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The effects of trichloroethane HCl and ion-implantation on the oxidation rate of silicon

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The thermal oxidation of silicon was studied using a large-scale industrial oxidation system. The characteristics of the oxides resulting from pure hydrogen/oxygen (H_2/O_2), trichloroethane/oxygen (TCA/O_2) and hydrogen chloride/oxygen (HCl/O_2) mixtures are compared. Both HCl and TCA addition to oxygen produced an enhanced oxidation rate. The oxidation rate for TCA/O_2 was approximately 30–40% higher than for HCl/O_2 mixtures. A molar ratio of TCA/O_2 of 1% gives an optimum process for very-large-scale industrial (VLSI) applications. However, 3% HCl/O_2 gives comparable results to 1% TCA. In addition, boron and phosphorus implantation are observed to increase the oxidation rate. Phosphorus doping of the silicon yields a higher rate than boron-doped wafers. This behaviour is explained in terms of surface damage and chemistry. It appears that the overall mechanisms governing all these processes are similar.

1. Introduction

The thermal oxidation of silicon wafers is an essential process in the fabrication of many modern electronic circuits [1]. Silicon-dioxide layers have many useful properties and are employed for a number of different functions [2]. For most applications, it is necessary to obtain high-quality silicon dioxide with a low defect density. Therefore, thermal oxidation of silicon is preferred over other methods of forming silicon dioxide [3]. The thermal oxidation process is generally carried out in several different ways, as described previously [4].

When a small quantity of HCl is added during the oxidation of silicon [4, 5–10], major process benefits can be achieved due to the following effects: a reduction in the defect density, the stacking faults, the mobile ion charges, the interface state and the surface-charge densities; improvements in dielectric breakdown characteristics; and an increase in minority-carrier lifetimes. However, the major drawback with HCl is it has a highly corrosive nature. Trichloroethane (TCA) is an attractive alternative to HCl and merits further investigation [11–13].

It has been shown that the surface characteristics can have a significant effect on various growth processes [14, 15]. The surface can have both catalytic or inhibitory effects on the rate of growth. Ion implantation is a versatile process which can be used to create a wide range of surface compositions and structures, thus modifying the resulting process behaviour [16]. More specifically, this can have a profound effect on the oxidation process of interest and it was thus investigated using both boron and phosphorus species.

In this paper, the results of an investigation into the oxidation of silicon using H_2/O_2, HCl/O_2 and TCA/O_2 mixtures are reported. In addition, the effects on the oxidation behaviour of boron and phosphorus implantation into the silicon substrates were investigated and compared.

2. Experimental procedure

In these experiments, chemically and mechanically polished silicon wafers in the form of circular slices 10 cm in diameter with $\langle 1\,1\,1 \rangle$-surface orientation were used. Prior to the oxidation, the test wafers underwent a standard semiconductor wafer cleaning process according to the following schedule. The wafers, obtained from a clean box of new wafers, which were going to be used for devices, were further cleaned in 2:1 H_2SO_4/H_2O_2 for 15 min. This was followed by a rinse in deionised water for 5 min and a 1:10 $HF–H_2O$ dip for 10 s to remove the oxide layer formed during the previous cleaning steps. After another deionized water clean, the wafers were dried in a N_2 atmosphere using a spin dryer for 5 min. For some of the experiments, the standard RCA Ltd. clean was employed [17, 18]. Similar cleaning processes were employed for the other steps in the fabrication sequence such as low pressure chemical vapour deposition (LPCVD) of polysilicon and phosphorus doping from $POCl_3$.

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The cleaned wafers were then loaded into a specially constructed fused silica boat which was pushed into the heated furnace. Test wafers were placed into predetermined slot positions with dummy wafers in the other slot positions, to simulate actual production runs. The wafers were slowly heated to the required temperature and controlled to within ± 1 °C using a Thermco three-zone temperature-control system. A flat temperature profile was maintained for these investigations unless stated otherwise. The process gases, H_2, N_2, O_2, HCl and TCA, were introduced and precisely controlled using high-precision mass-flow controllers. The TCA was held in a temperature-controlled bubbler system. The wafers were introduced slowly, in an O_2 atmosphere, into the reactor using a soft-contact loader to minimize contact with the tube and thus reduce particulate levels, which result from the sliding action of the boat in the furnace tube, and can have a detrimental effect on device performance and yields. A two-stage loading sequence was used to minimize thermal stresses. The wafers were introduced into the furnace at a lower temperature, which was then gradually ramped to the desired processing temperature. This gradual ramp was a second way of minimizing the thermal stresses. The wafers were pushed in at 800 °C and then ramped up to 1000 °C followed by a 1100 °C anneal in N_2. Prior to unloading the wafers, the furnace was ramped down to 800 °C in N_2. The wafers were pushed in an atmosphere of O_2 to prevent pitting. This resulted in the growth of approximately 20.0 nm of silicon dioxide. TCA was only introduced into the process when the furnace was at 1000 °C. The O_2 continued to flow even after TCA flow had been terminated. This step is effective in minimizing the interface state change density, Q_{ss}.

