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RESEARCH OF THE IMPACT OF SILICON DOPING WITH HOLMIUM ON ITS STRUCTURE AND PROPERTIES USING RAMAN SCATTERING SPECTROSCOPY METHODS

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Each crystal structure has its own phonon modes, which appear in the Raman spectrum of Raman scattering. In the case of silicon, phonon modes associated with the diamond structure of silicon can be detected. In a 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 application in the study of semiconductors and nanomaterials provides important information about their structure and properties. In this study, the spectra of two types of silicon were analyzed: n-Si and p-Si, as well as their doped analogues n-Si<Ho> and p-Si<Ho>. The obtained Raman imaging results demonstrated spatially varying nanocrystallinity and microcrystallinity of the samples. The n-Si<Ho> and p-Si<Ho> spectra indicate the appearance of a Raman band at 525 cm^{-1} with a shift of -5 cm^{-1} and +5 cm^{-1}, respectively, relative to the position of the silicon substrate peak, indicating the presence of tensile strain in the materials. The absence of other impurity peaks indicates the high purity of the n-Si<Ho> and p-Si<Ho> samples. The holmium doped Si material exhibits additional peaks in the Raman spectra, which is attributed to the presence of vacancies and defects in the newly formed Si-Ho compositions. The results of the analysis of the spectra indicate the influence of doping silicon with holmium on its structure and properties, forming new bonds and defects.

Key words: *Silicon; Holmium; Rare Earth Elements; Raman Spectra; Diffusion; Heat Treatment; Defects*
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INTRODUCTION

When characterizing crystalline silicon, which is widely used in the production of semiconductor electronic devices, Raman spectroscopy methods are actively used [1-6]. Raman spectroscopy measures the change in frequency of light scattered by the molecules of a sample. These frequency changes are associated with molecular vibrations and can provide information about the chemical composition, structure and physical properties of the materials being studied. Raman spectroscopy technique is used in various fields such as chemistry, biology, physics, materials science and surface science [14]. Widely used for the analysis of chemical compounds, biological research, as well as quality control and materials research. To study the composition and structure of nanocrystalline silicon, a combination of transmission electron microscopy, Raman spectroscopy, and the effect of extremely small silicon grain sizes is used [7-10]. It is critical to recognize the consequences of nanocrystallinity in the Raman spectrum to avoid erroneously attributing spectral features of nanocrystals to deformation of microcrystalline or larger grains [15-17].

MATERIALS AND METHODS

n-Si and p-Si samples with an initial resistivity from 0.3 to 40 Ω×cm were selected for the study. Before alloying, the samples were subjected to thorough acid-peroxide washing, and the oxide layers were removed from the surface of the samples using a HF solution. After thoroughly cleaning the surface of the samples, films of holmium impurities of special purity (99.999%) were deposited onto the clean Si surfaces using vacuum deposition. 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. Doping of samples with Ho impurities was carried out by the diffusion method at a temperature of 1200 °C for 5 hours, followed by rapid cooling.

Raman spectra were studied using a SENTERRA II Bruker Raman spectrometer. This fully automated instrument combines excellent sensitivity and high resolution of 4.0 cm^{-1}. Senterra calibration was automatic and referenced to NIST acetaminophen and silica standards, resulting in wavelength accuracy of 0.2 cm^{-1}. The experiments were carried out using a laser with a wavelength λ_0=532 nm, maximum power P_{max}=25 mW, acquisition time 100 s and addition of two spectra. This device allows you to obtain spectra in the range from 50 to 4265 cm^{-1}. The Raman spectra were specially processed to be able to compare intensity ratios between samples. Before normalizing the spectra to the peak at 510 cm^{-1}, which corresponded to the most intense peak in the spectral region 4265-50 cm^{-1}, we subtracted the baseline for each spectrum.

