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Crystallization of hydrogenated amorphous-nanocrystalline silicon films under high-pressure annealing

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Crystallization of the hydrogen ion implanted silicon-on-insulator (SOI) layers under conditions of high-pressure (10.5 kbar) annealing at the temperature T_a = 450-1000 °C was investigated by Raman spectroscopy. The as-implanted films had composite structure consisted of the Si nanocrystals surrounded by the hydrogenated amorphous silicon. The retardation of hydrogenated Si crystallization was obtained under high-pressure annealing at the temperature higher than 600 °C. The SOI layers remained to be nanocrystalline up to the annealing temperature of 1000 °C. The average size of the nanocrystals and the crystalline volume fraction were estimated from the Raman spectra as a function of the annealing temperature. The origin of the pressure effect on the crystallization of hydrogenated silicon is discussed.

1 Introduction The hydrogenated silicon nanocrystals have attracted much attention because of their practical application and unique fundamental properties. Nanocrystalline silicon (nc-Si) is a very promising material for thin film solar cells [1]. In comparison with the amorphous silicon, nc-Si is more stable under light irradiation and possesses the higher carrier mobility. Their optical properties depend on the nanocrystalline fraction, nanocrystal size, grain boundary region and the interface quality. It is known, that hydrogen passivates the dangling bonds and reduces the surface recombination centres in the bulk silicon [2]. According to some of suppositions [3], the hydrogen termination on the Si nanocrystal surface forms abrupt potential barrier for exciton. It makes the H terminated nc-Si a good model system to understand the fundamental properties of zero-dimensional indirect-gap semiconductors. However, it is well-known that at the temperatures above 350 °C the hydrogen is no longer in a condensed state, but rather forms mobile dimers (i.e. H_2 molecules). In turn, the hydrogen dimers migrate to the microvoids formed in the H^+ ion implanted silicon, and form there the hydrogen bubbles. As result, the hydrogen gas pressure in a microvoid increases and reaches eventually a critical value P_c = 5-6 kbar [4]. As the critical pressure is achieved, the bubbles burst, and hydrogen gas leaves the silicon bulk. Under normal conditions, this process occurs at the temperature higher than 500 °C. An increase in the hydrostatic pressure of the annealing ambient above a certain critical value $P > P_{cr}$ may suppress the bubble formation in thin near-surface region [5]. Therefore, in this paper, we investigated the effect of the hydrostatic pressure annealing on the crystallization of thin silicon films implanted with high doses of hydrogen ions.

2 Methods SOI structures with the 280 nm thick top silicon layer and the 400 nm thick buried SiO_2 were implanted with hydrogen ions at an energy of 24 keV to dose of 5×10^{17} cm^{-2}. According to TRIM calculations, the implantation parameters produced Gaussian-like H concentration-depth profiles with the peak concentration of about 50

at.% at a depth of about 340 nm below the top surface. Subsequent annealing was carried out at the temperatures ranging from 450 to 1000 °C for 1 hour in an Ar ambient. Annealing was carried out under hydrostatic compression at the pressure of 10.5 kbar. Details of the annealing technique are given elsewhere [6]. Raman spectroscopy was employed to study the properties of the produced structures. Raman measurements were performed using a Horiba Jobin Yvon spectrometer having a triple monochromator with the spectral resolution of about 2 cm^{-1}. The probing beam diameter was about 6-8 μm. The emission power on the sample surface was about 2-3 mW. In order to suppress a signal from the silicon substrate Raman measurements were carried out in a backscattering geometry (⟨011⟩, ⟨011⟩) using 514.5 nm Ar laser excitation. Photoluminescence spectra were excited by the 514.5 nm wavelength of an Ar laser and registered at room temperature.

