Investigation of oxide thin films deposited by atomic layer deposition as dopant source for ultra-shallow doping of silicon

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ABSTRACT

Atomic layer deposition of solid dopant sources for silicon was carried out by using triethylantimony and ozone, and tris-(dimethylamido)borane and ozone as precursors for antimony or boron containing oxides, respectively. It was proved that homogenous antimony oxide deposition could be achieved on flat silicon wafers and in trench structures. Little growth was found below 100 °C deposition temperature and linear temperature dependence on the growth rate between 100 and 250 °C. The oxide films were not stable above 750 °C and therefore failed to act as dopant source for silicon so far. Boron containing films were only obtained at a deposition temperature of 50 °C. These films were highly instable after exposure to air but degradation could be delayed by thin films of antimony oxide or aluminium oxide that were in situ grown by ALD as well. Only little boron was found by ex-situ chemical analysis. However, rapid thermal annealing of such boron containing dopant source layers resulted in high concentrations of active boron close to the silicon surface. The dependence of the doping results on the thickness of the initial boron containing films could be shown.

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1. Introduction

The advanced silicon semiconductor technology requires doping methods for production of ultra-shallow junctions with sufficiently low sheet resistance. Very high concentrations of active dopants need to be introduced close to the semiconductor surface. Furthermore, advanced three-dimensional topologies may require controlled local doping that cannot be achieved by ion-implantation. Alternatives like plasma doping [1] were investigated in order to overcome limitations of conventional implantation. However, problematic damage-related phenomena as transient enhanced diffusion during dopant activation cannot be fully avoided. A different approach is the radiation-free deposition of a dopant source onto the silicon surface. Recently, chemical vapor deposition of pure boron layers from decomposition of diborane was demonstrated to result in very shallow p$^+$ doping of silicon [2]. Here, we present the application of the atomic layer deposition method for pre-deposition of dopant sources on silicon. Antimony oxide and boron oxide were investigated as materials for such application. The ALD technique is widely known to have benefits of high surface coverage, precise control of deposition and material properties. In principle, it allows to obtain highly reproducible films with low impurity levels [3]. It is compatible with silicon micro-fabrication technology where it has been accepted as one of the standard techniques for thin film production in the recent years. However, the ALD of antimony oxide [4,5] and boron oxide [6,7] is poorly investigated. Viirola and Niinistö [4] have described ALD processes involving antimony oxide deposition as dopant for tin dioxide films using $SnCl_4$, $SbCl_5$ and H_2O at 500 °C. Furthermore, tris(dimethylamido)antimony and ozone were used as precursors for the deposition of Sb_2O_5 [5]. At 120 °C a relatively high growth per cycle (gpc) of approximately 0.185 nm was found that only moderately varied in a temperature range between 120 and 270 °C. Boron oxide was deposited at room temperature by ALD by using boron bromide and water as precursors [7]. Halides are however quite difficult to handle and produce problematic corrosive by-products. So, we aimed to investigate the use of halogen-free precursors for the deposition processes.

2. Experimental

The experiments were carried out in a single wafer ALD reactor that was developed and build in our group. Typical process pressures were lower than 1 mbar. The reactor is a cold-wall system but is equipped with a special designed "inner chamber" that is heated by the susceptor plate. The antimony and boron precursors were triethylantimony ($SbEt_3$) and tris(dimethylamido)borane ($B(NMe_2)_3$), respectively. Dosing was achieved by "vapor-draw" into a nitrogen carrier flow by fast acting valves. The deposition cy-

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cles consisted of several sub-steps that could be individually defined (initial/pulse/exposure/purge). Typical durations of these steps were (in seconds) 1/0.015/3/8 for $SbEt_3$, 1/0.05/5/8 for $B(NMe_2)_3$, and 1/3/1/13 for O_3. The doping was carried out in a low-pressure single wafer RTP cluster module. Temperature measurement was carried out by a thermo-couple (TC) integrated in one of the wafer support pins close to the wafer edge. Thus, precise temperature determination of the central part of the wafer could not be obtained. However, the RTP system allowed very reproducible processing and more accurate absolute temperature measurement appeared to be nonessential at this stage of the experiments. A temperature correction was carried out by evaluating the lamp power during processing of a test wafer with an integrated thermocouple. The oxide thickness was measured by spectroscopic ellipsometry by using a wavelength range from 320 to 800 nm. Chemical analysis was carried out by X-ray photoelectron spectroscopy (XPS). The binding energy (BE) referencing of the spectra was done with respect to the C1s peak at 284.8 eV from adventitious carbon contamination of the as-received state of the sample. The sheet resistance measurements were carried out by an ordinary four-point probe (FPP) set-up. Negative-ion time-of-flight secondary ion mass spectrometry (ToF-SIMS) was performed with Bi^+ analysis source and Cs^+ erosion source.

