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## INTERACTION OF LIGHT WITH A SILICON CRYSTAL LATTICE MODIFIED WITH GADOLINIUM ATOMS

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### Abstract

The paper presents the results of a study of the effect of gadolinium on the structure of silicon samples, performed using scanning electron microscopy (SEM) and Raman spectroscopy. The distribution of carbon and silicon on the surface of gadolinium-doped substrates was studied using energy-dispersive analysis (EDS). An uneven distribution of carbon atoms was found, with noticeable clusters in certain areas of the surface. The analysis showed a high carbon content, indicating its significant presence in the samples. Small oxygen concentrations indicate the presence of oxide compounds. Doping with gadolinium led to the formation of defects on the surface and an uneven distribution of carbon. Analysis of the Raman spectra showed the presence of several vibrational modes, including scattering on acoustic and optical phonons, as well as modes associated with gadolinium and gadolinium oxide. In addition, the spectra revealed new signals that increase with increasing resistivity of the samples.

**Keywords:** *silicon, gadolinium, Rare Earth Element, Energy-dispersive spectroscopy, Raman Spectra, Diffusion, Heat Treatment, Defects*

Silicon is the main material of the modern semiconductor and optoelectronic industries (Utamuradova, Sh.B., Matchonov, Kh.J., Khamdamov, J.J., & Utemuratova, Kh.Y., 2023) due to its unique electrical and optical properties. At the same time, there is a need to further modify its characteristics to expand the areas of application. One of the ways to modify the characteristics of silicon is to in-

troduce rare earth elements such as gadolinium (Gd), which can significantly affect the magnetic and optical properties of silicon. Studies have shown that gadolinium atoms introduced into the silicon crystal lattice are able to change its interaction with light and magnetic characteristics, which makes such materials promising for use in optoelectronics, sensor devices and spintronics.

Modification of silicon with gadolinium atoms causes structural changes that significantly affect its optical and magnetic properties. In particular, the introduction of gadolinium into silicon leads to changes in the crystal lattice, which causes deformation and a change in the optical activity of silicon. According to studies, the presence of gadolinium atoms in the silicon lattice can change the photochemical activity of the material, improving its ability to interact with radiation. This is due to the fact that gadolinium retains its magnetic moments even when diffused into the silicon lattice, due to localized  $d$ -electrons, which is especially important for applications in spintronics (Jucui Yang, Yutong Feng, Xiaohong Xie, Huiwa Wu, and Yuming Liu., 2016; Sercheli M. S., Retto-ri C., 2002, June).

One of the key effects is the reduction in the density of “hanging” bonds of silicon when gadolinium is introduced. Studies have shown that trivalent  $Gd^{3+}$  ions help reduce the number of defects in the crystal structure, which improves the electronic properties of the material and reduces the number of defects on the surface. It was also found that gadolinium, interacting with silicon, improves the magnetic characteristics of the material, making it suitable for use in magnetic sensors and devices using spin effects.

Raman spectroscopy is widely used to study crystalline materials, including semiconductors, including silicon (Utamuradova, S.B., Daliev, S.K., Khaitbaev, A.K., Khamdamov, J.J., Matchonov, Kh.J., & Utemuratova, X.Y., 2024). In Raman spectroscopy, light interacts with phonons (quanta of sound vibrations of the crystal lattice). As a result of this interaction, Raman scattering of light occurs, which creates characteristic spectral lines.

Phonons interact with photons of light, causing changes in their energy and frequency. These changes are reflected in the Raman spectrum. Each crystal structure has its own phonon modes, which appear in the Raman spectrum. In the case of silicon, phonon modes associated with the diamond structure of silicon can be detected. In the Raman spectrum, the position of the lines, their intensity, and the width of the lines are usually measured. Raman spectroscopy is a powerful tool for studying crystalline materials at the molecular level, and its appli-

cation in the study of semiconductors and nanomaterials allows obtaining important information about their structure and properties (Jones, R. R., Hooper D. C., Zhang L., Wolverson D., & Valev V. K., 2019).

