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Dopant Activation Enhancement in Silicon by Hydrogen Treatment

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1. Introduction

Activation of dopants in shallow junctions required for CMOS device scaling is hampered by the need for high doping concentrations and possible dopant clustering. Process integration issues with high-k dielectrics and use of metal gates as well as problems such as transient enhanced diffusion (TED) impose thermal budget restraints, so alternative means must be found to lower the anneal temperature while retaining activation efficiency. Our previous work [1] demonstrated the enhancement of activation in boron implanted at a dose of 5E14/cm^2 and annealed at temperatures of 450 ^{o}C and below, by the incorporation of atomic hydrogen introduced by exposing the substrate to a hydrogen plasma. This study is based in part on theoretical results suggesting that the presence of atomic hydrogen reduces the activation energy for a dopant to enter the Si vacant site [2]. Here we report on further experiments involving P and Sb implantation, as well as B, to shed new light on the interactions among atomic hydrogen, point defects and dopants.

2. Experimental

(100) p- and n-type Si wafers were used in this experiment. Some of the wafer pieces were hydrogenated by exposure to an electron cyclotron resonance (ECR) hydrogen plasma at 250 ^{o}C. This causes atomic hydrogen to penetrate in significant concentrations into the top 0.2 μm of Si. The hydrogenated and unhydrogenated wafers were then implanted with boron, phosphorus and antimony dopants, and annealed at different temperatures. Table I shows the implant and annealing specifications. The wafers were then characterized using the SSM 2000 NanoSRP spreading resistance profiler. As-implanted samples with boron, phosphorus and antimony implants (i.e. without any annealing) were also characterized by SRP.

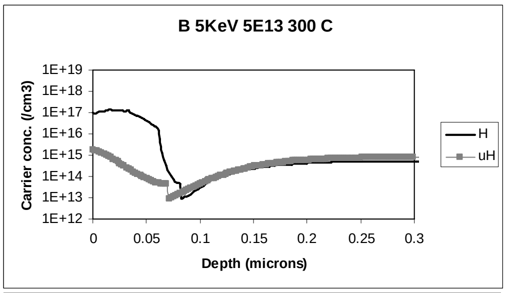
Table I. Types of samples processed

n –type wafers		p-type wafers		p-type wafers	
H treatment	--	H treatment	--	H treatment	--
B implant 5 keV 5E13 cm^{-2}		P implant 10 keV 1E14 cm^{-2}		Sb implant 30 keV 1E14 cm^{-2}	
Anneal 20 s at 300, 400 ^{o} C		Anneal 20 s, at300, 400, 500 ^{o} C		Anneal 20s at 300, 400, 500 ^{o} C	
Characterization with Spreading Resistance Profiling (SRP) to give carrier concentration vs depth					

2. Results and Discussion

In our earlier experiment, many reasons were postulated for the increase in dopant activation seen with boron, starting with the theoretical results of [2] cited above. Atomic hydrogen also is known to increase the movement of dislocations in silicon, and this could be causing the low-temp. activation enhancement. For T >500 ^{o}C, the Si-H bond breaks and hydrogen rapidly effuses out of the silicon, hence this effect is not seen at higher annealing temperatures. Plasma hydrogenation and the out-diffusion of hydrogen from silicon during annealing are both processes that create vacancies in silicon. A supersaturation of vacancies is also known to increase boron activation [3]. Implantation of boron at high doses and low energies results in the formation of immobile inactive defect clusters, and the hydrogen in the lattice could in some way be preventing boron-interstitial cluster formation or assisting cluster dissolution.

Figure 1 shows the SRP results obtained from the samples implanted with 5 keV boron but at a lower dose of 5E13 cm^{-2}, instead of the 5E14 cm^{-2} used in our earlier work.. Dopant activation enhancement due to hydrogen is seen in these samples at 300 and 400 ^{o}C. However, no difference in activation was seen at higher annealing temperatures (not shown). The junction depth is smaller in these samples compared to the previous ones [1]. Cluster formation is known to be lowered with a decrease in implant dose, yet a considerable enhancement of activation with H is still seen in this case. This result hence suggests that the hydrogen may not play any role in B cluster dissolution.



