Raman spectroscopy of monoatomic hydrogen at dislocations in silicon

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Abstract. A broad Raman peak at about 2000 cm⁻¹ was found in hydrogenated silicon foils with a regular dislocation network (DN) produced by silicon wafer bonding. It was not observed in the reference foils without a dislocation network. The hydrogenation was performed from acid water solution at room temperature. The peak was ascribed to monoatomic hydrogen in silicon bond centered position that became stable in a close vicinity to the dislocation cores in opposite to the case of the regular lattice where its molecular form is energetically favorable.

1. Introduction

Hydrogen (H) when introduced in crystalline silicon interacts effectively with various lattice defects. Such interaction results in the formation of H-defect complexes that change electric properties of the defects giving rise in many cases to a reduction of their recombination activity. The latter is known as hydrogen passivation of recombination active defects and widely used now to improve the efficiency of multi-crystalline silicon (mc-Si) solar cells in photovoltaic industry.

The most powerful techniques to identify H configuration in silicon by its vibrational mode energy are infrared absorption and Raman spectroscopies. In regular Si lattice the configuration of interstitial hydrogen H which is stable at room temperature is the molecule H₂ centered in T–site giving rise to a Raman peak at about 3600 cm⁻¹ [1,2]. According to the theoretical calculations, T-site H₂ configuration has significantly lower energy than the monoatomic one. The configuration of monoatomic H is in the center of Si-Si bonds (BC–site) that gives rise to the appearance of Si bond stretch mode in the vicinity of 2000 cm⁻¹ (f.i. 1980 cm⁻¹ for positive H⁺ [3–6]). It is metastable and was observed only in proton irradiated silicon at liquid helium temperature and disappeared above 200 K.

Vibration modes of H in complexes with vacancies or impurities lyse also in the region close to monoatomic H (1800-2200 cm⁻¹ [3,7,8]) as well as with the silicon surface states and with grain boundaries of unknown structure in mc-Si (2000-2100 cm⁻¹ [9,10]).

Previous experiments on H exo-diffusion from silicon and SIMS showed that hydrogen attracted by and accumulated at dislocations [11,12]. There are theoretical calculations of the stable configurations of H within a dislocation core [13,14] or at its vicinity [15]. In particular, it was predicted that in a close vicinity of a screw dislocation the H monoatomic configuration became more preferable that the molecular one. However, until now to the best of our knowledge there were no reports about successful measurements of vibration modes of hydrogen at dislocations.

In this work we investigated Raman spectroscopy of silicon foils prepared for transmission electron microscopy (TEM) investigations with a buried regular dislocation network (DN) that were
hydrogenated by wet-chemical etching (WCE). The combination of a high DN density and the reduction of the background signal from the bulk allowed us to detect a Raman peak (at 2000 cm$^{-1}$, FWHM $\sim$ 90 cm$^{-1}$) corresponding to the vibrational mode of monoatomic hydrogen both in p- and in n-type samples. The comparison of TEM images with the Raman signal spatial distribution revealed that the detected Raman peak is confined at DN and can be identified as a H-dislocation complex confirming the prediction of the theory [15].

2. Experimental
The samples were cut from hydrophilically bonded (100) Cz-Si doped with boron to about 10$^{15}$ cm$^{-3}$ or with phosphorus to 3$\times$10$^{14}$ cm$^{-3}$. DN was located at the depth of 160-180 nm from the surface. DN consisted of a square network of screw dislocations ($\sim$5-10 nm mesh) and rows of 60$^\circ$ dislocations (with an inter-dislocation distance of $\sim$60 nm). The detailed information about the dislocation structure obtained with TEM, electrical levels and hydrogen out-drift processed was reported earlier and can be found elsewhere [16,17].

For Raman spectroscopy we used a thin plan view of TEM foils that enabled us to reduce drastically the background Raman signal. The foils were formed by conventional WCE (7:1 HNO$_3$:HF) that produces a beveled edge of the sample near the hole in their middle as well as the sample hydrogenation. The dislocated/reference foils were obtained by etching of back/front sides of the bonded wafers. The foils had a standard TEM diameter of 3 mm with a hole in the middle. After the TEM foils preparation, the foils were kept in the air for more than one month that was sufficient to diminish the Raman signal from hydrogen on the surface [18].