Doping silicon with rare earth elements such as gadolinium (Gd) can significantly change its properties and, therefore, cause changes in the Raman spectra. Doping also affects the formation of defects and deformations in the crystal lattice. Changes in the Raman spectra can provide information about such structural changes. Studying the effect of gadolinium doping of silicon on Raman scattering can provide information about the possibility of technological applications of such materials in the fields of electronics, optics and nanotechnology.

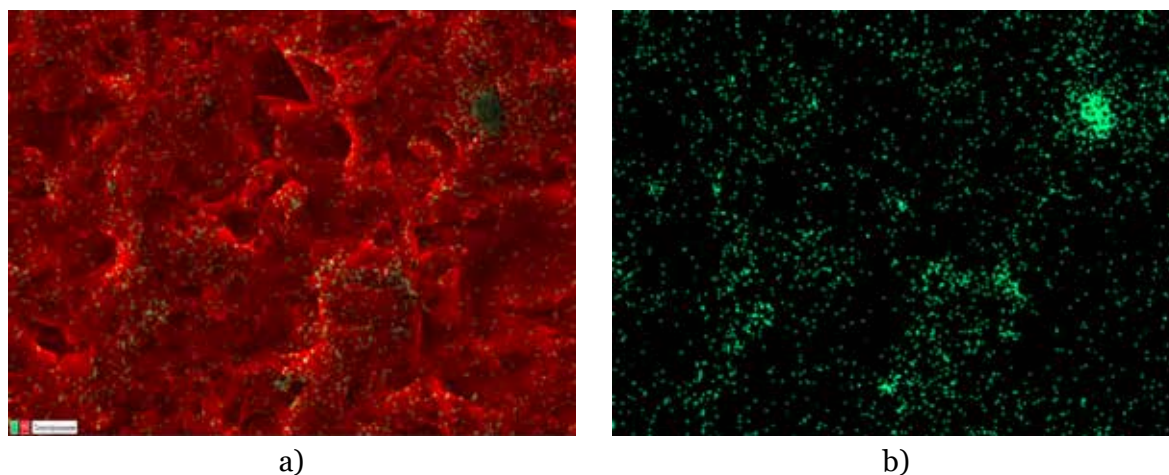
In this paper, we present the results of studying the one- and two-phonon Raman spectra of single-crystal silicon doped with Gd atoms.

For the study,  $n$ -Si and  $p$ -Si samples with an initial specific resistance from  $0.3$  to  $40 \Omega \times \text{cm}$  were selected. Before doping, the samples were subjected to thorough acid-peroxide washing, while the oxide layers were removed from the surface of the samples using an HF solution. After thorough cleaning of the sample surface, high-purity gadolinium impurity films (99.999%) were applied to the clean Si surfaces using vacuum sputtering. Vacuum conditions in the volume of the working chamber of the order of  $10^{-7}$ – $10^{-8}$  torr were provided by an oil-free vacuum pumping system.

Before diffusion annealing, the samples were placed in evacuated quartz ampoules. The samples were doped with Gd impurity by the diffusion method at a temperature of  $1200 \text{ }^\circ\text{C}$  for 20 hours, followed by rapid cooling. To study the interaction of impurity atoms in silicon, not only uniform doping of the material is necessary, but also maximum concentration. In this regard, we took into account the optimal conditions for doping silicon with these impurity atoms.

The study of the surface of silicon doped with gadolinium during the growth process using energy-dispersive spectroscopy (EDS) and scanning electron microscopy (SEM) made it possible to identify the structural and elemental features of the material.

