

Fundamental characterization of the effect of nitride sidewall spacer process on boron dose loss in ultra-shallow junction formation

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Abstract

A nitride spacer with an underlying deposited tetraethoxysilane (TEOS) oxide that behaves as a convenient etch stop layer is a popular choice for sidewall spacer in modern complementary metal oxide semiconductor (CMOS) process flows. In this work, we have investigated the effect of the silicon nitride spacer process chemistry on the boron profile in silicon and the related dose loss of B from Si into silicon dioxide. This is reflected as a dramatic change in the junction depth, junction abruptness and junction peak concentration for the different nitride chemistries. We conclude that the silicon nitride influences the concentration of hydrogen in the silicon dioxide and different nitride chemistries result in different concentrations of hydrogen in the silicon dioxide during the final source/drain anneal. The presence of H enhances the diffusivity of B in the silicon dioxide and thereby results in a significant dose loss from the Si into the silicon dioxide. In this work, we show that this dose loss can be minimized and the junction profile engineered by choosing a desirable nitride chemistry.

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1. Introduction

The rapid pace of improvements in the semiconductor industry has resulted principally from the exponential scaling down of device dimensions since both the speed and the number of transistors per unit area increase as device dimensions are decreased. In the last decade, in order to continue conventional scaling of the source/drain junctions, the semiconductor industry has relied heavily on decreasing the implant energy, and also on minimizing the thermal budget of the activation anneal. However, with transient enhanced diffusion (TED) being less pronounced for low implant energies and sharper anneal temperature profiles, surface reactions and related processes are starting to dominate the formation of ultra-shallow junctions [1]. Recent work by Kohli et al. has emphasized the importance of interactions of dopants with silicon nitride spacer layers on ultra-shallow junction for-

mation [2]. They investigated the influence of silicon nitride spacer (from now on we will refer to silicon nitride as nitride and silicon dioxide as oxide) with an underlying deposited tetraethoxysilane (TEOS) oxide on B dose loss from the Si into the oxide. They showed that the as-deposited TEOS oxide has very high concentrations of H. This H diffuses out readily upon annealing. However, the presence of nitride acts as a diffusion barrier for the out-diffusing H, resulting in high concentration of retained H in the TEOS even after annealing. The presence of this high level of retained H causes an enhancement of B diffusivity in the oxide [2–6] and thereby enhances the amount of B dose loss into the oxide from the Si. Lesser retained dose leads to shallower profile because of Fermi level effects, coupled diffusion effects and also due to the fact that shift of the profile downwards (due to lesser concentration/dose) moves the point where concentration of B drops to a certain value towards the surface (to the left). In this work, we study the effect of different nitride chemistries on the hydrogen concentration in the oxide after annealing and the corresponding B dose loss.

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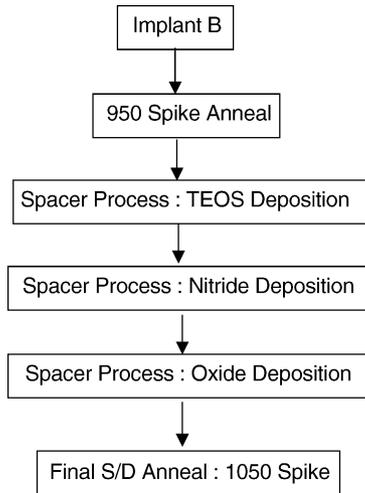


Fig. 1. Experimental procedure for standard VLSI p-MOS source/drain extension formation with nitride sidewall spacer.

2. Experiment

The experimental procedure was designed for standard source/drain extension formation with nitride spacer in the complementary metal oxide semiconductor (CMOS) device flow, as shown in Fig. 1. After the source/drain extension implants, Si is first capped with a TEOS oxide layer (oxide 1) followed by a nitride layer. For thin nitride spacer layer, the nitride deposition is followed by another oxide layer (oxide 2) in order to obtain the desired thickness (in our case 800 Å) of the sidewall spacer. Two different nitride chemistries were used in this work: BisTertiaryButylAminoSilane (BTBAS) and DiChloroSilane (DCS). In both chemistries NH₃ is the reacting gas. The deposition cycle for BTBAS chemistry is at 550 °C for 2 h and for DCS chemistry it is at 740 °C for 1 h.

