RAMAN SPECTROSCOPIC ANALYSIS OF TUNGSTEN SILICIDE (WSI_2) PHASE FORMATION AND LATTICE STRESS IN P-TYPE SILICON.

Sh.B. Utamuradova, Sh.Kh. Daliev, J.J. Khamdamov, Y.Z. Mardiyev
Institute of Semiconductor Physics and Microelectronics at the National University of Uzbekistan, Tashkent, Uzbekistan
E-mail: yolqinmardiyev96@gmail.com

https://doi.org/10.5281/zenodo.17910997

Abstract: In this study, the effect of tungsten (W) incorporation on the compositional and structural properties of p-type single-crystal silicon (p-Si) samples via high-temperature (1573 K, 5 hours) thermal diffusion was investigated. The properties of the samples were analyzed using Raman scattering spectroscopy. Raman spectroscopy analysis confirmed a decrease in the intensity of the main silicon LO peak in the p-Si<W> sample, as well as the appearance of new, sharp peaks at frequencies of ~244 cm^{-1} and ~429 cm^{-1}. These changes indicate the formation of a new stable phase – tungsten silicide (WSi_2) – on the silicon surface. Furthermore, the shift of the 2TA peak center to a higher frequency (~319 cm^{-1}) indicated the emergence of strong compressive mechanical stresses in the lattice.

Keywords: single-crystal silicon (p-Si), tungsten (W), thermal diffusion, Raman spectroscopy, resistivity, tungsten silicide (WSi_2), phonon bands (TA, LA, 2TO).

АНАЛИЗ ФОРМИРОВАНИЯ ФАЗЫ СИЛИЦИДА ВОЛЬФРАМА (WSi_2) И НАПРЯЖЕНИЙ КРИСТАЛЛИЧЕСКОЙ РЕШЕТКИ В КРЕМНИИ P-ТИПА МЕТОДОМ РАМАНОВСКОЙ СПЕКТРОСКОПИИ

Ш.Б. Утамурадова, Ш.Х. Далиев, Ж.Ж. Хамдамов, Ё.З. Мардиев
Институт физики полупроводников и микроэлектроники при Национальном университете Узбекистана, Ташкент, Узбекистан
E-mail: yolqinmardiyev96@gmail.com

Аннотация: В данной работе исследовано влияние внедрения вольфрама (W) на композиционные и структурные свойства образцов монокристаллического кремния p-типа (p-Si) методом высокотемпературной (1573 K, 5 часов) термической диффузии. Свойства образцов были проанализированы методом спектроскопии комбинационного рассеяния света (Рамановской спектроскопии). Анализ Рамановских спектров подтвердил снижение интенсивности основного LO-пика кремния в образце p-Si<W>, а также появление новых острых пиков на частотах ~244 $см^{-1}$ и ~429 $см^{-1}$. Эти изменения свидетельствуют об образовании на поверхности кремния новой стабильной фазы – силицида вольфрама (WSi_2). Кроме того, смещение центра пика 2TA в область более высоких частот (~319 $см^{-1}$) указало на возникновение сильных сжимающих механических напряжений в кристаллической решетке.

Ключевые слова: монокристаллический кремний (p-Si), вольфрам (W), термическая диффузия, Рамановская спектроскопия, удельное сопротивление, силицид вольфрама (WSi_2), фононные полосы (TA, LA, 2TO).

INTRODUCTION

With the rapid development of modern electronics, particularly in the fields of micro- and nanoelectronics, the demand for materials with improved physicochemical, structural, and electrical properties is increasing. In this regard, silicon (Si) occupies a leading position as the

most widely used base semiconductor material. Silicon crystals are used in the production of highly integrated circuits, high-speed photodiodes, radiation-resistant detectors, memory elements, as well as solar cells and many other electronic devices. One of the main factors determining the reliability and stability of such devices is the nature of internal and external defects in the material [1-3]. To further improve electronic devices made from silicon materials, it is necessary to introduce atoms of various elements. Introducing atoms of refractory elements into the silicon crystal lattice allows for significant modification of its properties and opens new possibilities for creating high-performance electronic devices.

The changes in the composition of tungsten (W) doped silicon were investigated using several modern devices and methods. Through experiments and measurements, the variation of resistivity across the thickness of the silicon sample was studied. Additionally, a Raman spectrometer was used to identify defects in the crystal structure. This involved studying the nature of the placement of introduced tungsten atoms within the silicon crystal lattice by analyzing defect formation and existing defects.

