Effect of nitride sidewall spacer process on boron dose loss in ultrashallow junction formation

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A nitride spacer with an underlying deposited tetraethoxysilane oxide, that behaves as a convenient etch stop layer, is a popular choice for sidewall spacer in modern complementary metal–oxide–semiconductor process flows. In this work we have investigated the effect of the silicon nitride spacer process on the boron profile in silicon and the related dose loss of B from the Si into the silicon dioxide. This is reflected as a dramatic decrease in the junction depth. We find that the silicon nitride influences the concentration 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 have shown this dose loss can be lowered by altering the silicon nitride stoichiometry. © *2004 American Vacuum Society.*
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I. INTRODUCTION

Improvements in the integrated circuit performance over the past 3 decades have been mainly possible by the downward scaling of device dimensions. Device scaling requires that all lateral and vertical dimensions of the transistor be scaled. 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. Decreasing the implant energy puts the excess interstitials closer to the surface. The surface acts as an efficient sink for the interstitials, thus reducing transient enhanced diffusion (TED), which results from the interaction of excess interstitials with the dopant atoms. For implant energies below 1 keV, TED can be nearly eliminated. Increasing the ramp rate of anneal, too, has greatly reduced TED effects. With TED less pronounced for low implant energies and sharper anneal temperature profiles, surface reactions and related processes emerge to dominate the formation of ultrashallow junctions. Interactions of dopant atoms and point defects with surface films and interfaces are becoming of paramount importance in determining the concentrations of dopants and point defects, and therefore the resulting device structures.[1]

In the standard complementary metal–oxide–semiconductor (CMOS) process flow, sidewall spacer is widely used to self align the deep source/drain from the shallow source/drain extension. Oxide spacers in deep submicron technology are limited by trenching in the field oxide, and occurrence of shorts between gate and drain/source, due to the salicidation step. 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 that behaves as a convenient etch stop layer, overcomes these difficulties.[2] The aim of this work is to analyze the effect of nitride spacer on the B dose loss from the Si into the overlying implantation oxide and TEOS oxide.

II. EXPERIMENT

The experimental procedure was designed for standard very large scale integrated (VLSI) source/drain extension

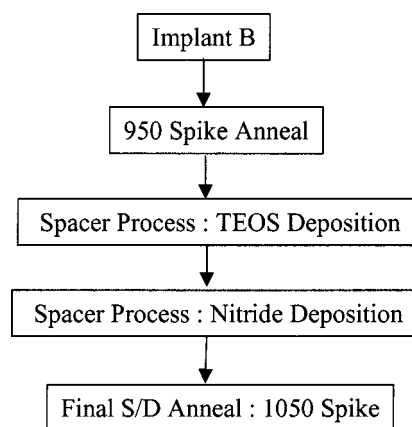FIG. 1. Experimental procedure for standard VLSI *p*-MOS source/drain extension formation with nitride sidewall spacer.