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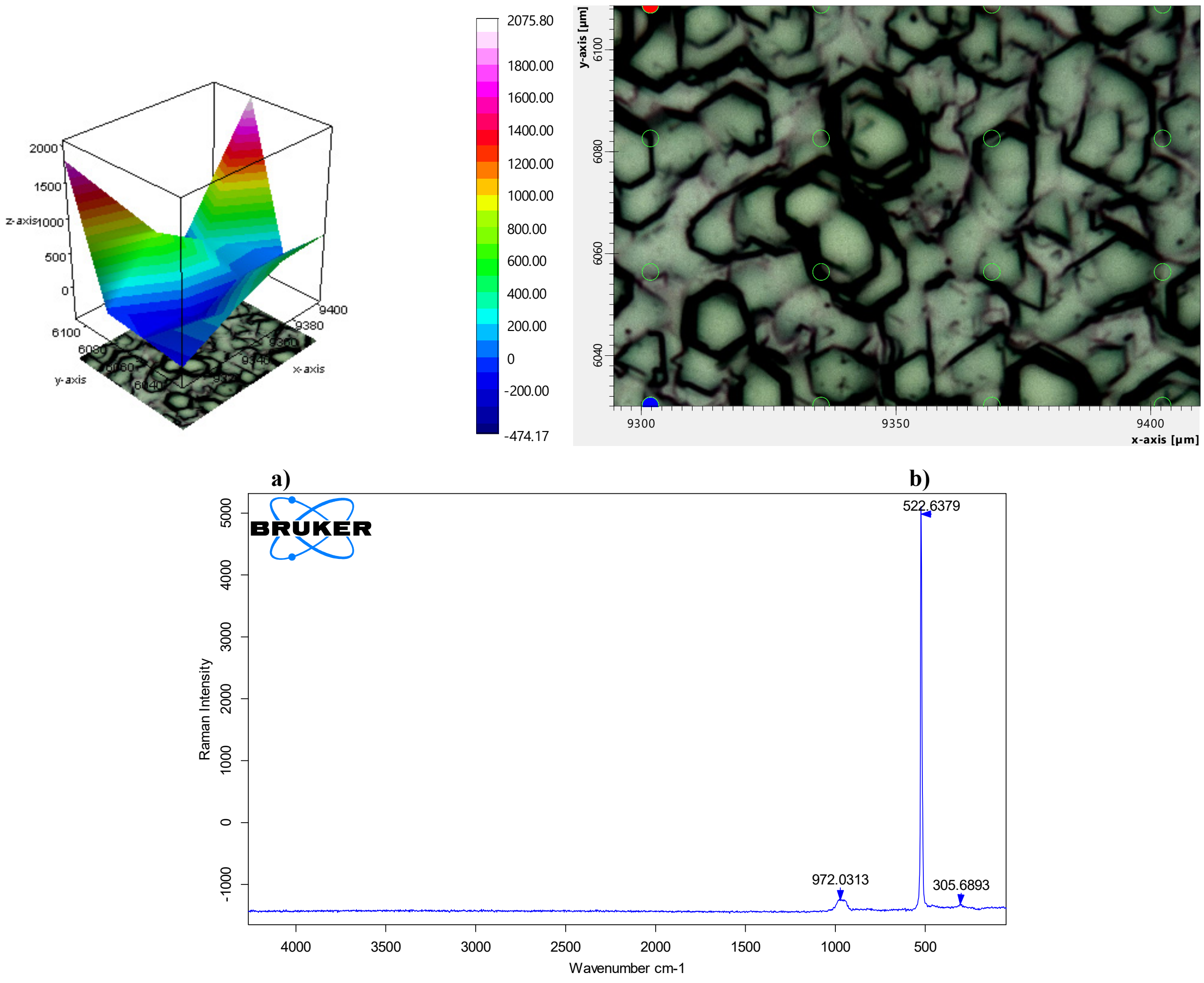
RESULTS AND DISCUSSION

