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Application of atomic layer deposited dopant sources for ultra-shallow doping of silicon

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The advanced silicon semiconductor technology requires doping methods for production of ultra-shallow junctions with sufficiently low sheet resistance. Furthermore, advanced 3-dimensional topologies may require controlled local doping that cannot be achieved by ion-implantation. Here, the application of the atomic layer deposition (ALD) method for pre-deposition of dopant sources is presented. Antimony oxide and boron oxide were investigated for such application. Ozone-based ALD was carried out on silicon wafers by using triethyl-antimony or tris-(dimethylamido)borane. Very homogeneous Sb_2O_5 deposition could be achieved on flat silicon wafers and in trench structures. The thermal stability of antimony oxide layers was investigated by rapid thermal annealing experiments. The layers were not stable above 750 °C. Therefore, this material failed to act as dopant source so far.

In contrast, ultra-shallow boron doping of silicon from ALD grown boron oxide films was successful. However, pure B_2O_3 films were highly unstable after exposure to ambient air. The boron oxide films could be protected by thin Sb_2O_5 or Al_2O_3 films that were in-situ grown by ALD. 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 boron oxide. Interestingly, it was observed that already one ALD cycle of TMA and O_3 resulted in significant increase in stability of the boron oxide in air.

1 Introduction In order to continue moore's scaling, there is need for new enabling semiconductor fabrication technology. As device dimensions get smaller, doping methods for production of ultra-shallow pn junctions with sufficiently low resistance becomes necessary. Ultra shallow junctions can be fabricated by introducing high concentration of dopant impurities close to the semiconductor surface before drive in by rapid thermal annealing (RTA). Moreover, fabrication of 3-dimensional integrated circuits may also require controlled local doping which cannot be achieved by ion-implantation. Plasma doping were investigated to overcome the limitation by conventional ion implantation [1,2]. But, crystal damage and also transient enhance diffusion during dopant activation cannot be totally avoided. An alternative approach is to avoid plasma or ion radiation. Sarubbi et al. investigated the application of chemical vapour deposited boron from decomposition of diborane, which resulted to very shallow p^+ silicon doping [3]. Here, we report the application of atomic layer predeposited dopant sources of boron and antimony, followed by drive in by RTA, to achieve ultra shallow silicon doping. Atomic layer deposition (ALD) is a variation of chemical vapour deposition (CVD) by dosing the precursors in vapour or gas phase, one at a time. After the first dosing step, there is efficient purge of reaction products and remaining unreacted precursor

before dosing the next precursor. In principle, the surface reaction stops once there are no active reaction sites on the surface and this gives highly conformal growth. Antimony oxide [4,5] and boron oxide [6,7] atomic layer deposition have been reported. The earlier work on boron oxide ALD [7] used boron bromide and water as precursor which can give a corrosive product. In this work, boron oxide were deposited from tris(dimethylamido)borane-ozone, and antimony oxide from triethylantimony-ozone. Both dopant sources were investigated for doping experiment.

2 Experimental The experiments were carried out in a single ALD reactor which was developed in our group. The reactor is a cold-wall system but is equipped with a special designed "inner chamber" that is heated by the susceptor plate [8]. Doping was carried out in a single wafer RTP (rapid thermal process) module. Temperature measurement was carried out by a thermocouple (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. A temperature correction was carried out by evaluating the lamp power during processing of a test wafer with an integrated thermocouple. Oxide thickness was measured by ellipsometric measurements in the wavelength range from 320 nm to 800 nm. Chemical analysis was done by X-ray photoelectron spectroscopy (XPS) measurement. Sheet resistance was measured by ordinary four point probe (FPP) set up. And, the doping profile was measured by negative-ion time of flight secondary ion mass spectrometry (ToF-SIMS) with Bi^+ analysis source and Cs^+ erosion source.

3 Results and discussion

3.1 Antimony oxide Stable and very homogenous antimony oxide Sb_2O_5 films were grown on flat silicon substrate and on trench structures. Antimony oxide ALD growth per cycle was found to increase approximately linearly with temperature between 100 °C and 250 °C. Below 100 °C, the growth per cycle was negligible and it was 0.75 Å at 250 °C [8].