MATERIALS AND EXPERIMENTAL METHODS

For the experiment, monocrystalline silicon samples with a resistivity of p-Si (KDB-0.3 Ω·cm) were selected. The initial thickness of the samples was d_0=2000 μm. To remove contaminants and oxide layers from the surface, 20 μm was removed from both sides of the sample using carborundum (silicon carbide) powders of grades M=20, M=14, and M=8. Subsequently, the samples underwent a 7-stage full chemical cleaning process [4].

After cleaning, a layer of high-purity (99.999%) tungsten was evaporated onto the silicon surface. To form the tungsten layer, evaporation was carried out using a VUP-4 device under high vacuum conditions (10^{-6} Torr), ensuring a uniform distribution of tungsten atoms on the silicon surface. The doping process was carried out using the thermal diffusion method. The prepared p-Si samples were placed in pure quartz ampoules. Initially, a vacuum (10^{-4} Torr) was created inside the ampoule, and diffusion was performed at a temperature of 1573 K (1300°C) for 5 hours. Subsequently, the samples were rapidly cooled (quenched) to study the formation of defects and the incorporation of tungsten atoms into the silicon crystal lattice. Rapid cooling helps prevent the excessive growth of internal defects in the samples, which could affect the formation of nanocrystallites and other compositional changes [5].

In this work, the effect of various technological treatments and impurity atoms on the compositional and structural properties of p-type silicon (p-Si) samples was studied using Raman scattering spectroscopy in the 0-1100 cm^{-1} wavenumber range. The obtained spectra were decomposed (deconvoluted) into constituent components using Gaussian functions; a comparative analysis was performed by determining the peak position (ν_0), relative intensity (I), and full width at half maximum (FWHM) for each component.

For comparison, special attention was paid to the main phonon modes in the spectra. The low-energy TA+LA region, the second-order 2TA mode, the first-order LO mode (~520 cm^{-1}) corresponding to the Si-Si bond, and the second-order 2TO modes (~950-1000 cm^{-1}) were investigated (Figure 1).

In the spectrum of the initial p-Si sample (Figure 1), the TO phonon peak was observed at 524 cm^{-1}. After the p-Si (Control sample) was heat-treated at 1573 K for 5 hours, significant positive changes occurred in the LO peak. The peak shifted to 523 cm^{-1}, which indicates that the compressive stress in the lattice was partially reduced as a result of the heat treatment.

The most significant change was the sharp increase in peak intensity (from 16444 to 107800) while its full width at half maximum (FWHM) remained almost unchanged (31 cm^{-1}). Such a large increase in intensity confirms an overall improvement in the degree of crystallinity throughout the sample, a reduction in defects, and an ordering of the lattice.

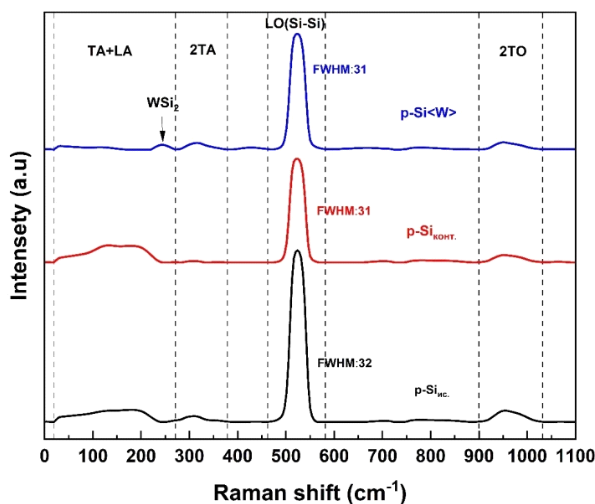

Figure 1. Raman spectra of the samples.

In the tungsten-doped p-Si<W> sample, the main LO peak of silicon changed its properties again. The peak's center remained at 524 cm^{-1}, indicating that the introduction of W atoms again created compressive stress in the lattice. The peak intensity decreased significantly compared to the heat-treated sample (from 107800 to 11058). This, as mentioned above, is explained by the formation of the tungsten silicide (WSi_2) phase resulting from the diffusion of tungsten into silicon. In the new near-surface phase, the volume fraction of pure silicon decreases, which in turn reduces the intensity of the main LO peak belonging to silicon.

The most important change is the formation of a new peak at 244 cm^{-1} with high intensity and a very small FWHM (30 cm^{-1}). The appearance of this peak signifies the emergence of a new stable phase-a tungsten silicide (WSi_2) compound-or Local Vibrational Modes (LVM) created by W atoms located in the silicon lattice.