3. Results and discussion

3.1. Antimony oxide

Very homogenous Sb_2O_5 deposition could be achieved on flat silicon wafers and in trench structures (Fig. 1). Little growth was obtained below 100 °C deposition temperature. Linear temperature dependence on the growth rate was found between 100 and 250 °C. At 250 °C a growth per cycle of 0.75 Å was achieved. Thickness maps of 69 data points measured by ellipsometry were obtained from flat silicon wafers of 150 mm diameter to analyze the deposition homogeneity. High/low variation of the thickness values of only 0.6% was obtained after 100 cycles at 250 °C deposition temperature.

High-resolution transmission electron microscope measurements of as-deposited films showed the existence of a SiO_2 interface layer and crystalline grains within the antimony oxide. The films were stable during storage in air. The thermal stability of antimony oxide layers was investigated by rapid thermal annealing experiments. The layers were not stable above 750 °C (Fig. 2). This thermal instability was assumed to be the reason that this material failed to act as dopant source for shallow antimony
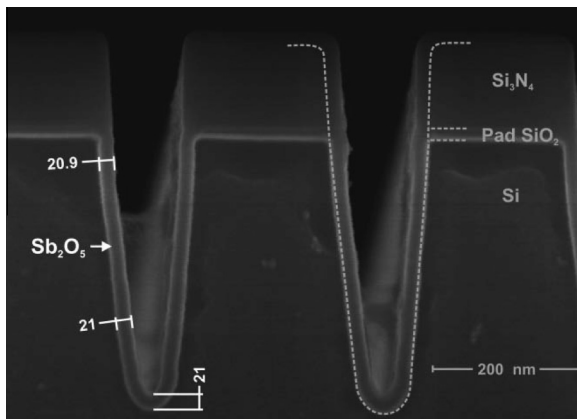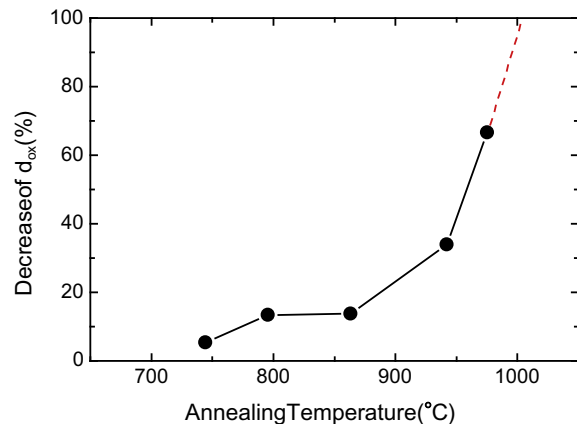

Fig. 2. Decrease in layer thickness of Sb_2O_5 after RTA processes for 5 s in 5 mbar O_2. (The initial Sb_2O_5 layer thickness was each time about 20 nm).

doping of silicon so far. TOF-SIMS measurements showed that after RTA treatment only traces of antimony were present close to the surface.

3.2. Boron oxide

In contrast, the deposition of pure B_2O_3 films was difficult. Preliminary results gave indication of little or no growth at higher temperatures so most of the experiments were carried out at 50 °C deposition temperature. ALD at room temperature gave similar results but 50 °C was chosen to obtain the same stabilized deposition temperature for all the experiments. The ex-situ analysis of the deposition results was complicated by severe instability of the grown film in air. Almost constant rate of decrease of film thickness was observed by time-dependent ellipsometric measurements after contact of the as-grown films to air (see Fig. 3, lower curve). This film instability was most likely dominated by the air humidity as already discussed in [7]. From the decay rate the film thickness before air contact was extracted. Constant growth per cycle of 0.3 Å was obtained at 50 °C deposition temperature.