Heterostructures (Ho-Si) and solid solutions (n-Si<Ho>) crystal lattice constants of Ho and Si materials are always different, therefore, if another (Ho) is grown on top of a substrate of one material (Si), built-in elastic stresses appear in the Ho layers, Si, Ho-Si multilayer structures. In this case, elastic stresses turn out to be so significant that they significantly affect the band structure of charge carriers and phonon spectra. The magnitude of the mismatch of crystal lattices largely determines the quality of structures, since stresses give rise to the formation of structural defects and in some cases greatly limit the possibility of creating perfect heterocompositions. Changes in composition and deformation of the material change the crystal structure, and thereby manifest themselves in changes in vibrational and phonon spectra. One of the methods of structural analysis that allows one to study phonon spectra and their changes is Raman spectroscopy. In this work, the Raman spectrum of an n-Si<Ho> sample ($x = 0.25$) grown on a Si substrate with (100) orientation was studied. The thickness of the solid solution layer is 5 microns. The solid solution contains Si-Si, Ho-Ho and Ho-Si bonds. Therefore, light scattering involving these vibrational modes should be expected.

Below are the Raman spectra of both the initial n-Si silicon material (Fig. 1.) and the resulting n-Si<Ho> sample (Fig. 2.). In this case, the Raman image was visualized using color coding.



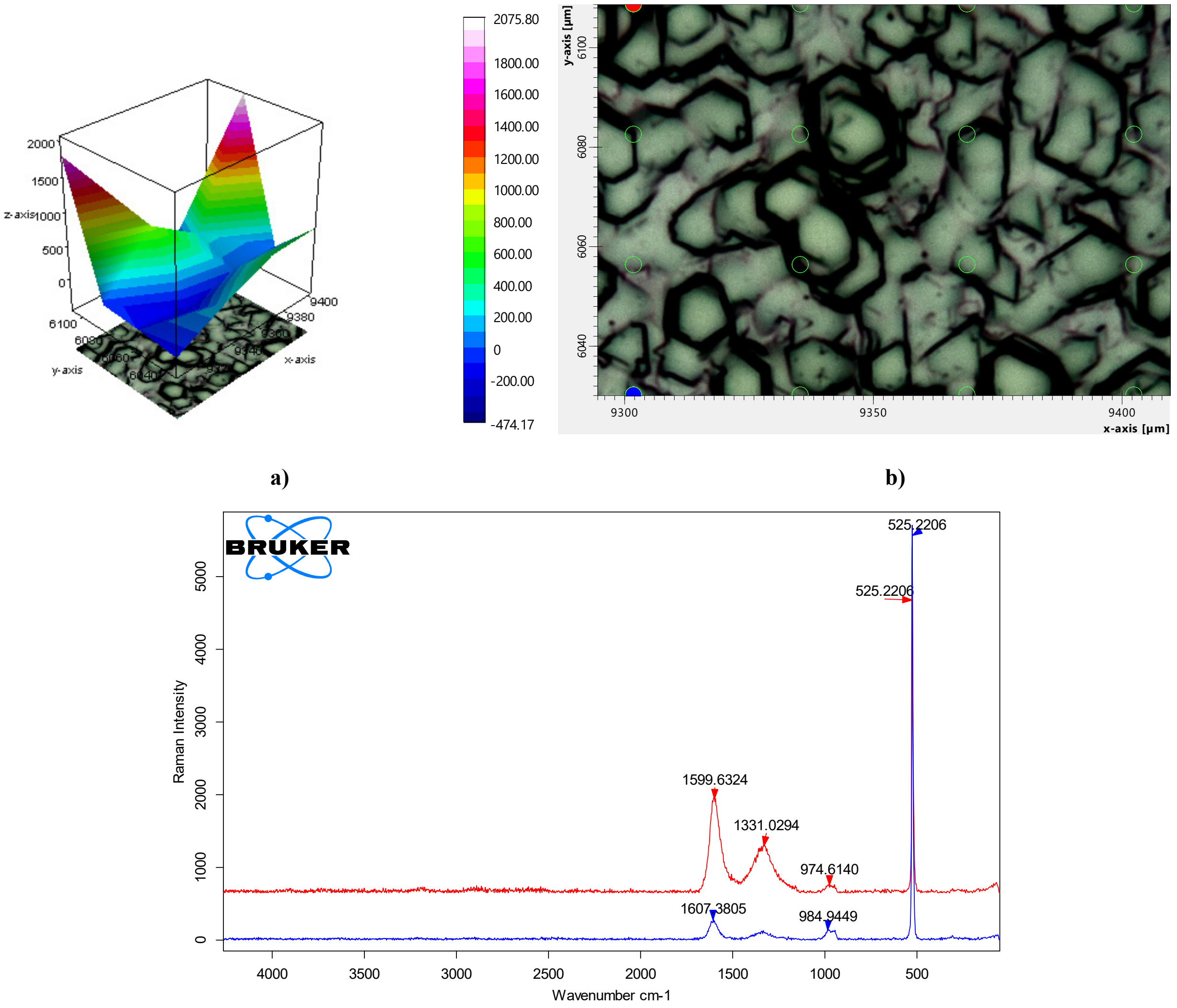
a) b)