To further study the changes formed in the samples, the results obtained from the Raman spectrometer were analyzed by dividing the spectra into separate regions. The changes in the peaks within the 0-250 cm^{-1}, 250-450 cm^{-1}, and 850-1000 cm^{-1} regions were studied separately using Gaussian distribution function fitting.

Initial p-Si sample. In the spectrum of the initial, untreated p-Si sample (Figure 2, a), three main peaks were observed: 45 cm^{-1}, 133 cm^{-1}, and 196 cm^{-1}. The appearance of these peaks is explained by the relaxation (weakening) of the momentum conservation law due to symmetry breaking in the crystal lattice, and the subsequent Raman activation of phonons from the Brillouin zone edges [6].

These peaks primarily correspond to silicon's Transverse Acoustic (TA) phonon branches and can be associated with high-symmetry points-X, L, and W-where the phonon density of states reaches a maximum [7]. The most intense L-peak at 133 cm^{-1} corresponds to TA phonons at the L-point of the Brillouin zone and is characteristic of silicon.

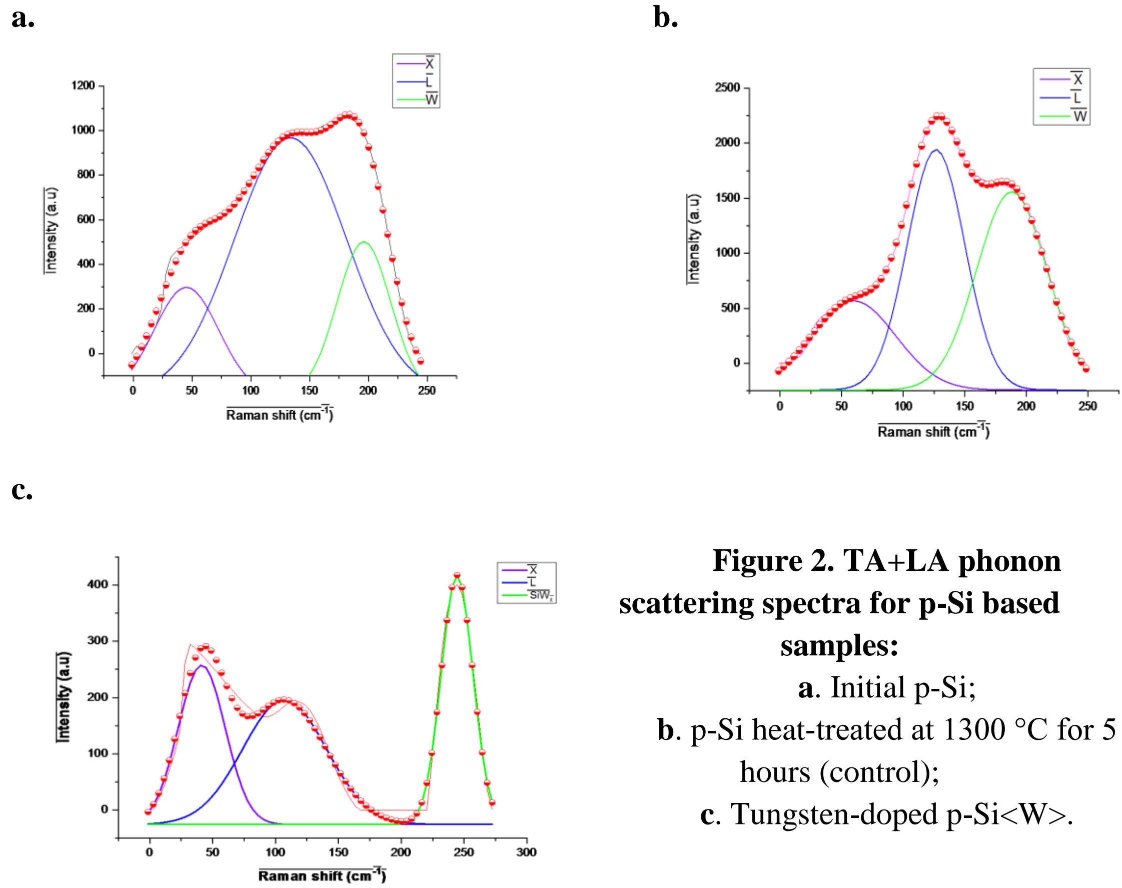

Figure 2. TA+LA phonon scattering spectra for p-Si based samples:
a. Initial p-Si;
b. p-Si heat-treated at 1300 °C for 5 hours (control);
c. Tungsten-doped p-Si<W>.