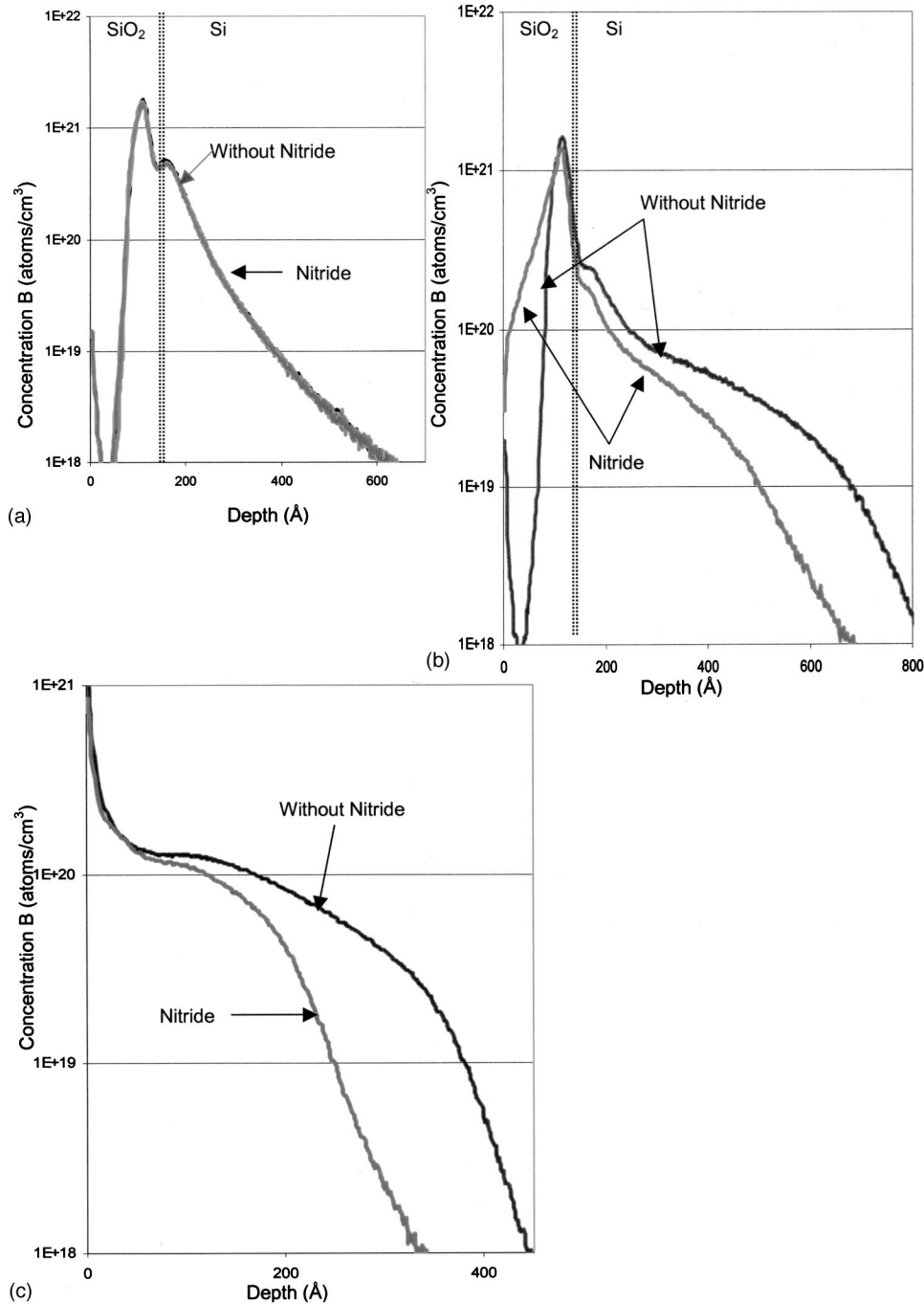[a)]Electronic mail: kohli@ece.utexas.edu

FIG. 2. (a) B diffusion profiles before 1050 °C spike anneal are identical for both the samples with and without the nitride. B was implanted in these samples. (b) B diffusion profiles after 1050 °C spike anneal. In the presence of nitride less B is retained in Si and more B is lost into the oxide. B was implanted in these samples. (c) B diffusion profiles after 1050 °C spike anneal. In the presence of nitride less B is retained in Si and more B is lost into the oxide. BF_2 was implanted in these samples. The trends are similar to Fig. 3 with B implants.

formation with nitride spacer in the CMOS device flow as shown in Fig. 1. The starting material was *n*-type Si with $\langle 100 \rangle$ crystal orientation. A 50 Å thermal oxide was grown on all the wafers. The wafers were then subjected to a B (or BF_2) implant at 1.3 keV (or 6 keV BF_2) and a B dose of $1.2e15$ atoms/cm^2. Wafers that were subjected to the BF_2 implant received a predamage implant. 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 300 Å thick room temperature chemical vapor deposited (RTCVD) nitride layer was deposited by flowing silane and ammonia at 700 °C. A nitride layer thickness of 1100 Å instead of the 300 Å thickness was deposited on some samples. Furthermore, for some samples during the nitride deposition step, no reaction gases were made to flow (only N_2 purge). This was to subject the wafers to the same thermal budget 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. Three different nitride deposition processes were employed with different flow rates of ammonia and silane, but the same thermal budget was used. Also, some samples were prepared with 1500 Å oxide. Some of these samples had thermally grown oxide, while others had a TEOS based deposited oxide, in order to study the diffusivity of B in oxide. A B dose of $5E13$ atoms/cm^2 was implanted at 18 keV into the 1500 Å thick oxide samples. Further, on some of these wafers 2000 Å RTCVD nitride was deposited. Nitride of this thickness enables comparison of two extreme conditions. Wafers both with and without the nitride were annealed at 1050 °C for 11 s. Some wafers were not annealed to serve as reference. Another set of wafers were deposited with 1200 Å thick TEOS oxide, and then with or without 300 Å thick nitride. Next the wafers were subjected to 1050 °C spike anneal. Some wafers were not subjected to anneal to serve as reference. This set of samples enables a study of hydrogen loss from the oxide upon annealing.

