

INVESTIGATION OF DEFECT FORMATION IN SILICON DOPED WITH SILVER AND GADOLINIUM IMPURITIES BY RAMAN SCATTERING SPECTROSCOPY[†]

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Silicon doped with gadolinium and silver impurities were studied using a Renishaw InVia Raman spectrometer. Registration and identification of both crystalline and amorphous phase components in the samples was carried out. Some changes are observed in the Raman spectra of gadolinium-doped silicon samples compared to the initial sample. It has been experimentally found that an increase in the silver impurity concentration in gadolinium-doped silicon leads to a smoothing of the Raman spectrum, which indicates the formation of a more perfect crystal structure.

Keywords: Silicon, Gadolinium, Silver, Raman spectrum, Doping, Complex defects

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INTRODUCTION

In recent years, silicon structures have been actively studied both theoretically and experimentally in order to realize their possible applications. Structured silicon is currently of great interest, since silicon itself is an extremely promising material not only for electronics, but also for optoelectronics and solar cells [1-3].

For many years, Raman scattering has become a standard tool for studying the structure of silicon crystal [4-7]. Raman scattering studies of materials give us information about energy dispersion, structure, bonds, and defects. The analysis of structures is usually based on the phonon confinement model, in which the finite size of crystallites is taken into account by estimating the efficiency of phonon scattering. Constraint effects in structures lead to modification of the electronic, optical, and vibrational properties. It should be noted that while the Raman spectrum of crystalline silicon has been sufficiently well studied, the Raman spectra of silicon doped with transition and rare earth metals have not yet been studied in full.

In this paper, we present the spectra of one- and two-phonon Raman scattering of light from single-crystal silicon doped with Ag and Gd atoms.

EXPERIMENTAL PART

Samples of n-Si and p-Si with initial resistivity from 1 to 100 Ohm·cm were chosen for the study. Doping of the samples with Ag and Gd impurities was carried out sequentially by the thermal diffusion method. Before doping, the samples were subjected to chemical cleaning and etching, while the oxide layers were removed from the surface of the samples using an HF solution. After thermal degassing of the samples, films of high-purity gadolinium and silver impurities (99.999%) were deposited on clean Si surfaces using vacuum deposition. Vacuum conditions in the volume of the working chamber of the order of 10^{-6} - 10^{-7} Torr were provided by an oil-free vacuum pumping system.

Before diffusion annealing, the samples were placed in evacuated quartz ampoules. The diffusion of Ag impurities into the Si volume was provided by heating the deposited samples in a diffusion furnace at a temperature of 1100°C, with a heating duration of 7-10 hours, followed by rapid cooling. To study the interaction of impurity atoms in silicon, it is necessary not only to uniformly dope the material, but also to maximize the concentration. In this regard, we not only took into account the mechanisms of diffusion and solubility in more detail, but also the optimal conditions for doping silicon with these impurity atoms.

Doped silicon samples were studied using a Renishaw InVia Raman spectrometer equipped with a confocal microscope. The Raman spectra were excited by a laser with a wavelength of 785 nm. The spectral resolution was ≤ 0.5 cm⁻¹ in the visible region. Brightness > 30% provided high resolution with maximum stability. Measurement reproducibility ≤ 0.1 cm⁻¹. The measurements used a diffraction grating with 1200 lines/mm and a standard Renishaw CCD detector. The laser power was varied to provide optimal experimental conditions. The minimum power at which the signal could be measured was limited by the signal-to-noise resolution of the detector in the spectrometer. A×50 lens was used. The exposure time was 10 s, the diameter of the laser spot on the sample was 10 μm. All measurements were carried out at room temperature in ambient atmosphere.

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RESULTS AND THEIR DISCUSSION

Under normal conditions (standard pressure and temperature), silicon crystallizes into the diamond lattice structure. The diamond structure of silicon allows the presence of only one Raman active phonon of the first order, located at the center of the Brillouin zone (BZ), which corresponds to a phonon wave vector of $520.0 \pm 1.0 \text{ cm}^{-1}$ with a full width at half maximum (FWHM) of 3.5 cm^{-1} .

The Raman spectra of an n-type silicon sample doped with Gd and Ag impurity atoms are shown in Fig. 1a. The Raman spectrum of Si<Gd> samples show a high peak in the region of $521\text{-}522 \text{ cm}^{-1}$. Intensity of first-order scattering due to optical phonons (TO - transverse optical vibrations, LO - longitudinal optical vibrations) at the central point Γ of the Brillouin zone (BZ).