The boron containing films could be stabilized by thin Sb_2O_5 or Al_2O_3 films that were in situ grown by ALD. Especially, low temperature ALD of Al_2O_3 at 50 °C from trimethylaluminium (TMA) and ozone was investigated in detail with respect of its protective effect on the boron oxide. A gpc of 1 Å Al_2O_3 was obtained at 50 °C on the silicon surface. Interestingly, it was observed that already
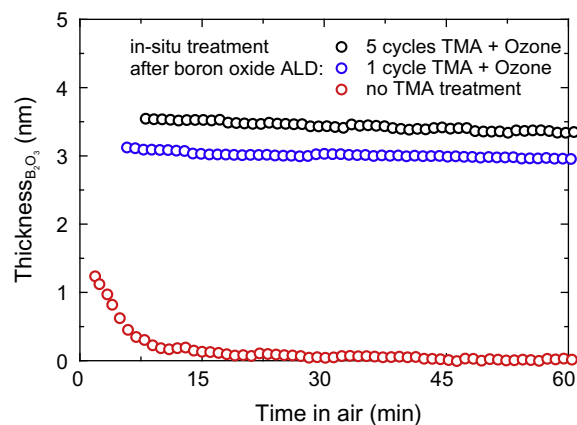

Fig. 1. Trench test structure with Sb_2O_5 sidewall deposition by ALD with $SbEt_3$ and O_3.

Fig. 3. Results of time-dependent measurements of film thickness in air: ALD of boron oxide at 50 °C (50 cycles of $B(NMe_2)_3$ and ozone) followed by different in situ ALD cycles of TMA and ozone.

one ALD cycle of TMA and O_3 after the boron oxide deposition resulted in significant increase in stability of these films in air (Fig. 3).

After storage of about 50 days, the films of Fig. 3 were analyzed by XPS (Fig. 4). The remaining film thickness of the stabilized layers was about three-fourth of the initial thickness. No boron and no aluminium were detected within the detection limits of the XPS system on the sample without post TMA treatment as it was expected. Interestingly, only very little boron was found in the stabilized films, they were mainly composed of aluminium oxide. However, the growth of such relatively thick films cannot have been resulted from normal Al_2O_3 ALD, with expected thicknesses of only 0.1 and 0.5 nm by applying one and five cycles, respectively. One conclusion could be that the boron oxide ALD is inhibited by competing deposition of reaction products on the surface at the low deposition temperature. When the Al_2O_3 deposition begins thereafter, the entire film present after the initial deposition sequence can readily react with the TMA precursor already during its first pulse. Hence, the boron oxide growth rate itself would be lower than the above obtained value of 0.3 Å per cycle. Presently, improved process parameters mainly with respect to the purge conditions will be tested in order to obtain boron oxide of higher quality.

On the other hand, ultra-shallow boron doping of silicon from the ALD grown boron containing films was successful. Rapid thermal annealing resulted in high concentration of active boron close to the silicon surface (see Fig. 5 with respective sheet resistance values).

Influence of oxidation enhanced diffusion seemed to have been occurred, which can be evaluated by comparing the results of annealing in O_2 and N_2 atmosphere. An important conclusion could be made after analysis of the doping results of the sample with stabilization by Sb_2O_5. It got the highest amount of boron after doping but more important is the observation that only traces of antimony could be found on the sample after such RTA treatment. The antimony did not seem to have noticeably contaminated the silicon material. Analysis of the SIMS surface profiling suggested that little remaining Sb is mostly located near the surface or on surface sites. Antimony is a very slow diffusor in silicon and is regarded as compatible to CMOS fabrication technology.

