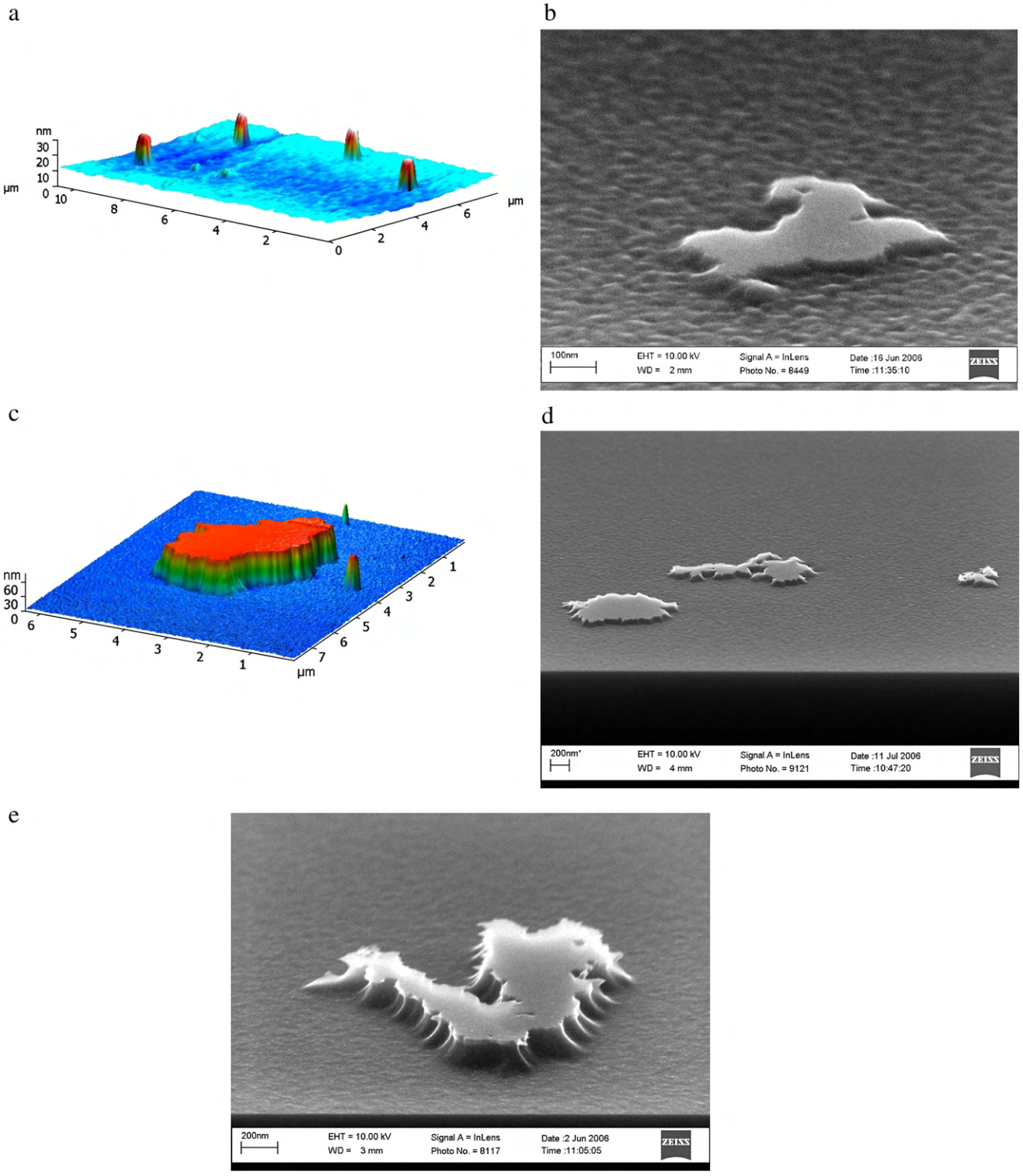

Fig. 2. AFM and SEM pictures of the structures grown during 5 cycles and etched for different time in cryo-DRIE: 1 s (a, b), 2 s (c, d), 5 s (e).