Investigation of thermal stability of antimony oxide was carried out by RTP of about 20 nm thick oxide layers. The samples were heated by equal ramp rates of about 10 K/s in 5 mbar oxygen up to different temperatures that were held for 5 s. It can be seen from Fig. 1 that significant film degradation started at about 750 °C. Such and similar annealing processes with faster ramp rates, higher temperatures, and different annealing atmospheres (N_2 or no additional gas) resulted in no significant antimony doping of silicon as confirmed by SIMS and sheet resistance measurements. The doping failed most likely due to the instability of the antimony oxide at the temperatures needed for diffusion. However, further experiments applying capping layers on top of the antimony oxide, using even higher oxygen partial pressures, or carrying out flash anneal processes might lead to better doping results.
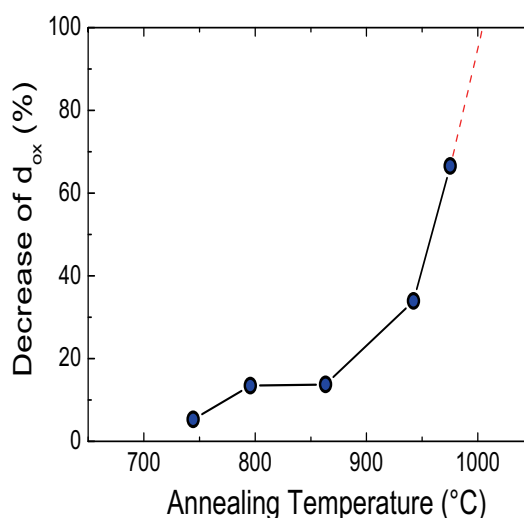
Figure 1 Decrease in layer thickness of Sb_2O_5 after RTA processes for 5 s in 5 mbar O_2 (The initial Sb_2O_5 layer thickness was each time about 20 nm.) [8].

3.2 Boron oxide On the other hand, boron oxide deposition was challenging. There was no growth at higher temperatures by using tris(dimethylamido)borane (TDMAB) and ozone. We could observe growth from room temperature to 100 °C. A growth per cycle of 0.3 Å was obtained at 50 °C, which decreased with temperature.
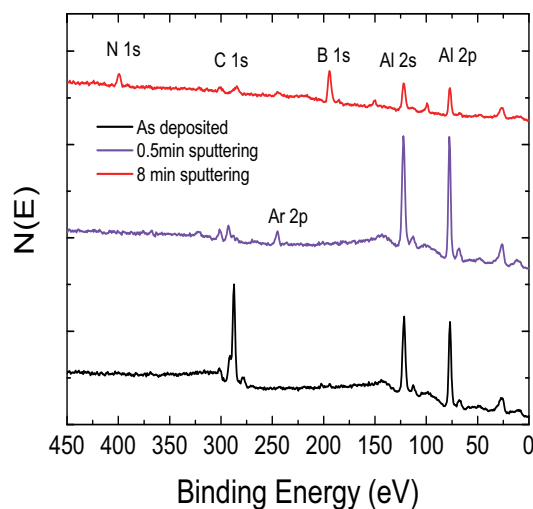
It was proved that reactive ozone was needed for the layer growth. No growth was obtained by using oxygen or TDMAB alone as shown in Fig. 2. Here, time dependent ellipsometric measurements were carried out in air after the depositions and fitting was done by assuming only one single layer since it was not possible to unambiguously distinguish between the layer and a SiO_2 interface by a fitting procedure with a two-layer model. No film was measured if the ozone generator was on standby or switched off during the depositions. Hence, the precursor does not react with oxygen since there was supply of oxygen even while the ozone generator was switched off. Also by dosing only the boron precursor, there was no layer build up, so the growth did not occur by simple condensation. One can also see from Fig. 2 that the as-deposited film is unstable in air. The instability is most likely due to humidity as already discussed in [7]. We could observe almost a linear decrease within the first few minutes after contact to clean room air until a stable remaining coverage is left. Boron oxide films can be stabilized by capping it with Al_2O_3 or Sb_2O_5 layer. Boron oxide is stable under vacuum, and the goal will be just to protect it from escaping before RTA. Antimony oxide can in-situ be grown by the above presented ALD process. The advantage is that this film is stable in