To minimize the contamination problem (which can arise in the oxidation of silicon from the quartz tube, the wafer boat and the associated quartzware used for wafer handling), the furnace containing all components except the test wafers was cleaned regularly using a 1% TCA/O_2 molar ratio for 4 h at 1100 °C. This process eliminated the majority of sodium and other metal contaminants from the quartzware and yielded a clean process adequate for the required device performances. The mobile charge density measured fell below the detection limit of approximately 2×10^9 cm^{-2}. This process was repeated after a specified number of runs which were dictated by practical experience. Non-destructive optical measurements of the film thicknesses were made using a Nanometrics Nanospec which gave thickness accuracies of approximately ± 2%.

A Lintott Series II ion-implanter, with a modified Freeman source was employed for this work; it has been described previously [19]. The dose and energy of both boron and phosphorus were altered to yield different concentrations and implant depths. In the present investigation, energy and dose combinations of 25 keV and 2×10^{15} for boron, and 80 keV and 5×10^{15} for phosphorus were employed, without heating the substrates. These arbitrary values of dose and energy were employed as the test wafers were placed in an industrial system during the production of electronic devices. The samples were subjected to various thermal cycles at different temperatures and times.

3. Results and discussion

The oxide-thickness variations with the TCA concentration were investigated as a function of the total oxidation time. The process temperature was held at 1000 °C and is shown in Fig. 1 along with the data obtained for H_2/O_2 and for TCA/O_2. The TCA/O_2 ratio was varied between 0 and 3%. For all the molar ratios considered, as expected, the oxide thickness increased linearly with time. Although, the addition of both TCA and HCl increased the oxidation rate, the fundamental oxidation process characteristics were not drastically altered. This is illustrated for both TCA/O_2 and HCl/O_2 molar ratios in Fig. 2. The oxidation rate increased rapidly for low percentages of TCA and then leveled off. For TCA a ratio of 1% gave nearly a maximum oxidation rate. However, for HCl/O_2 a higher ratio of 3% was required to observe a similar effect. The addition of TCA and HCl to oxygen enhanced the oxidation rate by approximately 30–40% compared to H_2/O_2. However, compared to pure O_2, the percentage increase with TCA and HCl was approximately 54%. This is slightly higher than previously observed in the literature [10]. This is again probably due to our experimental procedure for loading wafers in an O_2 atmosphere to eliminate charges and defects. In general, it is difficult to compare results obtained by various workers in the literature as each worker uses different experimental conditions, reactor dimensions and loading procedures. However, the previously reported results can be used to compare trends if not absolute values.

The addition of HCl or Cl_2 to oxygen has been suggested as a way of enhancing the oxidation rate due to their effect in weakening the Si–Si dangling bonds on the wafer surface [20]. A similar explanation is likely to be valid for the presence of TCA in the ambient oxygen. The TCA molecule decomposes readily at the high temperatures employed within the furnace to generate *in-situ* HCl molecules.

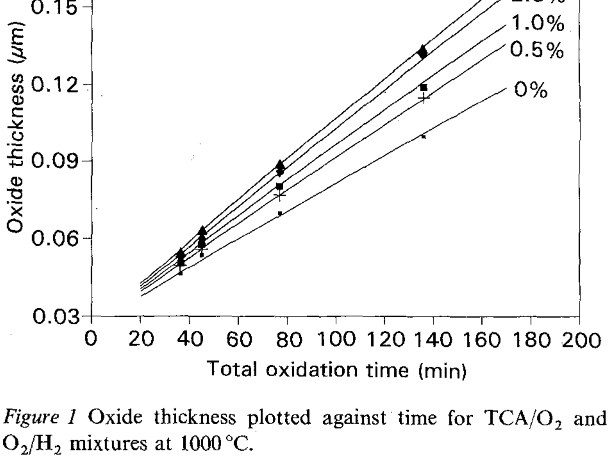

Figure 1 Oxide thickness plotted against time for TCA/O_2 and O_2/H_2 mixtures at 1000 °C.