Furthermore, the dependence of the doping results on the thickness of the initial boron containing films could be shown. Different sets with different number of ALD cycles were prepared and received identical annealing treatments. Here, fairly slow RTA was carried out: 10 K/s ramp rate and 5 s soak in 5 mbar oxygen at ap-
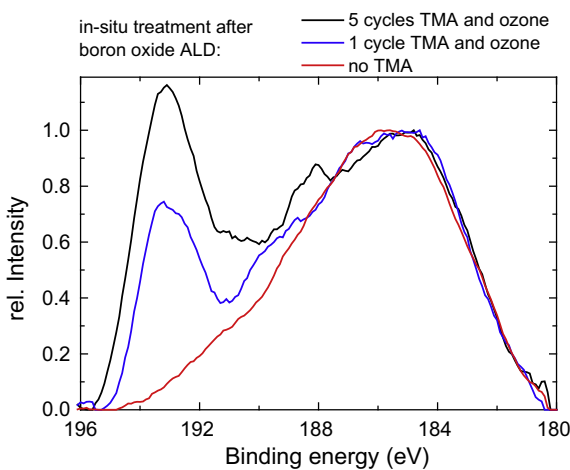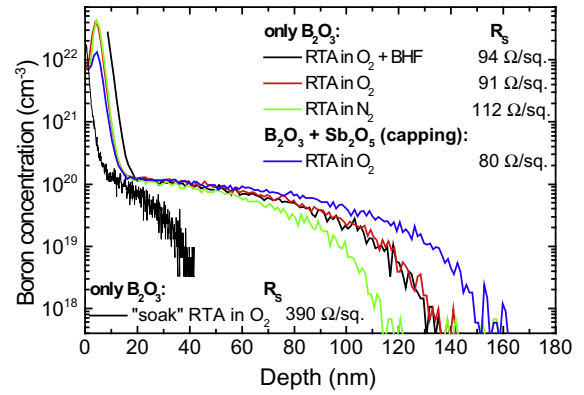

Fig. 5. Results of ToF-SIMS measurements on Si samples doped by different RTA treatments of ALD B_2O_3 surface sources.
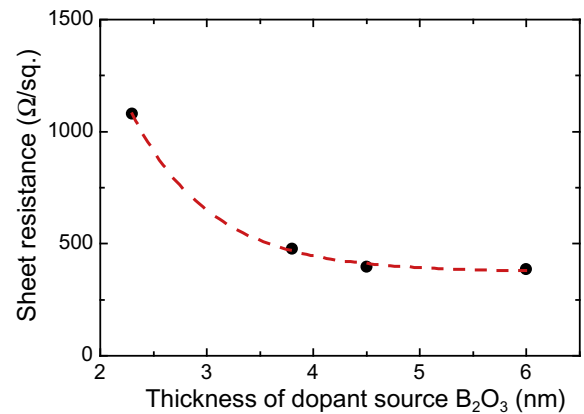
Fig. 6. Sheet resistance of silicon samples after identical RTA processes. The samples had different B_2O_3 layer thicknesses prior the RTA.

prox. 950 °C. The results of sheet resistance measurements of different samples after this procedure are shown in Fig. 6. Here, one important conclusion can be made regarding the control of the doping process using the atomic layer deposited dopant source. For thinner layers, the doping result depended on the thickness of the source layer while for thicker layers the extent of doping seemed to saturate for the chosen RTA process. Most likely, it could be further varied by changing the RTA conditions. Hence, by growing thin layers very precisely with the ALD method one should be able to control the dose of the dopants. One seems to be able to completely diffuse the dopants into the silicon in the case of carefully tuned layers with respect to the thermal budget of the annealing process. In our case, very thin layers close to 2 nm thickness resulted in fairly high sheet resistance (approximately 4 kΩ/sq., not shown in the figure) while no measurable sheet resistance was found for layers that only had the remaining layer thickness after their volatilization in air.

4. Conclusions

It could be shown that antimony oxide thin films can be grown by the atomic layer deposition method using the precursors $SbEt_3$ and O_3. It was proved that very good homogeneity of film thickness can be achieved even for the thinnest layers and that conformal growth in trenches can be carried using the presented ALD process. According to rapid thermal annealing experiments, Sb_2O_5 evaporation occurred at temperatures above 700 °C. Therefore, no efficient

Fig. 4. Results of XPS measurements of the films of Fig. 3, the smoothed data of the region of the B1s peak are shown, normalized to the energy loss peak at 184.7 eV caused by excitation of plasmons by Si 2s photoelectrons.

doping process for Sb doping of silicon from pure ALD Sb_2O_5 surface source was possible so far. Boron containing layers deposited by ALD from tris(dimethylamido)borane and ozone have been successfully used as dopant source for boron doping of silicon by RTA. The availability of an ALD process offers the possibility of very precise and controllable dopant pre-deposition on highly structured surfaces. Deep trenches, nano-rods or fin-shaped features become more and more important in advanced silicon technology. Controlled doping on such structures by ion-implantation faces severe limitations mainly due to shadowing effects of the highly directed beams or damage of the substrate materials. The pre-deposition by ALD does not damage the substrate and hence phenomena like transient boron enhanced diffusion due to damage-related interstitial super-saturation cannot occur.

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