c)

Figure 1. Raman spectrum n-Si$_{\text{initial}}$

As can be seen from the data in Figure 1, when studying the n-Si$_{\text{initial}}$, a strong signal appears in the region of 522 cm^{-1}, resulting from a first-order optical phonon in the Brillouin center region. An increase in band width indicates that there is a distribution of strains and the band shift is not the result of a single uniaxial stress. The shoulder at 522 cm^{-1} can be attributed to crystalline silicon.

When studying the Raman spectra of the resulting material, it was revealed that the studied material consists of a silicon substrate (or grown single-crystalline silicon) with different oxide thicknesses. The spatial variation of the material's Raman signal power closely matches the physical optical effect of the oxide thickness, and even small impurities or defects are visible in the reflected light image (Figures 1b and 2b). Moreover, due to the thinness of the silicon structure (Fig. 1a and 2a), it is possible to see through the picture the components of the resulting material. Note that the bright green dots in the Raman image correspond precisely to the black specks in the reflection of the light image. A careful examination of the central strip reveals the same speckles in the silicon deposited on top of it.



a) b)

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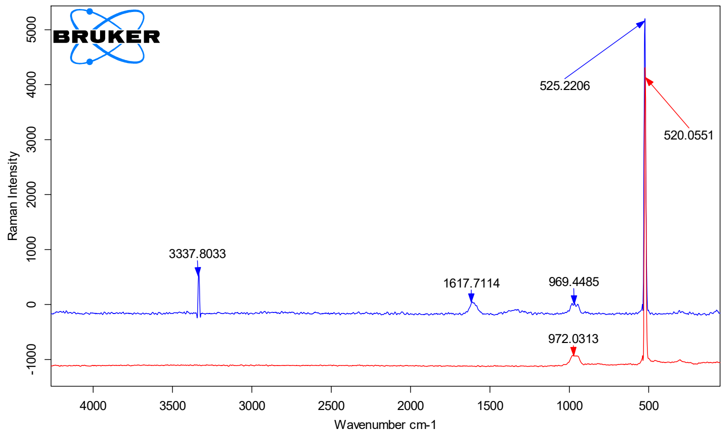
Figure 2. Raman spectra of n-Si<Ho>