In the Raman spectrum of Si<Ag> samples, a gentle slope of the main Si peak on the left wing in the region at $303\text{-}489 \text{ cm}^{-1}$ (Fig. 1b) is observed. It indicates the presence of an Ag-O type bond vibration [7]. The authors of [8] in this region observed modes at $302, 379, 429, 467,$ and 487 cm^{-1} associated with Raman vibrations of Ag-O. The violation of the symmetry of the peak at 521 cm^{-1} of the Raman spectrum at $1100 \text{ }^\circ\text{C}$ is associated with the formation of interstitial defects, since in the silicon lattice at this temperature an intense precipitation of free interstitial oxygen is observed [9]. As is known, the precipitates of the first phase of SiO_2 have a strong bond, and the concentration of Ag-O complexes under such a diffusion regime was insufficient for detection in the Raman spectrum.

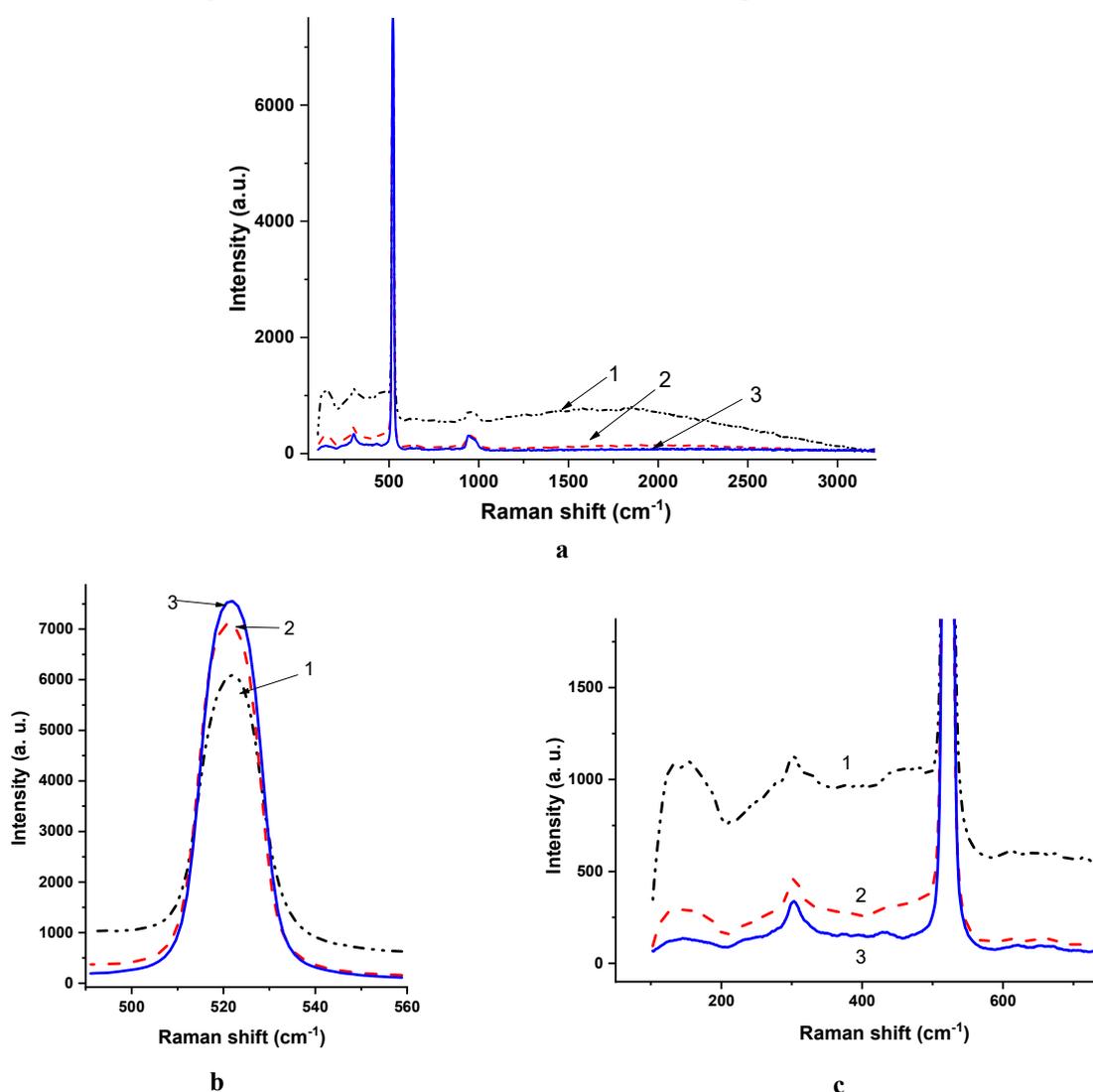


Figure 1. Raman spectrum of n-type silicon doped with Gd and Ag impurities: 1- Raman spectrum of Si<Gd> samples, 2- Raman spectrum of Si<Ag> samples, 3- Raman spectrum of Si<Gd, Ag> samples.

