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TRANSFORMATION OF STRUCTURAL DEFECTS AND THE HYDROGEN STATE UPON HEAT TREATMENT OF HYDROGENATED SILICON

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Transformations of structural defects, the hydrogen state, and electrophysical properties of silicon treated in hydrogen plasma are studied. Treatment in plasma (150°C) produces bands in Raman spectra at 2095 and 2129 cm^{-1} that are associated with scattering by Si–H vibrations. Subsequent heat treatment (275°C) causes a band for gaseous molecular H_2 to appear at 4153 cm^{-1}. A comparison of Raman spectra and scanning probe microscopy results shows that hydrogenation forms defects (platelets) of average size 43 nm and surface density $6.5 \cdot 10^9$ cm^{-2} that are due to precipitation of H_2 and formation of Si–H bonds. Inclusions of average size 115 nm and surface density $1.7 \cdot 10^9$ cm^{-2} that are filled with molecular H_2 are observed after heat treatment. The concentration of free charge carriers remains constant after treatment in plasma and subsequent heat treatment.

Keywords: *epitaxial silicon, hydrogen plasma, Raman scattering, scanning probe microscope, Hall effect.*

Introduction. Hydrogen (H_2) in silicon (Si) is an important technological dopant that affects its optical and electrical properties [1]. H_2 can passivate electrically active dopants and recombination impurities [1] or activate neutral ones such as oxygen, which enhances oxygen-related thermal donor (OTD) formation [2, 3], because of its high chemical reactivity and mobility. According to the literature [4], exposure to H_2 plasma and subsequent heat treatment can lead to hydrogen thermal donor (HTD) formation. HTDs were reported to form after implantation of hydrogen ions in Si and SiGe solid solutions [5–8]. Passivation and formation of electrically active centers during exposure to H_2 plasma was associated with structural defect (platelet) formation due to H_2 precipitation during plasma exposure and Si–H bond formation [9, 10]. Information about further development of structural defects initiated by hydrogen are contradictory. According to some researchers [10], further development starts at ~600°C. Conversely, a band at 3601 cm^{-1} in Raman spectra after plasma exposure at ≤150°C was assigned to vibrations of H_2 located near a tetragonal site in the Si lattice [11, 12]. A band at 4157 cm^{-1} characteristic of gaseous H_2 was observed at >150°C. These effects were explained by capture of diffusing H_2 in platelets and gaseous H_2 formation in them [11, 12].

The present work studied transformations of structural defects and Si–H_x complexes formed in Si by exposure to H_2 plasma and then heat treatment and their effects on the electrical and optical properties of hydrogenated Si.

Experimental. Epitaxial structures n-Si/p^+-Si were exposed to H_2 plasma in the work. The structures were grown in Si substrates (<111> orientation, 510–540-μm thick). The epitaxial layer (55.2–64.8 μm) was doped with phosphorus (ρ = 1 Ω·cm). Structures were exposed to high-frequency (13.5 MHz, 50 W) H_2 plasma for up to 10 h at 150°C.

Raman spectra were recorded at room temperature using a Nanofinder® HE micro-Raman spectrometer of 0.3 cm^{-1} resolution fitted with a back-scattering 3*D*-scanning confocal microscope. Power of 2 mW was directed at the sample. The exciting beam had a diameter of ~1 μm. A solid-state laser with 532-nm radiation was used for excitation.

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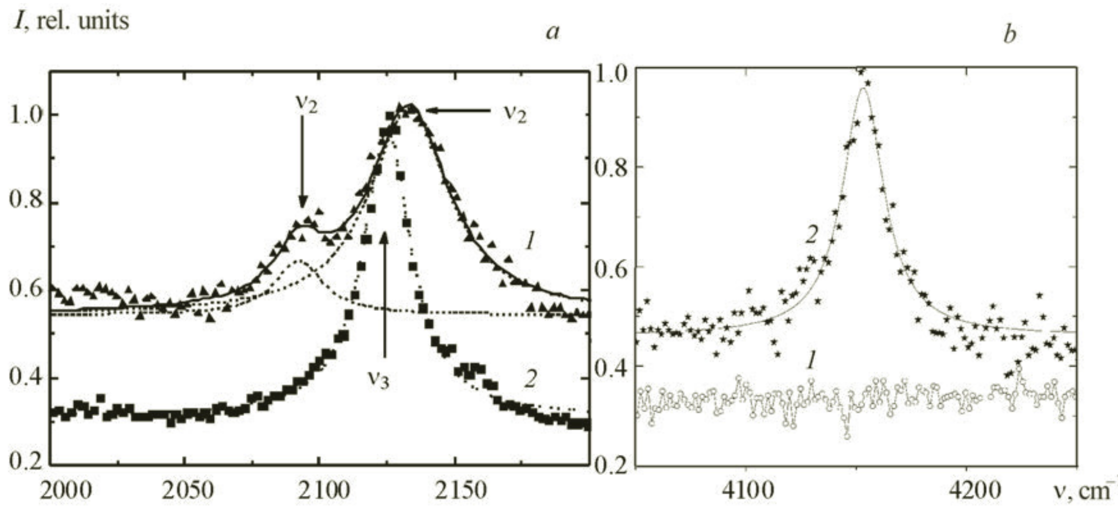

Fig. 1. Experimental Raman spectra in different frequency ranges of samples treated in H plasma (1) and subsequently annealed at 275°C for 20 min (2); dashed line, deconvolution of spectra into elementary Lorentzian oscillators.