density of small "nanoislands", of the order of 20 nm in size. These islands were underetched in the DRIE process, even though it was very short. The extremely short DRIE etching time is necessitated by the possible side underetch of nanometer-size structures of the ALD layer. Most likely, for 2 cycles of the ALD process even a 1 second etching time is too long, but this is already the limit for our ICP- RIE system. Of course, it is difficult to suppose that the plasma etching process can be already well established during such a short time. Therefore, both silicon etch rate and anisotropy, and also the mask etch rate can differ from the average values obtained for well established process. This was proved later by evaluating and comparing the etch depths in silicon.

The second tested structure was a layer grown during 5 cycles of ALD and etched for 3 different times in DRIE. The typical SEM and AFM pictures of the structures, etched for 1, 2 or 5 seconds are shown in Fig. 2. The main difference from 2 cycles is that during 5 applied cycles, "large islands" were already formed, and the largest ones still remain in place after the DRIE step. Their shape and distribution is quite random, and the size ranges from 100 nm to a few micrometers. More small islands (about 100 nm in diameter) can be seen after the short

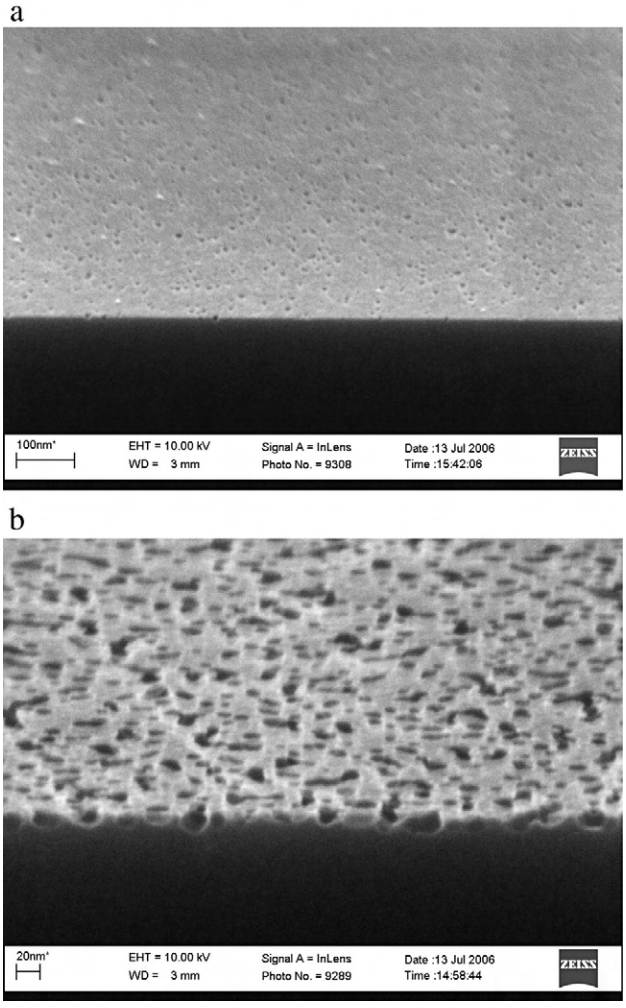

Fig. 3. SEM pictures of the structures grown during 8 cycles and etched for 1 s (a) and 2 s (b) in cryo-DRIE.

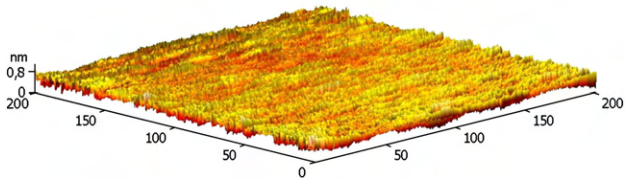

Fig. 4. AFM scan of the structure grown during 10 cycles and etched for 2 s in cryo-DRIE.