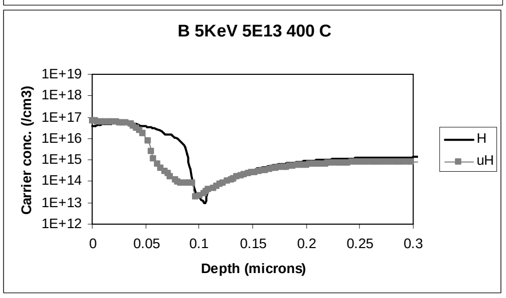
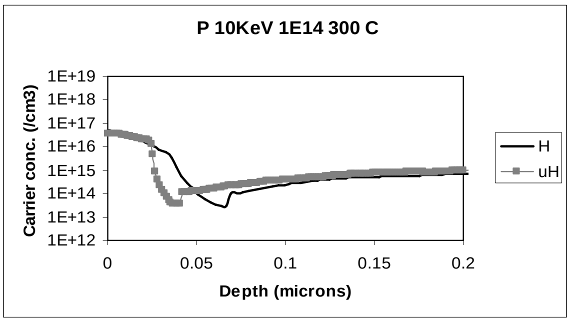
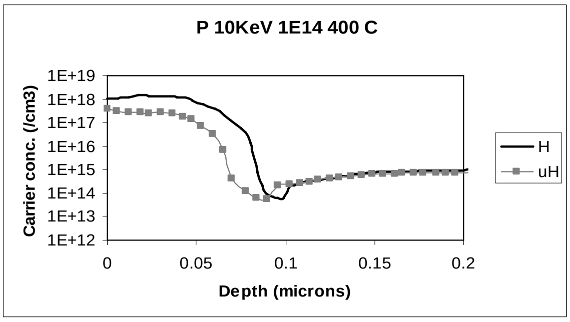


Fig. 1. SRP depth profiles of carrier concentration for hydrogenated (H) and unhydrogenated (uH) samples implanted with boron and annealed at 300 ^{o}C (a) and 400 ^{o}C (b) for 20 s

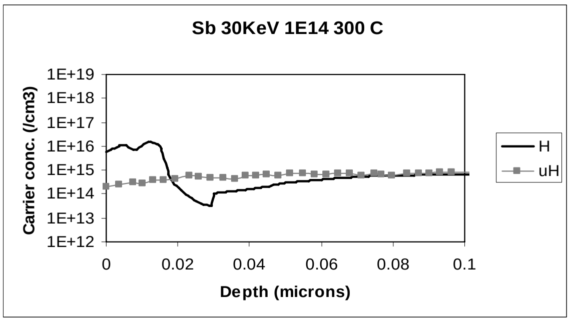
Fig. 2 shows the SRP data for the samples implanted with P at 10 keV, 1E14 cm^{-2} and annealed at 300 ^{o}C (A) and 400 ^{o}C (B). Also shown in (C), (D) are the corresponding SRP data for Sb-implanted samples. Greater dopant activation is seen in both the P and Sb implanted samples due to the hydrogenation treatment. The results the Sb samples annealed at 300 ^{o}C are particularly noteworthy because there is no dopant activation at all seen in the unhydrogenated sample, whereas it is clearly apparent in the hydrogenated samples.



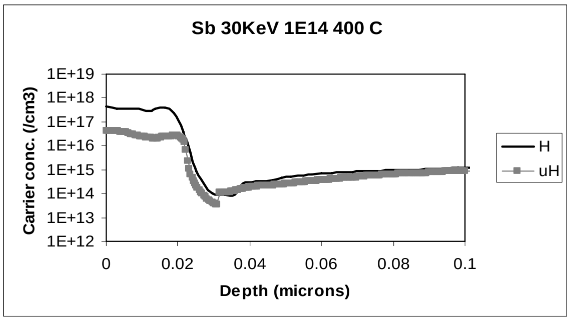
A



B



C



D

Fig. 2. SRP data for the phosphorus-implanted samples (10 keV, 1E14 cm^{-2}) and annealed at 300 ^{o}C, (A) & 400 ^{o}C (B), and the antimony-implanted samples (30 keV, 1E14 cm^{-2}) annealed at 300 ^{o}C (C) & 400 ^{o}C (D). H indicates hydrogenated samples and uH indicates samples that were not hydrogenated.

The enhancement in dopant activation was not seen in the P- and Sb-implanted samples at anneal temperatures > 500 ^{o}C . The Si-H bond breaks around 500 ^{o}C, and so most of the hydrogen would have diffused out of the Si. Since B and P/Sb are different dopant types, and each show activation enhancement, this rules out any effects due to dopant charge states. This also rules out any effects due to hydrogen thermal donors. B and P diffuse by an interstitialcy-assisted mechanism whereas Sb diffuses by a vacancy-assisted mechanism. However, activation enhancement is seen in all the cases. Hence, it is unlikely that the diffusion mechanism has any anything to do with the activation enhancement. Nor is it likely that the hydrogen interacts with the Si interstitials that cause TED and dopant deactivation in boron.

Additional results to be presented include SIMS data that reveal the absence of any dopant redistribution due to the hydrogen in the lattice, as well as Hall measurements to confirm that the SR changes arise principally from dopant activation, not due to reduced carrier scattering by hydrogen passivation of defects.

3. CONCLUSIONS

We have demonstrated that the presence of hydrogen in the lattice of crystalline Si causes an enhancement of dopant activation regardless of the implanted dopant type - B, P or Sb. The presence of hydrogen near a vacancy is theoretically known to reduce the energy barrier for a dopant to enter the vacancy site. This mechanism is believed to be the cause of the increased activation observed in hydrogenated samples. Further efforts are required to optimize the hydrogenation and annealing conditions, as well as gain a deeper understanding of the phenomenon.

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