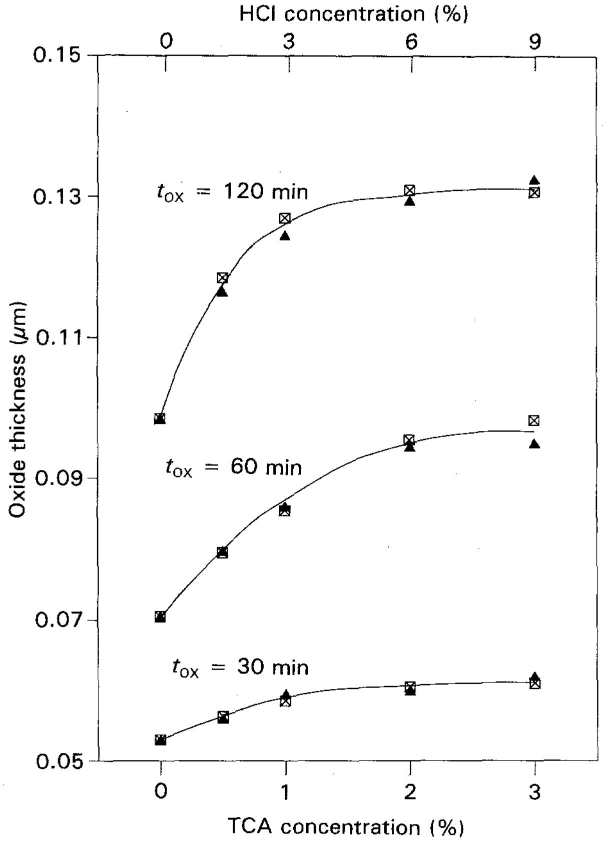

Figure 2 Oxide thickness plotted against various ratios of TCA/O_2 and HCl/O_2 mixtures, for different oxidation times at 1000 °C: (▲) TCA oxides, and □ HCl oxides.

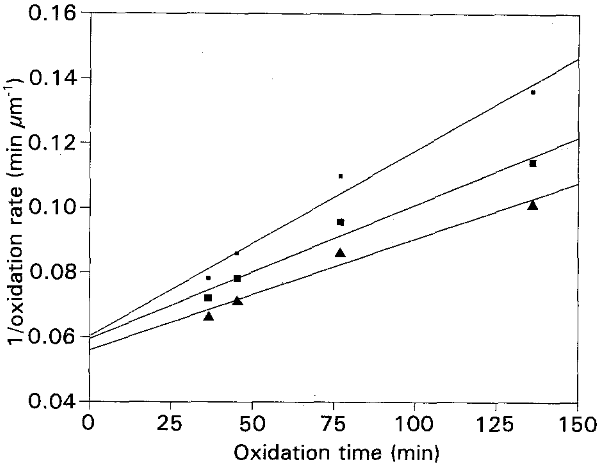

Figure 3 Oxidation time versus the reciprocal of the oxidation rate for TCA/O_2 mixtures at 1000 °C: (▪) H_2O_2, (■) 1% TCA/O_2, and (▲) 3% TCA/O_2.

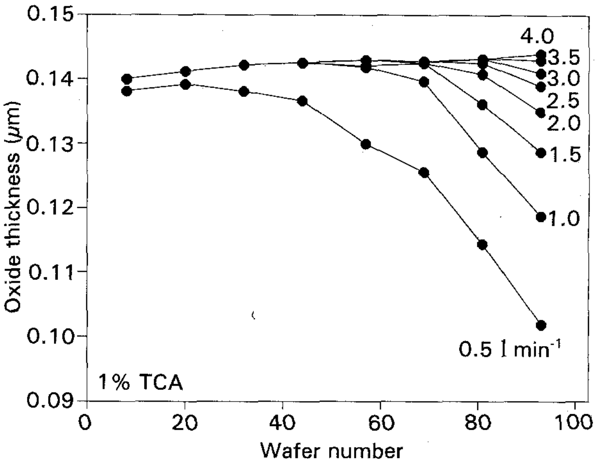

Figure 4 Oxide thickness versus wafer position for TCA/O_2 for different flow rates (L min^{-1}) at 1000 °C.