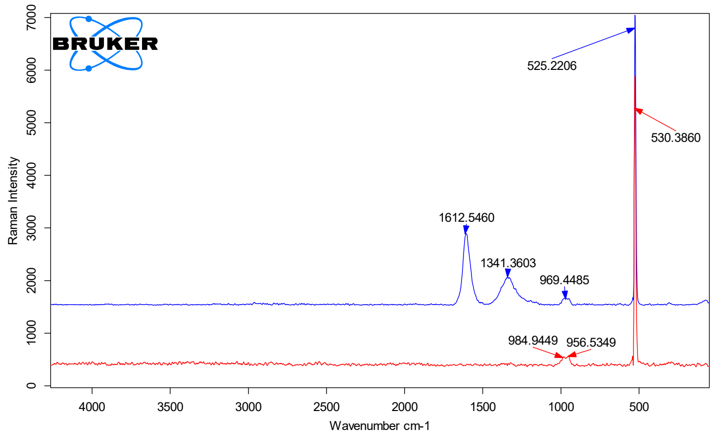
As can be seen from the given spectrum (Fig. 3.) silicon consists of Raman scattering of light at 525 cm^{-1} for n-Si and 530 cm^{-1} for p-Si, respectively, resulting from the first order of optical phonon in the Brillouin center region, Raman the band in the spectra of the resulting n-Si<Ho> appears at 525 cm^{-1} (shift -5 cm^{-1}), and in the case of p-Si<Ho> appears at 525 cm^{-1} (shift +5 cm^{-1}) relative to the position peak of the silicon substrate, thereby indicating the presence of tensile strain. The absence of other impurity peaks of the samples indicates a higher purity of the samples. Both types of Si and Si<Ho> samples obtained on their basis have a strong, broad absorption at ~960 cm^{-1}, which corresponds to the Si-O-Si stretching vibration. Apparently, the above results demonstrate the successful production of the Si<Ho> composite on the surface of the material. When studying Raman spectroscopy of materials, two Si peaks located at ~522 and ~950 cm^{-1} correspond well to the Si peak symbol, which can also be observed in the resulting Si<Ho> materials. The increased Raman bandwidth of silicon indicates that there is a distribution of strains and the band shift is not the result of a single uniaxial stress. The shoulder at~522 cm^{-1} can be attributed to crystalline silicon.

Ho-doped Si material also has additional peaks in its Raman spectra, which is expected due to the presence of vacancies, defects in the newly formed Si<Ho> compositions. Ho-doped silicon surfaces exhibit higher absorption rates after grinding to 50 µm. An additional peak at 805 cm^{-1} is assigned to the hydrogen wagging mode. The frequency range (2000-2150 cm^{-1}) is deconvoluted to study possible local vibrational modes arising from defects and new bonds formed in which Ho is involved. Peaks between 2021 cm^{-1} and 2150 cm^{-1} usually result from Ho-Ho stretches. The peak at 2060 cm^{-1} is due to adsorbed hydrogen at defect sites. The peaks at 2058 cm^{-1} and 2098 cm^{-1} are attributed to Ho-Si and Si-Ho$_2$, respectively. The peak at 2074 cm^{-1} corresponds to db-Si-Si-H, where db means dangling bond. The small peak at 2190 cm^{-1} may be due to Ho-induced microcrystallites.

Raman spectra of two types of silicon n-Si and p-Si, and n-Si<Ho> and p-Si<Ho> obtained on their basis, deposited on crystalline Si substrates and annealed at 1373 K for 5 hours, are presented in Fig. 1-3. a tail that does not develop into a clearly visible peak in any sample. We hypothesize that the tail is primarily scattering from annealed-grown silicon nanocrystals, and this is supported by a similar low-energy tail observed in other Raman scattering studies of silicon nanocrystals [11-13,19]. In these studies, the peak of the Raman band is slightly shifted relative to the Si single crystal band, but its low-energy tail is highly asymmetric and extends to 480 cm^{-1}, similar to the tail of our Raman spectra. However, some small portion of the scattering in the low-frequency tail of our spectra may be due to n-Si, whose Raman peak [12,13,18] at 480 cm^{-1} extends asymmetrically to 242-341 cm^{-1}. We do not observe any scattering below 400 cm^{-1}, which means that most of the scattering in the low-energy tail of our spectra is due to Si nanocrystals.



a). n-Si (−); n-Si<Ho> (−).



b) p-Si (−); composite p-Si<Ho> (−)

Figure-3. Comparative analysis of Raman spectra

CONCLUSION

The spectra of two types of silicon, n-Si and p-Si, and samples obtained on their basis, n-Si<Ho> and p-Si<Ho>, were studied. Raman imaging studies revealed spatially varying nanocrystallinity and microcrystallinity of the resulting samples.