All B profiles in Si and in the oxide were obtained using dynamic secondary ion mass spectroscopy (DSIMS). H profiles in the oxide were obtained using nuclear reaction analysis (NRA). Fourier transform infrared spectroscopy was also used to analyze some samples. Sheet resistance values were obtained using a four-point probe.

III. RESULTS

The following is the effect of the presence of nitride on the B diffusion profile. Figure 2(a) shows the B diffusion profiles in the Si/TEOS oxide stack 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. Samples implanted with BF$_2$ into predamaged Si also show identical profiles for samples with and without the nitride, before the final anneal at 1050 °C. Figures 2(b) and 2(c) show the B diffusion profiles for samples with and without the nitride after the 1050 °C spike, for B and BF$_2$ implant cases, respectively. For B and BF$_2$ implant cases, after the final activation anneal, samples with the nitride show lower retained B dose in Si than those without the nitride. So during the 1050 °C spike, the presence of nitride on top of TEOS oxide seems to influence the final B diffusion profile. Samples with the nitride on top of TEOS show lower B concentration at each depth in Si and consequently shallower junctions in Si compared to samples without the nitride. However, the B concentration in the TEOS oxide is higher at all depths for the samples with the nitride compared to the samples without the nitride. It is clear from the profiles that the reduction in junction depth in the presence of nitride comes along with a lower B peak concentration. The average conductivity of the junctions (calculated as the inverse of the product of sheet resistance and junction depth) indicates formation of a lower conductivity junction in the presence of nitride for both B and BF$_2$ implants. Eyben *et al.* have reported that nitride spacer en-
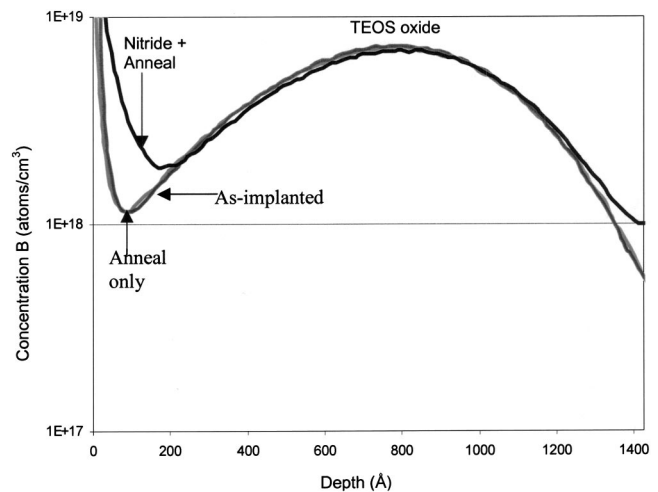

FIG. 3. B diffusion profiles in TEOS oxide after anneal. In the presence of nitride, B diffuses faster. The B annealed profile without the nitride is identical to the as-implanted profile.

hances lateral diffusion of B while having no effect on the vertical diffusion of B. Clearly, our results do not agree with their observation.[3]

The effect of the presence of nitride on B diffusion in thermal and TEOS oxide is as follows. Figure 3 shows the three B diffusion profiles in TEOS oxide for different processing conditions. The as-implanted profile of B in TEOS oxide does not show any measurable broadening even after relatively long high temperature anneal at 1050 °C for 11 s. However, with the nitride present the same profile shows measurable diffusion. It is the presence of nitride on top of the TEOS oxide that influences the B diffusivity during the high temperature anneal. For samples with thermal oxide instead of the TEOS oxide, the three profiles corresponding to the processing conditions of the profiles in Fig. 3 look identical. The presence of the nitride seems to substantially enhance the diffusivity of the B in the oxide in the case of TEOS oxide, while it does not seem to influence the B diffusivity in the case of thermal oxide.