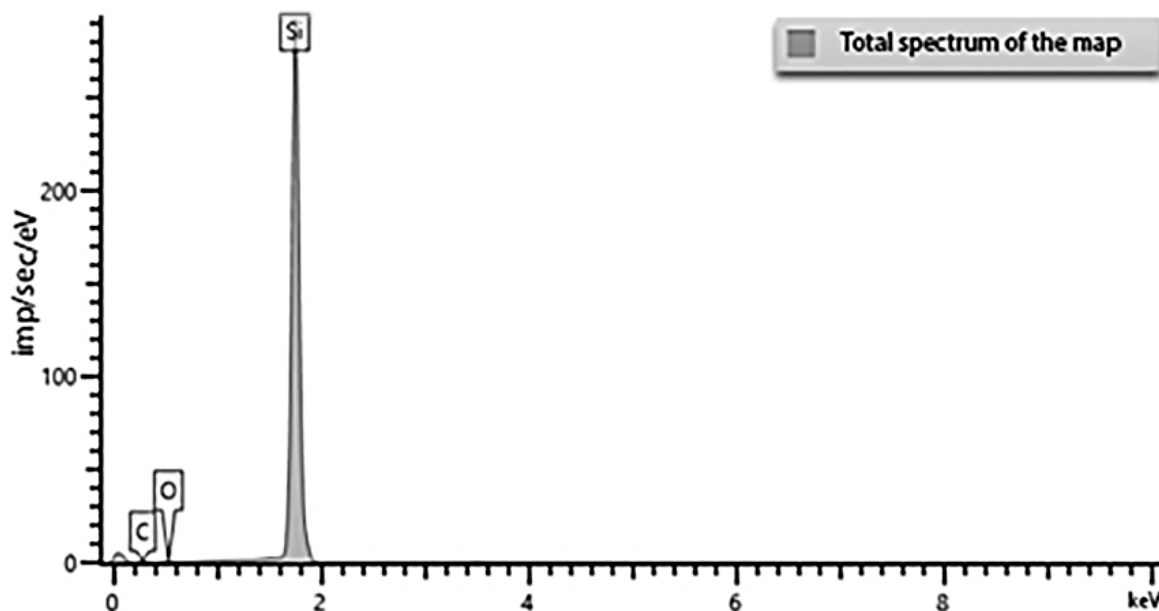
**Figure 1.** SEM images of the surface of silicon doped with gadolinium during the growth process



The SEM image (Fig. 1 a) showed that the carbon (green) and silicon (red) atoms were distributed unevenly over the sample surface, with noticeable areas of carbon accumulation. This is confirmed by the carbon distribution map (Fig. 1 b), which shows significant accumulations of this element in certain areas of the surface.

The EDS spectrum revealed a dominant peak of silicon (Si) with minor peaks of oxygen (O) and carbon (C) (Fig. 2). The bulk of the material is silicon, as expected for silicon substrates doped with gadolinium during growth. The presence of oxygen and carbon indicates possible contamination or oxidation of the surface.

**Figure 2.** EDS spectra of silicon samples doped with gadolinium during growth



According to the quantitative analysis (Table 1), the weight fraction of silicon is 86.79% and carbon is 11.90%, which confirms the significant presence of carbon on the surface. The atomic concentration of carbon (23.81%) indicates its high proportion in the sample composition. Oxygen (1.96%)

may indicate the presence of oxides, probably formed on the surface during the growth process or subsequent storage.

Gadolinium doping during growth may have affected the silicon surface structure, creating defects that contributed to the uneven distribution of carbon. The presence of

oxygen and carbon may be due to processes occurring during gadolinium doping, as

well as possible contamination that occurred during sample handling or storage.