The starting material was n-type Si with (1 0 0) crystal orientation. On the first set of wafers (set A) a 50 Å thermal oxide was grown. The wafers were then subjected to a B (or BF₂) implant at 1.3 keV (or 6 keV BF₂) and a B dose of 1.2E15 atoms/cm². Wafers that were subjected to the BF₂ implant received a pre-damage implant to prevent dopant channeling. All wafers were subjected to a 950 °C spike anneal. A

150 Å thick TEOS oxide layer was then deposited at 650 °C as part of the sidewall spacer process. Next a BTBAS nitride (300 Å) or DCS nitride (800 Å or 300 Å) layer was deposited. For some samples, no reactive gases were flowed during the nitride deposition step (only N₂ purge). This was to subject the wafers to the same thermal budget as BTBAS or DCS nitride without actually depositing any nitride. Finally, wafers were subjected to the source/drain spike anneal at 1050 °C. Some wafers were not subjected to the final anneal to serve as a reference (as indicated in Table 1). For the two different DCS nitride thickness recipes (300 Å and 800 Å) the thermal budgets were very similar.

Another set of wafers (set B) was deposited with 1200 Å thick TEOS oxide, and then 300 Å thick BTBAS nitride or 800 Å DCS nitride or just the equivalent thermal budget. Next the wafers were subjected to 1050 °C spike anneal. Again, some wafers were not subjected to an anneal to serve as a reference (as indicated in Table 1). These samples enable a study of hydrogen loss from the oxide upon annealing, using the nuclear reaction analysis (NRA) technique.

The wafer splits for sets A and B are shown in Table 1.

Hydrogen profiles in the oxide were obtained using nuclear reaction analysis at the State University of New York, Albany.

All B profiles in Si and in the oxide were obtained using dynamic secondary ion mass spectroscopy (DSIMS) at Texas Instruments. All B profiles shown in oxide only were obtained using time-of-flight SIMS. Nitrogen and C profiles were also obtained for some samples by dynamic SIMS. Wafer bow was also measured. Sheet resistance values were obtained using a four-point probe and the standard deviation was less than 5%.

3. Results and discussion

3.1. Effect of presence of BTBAS nitride on B diffusion profile

The target BTBAS nitride thickness was 300 Å. Fig. 2a and b show the B diffusion profiles in the Si and the TEOS

Table 1
Summary of wafer processing conditions

Process steps \ wafers	Set A										Set B			
	1	2	3	4	5	6	7	8	9	10	11	12	13	14
B implant	X	X	X	X	X	X	X	X	X	X				
BF ₂ implant (into pre-damaged Si)											X	X		
TEOS 150 Å	X	X	X	X	X	X	X	X	X	X	X	X		
TEOS 1200 Å													X	X
BTBAS 300 Å			X		X						X			
BTBAS thermal cycle				X		X							X	
DCS 300 Å									X					
DCS 800 Å							X			X			X	
DCS thermal cycle								X			X			
1050 °C spike				X	X				X	X	X	X	X	X

