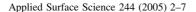
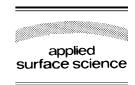


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Hydrogen and helium interactions in Si: phenomena obscure and not-so-obscure

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Abstract

The deliberate use of H- and He-related phenomena in crystalline Si (c-Si) has at times been hampered by concerns of the mobility of these light elements and hence potential device instability. However H is inevitably present in many Si processing steps, though not necessarily in the finished device. Accordingly one could differentiate between a transient or catalytic interaction of H with c-Si, and one where H resides permanently during device operation. We have uncovered phenomena on both domains, and these involve trapping and de-trapping of H by defective regions, thermal activation of latent defects in hydrogenated c-Si, and low-temperature activation of ion implanted dopant atoms. He differs from H principally by its electrical inactivity, but plays a significant role in altering the microstructure. The strong interaction of He with vacancy clusters results in nanocavities that act as excellent gettering sites and also enable localized minority carrier lifetime control. H and He thus offer possibilities for defect and impurity engineering in Si.

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1. Introduction

The influence of H and He on the electrical and structural properties of crystalline Si (c-Si) has been widely investigated over the years and a number of interesting phenomena uncovered in the process [1,2]. However, in contrast to its essential and accepted presence in amorphous Si and a somewhat lesser role

in polycrystalline Si, the application of H in conventional c-Si technology has been hampered by concerns of possible device instability due to migration of the hydrogen atoms. Nevertheless a number of applications are now well entrenched and a few others have emerged in recent years.

H is inevitably present in Si processing steps such as plasma etching/deposition, cleaning and surface passivation. The interaction of H with c-Si encompasses a variety of topics, such as dopant-hydrogen complexes [1], passivation of defects [3], hydrogen-

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induced defects [4], and enhancement of thermal donor (TD) formation [5]. Experimental observations and theoretical results in recent years have attested to its potential in improving gate oxide integrity with deuterium passivation [6] or high-temperature wafer anneal in H_2 [7], reducing post-implant dopant anneal temperature [8], and formation of deep junctions using hydrogen-enhanced TDs [9]. Yet another interesting use of hydrogen is in wafer splitting technologies [10]. In our own work, we have uncovered additional phenomena relating to trapping and de-trapping of H by defects, interaction with ion implantation damage, thermal activation of latent defects in hydrogenated c-Si, and evidence for hydrogen-promoted low-temperature activation of ion-implanted dopant atoms.

He differs from H principally by its electrical inactivity, but plays a significant role in altering the microstructure. The strong interaction between vacancy clusters and He results in nanocavities that are useful in gettering and localized minority carrier lifetime control. They also offer prospects in sensing and optoelectronics. Our recent efforts in this area have focused on generating multilayer nanocavities as well as controlling their nucleation and size with additional hydrogen plasma treatment.

In this paper, we will outline some of our results on H- and He-related phenomena with implications for defect and impurity engineering in Si. Hydrogen being electrically active, two distinguishing aspects of using hydrogen in Si are emphasized: (i) where the hydrogen is present transiently or catalytically in one or more of the processing steps, and (ii) where H is permanently ensconced as a passivant in the finished device. Ion implantation and electron cyclotron resonance (ECR) plasma are the typical techniques used to introduce the species into Si.

2. Hydrogen trapping and de-trapping in disordered regions in Si

This study follows the observation of extremely high Schottky barrier heights (>0.85 eV) in Al/p-Si Schottky contacts when the p-type Si sample was first damaged with an Ar implant prior to (low-energy) hydrogenation. Normally such high barriers on p-Si are seen only with exotic metals such as Ir that are not compatible with Si technology. Since acceptor

deactivation by B-H complex formation is a wellknown phenomenon [1], scanning the carrier concentration from the surface by capacitance-voltage (C-V) or spreading resistance (SR) measurement gives a signature of the H profile in the material. Fig. 1 shows such an SR profile for (a) hydrogenation only (from a 0.4 keV Kaufman source at 1 mA/cm², 10 min, no intentional substrate heating, with similar results for ECR H plasma), (b) 20 keV, 10^{13} cm⁻² Ar implant prior to hydrogenation, and (c) 20 keV, 10¹⁵ cm⁻² Ar implant prior to hydrogenation. Curve a displays the well-known H-induced deactivation of boron by over two orders of magnitude at depths of up to 6 µm from the surface. Under identical hydrogenation conditions, the p-Si sample that had earlier been implanted with Ar to a dose of $10^{13} \, \mathrm{cm}^{-2}$ displays considerably reduced depth as well as extent of deactivation (curve b). A much more drastic change is evident under a higher Ar dose of 10¹⁵ cm⁻² (curve c) - the change in carrier concentration due to hydrogenation is hardly noticeable here.

Further elucidation of the role of the Ar implanted (damaged) layer in inhibiting acceptor deactivation was obtained with SIMS profiling (H replaced with deuterium here for enhancing SIMS sensitivity). The SIMS data (not shown) confirms that the implantinduced disordered region - or any other type disordered region such as a poly-Si or amorphous Si thin film deposited on the c-Si surface – acts as a sink or sponge for atomic hydrogen, and prevents its further penetration into the bulk. This is contrary to the usual association of defects with enhanced impurity diffusion in semiconductors. A later study on passivation of fine-grain poly-Si by atomic hydrogen in fact confirms that the (disordered) grain boundary regions act as efficient traps for H rather than as paths for enhanced diffusion [11].

The implant-induced disordered region not only acts as a sink for H, but also as a *source* of *atomic* hydrogen if subsequently impelled by suitable thermal excitation. We discovered this while investigating the anomalous thermal anneal behavior of ion implanted and hydrogenated Si. With rapid thermal anneal of a sample such as that of Fig. 1(c), we found that the acceptor deactivation, so far inhibited by the implant damage at the surface, spreads further into the Si! This implies that the hydrogen impregnated in the damage region is by and large still in atomic form capable of

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