In contrast to the 521 cm^{-1} mode, in the Raman spectrum of the Si<Gd> samples one can observe a peak having several vibrational modes. Using the Gaussian distribution of this peak (Fig. 2a), it was found that the Raman scattering at 123 and 186 cm^{-1} belongs to the vibrational modes of the first and second order of Gd [8-10], and the 150 cm^{-1} mode belongs to the first-order scattering by acoustic phonons (TA), which characterizes the SiO_2 bond. The last peak indicates the presence of silicon in the amorphous state [9-11]. A peak in the region $420\text{-}500 \text{ cm}^{-1}$ with a weak intensity is the result of scattering by optical phonons (LO) at 440 cm^{-1} and vibrations of the Gd-O structure (Fig. 2b).

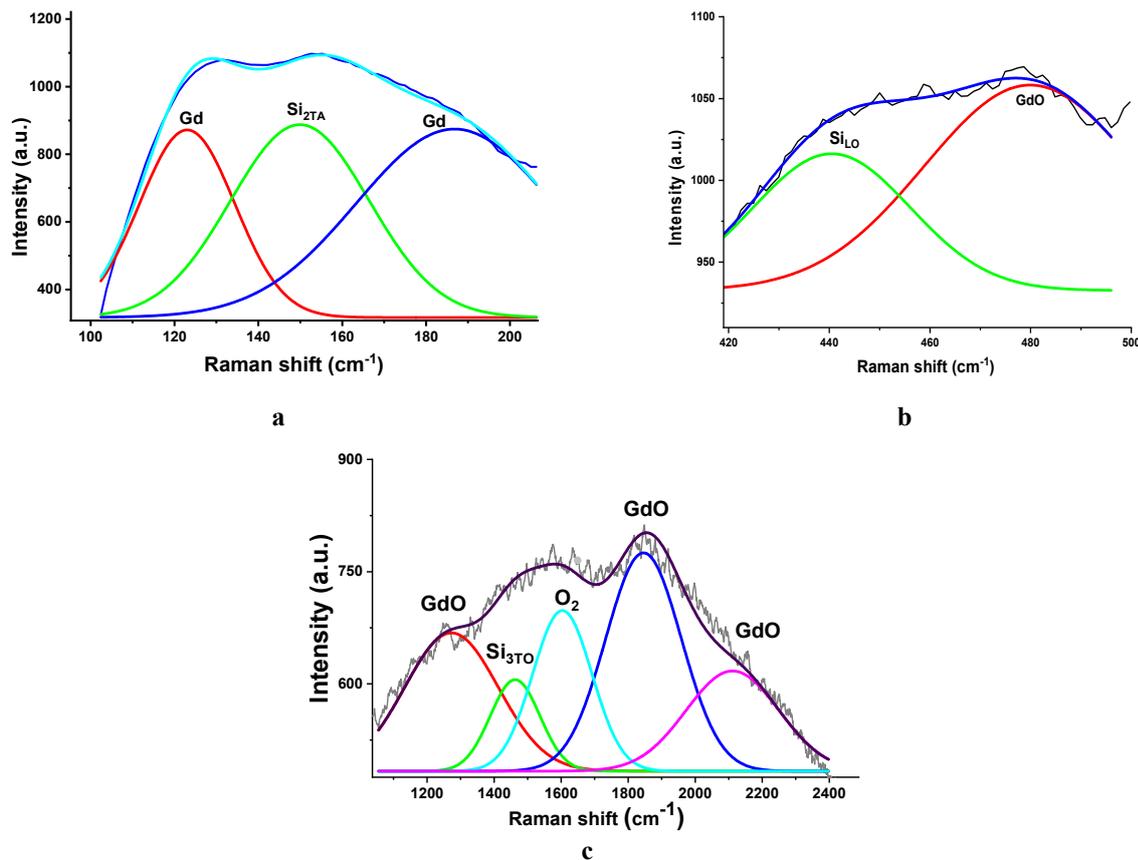


Figure 2. Gaussian distribution of peaks in the region (a) 102-206 cm^{-1} and (b) 420-500 cm^{-1} and (c) 1046-3176 cm^{-1}

The second order spectrum is much weaker than the first order LTO (Γ) peak with characteristics in the range of 100-1100 cm^{-1} . The second-order spectrum of transverse 2TA acoustic phonons is clearly observed near 303 cm^{-1} . Some authors suggest that this peak corresponds to the LA modes [10-12], but there is no exact confirmation of this fact. We are probably observing a superposition of transverse and longitudinal acoustic modes. There is also a broad peak between 900–1000 cm^{-1} , which is due to the scattering of several transverse optical phonons \sim 2TO phonons [11-13].