3 Results and discussion Figure 1a shows Raman spectra plotted in the 440-530 cm^{-1} wavenumber range both from the as-implanted SOI layers and from the samples annealed at the temperatures of 450-800 °C under pressure of 10.5 kbar. Figure 1b shows the respective spectra obtained from the samples annealed at the temperature of 900-1000 °C as well as from the crystalline silicon. In order to analyze quantitatively the phonon modes, the experimental spectra were fitted by multiple Gauss or Lorentz functions. Spectrum measured from the as-implanted sample showed a broad peak located at 472 cm^{-1} corresponding to TO phonon mode in hydrogenated amorphous silicon [7]. As annealing temperature increased, the intensity of the peak connected with the amorphous phase dropped and after annealing at the temperature of 1000 °C, this peak disappeared completely. Along with the broad amorphous Si peak, a low-intensity shoulder near 513 cm^{-1} was seen. Under annealing, the shoulder transformed to strongly pronounced peak and its maxima position shifted to 517.4 cm^{-1}. The origin of this peak is associated with the optical phonons localized in silicon nanocrystals [8]. As annealing temperature increased to 700 °C, this peak position shifted to 519.5 nm. Further increase in the temperature up to 1000 °C kept the crystalline peak position invariable. These results differ from the data obtained after annealing at the atmospheric pressure [9]. Table 1 shows the peak position and FWHM corresponding to the phonon mode localized in the crystalline phase of the samples annealed both under high-pressure and atmospheric conditions. In the case of the atmospheric conditions, the high-temperature annealing was accompanied by the appearance of the Raman peak of 520.4 cm^{-1} corresponding to optical phonon mode in the crystalline silicon.

The Raman shift due to the confinement effect in the sphere-shaped Si nanocrystals can be described by a phenomenological expression [10]:

$$\Delta\omega = \omega_{Si} - \omega_{nc} = A(a/D_{nc})^{\gamma}, \quad (1)$$

where a =0.543 nm is the lattice constant of silicon, D_{nc} is the nanocrystal diameter, ω_{Si} is the frequency of the optical phonon in monocrystalline bulk silicon, ω_{nc} is the frequency of the optical phonon in a nanocrystal with the size D_{nc}, A = 47.41 cm^{-1} and γ = 1.44 are the parameters used to describe the vibrational confinement due to the finite size of the nanocrystals. The respective nanocrystal diameters obtained with the expression (1) are presented in Table 1.

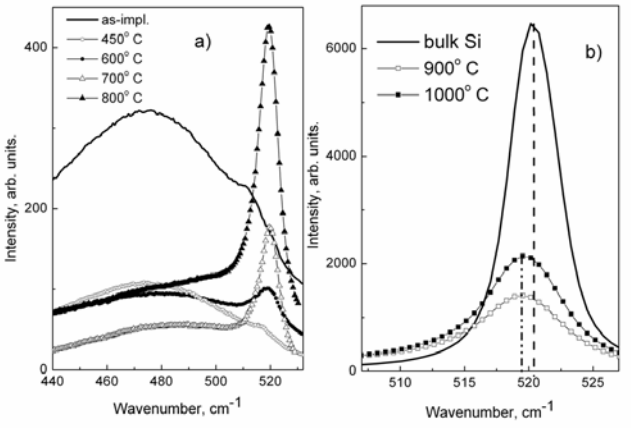

Figure 1 Raman spectra from the SOI layers implanted with hydrogen ions at an energy of 24 keV to dose of 5×10^{17} cm^{-2} before and after annealing at the temperature of 450-1000 °C under hydrostatic pressure 10.5 kbar.

So, we have obtained that the high-dose hydrogen ion implanted silicon layer has two-phase structure. Quantitative characterization of the measured Raman spectra allows to determine both the amorphous (a) and crystalline (c) volume fraction. For example, the crystalline fraction ρ_c can be expressed by [11]

$$\rho_c = I_c/(I_c + yI_a), \quad (2)$$

in which I is the respective integrated scattered intensity, $y=\Sigma_c/\Sigma_a$, where Σ is the respective integrated backscattering cross section over the measured frequency range. The integrated Raman cross section of the TO mode is changing as a function of the crystalline size D_{nc} [11]:

$$y = 0.1 + \exp(-D_{nc}/25), \quad (3)$$

where D_{nc} is the nanocrystal diameter expressed in nanometers. Using the results presented in Table 1 and expressions (2)-(3), we estimated the crystalline volume fraction as a function of the annealing temperature under atmospheric and high-pressure conditions. These results are shown in Fig. 2a. As follows from Fig. 2a, the crystalline volume fraction obtained from the layers annealed under pressure is 30-50% lower than that obtained after the atmospheric pressure anneals. In other words, hydrostatic compression employed during annealing results in the retardation of the crystallization process. The suppression of the critical pressure within the hydrogen bubbles may be a possible reason of this effect. It provides the confinement

of hydrogen within the silicon bulk at the temperature higher than that corresponding to hydrogen out-diffusion from the silicon under normal conditions.