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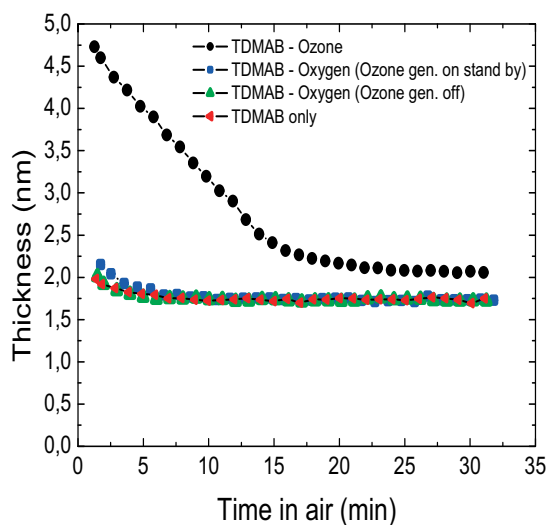
Figure 2 Investigation of film thickness and film stability in air using tris(dimethylamido)borane and ozone

Figure 3 XPS measurement of 30 nm boron oxide capped with 10 nm aluminium oxide

air but volatile and hence "self-destructive" at the boron diffusion temperatures, as shown before. Unfortunately, it can hardly be grown at the low temperatures needed for the boron oxide deposition. In order not to change the deposition temperature for the capping layer, the growth of Al_2O_3 from trimethylaluminium and ozone at low temperatures was investigated in detail. At 50 °C deposition temperature, growth per cycle of 1 Å was obtained with optimum uniformity. These films were later used as capping layers for the protection of boron oxide. The disadvantage here is that during high-temperature anneal also aluminium, which has higher diffusivity than boron, diffuses deep into the silicon and the remaining Al_2O_3 layer is very difficult to remove after the annealing. Hence, this type of capping might not be useful for standard doping applications but is used here for further analyzing the as-deposited boron oxide films.

Thick boron oxide layer of about 30 nm was grown at 50 °C with 1200 cycles of TDMAB and ozone, and capped with 10 nm Al_2O_3 layer. By fitting the whole layer in ellipsometric measurement, the total thickness increases slightly with time in air. One reason for this could be that humid air diffused through the capping, and the underneath boron oxide layer expanded, thereby increasing the thickness. On the other hand, the thickness of freshly grown pure aluminium oxide layer also increases with time in air, most likely due to coverage by adsorbate. The depth profile of this sample was analysed by XPS measurement. This was done by taking the XPS measurement, and then gentle sputtering each time before taking the next XPS measurement, until the silicon peak is detected.
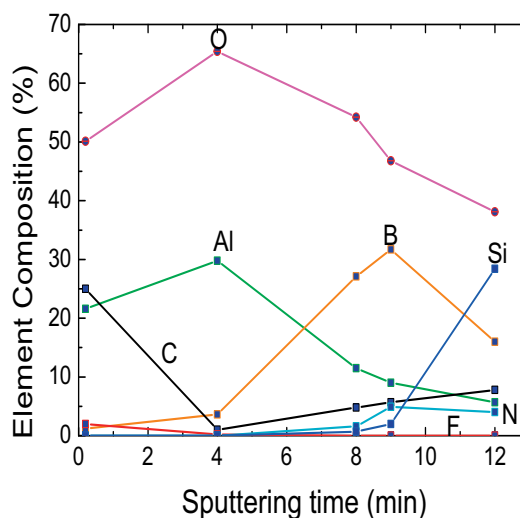

Figure 4 Element composition with the sputtering time for sample of Fig. 3.

We could detect surface contamination from adventitious carbon in the as-deposited state and this was almost totally removed after 0.5 min sputtering (Fig. 3 and 4). Again, after 0.2 min, 4 min, 8 min, 9 min and 12 min sputtering, aluminium content (%) decreases gradually while boron content (%) increases, which means aluminium ox-

ide actually formed a capping and not just mixing of the oxides (Fig. 4). In addition, carbon and nitrogen peak also increase slightly with a final height of 4% for nitrogen and 7.8% for carbon. This means, there were still carbon and nitrogen ligands in the film. This is an indication that the carbon and nitrogen ligands could not be totally removed during boron oxide deposition at the low temperature. We believe that, increasing the deposition temperature up to the limit at which we can still have boron oxide deposition will enhance ligand removal.
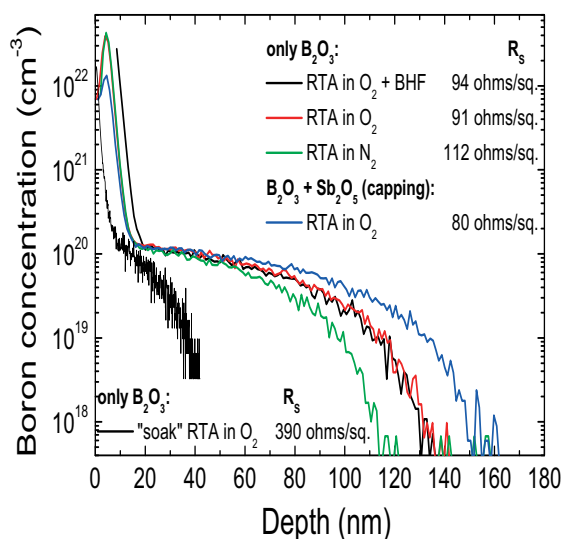
Figure 5 Results of ToF-SIMS measurements on Si samples doped by different RTA treatments of ALD B_2O_3 surface sources. RTA: $T_{max} \approx 1050\ ^{\circ}$C for 0.1 s, ramp rate 60 K/s, "soak" RTA: $T_{max} \approx 950\ ^{\circ}$C for 5 s, ramp rate 10 K/s