To summarize, the intensity variations of monocrystalline silicon correspond to the physical optical effects of varying oxide film thicknesses and surface contaminants. In addition, Raman imaging shows the spatial variation of nanocrystallinity and microcrystallinity in silicon. From the studies conducted, we can conclude that these structural differences arise either as a result of processing conditions, or from interaction with neighboring or host materials in which silicon is in contact with other components.

Spectral analysis of silicon shows characteristic Raman peaks at 520 cm^{-1} for n-Si and 530 cm^{-1} for p-Si, caused by the first order of the optical phonon in the Brillouin center region. The n-Si<Ho> and p-Si<Ho> spectra show the appearance of a Raman band at 525 cm^{-1} with a shift of -5 cm^{-1} and +5 cm^{-1}, respectively, relative to the position of the silicon substrate peak. This indicates the presence of tensile strain in the materials. The absence of other impurity peaks indicates the high purity of the n-Si<Ho> and p-Si<Ho> samples. Both types of Si and Si<Ho> samples have a strong broad absorption at ~960 cm^{-1}, which corresponds to the Si-O-Si stretching vibration. An increase in the Raman bandwidth of silicon indicates the distribution of strains and the absence of uniaxial stress. The Si material doped with Ho exhibits additional peaks in the Raman spectra, which is explained by the presence of vacancies and defects in the newly formed Si-Ho compositions. Peaks at 805 cm^{-1} and in the frequency range 2000-2150 cm^{-1} indicate hydrogen vibrations arising from defects and the formation of new bonds in which Ho is involved. Peaks between 2021 cm^{-1} and 2150 cm^{-1}, including peaks at 2058 cm^{-1} and 2098 cm^{-1}, indicate the interaction of Ho with Si and the formation of Ho-Si and $Si\text{-}Ho_2$ type bonds. The peak at 2190 cm^{-1} may be due to Ho-induced microcrystallites.

In general, the results of the analysis of the spectra indicate that doping silicon with holmium affects its structure and properties, forming new bonds and defects.

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ДОСЛІДЖЕННЯ ВПЛИВУ ЛЕГУВАННЯ КРЕМНІЮ ГОЛЬМІЄМ НА ЙОГО СТРУКТУРУ ТА ВЛАСТИВОСТІ МЕТОДАМИ СПЕКТРОСКОПІЇ КРЕМНІЮ

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Кожна кристалічна структура має власні фононні моди, які з’являються в спектрі комбінаційного розсіювання. У випадку кремнію можна виявити фононні моди, пов'язані з алмазною структурою кремнію. У раманівському спектрі зазвичай вимірюють положення ліній, їх інтенсивність і ширину ліній. Раманівська спектроскопія є потужним інструментом для вивчення кристалічних матеріалів на молекулярному рівні, і її застосування у вивченні напівпровідників і наноматеріалів дає важливу інформацію про їх структуру та властивості. У даній роботі проаналізовано спектри двох типів кремнію: n-Si та p-Si, а також їх легованих аналогів n-Si<Ho> та p–Si<Ho>. Отримані результати комбінаційного зображення продемонстрували просторово змінну нанокристалічність і мікрокристалічність зразків. Спектри n-Si<Ho> та p-Si<Ho> вказують на появу раманівської смуги при 525 см$^{-1}$ зі зсувом на -5 см$^{-1}$ та +5 см$^{-1}$ відповідно відносно положення пік кремнієвої підкладки, що вказує на наявність деформації розтягу в матеріалах. Відсутність інших домішкових піків свідчить про високу чистоту зразків n-Si<Ho> та p-Si<Ho>. Si-матеріал, легований гольмієм, демонструє додаткові піки в спектрах комбінаційного розсіювання, що пояснюється наявністю вакансій і дефектів у новоутворених композиціях Si-Ho. Результати аналізу спектрів свідчать про вплив легування кремнію гольмієм на його структуру та властивості, утворення нових зв'язків і дефектів.

Ключові слова: *кремній; гольмій; рідкоземельні елементи; Раманівські спектри; дифузія; теплоносій; дефекти*