1 second etching (Fig. 2 a,b), but they are mostly underetched after 5 seconds step, leaving the largest (over micrometer size) in place (Fig. 2 c–e). Flat and smooth top and uniform height of the islands are additional proof that the aluminum oxide layer remains, resistant to the plasma etching. The sloping sidewalls of the structures (Fig. 2e) show that the anisotropic plasma etching process is not completely established during initial seconds. The etch depth in silicon obtained after different etching time can be evaluated both from SEM and AFM pictures: 20 nm (after 1 s), 70 nm (after 2 s), 160 nm (after 5 s). The etch rate is still not constant.

It could be quite logical that during the further increase of ALD cycle number the large islands will grow and join together, finally forming a continuous layer. Therefore, 8 and 10 cycles were tested next. In the case of 8 cycles of ALD growth, we obtained an almost continuous layer, with only minor nanoholes (Fig. 3). Depending on the DRIE etch step, those nanoholes can be more "developed": the largest are only about 5 nm in diameter after 1 s etching step (Fig. 3a), and they become larger and denser after 2 s etching (Fig. 3b). The AFM scan could not resolve the individual nanohole due to the size of the AFM needle: the needle tip radius was 10 nm. Therefore, special ultra-sharp AFM needle tip would be needed for this type of structures.

In the case of 10 ALD cycles, both SEM and AFM studies showed an extremely uniform surface, without any defects, even after 5 s etching. AFM picture is shown here (Fig. 4) SEM does not provide additional information of a continuous layer. The roughness fluctuations, evaluated from the AFM scan, are about±0.5 nm. This proves that a continuous layer is grown after 10 cycles of ALD process.

Even though aluminum oxide being one of the most thoroughly investigated ALD materials, there is still insufficient data about the initial phase of the layer growth during the incubation period. At the same time, the selection of the most reliable growth mode is important task at initial growth stage. Three classes of ALD growth mode can be considered: two-dimensional growth, random deposition, and island growth [2,3,16]. Our results of plasma defect etching obtained for the initial ALD cycles of aluminum oxide growth confirm the island formation on hydrogen- terminated silicon surface. It corresponds well enough with the results of Puurunen [5], where nano-islands have been identified by TEM measurements. Actually, they observed Al_2O_3 islands even after 15 cycles, but this discrepancy can be caused by different precursors and purge pulses used, which is quite important at initial phase. Also, Frank [17] showed that a "standard" incubation period of about 15 cycles can be shortened by

increasing the TMA pulses length. We can see sufficient agreement with results of Gusev [6], where 2.2 nm thick aluminum oxide layer was found to be uniform and without defects. It could correspond to 25–30 cycles, and from our results, already 10 cycles are enough to produce a continuous layer.

4.2. TMA + ozone process

Growth on HF-passivated silicon is nonlinear, exhibiting an incubation period due to inhomogeneous nucleation. A thin silicon oxide layer is produced, which is necessary for subsequent aluminum oxide growth. When ozone is used instead of water, the incubation period may be shorter, and it can be explained by higher activity of ozone when breaking Si–H bonds and forming interfacial SiO_2 [5,7,14]. In the case of ozone process, a 1.5 nm thick interfacial silicon dioxide layer has been reported [8], while for the water process only a 0.15 nm thick interfacial oxide layer was resolved using high resolution transmission electron microscopy [7].