**Table 1. Summary Spectrum of the Map**

Element	Line Type	Conditional Concentration	Wt%	At. %
C(Carbon)	K-series	0.61	11.90	23.81
O(Oxygen)	K-series	0.56	1.31	1.96
Si(Silicon)	K-series	92.59	86.79	74.23
Total:			100.00	100.00

Raman spectra were studied using a Bruker SENTERRA II Raman spectrometer. This fully automated instrument combines excellent sensitivity with a high resolution of  $4.0 \text{ cm}^{-1}$ . Senterra calibration was performed automatically and was linked to NIST standards, acetaminophen and silicon, resulting in a wavelength measurement accuracy of  $0.2 \text{ cm}^{-1}$ . The experiments were performed using a laser with a wavelength of  $I_0 = 532 \text{ nm}$ , a maximum power of  $P_{\text{max}} = 25 \text{ mW}$ , an acquisition time of 100 s and addition of two spectra. This instrument allows obtaining spectra in the range from 50 to  $4265 \text{ cm}^{-1}$ . Raman spectra were specially processed to be able to compare intensity ratios between samples. Before normalizing the spectra to the peak at  $510 \text{ cm}^{-1}$ , which corresponded to the most intense peak in the spectral region  $4265\text{--}50 \text{ cm}^{-1}$ , we subtracted the baseline for each spectrum.

It is known that the lattice constants of Gd and Si differ, therefore, if a substrate of one material (Si) is grown on top of another (Gd), built-in elastic stresses appear in the Gd, Si layers, as well as in multilayer Gd-Si structures (Ramabadran, U., & Roughani, B., 2018). In this case, the elastic stresses are so significant that they significantly affect the band structure of charge carriers and phonon spectra. The magnitude of the lattice mismatch largely determines the quality of the structures, since stresses generate the formation of structural defects and in some cases greatly limit the possibilities of creating perfect heterocompositions. In the case where the layer material is a solid solution, the lattice mismatch becomes smaller than in the case of a structure of pure Si and Gd composition, the deformations of the material change the crystal structure, and thus mani-

fest themselves in changes in the vibrational, phonon spectra.

We have studied the Raman spectrum of the  $\text{Gd}_x\text{Si}_{1-x}$  solid solution ( $x = 0.25$ ) grown on a Si substrate with the (100) orientation. The thickness of the solid solution layer is  $5 \mu\text{m}$ . This means that such a layer is relaxed. It follows that the lattice constant of the  $\text{Gd}_x\text{Si}_{1-x}$  layer will lie in the interval between the lattice constants of Gd and Si.

Raman spectra of epitaxial films of Gd-Si solid solutions with different Gd and Si contents, grown on Gd substrates in the case of a low percentage of Si, and on Si in the case of a low percentage of Gd. The shift of the peaks of local Gd-Gd and Si-Si vibrations associated with the change in the values of deformations is clearly visible.

In the KPC spectra, three ranges of Raman shift frequencies can be distinguished, determined by the masses of the constituent elements and the elasticity coefficients of the present bonds: these are vibrations of the atoms of the Gd-Gd bonds (about  $238 \text{ cm}^{-1}$ ), Gd-Si bonds ( $783 \text{ cm}^{-1}$ ), and Si-Si ( $510 \text{ cm}^{-1}$ ). The built-in stresses caused by the significant difference in the lattice constants of Gd and Si have a significant effect on the position of the lines in the spectra.

It is known that (Vas'kovskiy, V.O., Svalov, A.V., Gorbunov, A.V., Schegoleva, N.N., & Zadvorkin, S.M., 2014) when growing a layer with a different lattice constant on a substrate, the layer being grown initially grows with the lattice constant of the substrate (i.e. deformed), but starting from a certain layer thickness, the formation of dislocations is energetically favorable, after which the layer continues to grow with its lattice constant. Such layers are called relaxed or unstressed.

