

Defect creation and passivation by hydrogen plasma in silicon and germanium

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The presence of hydrogen in semiconductors can strongly influence the formation of defects in group IV elemental semiconductors as silicon and germanium, and thus has an influence on the reliability of devices. Exposure of a material to hydrogen plasma is a very common method to introduce hydrogen.

In this work specific topics will be discussed related to defect creation and passivation by means of hydrogen plasma treatments both on Si and Ge.

A first example of defect creation in Si is the catalytic effect of hydrogen on the formation of oxygen thermal donors (OTDs), and thus an unexpected amount of additional donors can be formed during the processing of Si devices. Recently strong indications were obtained by means of Deep Level Transient Spectroscopy (DLTS) in combination with Capacitance Voltage profiling (CV) that hydrogen not only acts as a catalyst for the formation of OTDs but plays an active role in the formation of hydrogen related shallow thermal donors (STDs). In particular for short annealings at low temperatures, which are common in semiconductor technology, an unexpected increase in shallow donors was observed. To unambiguously link this observation to the creation of H-STDs samples were examined by means of far-infrared spectroscopy, which will be discussed here

Due to the fact that Si and Ge have similar properties, in general one would not expect qualitative differences in the behaviour of H between the two semiconductors. Also the chemistry of Si-H and Ge-H compounds is very similar. However Estreicher and Maric noted that whenever identical experiments involving H are performed on comparable Si and Ge samples, the results are very different, and thus one can conclude that qualitative differences do exist. Since one could expect from thermal effusion experiments that the incorporation of hydrogen in Ge seems to be more difficult, a more aggressive parallel-plate direct plasma system has been built and used to hydrogenate Ge.

Structural characterization of a Ge <100> wafer after hydrogenation allowed to distinguish defects which could be distinguished. As will be shown, close to the surface within the first 10nm, Ge-H bonds and H₂ molecules are observed by means of Raman spectroscopy. No

polarization sensitive measurements were performed, but the similar position and shape of the observed Raman peak comparing to the work of Hiller et al. allow to assign the vibrational modes to Ge-H bonds and H₂ within <111> platelets. The first micron was probed with TEM. Within this micron two regions could be distinguished. The first region until 70nm is heavily damaged and contains mostly <111> platelets. A second region (70 - 1100nm) contains plate-like cavity clusters oriented in <100> and <111> planes. The cavities inside are 2-5nm in diameter. Slow positron annihilation spectroscopy probes about the same region as examined by TEM. To first order the region with the defects observed can be approximated as 300nm thick. The positron signature corresponds with open volume defects of at least 3 vacancies. The S-parameter might be influenced by the presence of hydrogen, so the positrons possibly annihilate in the cavities observed by TEM. It may be emphasized that the depth of these structures is in good agreement with the one calculated from the size of the blisters. Infrared absorption spectroscopy in general measures the absorption integrated over the total sample thickness, but the disappearance of the bands after removal of approximately the first 2 micron demonstrates that the signal originates from this layer. It is shown that both the stretch and wag mode of Ge-H bonds in this region could be observed. The position of these bands is close to the frequencies calculated by Cardona.

Another interesting effect of hydrogenation with respect to applications is the possibility to passivate electrically active defects through binding with a hydrogen atom. In Si passivation of shallow dopants and of transition metal impurities by complex formation with hydrogen has been well established. As a last topic we will discuss the passivation of transition-metal impurities in Ge by means of direct-plasma treatments. The occurrence of defect complexes with hydrogen in Ge is known since the development of high purity Ge for radiation detector applications in the 1970's. This material is grown in a hydrogen containing atmosphere in order to suppress trapping, suggesting that deep traps become passivated by hydrogen. On the other hand, the neutral impurities Si, C and O become 'activated' and form shallow complexes such as (Si,H) and (C,H) acceptors and (O,H) donors, as was observed with Photo Thermal Ionization Spectroscopy by Haller et al. Also a deep level inducing severe trapping is formed by the V₂H complex. Partially passivated multivalent acceptors in Ge are very interesting since they remain experimentally accessible through their electronic level spectrum. The double acceptors Be and Zn become single acceptors (Be,H) and (Zn,H) with trigonal symmetry, through binding with a

hydrogen atom. Probably the most interesting case in the present context is passivation of the triple acceptor copper, which is presented in the next section. A simple model to explain passivation of multiple acceptors is that hydrogen is a single donor which is attracted by the negatively charged acceptor, forming a donor-acceptor pair. The acceptor multiplicity is then reduced with one unit for every hydrogen added. To study the passivation effect of plasma hydrogenation metal impurities, transition metal implanted Ge samples have been hydrogenated for 4h at 200°C. The most interesting observation by means of DLTS undoubtedly is the appearance of transition metal specific levels, which may be tentatively assigned to transition metal-hydrogen complexes. No obvious trend in the (metal,H) levels compared with the substitutional metals was observed, similar to the well-known case of Cu-passivation. Only for Cr a similar hierarchy of (Cr,H) with respect to Cr is observed as for (Cu,H) with respect to Cu. In both cases we are concerned with a triple acceptor + a donor level close to the valence band for the substitutional metal. Thus the metal specific levels in the Cr implanted hydrogenated specimen may be tentatively assigned to the Cr-H complex.