The experimental observation that the oxidation rate for TCA/O_2 is greater than for HCl/O_2 and the good correlation between the 1% TCA and 3% HCl oxidation rates suggests that the reaction proceeds by the decomposition of one molecule of TCA into three of HCl.

The effect of oxidation time on the oxidation rate is shown in Fig. 3. It appears that the inverse of the oxidation rate is linear. In addition, the extrapolation of the oxide thickness back to time zero gives a finite value. The Deal and Grove model [21] for the oxidation of silicon using pure O_2 may be used to explain the observed behaviour with TCA/O_2. The relatively large value of the oxide thickness [20] at time zero is perhaps largely due to loading the wafers into the furnace in an oxidizing atmosphere in order to reduce defects such as pitting. The trend in TCA/O_2 shown in Fig. 3 is similar to those obtained for pure O_2, H_2/O_2 and HCl/O_2 [8]. It is, therefore, reasonable to assume that the fundamental mechanism governing the oxidation process remains largely unaltered with the addition of HCl or TCA. The addition of either HCl or TCA has only a catalytic effect on the oxidation rate.

Fig. 4 shows the oxidation rates plotted as a function of wafer position in the furnace for various total flow rates for 1% TCA/O_2 and an oxidation temperature of 1000 °C. For a low flow rate of 0.5 L min^{-1}, a uniform profile is observed for only the first 40 wafers and the wafers near the end of the boat are approximately 40.0 nm thinner than the wafers at the start of the hot zone. The most likely explanation for this effect involves postulating the depletion of the reactive species involved in this process which, in this case, is oxygen. The impact of HCl and TCA is to interact with the surface to weaken the Si–Si bonds and thus to enhance the oxidation rate. This results in more severe depletion, due to a higher oxidation rate, as more oxygen is consumed near the inlet end of the furnace. The supply rate of oxygen remains unaltered as the flow rate and pressure conditions in the reactor have been kept constant. However, as the flow rate is increased, a more uniform distribution of reactants along the length of the wafer region is achieved. The concentration of oxygen is increased near the gas outlet end resulting in a more uniform concentration gradient. For example, a flow rate of 2.5 L min^{-1} or more, results in very little depletion of reactants, with wafers being uniform right along the hot zone to about ± 1%. Therefore, for a successful production process it is necessary to optimize the flow conditions to obtain maximum device yield per oxidation run. As expected, the flow rate also has a significant effect on the within-wafer uniformity of the oxide thickness. The effects of the flow rates and the wafer position on the within-wafer thickness uniformity were investigated and the results are presented in Fig. 5. It is evident that the wafers near the gas flow show good uniformity for both low and high flow rates. However, for low flow rates the uniformity degrades with wafer positions much closer to the gas inlet end of the furnace (that is, for lower wafer numbers) resulting in a lower number of wafers with acceptably good uniformity. This again corresponds to the onset of depletion of the oxidizing species, as less gas is available for reaction with the silicon. As the flow rates are increased, the onset of depletion occurs further away from the gas inlet and therefore more uniform wafers are obtained. Only the wafers furthest from the gas-inlet end displayed non-uniformity problems. These could easily be rectified with a further increase in the gas flow rate. The trends are similar in pure O_2, H_2/O_2 and HCl/O_2 mixtures.

Fig. 6 shows the effect of the furnace time on the oxide thickness for 80 keV and 5×10^{15} phosphorus ions per cm^2 of implanted samples at temperatures of 800, 900 and 950 °C. There is a linear relationship between the oxide thickness and time in all the cases considered. However, for higher temperatures, the larger value of the resultant oxide thickness is due to the higher oxidation rate. The oxidation rates are also higher for implanted samples than those for unimplanted silicon slices. This suggests that, as expected, the implantation process has altered the surface characteristics and these have a significant effect on the oxidation rate. It has been suggested that implantation creates surface damage such as dislocation loops [22]. These damaged regions can behave as active surface sites for the adsorption of oxygen. After the first few monolayers of coverage the active species interacts with the surface in the same way as an undoped surface. It is the initial interaction which produces the enhancing effect, which may continue, as this could have an effect on the subsequent surface morphology. In addition, the implantation process, by its very nature, breaks surface Si–Si bonds in the near-surface region, creating dangling bonds which can interact strongly with oxygen thus forming Si–O bonds more readily than in the unimplanted case.