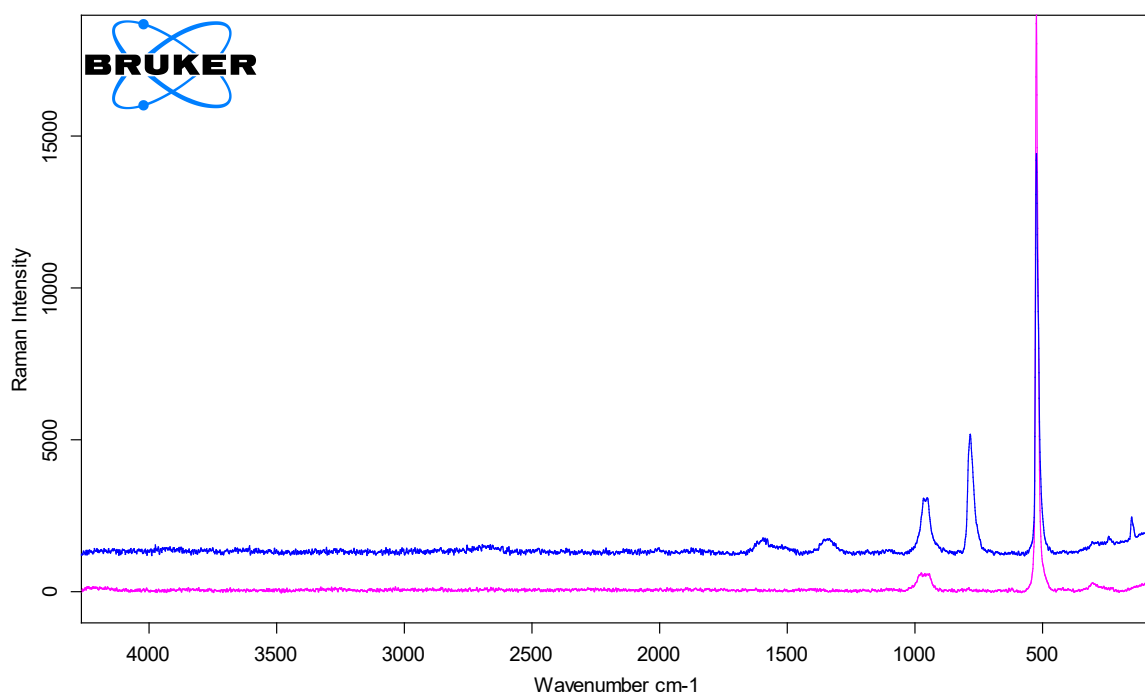
When analyzing the spectra, the intense band of asymmetric stretching vibrations  $\nu_{as}(\text{Si-O})$  at  $1067 \text{ cm}^{-1}$  was chosen as an internal standard. The baseline was drawn through the absorption minima at wave numbers of  $4000$  and  $755 \text{ cm}^{-1}$ . The analyzed samples were compared based on the relative optical density of the characteristic bands in the reduced form to the optical density of the internal standard band.

Thus, the detected changes in the Raman spectra of gadolinium-doped silicon samples

suggest that a bond is formed between gadolinium atoms and silicon atoms in the sample under study.

The Raman spectra of the n-type silicon sample doped with Gd impurity atoms are shown in (Fig. 3). The Raman spectrum of the Si <Gd> samples shows a high peak in the region of  $521\text{--}522 \text{ cm}^{-1}$ . The intensity of the first-order scattering caused by optical phonons (TO - transverse optical vibrations, LO - longitudinal optical vibrations) at the central point  $\Gamma$  of the Brillouin zone (BZ).

**Figure 3.** Raman spectrum of n-type silicon doped with Gd impurities: 1 – Raman spectrum of  $\text{Si}_{\text{original}}$  samples, 2 – Raman spectrum of  $\text{Gd}_x\text{Si}_{1-x}$  samples,  $\rho_{\text{original}} = 40 \Omega \times \text{cm}$



C:\spectry\EXTRACT_p=40 Gd-Si 1200 20 s.0_000002.2	Sample	Senterra II	4/13/2023
C:\spectry\EXTRACT_p=40 Gd-Si 1200 20 s.0_000015.0	Sample	Senterra II	4/13/2023