Raman spectroscopy was carried out by a Senterra unit with backscattering geometry at room temperature in the air using a 532 nm Nd laser for excitation as it is schematically shown in figure 1. One can easily recognize from figure 1 that there is a region of the foil at its internal edge where DN is absent. The lateral size of the dislocation-free region is as long as 20 micrometers that exceeds well the laser beam diameter of 6-7 um. That makes possible to acquire Raman spectra both from dislocation-free and from dislocation-rich regions of the sample. The exact position of the intersection of DN with the sample surface was obtained from TEM investigations. For this goal, a sequence of multiple TEM images with a sufficiently high magnification was obtained with a Zeiss-Libra 200 FE and they were then mated all together.

Figure 1. Schematic diagram of Raman spectroscopy measurements of a TEM foil with a dislocation network.

3. Results and discussion
The broad Raman peak in the vicinity of 2000 cm$^{-1}$ with a full width at half maximum (FWHM) of about 90 cm$^{-1}$ was observed both in p- and n-type foils in the region which contains DN (see in figure 2 (a)). As it was mentioned in Introduction, the position of the peak corresponds to the spectral range of the stretched mode of atomic hydrogen in BC-site. The peak was not observed in bulk samples, in dislocation-free reference foils prepared together with dislocated ones as well as under excitation of dislocation-free part of the foils as it is illustrated in figure 2 (b).
One should firstly note that the dependences of the Raman peak intensity on the distance from the foil edge presented in figure 2b and figure 3 exhibit oscillations which are caused by the phenomenon of light interference in thin films and so will not be further discussed in details.

The intensity profiles of the 2000 cm\(^{-1}\) Raman peak presented in figure 2b and 3 can be divided into several parts. The first one is near the foil edge at the central hole where the Raman peak of 2000 cm\(^{-1}\) was absent while the signal of optical phonon mode of Si at 520 cm\(^{-1}\) [19] was already present (figure 3). The second part is characterized by a surge of the 2000 cm\(^{-1}\) peak intensity at the distance from the hole edge where DN intersects the foil surface. With moving further away from the foil edge, the intensity of the 2000 cm\(^{-1}\) Raman peak decreases but the intensity of the 520 cm\(^{-1}\) peak continues to increase with the distance. The increase of the silicon-lattice-related signal is obviously due to increase of the generation volume with the foil thickness whereas the decrease of the hydrogen-related signal is due to increase of the optical path length towards and from the DN plane that increases the light absorption. The theoretical curve of Raman signal profile calculated taking into account the excitation laser light absorption is down as the black dotted line in figure 3. The impact of the light absorption can be also noted from the examination of Raman profiles in figure 3 as a reduction of the interference oscillation amplitude at their most remote parts.

Figure 4 represents the results of thermal treatment of a p-type sample at a pressure of 10\(^{-5}\) Torr for one hour. The intensity of the hydrogen-related signal reduced upon annealing already at 150°C but it is still present even after the treatment at temperature as high as 500°C. This indicates the variety of binding strengths of hydrogen with the lattice. The thermal stability of the peak at 500°C is in
accordance with previous data of exo-diffusion experiments that have shown not complete removal of hydrogen from dislocated silicon at this temperature [11].

Figure 3. The intensity of the 2000 cm\(^{-1}\) peak as a function on the distance from the inner edge of the foil compared to the optical-phonon mode of Si 520 cm\(^{-1}\). The dotted line shows the theoretical curve calculated with corrections for excitation laser beam width and light absorption.

Figure 4. Raman spectra in a p-type bonded sample before and after annealing at different temperatures for one hour in vacuum (10\(^{-5}\) Torr).

4. Conclusion
In our work we provide first observation of a monatomic hydrogen-related Raman peak at 2000 cm\(^{-1}\) at dislocations, using a TEM foil of bonded silicon wafer with well defined DN. We suggest that the origins of the Raman peak at 2000 cm\(^{-1}\) can be attributed to the stable BC-site Si-H configuration in the region close to the dislocation core. The observation of the stable signal corresponding to the silicon bond stretch mode of hydrogen in BC site confirms qualitatively recent results of theoretical calculations [14,15] predicting an increase of the binding energy of hydrogen in BC-Si atomic configuration in a close vicinity of the screw dislocation core due to lattice distortion. Temperature behavior of the peak height upon annealing and its broadness can be associated then with the variation of the binding energy for hydrogen in BC with the distance from the dislocation core.

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