The effect of nitride stoichiometry and thickness variation is as follows. Figure 4(a) shows B diffusion profiles in Si/TEOS stack after final source/drain anneal for three different nitride stoichiometries for B implanted samples. Figure 4(a) also shows the B diffusion profile for B implant after annealing without a nitride. The x-ray photoelection spectroscopy results for the three nitrides show that Nitride 1 has the highest concentration of N (46.15%) while Nitride 3 has the least concentration of N (43.27%). The total thermal budgets involved in the nitride deposition using different flow rates for the same nitride thickness were made identical. All four B profiles were identical right before the 1050 °C anneal. However, during annealing different nitrides seem to influence B diffusion in different ways. Boron concentration in Si, after the final anneal, is highest for Nitride 1 followed by Nitride 2, and then Nitride 3; while the B concentration in the TEOS oxide is highest for Nitride 3 followed by Nitride 2 and then Nitride 1. It is important to note that during DSIMS analysis
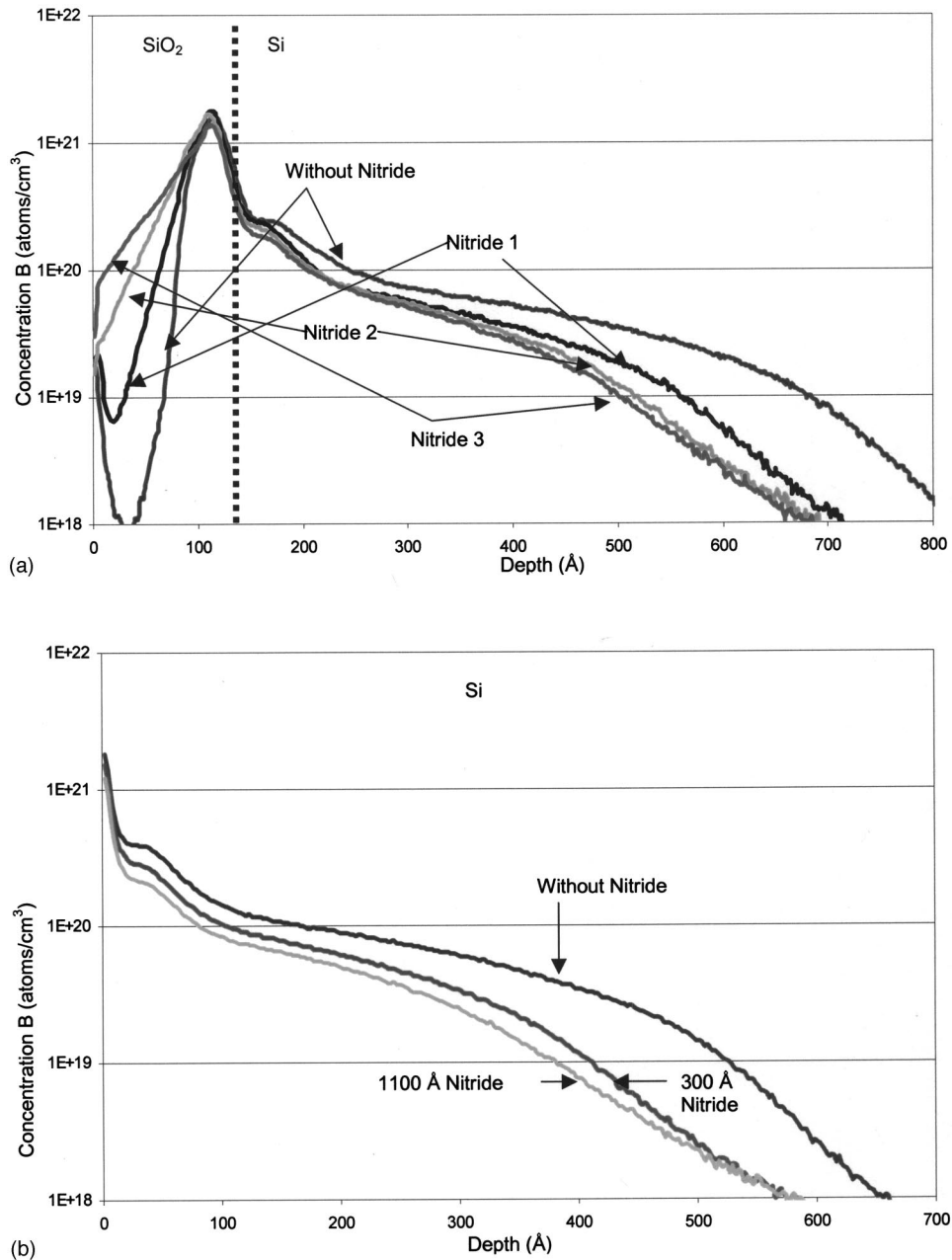
FIG. 4. (a) Effect of nitride stoichiometry on B diffusivity in oxide and B profile in Si. Nitride 1 seems to retain most B dose in the Si without any substantial tradeoff in junction depth. (b) Effect of nitride thickness on B dose loss. Thicker film results in more B dose loss from Si into oxide.