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In contrast to the  $521 \text{ cm}^{-1}$  mode, the Raman spectrum exhibits a peak with several vibrational modes. Using the Gaussian distribution of this peak, it was found that the Raman at  $123$  and  $186 \text{ cm}^{-1}$  belongs to the vibrational modes of Gd (Kasirajan, K., Bruno Chandrasekar, L., Maheswari, S., Karunakaran, M., & Shunmuga Sundaram, P., 2021), and the  $148 \text{ cm}^{-1}$  mode is related to the first-order scattering on acoustic phonons (TA), which characterizes the  $\text{SiO}_2$  bond. The weak peak at  $456 \text{ cm}^{-1}$  is the result of scattering on optical phonons (LO). The latter

peak indicates the presence of silicon in the amorphous state (Tony, D.K., James, C.P., John, W.M., Volodymyr, T.A., Yaroslav, V.B., Bohdan, V.P., Ihor, M.T., Ning Lu, Lu Wang, Wai-Ning Mei and Peter, A.D., 2014).

The second-order spectrum is much weaker than the first-order LTO ( $\Gamma$ ) peak with characteristics in the range of  $100\text{--}1100 \text{ cm}^{-1}$ . The second-order spectrum of transverse 2TA acoustic phonons is clearly observed near  $303 \text{ cm}^{-1}$ . Some authors suggest that this peak corresponds to the LA modes (Daliev, K.S., Utamuradova, Sh.B.,



Khaitbaev, A., Khamdamov, J.J., Norkulov, Sh. B., and Bekmuratov, M. B., (2024), but there is no exact confirmation of this fact. Probably, we observe a superposition of transverse and longitudinal acoustic modes. There is also a broad peak between 900–1000  $\text{cm}^{-1}$ , which is due to the scattering of several transverse optical phonons  $\sim 2\text{TO}$  phonons (Daliev, K. S., Utamuradova, Sh. B., Khaitbaev, A., Khamdamov, J. J., Norkulov, Sh. B., and Bekmuratov, M. B., 2024).

The peak broadening can be caused by the high defect density and local composition fluctuations (Daliev, K. S., Utamuradova, Sh. B., Khaitbaev, A., Khamdamov, J. J., Norkulov, Sh. B., and Bekmuratov, M. B., 2024). From the comparison of our results with the literature data, it was found that the modes at 954, 1340 and 1610  $\text{cm}^{-1}$  are associated with combination vibrations of the GdO structure. Whereas, the peaks at 1462 and 1600  $\text{cm}^{-1}$  are related to third-order Si scattering vibra-

tions caused by optical phonons (TO) (Tony, D. K., James, C. P., John, W. M., Volodymyr, T. A., Yaroslav, V. B., Bohdan, V. P., Ihor, M. T., Ning Lu, Lu Wang, Wai-Ning Mei and Peter, A. D., 2014; Daliev, K. S., Utamuradova, Sh. B., Khaitbaev, A., Khamdamov, J. J., Norkulov, Sh. B., and Bekmuratov, M. B., 2024; Hong, W.-E., & Ro, J.-S., 2013) and vibrations of interstitial oxygen ( $\text{O}_2$ ), respectively (Daliev, K. S., Utamuradova, Sh. B., Khaitbaev, A., Khamdamov, J. J., Norkulov, Sh. B., and Bekmuratov, M. B., 2024; Hong, W.-E., & Ro, J.-S., 2013).

Thus, with an increase in the specific resistance of the studied samples from  $\rho_{\text{inh}} = 0.3 \Omega \times \text{cm}$  to  $\rho_{\text{inh}} = 40 \Omega \times \text{cm}$ , new signals appear in the region of: 68, 123, 148, 238, 303, 456, 784, 954 1340 and 1610  $\text{cm}^{-1}$  and then their intensities increase. The most significant band observed at 784  $\text{cm}^{-1}$ , in our case, corresponds to the stretching vibrations of the Gd – Si bond.

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