Figure 2b shows PL spectra recorded at room temperature from the as-implanted samples and those from ones annealed under hydrostatic pressure at the temperature of 450 and 600 °C. The high-intensity PL peak around 750 nm (1.64 eV) was observed for the as-implanted SOI film. Its FWHM was about 0.3 eV. Annealing at the temperature of 450 °C resulted in a decrease of the PL intensity by the factor of 5. The energy peak position was practically invariable. Further increase in annealing temperature to 600 °C extinguished the PL completely. The quantum confinement energy obtained from the PL peak position corresponds to the nanocrystals with the average diameter of (2.0-2.5)±0.2 nm. That is in good agreement with the nanocrystal size estimated from the localized optical phonon frequency.

Table 1 TO phonon mode frequency, Raman peak FWHM, and the nanocrystal diameter obtained from the H^+ ion implanted SOI layers after high-pressure and atmospheric pressure anneals.

T_a (°C)	P=10.5 kbar			P=1 bar		
	ω_{nc} (cm^{-1})	FWHM (cm^{-1})	D_{nc} (nm)	ω_{nc} (cm^{-1})	FWHM (cm^{-1})	D_{nc} (nm)
Bulk Si	520.4	4.0		520.4	4.0	
As-impl.	513.4	10.1	2.0	513.4	10.1	2.0
200				515.4	12.3	2.4
300				515.1	11.8	2.3
450	517.4	8.5	3.2			
600	518.6	9.4	4.5	518.0	9.4	3.8
700	519.5	8.6	7.0	519.6	9.2	7.5
800	519.1	8.7	5.4	520.2	7.3	bulk Si
900	519.3	7.3	6.0	520.3	5.4	bulk Si
1000	519.5	6.9	7.0	520.3	5.9	bulk Si

4 Conclusion The two phase Si layers consisted of the nanocrystalline and amorphous silicon were formed as result of the hydrogen ion implantation into SOI structures. Crystallization of the hydrogenated Si films was investigated as a function of annealing temperature under conditions of high-pressure compression. It was observed that crystallization of hydrogenated Si slows down under high-pressure annealing in comparison with that at the atmospheric pressure annealing. The SOI layers remain to be the nanocrystalline up to the annealing temperature of 1000 °C. The average size of the nanocrystals obtained from the shift of the transverse optical phonon frequency ranged from 3 to 7 nm as annealing temperature grew from 450 to 1000 °C, respectively. The crystalline volume fraction obtained from the layers annealed under high pressure was 30-50% lower than that observed from the respective samples annealed at the atmospheric pressure. The origin of the pressure effect on crystallization of hydrogenated silicon is ascribed to the compensation of the critical pressure within the hydrogen bubbles.

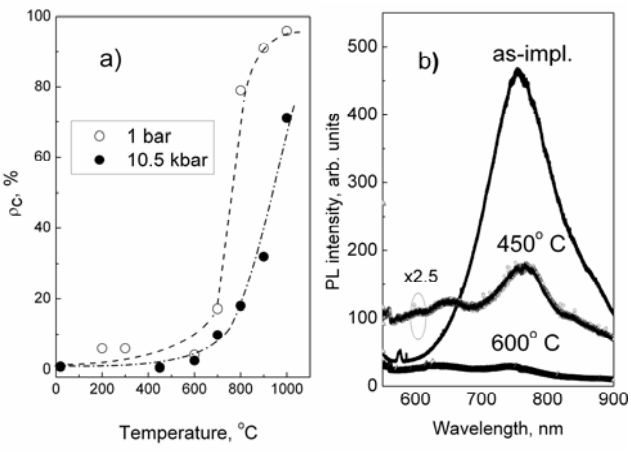

Figure 2 (a) The crystalline volume fraction as a function of the annealing temperature in the hydrogen ion implanted samples treated at the atmospheric pressure and under hydrostatic compression at the pressure 10.5 kbar. (b) PL spectra of the hydrogen ion-implanted SOI layers before and after subsequent annealing under pressure 10.5 kbar at the temperature of 450 and 600 °C.

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