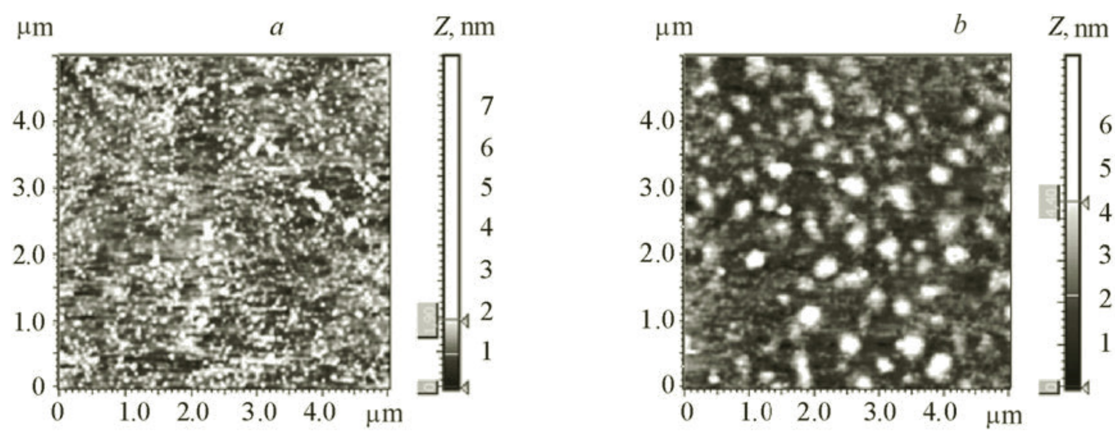

Fig. 2. Surface morphology of hydrogenated silicon before (a) and after (b) heat treatment at 275°C for 20 min.

Resistance and the Hall effect were measured using an HEMS high field measurement system (Cryogenic Ltd., London) that allowed the sample temperature to be held at 2–300 K with 0.05 K accuracy. A Keithley 6430 source/meter and Keithley 2821*A* nanovoltmeter were used as the source and meter of DC and potential.

Surface morphology was studied using a Solver nano scanning probe microscope (SPM) (NT-MDT) in semi-contact mode.

Results and Discussion. *Evolution of Raman spectra.* Figure 1 shows Raman spectra of samples after exposure to H_2 plasma and subsequent annealing at 275°C for 20 min. Plasma exposure produced two overlapping bands with maxima at 2095 (ν_2) and 2129 cm^{-1} (ν_1). These bands disappeared and a narrow band with a maximum at 2125 cm^{-1} (ν_3) appeared after annealing at 275°C for 20 min. The observed bands corresponded to various Si–H vibrations (Si–H_x, where x = 1–4) localized on platelets [10, 12]. Furthermore, subsequent heat treatment produced a new band at 4153 cm^{-1} in the Raman spectrum (Fig. 1b) that was reported to correspond to vibrations of isolated gaseous H_2 [11, 12].

Surface morphology. Sample surface morphologies were measured to establish the relationship between thermal evolution of hydrogen defects and transformation of structural defects. Figure 2a shows the surface morphology of Si after exposure to plasma. The surface was characterized by highly concentrated fine inhomogeneities. Computer processing found that 1618 inhomogeneities were detected in an arbitrarily selected 5 × 5-μm section of the sample (surface density

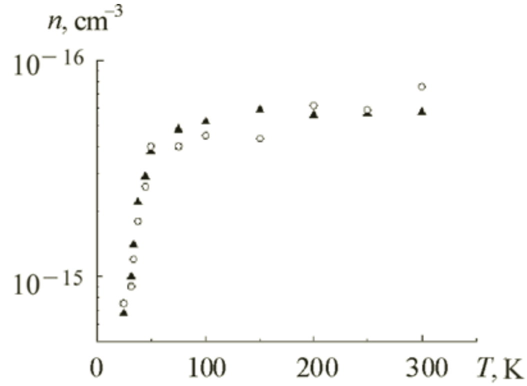

Fig. 3. Temperature dependences of charge carrier concentration in silicon samples after hydrogenation without (▲) and with subsequent heat treatment (○).

$6.5 \cdot 10^9$ cm^{-2}), the average size of which was 43 nm. The surface roughness was 1.1 nm. Heat treatment at 275°C changed considerably the surface morphology (Fig. 2b). The inhomogeneity diameter increased to an average of 115 nm. The surface density decreased to $1.7 \cdot 10^9$ cm^{-2}. The surface roughness about doubled.

The Raman and SPM results led to the conclusion that the inhomogeneities observed in Fig. 2a were platelets due to slippage of Si–H_x bonds [7–9]; the inhomogeneities in Fig. 2b, vacancies filled with gaseous molecular H_2.

Temperature dependences of electron concentrations. Figure 3 shows temperature dependences of electron concentration at 20–300 K from Hall-effect potentials for Si samples after exposure to plasma and subsequent heat treatment. Data analysis showed that the electron concentration of $\sim 6 \cdot 10^{15}$ cm^{-3} near an impurity-depleted region corresponded to the initial donor concentration. Therefore, hydrogenation and heat treatment of Si under these conditions did not passivate the impurities and form hydrogen donors.

Conclusions. A comparison of Raman spectra and SPM results showed that Si exposed to H_2 plasma (150°C) formed inhomogeneities (platelets) due to H_2 precipitation and Si–H_x (where $x = 1$–4) bond formation. This was consistent with known Raman bands at ~2000 cm^{-1}. Addition heat treatment of the samples at 275°C formed platelets and larger inhomogeneities. A band at 4153 cm^{-1} for molecular H_2 vibrations appeared in the Raman spectrum. Therefore, high-temperature annealing formed Si voids in the lattice that were filled with gaseous H_2. Transformations of structural defects and hydrogen centers (aggregates of Si–H_x complexes) did not affect the concentration of fundamental charge carriers.

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