The broad peak in the region of 1100–2400 cm^{-1} is associated with vibrations of Si, Gd, and O atoms, since such scattering was not observed in the original silicon. The broadening of the peak may be due to the high density of defects and local composition fluctuations [12-14]. The procedure for approximating the spectral bands of the Raman spectrum (Fig. 2c) performed using the standard software option of the spectrometer showed peaks with a Gaussian distribution located at 1273, 1462, 1600, 1845, and 2111 cm^{-1} . Comparing literature data, it was found that the modes at 1273, 1845, and 2111 cm^{-1} are associated with Raman vibrations of the Gd–O structure [13-15]. Whereas, the peaks at 1462 and 1600 cm^{-1} refer to vibrations of Si scattering of the third order due to optical phonons (TO) [14-16] and vibrations of interstitial oxygen (O_2), respectively [15-17].

As can be seen from Fig. 1a, the Raman spectrum of the Si<Gd> sample smoothes out after the introduction of the Ag impurity. The Raman spectrum of the main Si peak with a Gaussian distribution was also obtained and data on the peak position, peak intensity, and full width at half maximum (FWHM) were analyzed. As indicated in Table 1, the intensity and FWHM changed significantly in the Si<Gd, Ag> samples. At the same time, the position of the peak remained almost unchanged. A higher peak position at lower FWHM values corresponds to a higher crystallization quality [11-13]. This indicates that the presence of Ag atoms in doped Si, Gd impurities increases the degree of perfection of the crystal.

Table 1. Raman peak parameters of the samples.

Sample	Peak position, cm^{-1}	Intensity, a.u.	FWHM, cm^{-1}
Si<Gd>	521.62	6621	15
Si<Ag>	521.23	7098	13.38
Si<Gd, Ag>	521.68	7503	13.5

It was noted that the scattering in the range of 102-206 cm^{-1} and 1100-2400 cm^{-1} associated with Gd, Si and O atoms, after doping with Ag impurity atoms, is completely smoothed out as the concentration of silver atoms increases. It is likely that in the process of diffusion, silver atoms in silicon form neutral clusters and structural defects, such as Ag-Gd and Ag-O, due to which the intensity of this peak decreases. A change in the oxygen concentration in silicon upon

doping with silver was also observed by us earlier [16-18], when, based on the analysis of IR absorption spectra, it was shown that the concentration of optically active oxygen (N_0^{opt}) in samples of silicon doped with silver was, on average, 10-25% less than in controls.

CONCLUSION

The applied experimental procedure made it possible to obtain characteristic Raman spectra of silicon doped with Gd and Ag impurities. An analysis of the Raman spectra showed that, in contrast to the fundamental vibrations of silicon, the Raman spectrum of the Si<Gd> samples exhibit peaks characteristic of the first and second order scattering of the Gd impurity. It is shown that in the process of diffusion, silver atoms in silicon form neutral complex defects of the Ag-O type, which is typical for the case of a decrease in the oxygen concentration in silicon. It was also revealed that the presence of Gd atoms in the volume of Si, with the diffusion introduction of silver atoms, leads to the formation of aggregates of the Ag-Gd type, which, in turn, leads to a smoothing of the Raman spectrum and an improvement in the defect structure of the Si single crystal.

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ДОСЛІДЖЕННЯ ДЕФЕКТОУТВОРЕННЯ КРЕМНІЮ, ЛЕГОВАНОГО ДОМІШКАМИ СРІБЛА ТА ГАДОЛІНІЮ, МЕТОДОМ СПЕКТРОСКОПІЇ КОМБІНАЦІЙНОГО РОЗСІЮВАННЯ

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Кремній, легований домішками гадолінію та срібла, досліджували на раманівському спектрометрі Renishaw InVia. Проведено реєстрацію та ідентифікацію компонентів як кристалічної, так і аморфної фази у зразках. Спостерігаються деякі зміни спектрів комбінаційного розсіювання зразків кремнію, легованих гадолінієм, проти вихідним зразком. Експериментально встановлено, що збільшення концентрації домішки срібла в легованому кремнії гадолінієм призводить до згладжування спектра комбінаційного розсіювання, що свідчить про формування більш досконалої кристалічної структури.

Ключові слова: кремній; гадоліній; срібло; спектри комбінаційного розсіювання; легування; складні дефекти