Table 1. Positional parameters of the TA+LA phonon modes of the samples.

Initial p-Si			
№	Peak center	Peak height	FWHM
X	45	482	64
L	133	1153	112
W	196	686	53
X	59	810	81
L	126	2184	55
W	188	1800	67
X	41	283	44
L	107	221	78
SiW_x	244	443	30

Heat-treated p-Si sample (control). After the initial sample was heat-treated at 1300 °C for 5 hours (Figure 2, b), complex and multifaceted changes were observed in the spectrum. Alongside the sharp increase in the intensity of the main silicon peak (~523 cm^{-1}), the height of the low-frequency acoustic peaks, particularly the L-peak, also nearly doubled (from 1153 to 2184).

At first glance, these two phenomena might seem contradictory, but they demonstrate the dual effect of the heat treatment. While the strengthening of the main peak indicates the annealing of surface defects and amorphous phases and the restoration of overall crystallinity, the increase

in the intensity of the acoustic peaks is explained by a secondary effect of the process. Specifically, the high-temperature heat treatment leads to the formation of new types of local defects within the crystal bulk, such as oxygen precipitates and thermal dislocations that arise during the cooling process.

It is precisely these new, bulk defects that locally disrupt the periodicity (symmetry) of the lattice. These disruptions, in turn, relax the momentum conservation rule, drastically enhancing the contribution of disorder-activated acoustic phonon modes to the Raman scattering [8]. Thus, while the heat treatment improved the overall crystal quality of the sample, it also created new defect centers in its bulk that are sensitive to acoustic vibrations.

Tungsten-doped p-Si<W> sample. Doping with tungsten atoms had the most significant impact on the vibrational properties of the lattice (Figure 2, c). First, the intensity of all acoustic peaks characteristic of silicon decreased sharply. Second, the center of the L-peak shifted significantly to a lower frequency (from 133 cm^{-1} to 107 cm^{-1}). This phenomenon is termed “phonon softening” (or phonon weakening) and is related to the weakening of Si-Si bonds and the creation of local strains in the lattice due to the incorporation of large W atoms [9].

Third, and most importantly, a new peak appeared in the spectrum at 244 cm^{-1} with a very small full width at half maximum (FWHM=30 cm^{-1}). The sharpness of this peak indicates that it belongs to a specific, ordered crystalline phase. A review of the literature shows that this frequency closely matches the characteristic Raman vibrations of the tungsten silicide (WSi_2) phase [10]. Therefore, during the doping process, a new chemical compound-tungsten silicide-was formed on the silicon surface or in the near-surface region of the bulk as a result of the reaction between tungsten and silicon.

In the second stage of studying the Raman spectrometer results, the 250-450 cm^{-1} range was analyzed. In the spectrum of the initial sample (Figure 3, a), a broad and intense peak centered at ~308 cm^{-1} is prominent. This peak corresponds to silicon's fundamental 2TA(X) mode [9].

Its large FWHM value (~43 cm^{-1}) is a natural characteristic of two-phonon processes, which involve phonons from a range of frequencies at the zone edge. Other, weaker peaks in the spectrum (X and W) may also be attributed to other two-phonon combinations (e.g., LA+TA). In general, the clear and intense observation of the 2TA peak indicates that the sample has a good crystalline structure.

Heat-treated p-Si sample (control). After heat treatment (Figure 3, b), an unexpected and interesting change occurred in the spectrum: the intensity of all peaks decreased sharply (e.g., the L peak dropped from 531 to 172), and their FWHM decreased by almost half (for the L peak, from 43 to 23).

The narrowing of the peaks (decrease in FWHM) is a very clear sign that the degree of order in the crystal lattice has increased and the phonon lifetime has lengthened. This conclusion is in full agreement with our previous analysis of the strengthening and quality improvement of the main silicon peak (~523 cm^{-1}), and it confirms once again that surface defects were annealed and overall crystallinity was restored as a result of the heat treatment. The decrease in second-order scattering intensity, however, is a more complex phenomenon and may be related to phonon-phonon interaction mechanisms and changes in the Raman scattering cross-section. But the change in the FWHM parameter is the key indicator here.