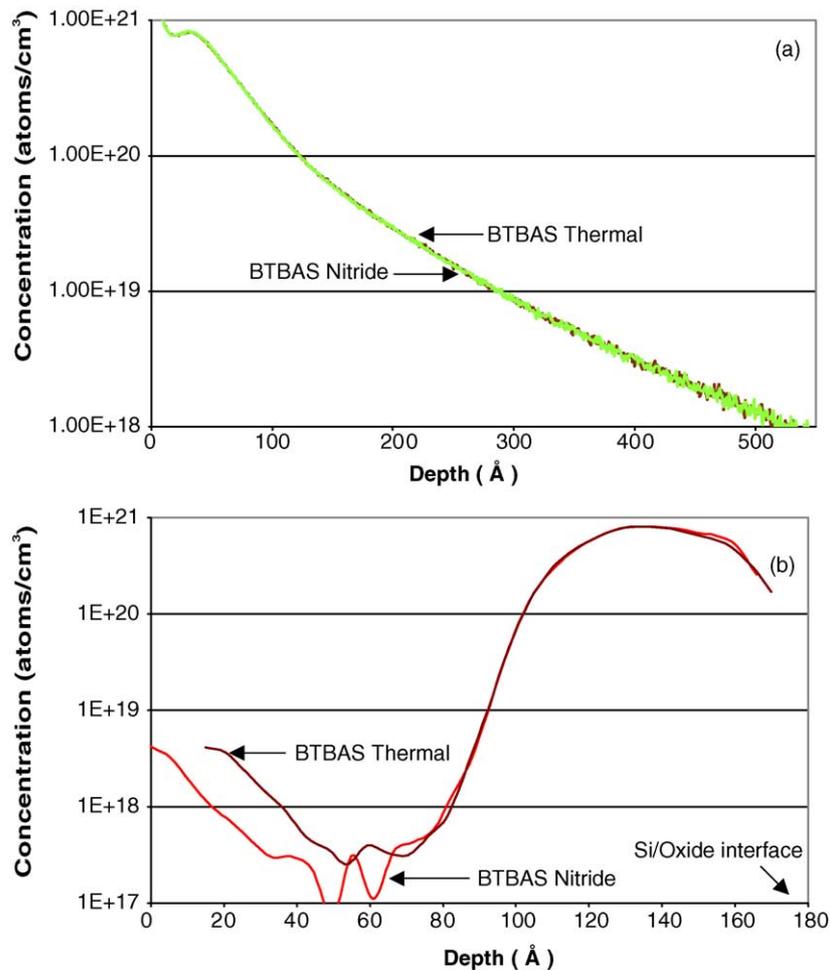


Fig. 2. (a) B diffusion profiles in Si (from DSIMS) before 1050 °C anneal are identical for samples with and without BTBAS nitride. It is important to note that both samples are subjected to the same thermal budget irrespective of whether BTBAS nitride is deposited or not. (b) B diffusion profiles in TEOS oxide stack (from TOF SIMS) before 1050 °C anneal are identical for samples with and without BTBAS nitride. It is important to note that both samples are subjected to the same thermal budget irrespective of whether BTBAS nitride is deposited or not.

oxide stack, respectively, right before the final source/drain activation anneal (for samples implanted with B). It is important to note that both samples were subjected to the same thermal budget, irrespective of whether nitride was deposited on top of the TEOS or not. Furthermore, we found that the B profile in both Si and TEOS oxide stack was not affected by the nitride deposition thermal budget. BTBAS deposition is a very low temperature process (550 °C/2 h) and therefore no significant dopant movement in Si or the TEOS oxide stack is expected during the BTBAS nitride dep/BTBAS thermal cycle only. Fig. 3a and b show the B diffusion profiles in Si and TEOS oxide stack, respectively, for samples with and without the BTBAS nitride after the 1050 °C spike. After the final activation anneal, SIMS profiles for samples with the nitride show lower retained B dose in Si than those without the BTBAS nitride. So during the 1050 °C spike, the presence of BTBAS nitride on top of TEOS oxide seems to influence the final B diffusion profile. Samples with the BTBAS nitride on top of TEOS show a lower B concentration over most of the

profile in Si and consequently shallower junctions in Si compared to samples without the BTBAS nitride. However, the B concentration in the TEOS oxide is higher for the samples with the BTBAS nitride compared to the samples without the BTBAS nitride. It appears from the profiles that the reduction in junction depth in the presence of BTBAS nitride comes along with a lower B concentration in Si.

Fig. 4 shows the H profiles obtained by NRA in the TEOS oxide after annealing, with and without BTBAS nitride. The H profile for as-deposited TEOS oxide is also shown. It is important to note that the H levels in the as-deposited TEOS are very high. Instead of BTBAS nitride acting as a source of H and thereby increasing the H in the underlying oxide upon annealing, we find that BTBAS nitride seems to be acting as a barrier for the H out-diffusion from the underlying TEOS during annealing. The H concentration in the TEOS after annealing is much higher (2.6E21 atoms/cm³) if the nitride is present during annealing as compared to the H concentration in the TEOS after annealing without nitride (1.9E21

