Abs. 1085, 206th Meeting, © 2004 The Electrochemical Society, Inc.

Thermal evolution of hydrogen related defects in silicon investigated by µ-Raman spectroscopy

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H-plasma treatment on Czochralski (Cz) silicon wafers creates lots of kinds of hydrogen related defects, such as Si-H bonds, H_2 molecules, and hydrogen induced platelets (HIPs). The Si-H bonds in silicon have been investigated for more than three decades. However, because of the various configurations of the Si-H bonds in the hydrogenated silicon substrate, the vibration spectra (such as IR or Raman spectra) related to the Si-H bonds are extremely complex and broad with tens of sub-peaks depending on the plasma conditions. Therefore, the decomposition of the Si-H bond related IR or Raman spectra can be somewhat problematic, and it is difficult to identify the respective sources of the various Si-H sub-peaks. H_2 molecules in hydrogenated Cz silicon have also been found in recent years. It is concluded that with high probability the H_2 molecules are trapped in the HIPs, which play an important role on the so-called "smart-cut®" technology. Recently, when applying Raman spectroscopy and scanning electron microscopy on the beveled surface of the hydrogenated Cz silicon wafers, a three-layer structure has been found and some of Si-H sub-peaks have been tentatively assigned [1]. Via combining the Raman spectra of the Si-H bonds and the H_2 molecules, as well as atomic force microscopy and cross-sectional transmission electron microscopy (XTEM) investigations on the post-hydrogenation annealed Cz silicon samples, the assignment of some other Si-H sub-peaks and the thermal evolution of the hydrogen related defects are reported and discussed in present publication.

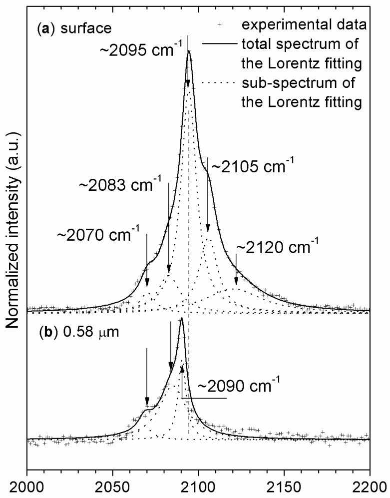

Fig. 1: Si-H bond Raman spectra on original surface (a) and beveled surface (b) of as plasma sample

Fig. 1 shows two Raman spectra of the as plasma treated samples. Spectrum (a) is measured on the original surface, while spectrum (b) is measured on the beveled surface where the corresponding depth is ~0.58 µm. Several sub-peaks at ~2070, ~2083, ~2095, ~2105, and ~2120 cm^{-1} are decomposed from the experimental data of the original surface based on the Lorentz fitting. The sub-peaks at ~2070 and ~2083 cm^{-1} can also be found on the Raman spectrum of the beveled surface. The former highest sub-peak at ~2095 cm^{-1} vanishes, while a new sub-peak at ~2090 cm^{-1} appears. Comparing these two spectra, one can conclude that the sub-peak at ~2095 cm^{-1} stems from the Si-H bonds at the hydrogen plasma damaged surface layer, which extends from the surface to a depth of ~0.2 µm [1]. The sub-peaks at ~2070 and ~2120 cm^{-1} are similar to the stretch mode frequencies of the monohydrogen-vacancy (VH) and the dihydrogen-vacancy (VH_2) complexes. Only the VH remains in the region of ~0.58µm, possibly because there are not enough hydrogen atoms. With high probability the somewhat hidden sub-peak at 2083 cm^{-1} is caused by the monohydride species (SiH) located at the inner surface of (111) HIPs, as reported by Higashi *et al.*

Considering the Si-H and H_2 Raman spectra of the sample with post-hydrogenation annealing at 450 °C (see Fig. 2), the source of the sub-peak at ~2105 cm^{-1} can also be clarified. As shown in the inset of Fig. 2, the annealing duration dependence of the integrated intensities of the sub-peak at ~2105 cm^{-1} is roughly proportional to that of the H_2 molecules. The correlation indicates that the ~2105 cm^{-1} and H_2 molecule related signals result from the same source. Furthermore, the frequency of ~2105 cm^{-1} is identical to the reported frequency of the dihydride species (SiH_2) on the (100) hydrogenated silicon surface. Thus, we assign this sub-peak to the SiH_2 located at the inner surface of the (100) HIPs.

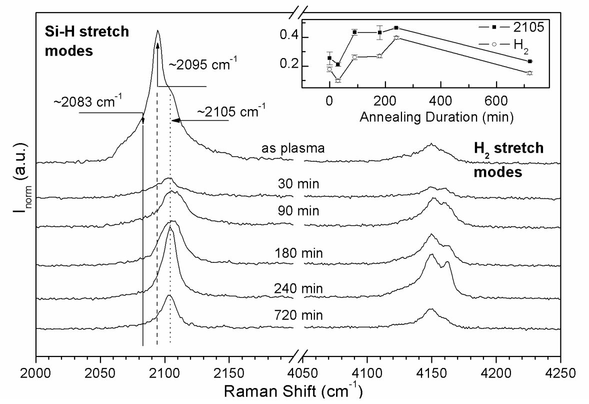

Fig. 2: Raman spectra of the samples with post-hydrogenation annealing. The inset shows the integrated intensities of the sub-peak at ~2105 cm^{-1} and of the H_2 molecules in dependence on the annealing duration

As shown in Fig. 2, the Si-H bonds at the damaged surface layer and on the inner surface of the (111) platelets dissociate more easily than the Si-H bonds on the inner surface of the (100) HIPs. Combined with the XTEM results (See Fig. 3(a) and (b)), we can conclude that when annealing, the (111) HIPs will gradually anneal out in such a way that they appear as "chains of dots", while the (100) HIPs trap more hydrogen atoms released from the damaged surface layer, so that the intensities of H_2 molecules and of the sub-peak at ~2105 cm^{-1} increase with the annealing duration up to 4 hours. However, when annealing duration reaches 12 hours, possibly due to the cracking of some of the (100) HIPs, the intensities of the Si-H bonds and the H_2 molecules decrease again.

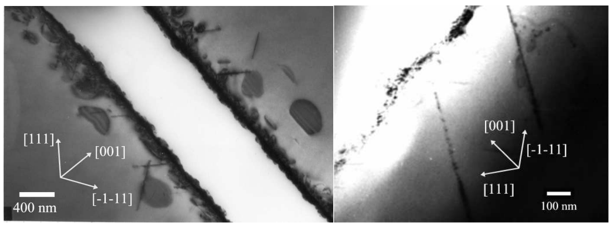

Fig. 3: XTEM graph of as plasma treated sample (a), and subsequent annealing at 550 °C for 20 minutes in air (b).

[1] Y. Ma, R. Job, Y. L. Huang, W. R. Fahrner, M. F. Beaufort, and J. F. Barbot, J. Electrochem. Soc. (accepted for publication).