for different processing conditions we never observed any B in the nitride. It is apparent that different nitrides influence the amount of B dose loss from the Si into the TEOS oxide differently, and therefore result in different junction depths and B peak concentrations. Figure 4(b) shows B diffusion profiles in Si for two different nitride thicknesses. The thicker nitride evidently results in higher dose loss from the Si into the oxide. The total thermal budgets involved for the recipes resulting in different deposition thicknesses were identical with the actual deposition times being different. In addition to the nitride chemistry it is apparent that the nitride thickness also influences the B diffusion profile.

IV. DISCUSSION

From Figs. 2(b) and 2(c) it is evident that the presence of the nitride influences the oxide in a way that it results in higher B dose loss from the Si into the TEOS oxide. From the B profiles in Fig. 3, one understands that the presence of nitride on the TEOS oxide enhances the B diffusivity in the oxide. Assuming simple Fickian diffusion, the B diffusion profile in the TEOS oxide in the presence of nitride can be modeled by increasing the B diffusivity in oxide by a factor of 2000.

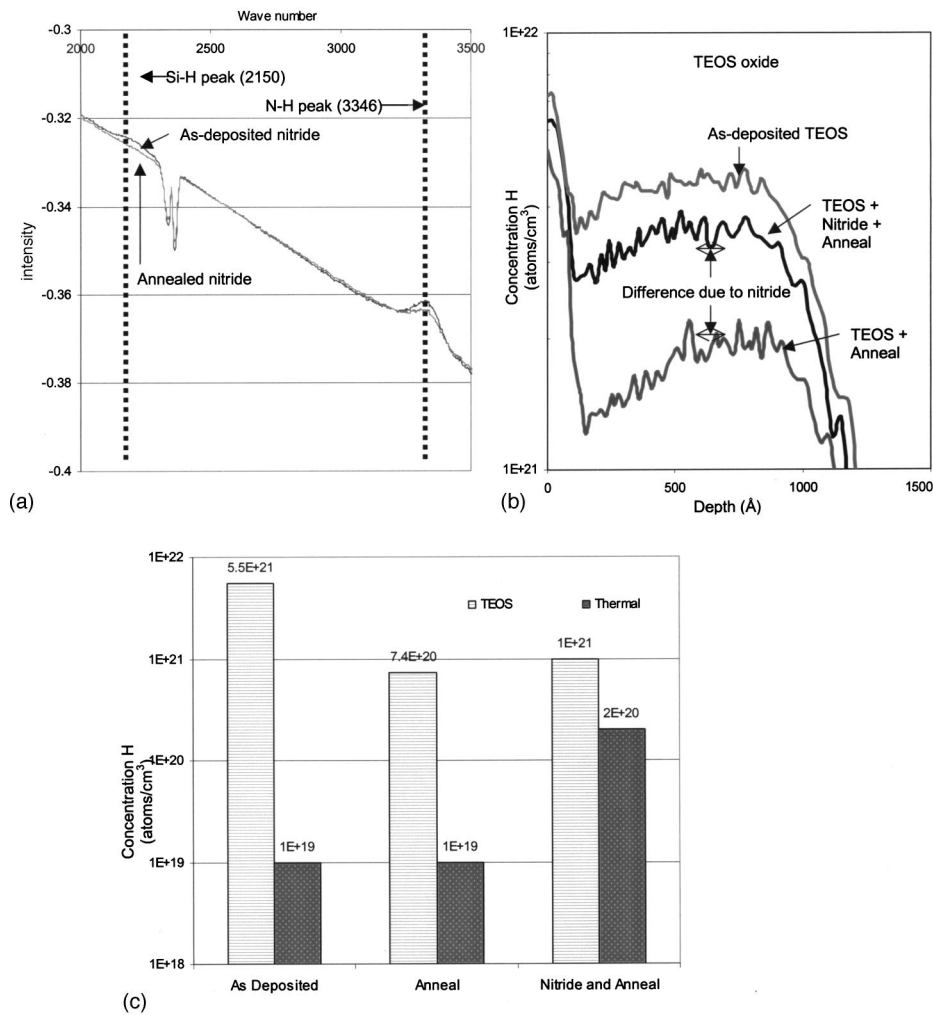In order to understand the effect of nitride we profiled N