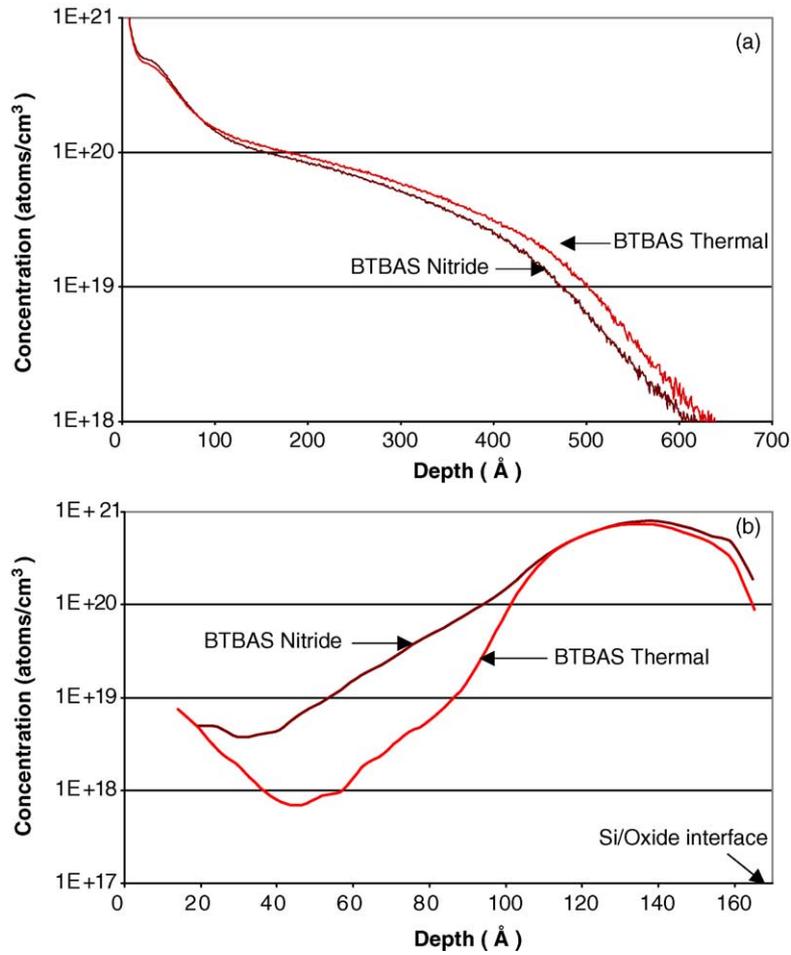


Fig. 3. (a) B diffusion profiles in Si after 1050 °C anneal (from DSIMS). In the presence of BTBAS nitride less B is retained in Si. (b) B diffusion profiles in TEOS oxide stack after 1050 °C anneal (from TOF SIMS). In the presence of BTBAS nitride B diffusivity is enhanced in the oxide resulting in higher dose of B in the oxide.

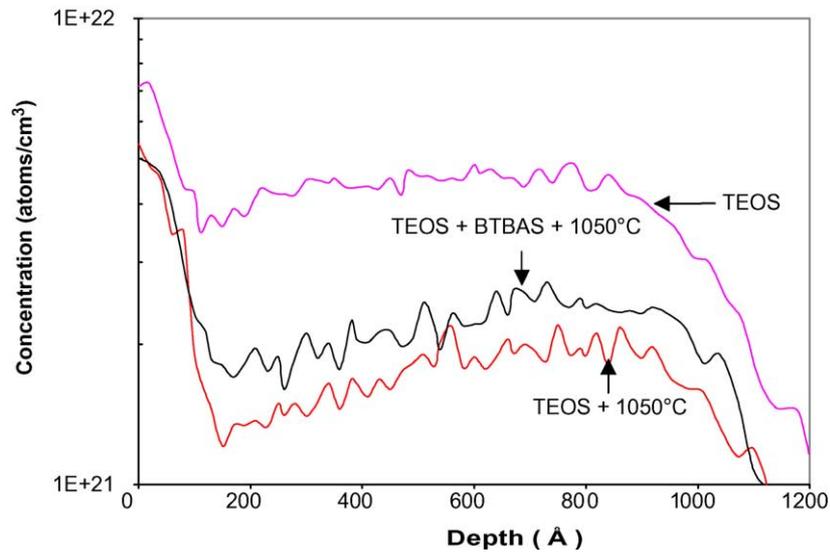


Fig. 4. H profiles (from NRA) showing as-deposited TEOS oxide has high levels of H. BTBAS nitride acts as a barrier for H out-diffusion.