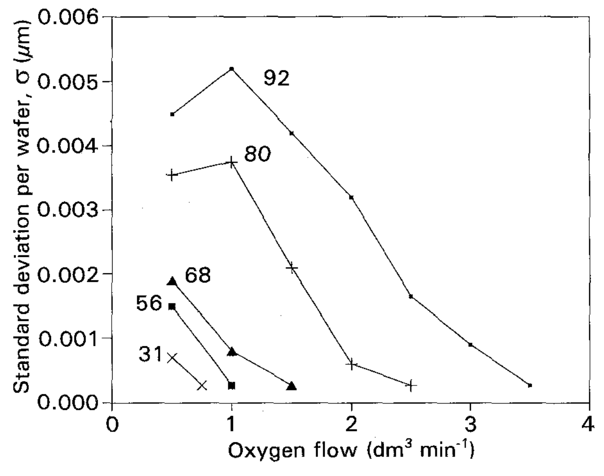

Figure 5 Standard deviation per wafer versus gas flow rates for wafers at various positions, for 1% TCA at 1000 °C.

Fig. 7 shows the oxide thickness plotted against time for 25 keV, 2×10^{15} boron ions per cm^2 of implanted silicon at 800, 850 and 900 °C. As with phosphorus, a linear relationship is observed, with the oxidation being higher than in the unimplanted silicon. A similar explanation is again valid for this case. However, phosphorus yields a higher oxidation rate than boron. There are several possible explanations for this. First the phosphorus dose and energy were higher than for boron. The dose is only slightly different, whereas the energy difference is much greater and is, therefore, likely to have the larger contribution. Secondly, phosphorus, being a physically larger atom than boron, can create greater surface damage than boron, whilst the lighter boron is expected to penetrate the silicon to a much greater depth. Thirdly, the presence of a different surface species could have a chemical effect which enhances the oxidation rate.This could, in some way, enhance the nucleation behaviour on the implanted surface.

A comparison of the effect of the furnace time on the oxide thickness grown on phosphorus- and boron-implanted silicon wafers is shown in Fig. 8. The dashed line represents the oxide grown on bare silicon wafers whilst the solid line indicates the thickness of

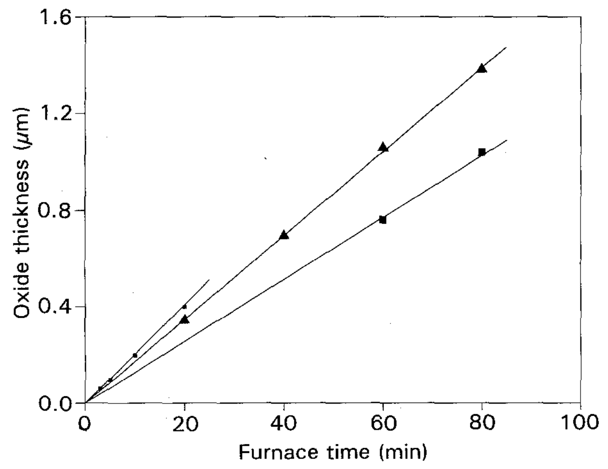

Figure 6 Oxide thickness versus furnace time for phosphorus-implanted silicon wafers (80 keV and 5×10^{15} ions per cm^2) at different temperatures: (■) 800 °C, (▲) 850 °C, and (▪) 900 °C.

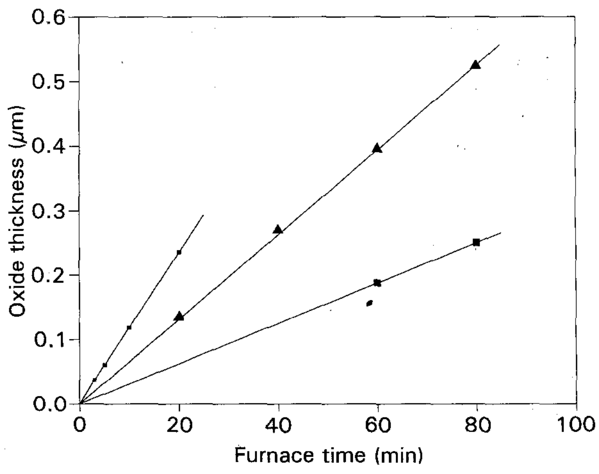

Figure 7 Oxide thickness versus furnace time for boron-implanted silicon wafers (25 keV and 2×10^{15} ions per cm^2) at different temperatures: (■) 800 °C, (▲) 850 °C, and (▪) 900 °C.