We have applied our PDE technique for layers, grown during 2, 5 and 8 cycles of TMA + ozone pulses in ALD reactor. It must be mentioned, that there was no reason to include SEM and AFM pictures of etched structures, because no major difference was found with corresponding (different number of cycles) figures for the TMA + water process. In the case of 2 cycles, the same type of "wavy" structure was observed, as for 2 cycles of TMA + water (Fig. 1). It can be concluded, that the very initial cycles were consumed to form the interfacial silicon oxide, both for water and ozone process. When 5 cycles of TMA + ozone process were applied, the PDE step revealed almost continuous aluminum oxide layer containing separate holes, their size being dependent on the plasma etching time. The SEM and AFM pictures were identical to those obtained with 8 cycles of TMA + water process (Fig. 3). Furthermore, 8 cycles of TMA + ozone produced an already completed continuous layer, similar to 10 cycles of TMA + water (Fig. 4). Therefore, we assume that, in the case of water, layer nucleation is "delayed" by 2–3 cycles, compared to the ozone process. We see the difference in activity of water and ozone when forming interfacial oxide as the main explanation for this delay [7,14]. There is one major difference, comparing water and ozone processes: we have not observed large island formation for the latter one. The first assumption is that the islands could be formed during the 3–4 cycles, the second one is that maybe two-dimensional growth is the initial growth mode [2] in the case of ozone as a precursor. We can only conclude, that ozone helps to oxidize silicon surface, and the aluminum oxide layer starts to grow earlier, already during the initial cycles.

It is worth mentioning again that all the experiments were performed on hydrogen-terminated silicon substrates, in order to guarantee identical conditions for the ALD process initialization. Of course, processing of oxidized substrates would offer faster establishment of the growth rate per cycle, especially in the case of TMA + water process [8], because the incubation period, during which interfacial SiO_2 is formed, would be skipped.

As it was mentioned in the Introduction, the investigation of the layers thinner than 1 nm is quite a challenging task. For example, the scanning tunneling microscope (STM) can reach even atomic resolution, but from the obtained steps in the limited scanned area it is difficult to distinguish if the step is caused by few layers of aluminum oxide or just by the initial roughness of the silicon substrate. On the other hand, SIMS, for example, can reach extremely high sensitivity in recognition of every chemical element presented at the surface [9], but data interpretation is not so trivial, and the spatial resolution cannot reach tens of nanometers. One of the most clear direct methods is high resolution TEM, where also individual atomic planes can be recognized [6,7]. But this technique requires a delicate sample preparation step, sometimes even deposition of additional top layer, and cannot give a 2-dimensional picture. On the other hand, the new PDE technique, allows us to get a 2-dimensional picture of the structure that enables the shape and distribution of the grown islands to be determined. The main advantage of this method is the ultimate thickness of the investigated layers, and this is possible because we are not observing the layer itself, but looking for the etch pattern repeating the defects of the layer. This allowed us to start observations after just 2 ALD cycles, when best result with TEM was 15 cycles [5]. Actually, in [4] *in situ* infrared absorption measurements were performed on a pulse-by-pulse bases, and interfacial oxide formation and Al_2O_3 growth was studied from the spectra, but no visual picture or information about the growth mode could be extracted this way. Comparing our SEM and AFM, we found SEM to be more suitable for PDE examination because of larger possible test-area, direct visual information and faster operation. Of course, spatial resolution of AFM would be reasonable better, if special ultra-sharp probe with a tip curvature radius close to 1 nm could be used.

5. Conclusions

Ultra-thin layers of aluminum oxide (less than 1 nm) were grown by (ALD) technique on hydrogen-terminated silicon substrates. A new technique is proposed for studying the continuity of such a layer. Layers were examined by using them as a mask in silicon etching at cryogenic temperatures in DRIE reactor. The etch profile was characterized by scanning electron microscopy and atomic force microscopy. This technique can be described as "plasma defect etching" (PDE). PDE shows that in the case of water as an oxidation precursor, 5 ALD cycles form only separate islands of aluminum oxide. On the other hand, the use of ozone precursor helps to oxidize silicon surface and facilitates growth of a layer: 5 cycles produce a layer with minor pinholes few nanometers in diameter. After 10 ALD cycles (for water) or 8 ALD cycles (for ozone) the layer is already continuous, without microscopic defects or holes. The island growth model is therefore confirmed, at least for the TMA + water process. The plasma defect etching technique can give additional information about the uniformity or defectivity of ultra-thin ALD layers, especially during the initial, "incubation period", where other measurement techniques are not applicable because of low resolution or complicated data interpretation.

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