FIG. 5. (a) Fourier transform infrared data showing decrease in both H associated peaks in nitride upon annealing. H out-diffuses from the nitride film upon annealing. (b) NRA H data showing as-deposited TEOS oxide has high levels of H. Nitride acts as a barrier for H out-diffusion. (c) NRA H data showing in the case of TEOS oxide, nitride acts as a diffusion barrier for H, while in the case of thermal oxide nitride acts as a source of H during annealing.

in the TEOS oxide. Our results from time-of-flight SIMS as well as DSIMS showed very similar levels of N in the TEOS oxide both with and without the presence of nitride after the 1050 °C anneal. Recent reports have discussed the effect of stress due to thin films on B diffusion in Si. However, we noted before that while the B implanted TEOS oxide sample showed enhanced B diffusion during anneal in the presence of nitride, the thermal oxide sample implanted with B did not show any B enhanced diffusion during annealing even in the presence of nitride. The stress values obtained using wafer bow measurements with the nitride were on the order of $1E10$ dynes/cm^2 tensile. According to the literature,[4] much higher stress values would be required to change the B diffusivity by a factor of 2000, as seen for the B implanted TEOS sample with nitride. Also, different nitride chemistries (which will be discussed elsewhere) result in very similar values of stress; however, they result in very different B diffusion profiles.

Extensive reports in the literature have discussed the nitride acting as a source of H that diffuses in the underlying oxide during nitride deposition and/or during annealing.[5,6]

This H is believed to form H-related defects in the oxide, which lower the B diffusion activation energy in the oxide.[7] Nitride FTIR measurements before and after anneal in Fig. 5(a) shows that both peaks corresponding to wave numbers for the Si–H and N–H bonds decrease in intensity after the nitride has been annealed, indicating out-diffusion of H from the nitride during annealing.

Figure 5(b) shows the H profiles obtained by NRA in the TEOS oxide with and without nitride, after anneal. 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 nitride acting as the source of H and thereby increasing the H in the underlying oxide upon annealing, we find that 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 ($3.5E21$ atoms/cm^3) if the nitride is present during annealing as compared to the H concentration in the TEOS after annealing without nitride. Figure 5(c) shows the H concentrations in the TEOS and thermal oxide, for samples corresponding to the processing conditions indicated

in Fig. 3. It is interesting to note that the H concentration for as-deposited TEOS is very high while that of as-grown oxide is very low. After annealing, the H concentration in TEOS oxide decreases both with and without the nitride. For thermal oxide with the nitride, upon annealing we find an increase in H concentration. This indicates the possibility of nitride acting as a source of H. However, for TEOS the out-diffusion flux of H from the TEOS seems to be the dominant one. It is the high H concentration during anneal in the presence of nitride that causes enhanced B diffusion. Also it appears that below a certain threshold value of H, no enhancement of B diffusivity is observed (as in the case of TEOS annealed without nitride).

We know that the H concentration in as-deposited TEOS oxide is very high and that upon annealing this H out-diffuses from the oxide directly into the ambient if there is no nitride present, or through the nitride into the ambient if nitride is present. H diffusion through the nitride is the rate-limiting step since the presence of nitride results in higher retained H in the oxide. As indicated in the schematic the higher concentration of H in the TEOS oxide due to the presence of nitride results in increase in B dose loss from Si into the oxide. This B dose loss reduces the extent of B diffusion in Si by reducing the concentration-dependent diffusivity. This model also explains the experimental observation of more dose loss into the oxide in the presence of thicker nitride. Since H diffusion through the nitride is the rate-limiting step, a thicker nitride would result in less H out-diffusion from the TEOS oxide for the same anneal. This implies that a thicker nitride would result in a higher retained

H concentration in the TEOS oxide, resulting in a greater enhancement of B diffusivity and thereby more B dose loss from the Si into the oxide, as is experimentally observed. The variation of nitride stoichiometry possibly influences the diffusivity of H through the nitride, and thereby results in different H concentrations in the TEOS oxide upon annealing for the different stoichiometries. However, NRA profiling did not show any significant differences in H concentration in the TEOS for the three different stoichiometries studied here.

V. CONCLUSIONS

An investigation of the influence of the nitride spacer on B dose loss from the Si into the oxide has been done. We showed that the as-deposited TEOS oxide has very high concentration 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 and thereby enhances the amount of B dose loss into the oxide from the Si. It is imperative to optimize the sidewall spacer stoichiometry and thickness in order to form very conductive shallow junctions.

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