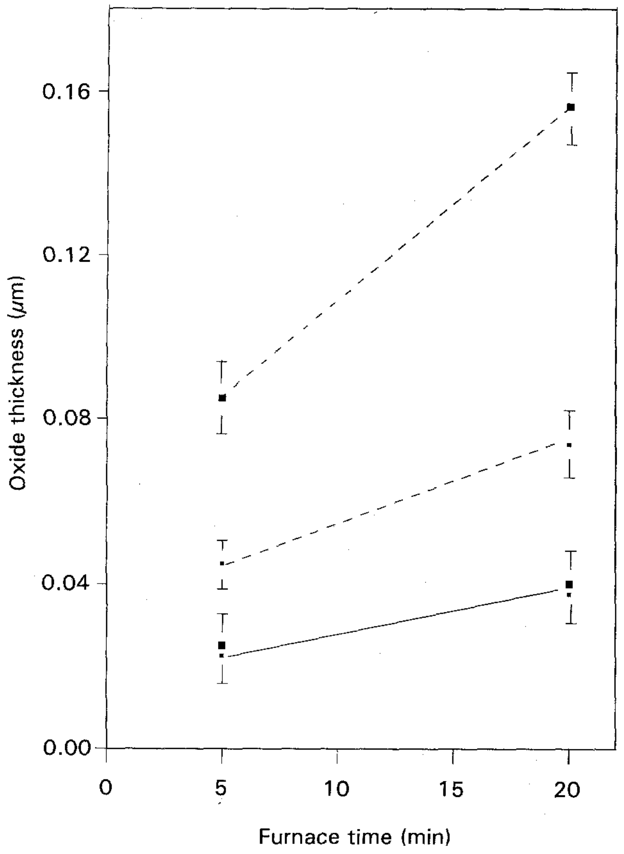

Figure 8 Oxide thickness versus furnace time for: (■) phosphorus-implanted and (▪) boron-implanted silicon wafers; (– – –) bare silicon, and (——) vapox. (The oxygen annealing temperature was 900 °C.)

the oxide grown under a 0.2/0.8 μm undoped/doped chemical vapour deposition (CVD) oxide (vapox) layer. The wet oxygen annealing was carried out at 900 °C. In general, for both phosphorus- and boron-implanted wafers the oxide thickness increases with longer annealing times. As observed in Figs 6 and 7, a linear increase in the oxide thickness with time is expected. In addition, the oxidation rate for phosphorus-implanted silicon substrates is enhanced in comparison to boron-implanted substrates. The oxide growth rate under the vapox is same for both phosphorus- and boron-implanted silicon wafers. In this case, the oxidation rate depends on the diffusion of oxygen through the two layers to the silicon interface, and it is thus transport limited. Therefore, as expected, the oxide growth is not as dependent on the surface properties of silicon.

4. Conclusion

The growth characteristics of oxides grown using H_2/O_2, HCl/O_2 and TCA/O_2 were compared in an industrial oxidation system. Both TCA/O_2 and HCl/O_2 resulted in increased deposition rates compared to H_2/O_2. The enhanced oxidation rate for TCA/O_2, in comparison to HCl/O_2, and the good correlation between the 1% TCA and 3% HCl oxidation rates suggests that the reaction proceeds through the decomposition of one molecule of TCA into three of HCl. The onset of depletion occurs further away from the gas inlet for high gas-flow rates than for low gas-flow rates, resulting in improved thickness uniformity both within the wafers and within the batch.

Phosphorus-implanted silicon wafers showed an enhanced oxide growth rate compared to boron-implanted and unimplanted substrates. It has been suggested that surface damage – the chemical and process effects of implantation – acts as active dopant sites for the adsorption of oxygen and it is probably the main reason for the increased growth rate. Surface effects were shown to be far more important for thermal oxidation than they are for deposited oxides by CVD. In addition, higher temperatures yield a reduced surface concentration because of increased diffusion into the bulk silicon.

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