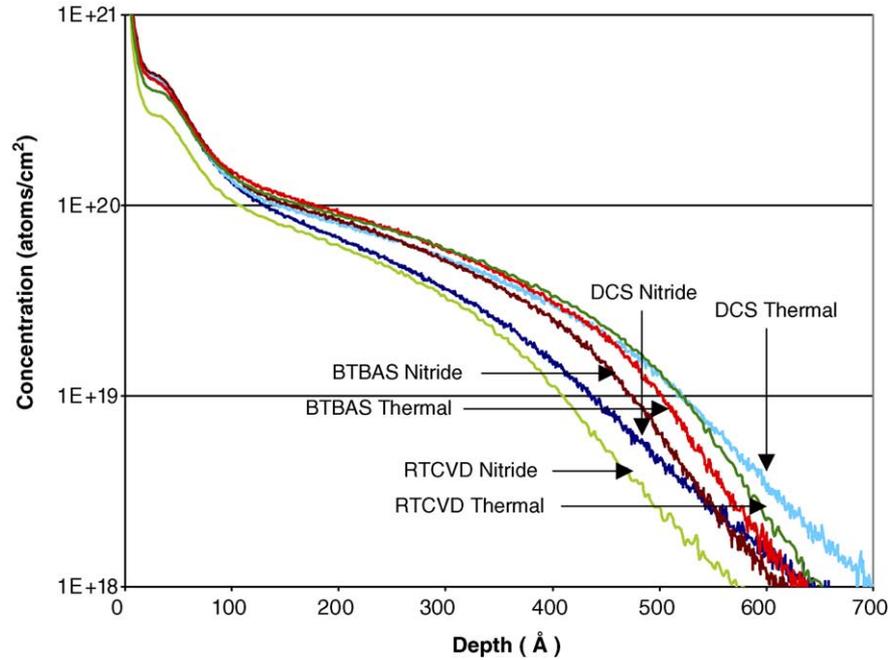


Fig. 5. Comparison of final annealed B junctions in Si (from DSIMS) formed using BTBAS, RTCVD or DCS nitride spacer process. Also shown are the final annealed B profiles in Si obtained without nitride deposition. BTBAS nitride results in the highest retained B dose in Si.

atoms/cm³). This suggests that it is the high H concentration during anneal in the presence of BTBAS nitride that causes enhanced B diffusion [2].

3.2. Comparison of different nitride chemistries on B diffusion profiles

Boron diffusion data with RTCVD nitride after 1050 °C spike anneal has been reported [2]. Fig. 5 shows the final

annealed profiles obtained with and without nitride for BTBAS, DCS and RTCVD nitride. It is evident (as discussed above) that the presence of nitride results in shallower junctions. BTBAS nitride results in the highest retained dose in the Si followed by DCS nitride and RTCVD nitride, respectively. Fig. 6 shows the peak H concentration in TEOS after 1050 °C spike for the different nitrides. BTBAS nitride that results in the highest retained B dose in Si and therefore the least B dose loss from Si into oxide shows the lowest H peak concentration, whereas RTCVD nitride which shows

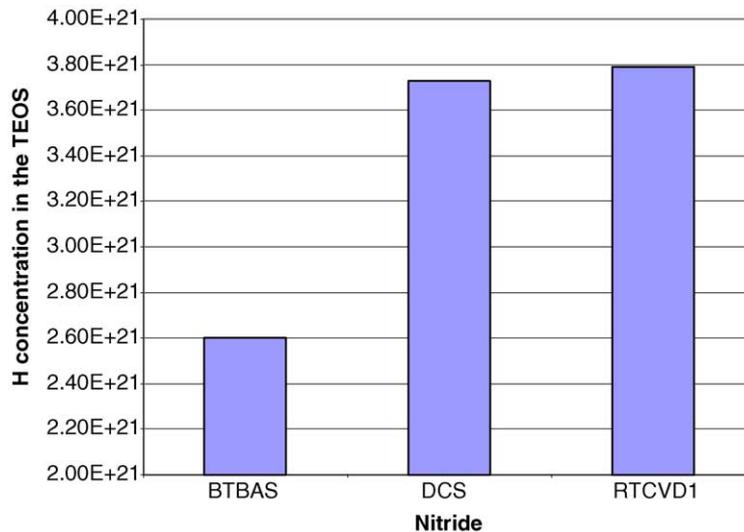


Fig. 6. H concentration in the TEOS oxide stack after 1050 °C anneal for BTBAS, DCS, and RTCVD nitride. BTBAS nitride results in the lowest concentration of H in the TEOS oxide. RTCVD nitride acts as the most effective barrier for H out-diffusion.