Furthermore, doping experiments with ALD grown B_2O_3 dopant source were successful (Fig. 5). After rapid thermal annealing, SIMS profiles show high concentration of dopant found close to the silicon surface. One sample was etched in buffered hydrofluoric acid after the annealing and before the SIMS measurement. (This profile was shifted in the figure to match the un-etched sample.) Also from Fig. 5, we could observe influence of different annealing environment. With same annealing temperature, boron could diffuse deeper with RTP in oxygen than in nitrogen. Also, the sample that was capped with Sb_2O_5 had the highest doping result, since Sb_2O_5 protect the underneath B_2O_3 layer. The capping here was proved to be "self-destructive" during this annealing step since only traces of antimony were detected by the SIMS measurements.

Dependence of the B_2O_3 thickness with the sheet resistance (doping) was also determined (Fig. 6). Different thickness of ALD grown B_2O_3 samples were prepared and
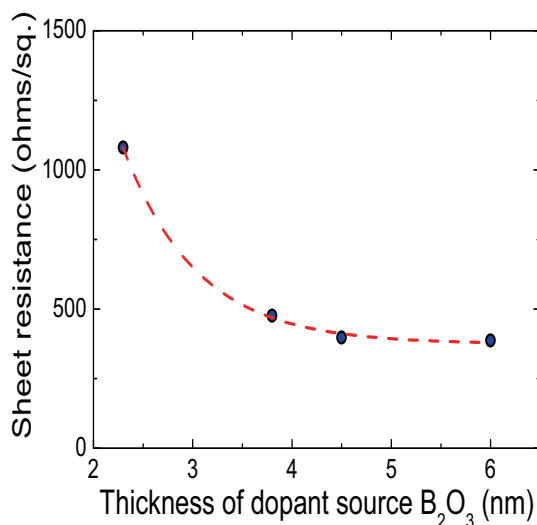
Figure 6 Sheet resistance of silicon samples after identical RTA processes. The samples had different B_2O_3 layer thicknesses prior the RTA.

all samples annealed under same condition, 10 K/s ramp rate, 5 s soak in 5mbar oxygen at approximately 950 $^{\circ}$C. The transfer in air of the non-capped samples after thickness measurement was carried out by tight time-coupling of less than a minute. We could see that the sheet resistance decreases with increasing B_2O_3 thickness, up to saturation. This means, we can control the sheet resistance with B_2O_3 thickness for sufficiently thin B_2O_3 layers.

4 Conclusion Atomic layer deposition (ALD) can be used for fabrication of dopant source for ultra shallow silicon doping. B_2O_3 dopant source was grown by ALD from tris-(dimethylamido)borane-ozone and successfully applied for ultra shallow p^+ doping. Boron oxide did not grow from tris-(dimethylamido)borane and oxygen. In addition, boron oxide process from tris-(dimethylamido)borane and ozone is not totally efficient at this 50 $^{\circ}$C temperatute because there were unremoved boron precursor carbon and nitrogen ligands in the film. Increasing the temperature up to the limit could give purer boron oxide film but even lower growth per cycle. Sb_2O_5 was grown by ALD from triethylantimony and ozone but was not stable beyond 750 $^{\circ}$C. Sb_2O_5 was not successfully used for doping. Controlled doping with thickness of dopant source is possible and this can be useful in doping some more complicated structured such as deep trenches, nano rods and fin shaped structures. Pre deposition by ALD offer a solution to damage related problem and transient enhanced diffusion caused by ion radiation doping.

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