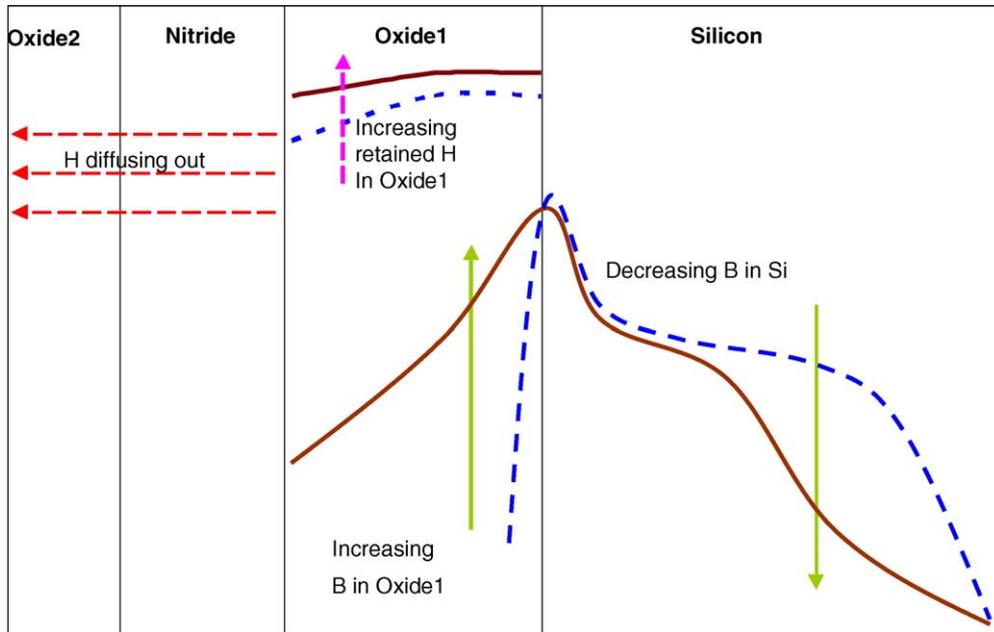


Fig. 7. Schematic illustration of the H model and B diffusion in oxide. The presence of H in oxide enhances the B diffusivity in oxide.

the least retained B dose in Si shows the highest H peak concentration in TEOS after the final anneal. These observations correlate well with the dose loss model proposed by us before [2]. Based on our observations, BTBAS seems to be a less effective barrier to H out-diffusion from the TEOS into the ambient through the nitride compared to DCS or RTCVD nitride.

The stress values obtained using wafer bow measurements with the nitride (DCS\BTBAS\RTCVD) were of the order of $1E10$ dynes/cm² tensile. According to the literature [7], much higher stress values would be required to change the B diffusivity in order to be able to match the B profiles in the oxide in the presence of nitride. Also, it is important to note that different nitride chemistries result in very similar values of stress; however, they result in very different B diffusion profiles. In order to understand the effect of nitride we profiled N in the TEOS oxide (and C in addition to N in the case of BTBAS, since BTBAS chemistry has C). Our results from DSIMS showed very similar levels of N (and C) in the TEOS oxide both with and without the presence of nitride after the 1050 °C anneal. We, therefore, believe that it is indeed the high concentration of H in the TEOS in the presence of nitride that results in enhanced B diffusivity in the TEOS oxide and the related B dose loss.

4. Proposed model

Fig. 7 represents a schematic illustration of the models and interactions considered in this work. Primarily, we model the diffusion of H through various spacer layers (oxide 1/nitride/oxide 2) and its effect on B diffusion in Si and oxide.

As has been suggested in literature [2] and also in this work, deposited oxides contain large amount of H. This H is highly volatile and out-diffuses readily. A nitride on top of oxide acts as a barrier to the out-diffusing H. Due to the differences in composition, different nitrates lead to different concentrations in the oxide (oxide 1) after final source/drain anneal. Higher concentrations of H in oxide enhance B diffusion in oxide resulting in an increase in dose loss of B from Si into the oxide. This reduces the extent of B diffusion in Si as observed by experimental data.

5. Summary

An investigation of the influence of the nitride spacer chemistry on B dose loss from the Si into the oxide has been concluded. We find that the as-deposited TEOS oxide has very high concentration of H. This H typically diffuses out readily upon annealing. However, the presence of nitride acts as a diffusion barrier for the out-diffusing H, resulting in higher concentration of retained H in the TEOS after annealing. The presence of this high level of retained H causes an enhancement of B diffusivity in the oxide and thereby enhances the amount of B dose loss into the oxide from the Si. Different nitride chemistries result in different concentrations of H in the TEOS upon annealing and therefore different B dose loss. BTBAS nitride, by acting as the least effective barrier for H out-diffusion from the TEOS, relative to DCS and RTCVD nitride, results in the highest retained B dose in Si and therefore results in most conductive source/drain junctions.

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