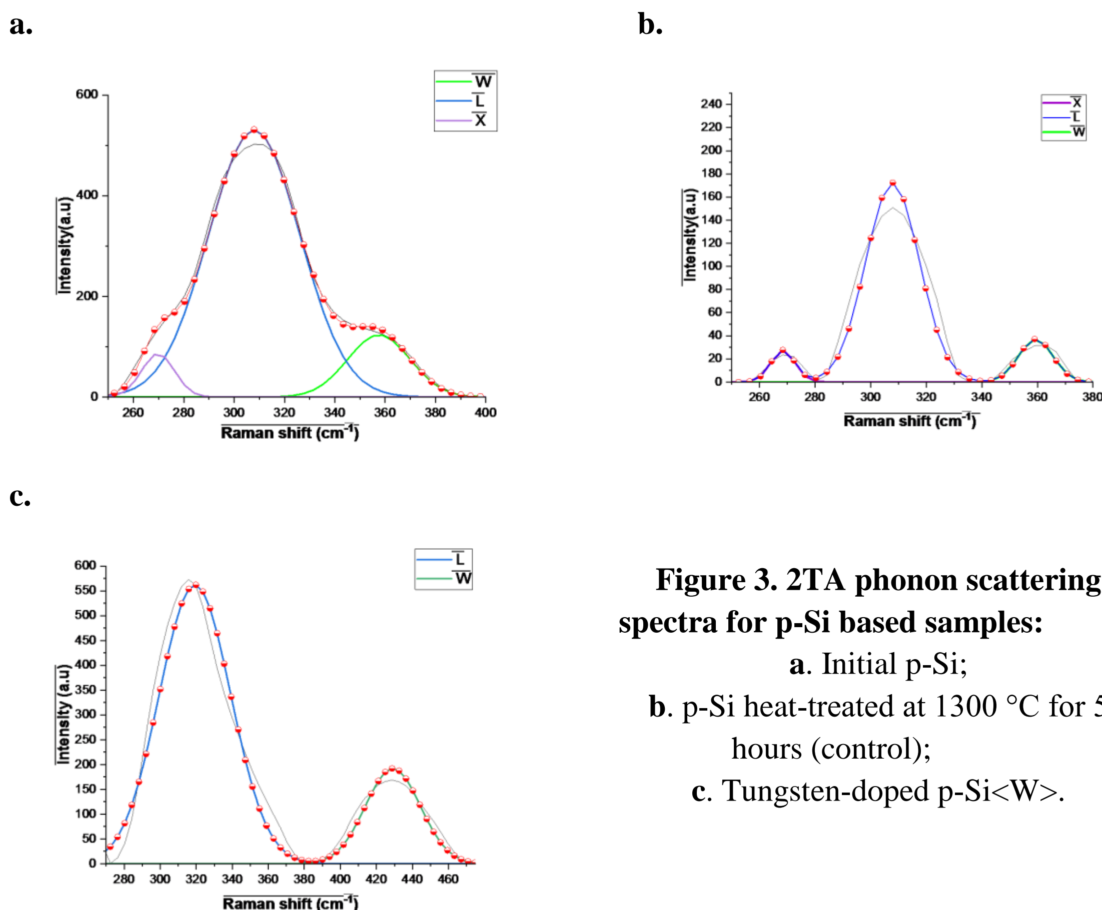

Figure 3. 2TA phonon scattering spectra for p-Si based samples:
a. Initial p-Si;
b. p-Si heat-treated at 1300 °C for 5 hours (control);
c. Tungsten-doped p-Si<W>.

Table 2. Positional parameters of the 2TA phonon modes of the samples.

Initial p-Si			
№	Peak center	Peak height	FWHM
X	269.794	86.9684	15.4629
L	307.9706695	531.31	42.6674
W	357.4266718	123.601	29.3366
X	268.4056888	27.7095	10.1483
L	307.8590893	172.438	22.7817
W	359.4035506	37.2477	14.5367
X	0	0	0
L	319.2826713	562.123	46.773
W	429.120271	192.027	35.9581

Tungsten-doped p-Si<W> sample. Tungsten doping radically changed the spectrum (Figure 3, c). Peak Shift: The main 2TA peak (L) shifted significantly to a higher frequency (308 $cm^{-1} \rightarrow 319\ cm^{-1}$). Such a high-frequency shift (or “blue shift”) of the peak center is a classic sign of compressive stress in the lattice [8].

The incorporation of large-sized tungsten atoms, “squeezing” into the silicon lattice, resulted in strong compressive deformation. This conclusion contrasts with the phonon softening (weakening) observed in the low-frequency acoustic peaks, indicating that the strain field created by the W atoms has a complex nature and affects different phonon modes differently.

Appearance of a new peak: A new, relatively intense peak (W) appeared in the spectrum at ~429 cm⁻¹. This frequency does not correspond to silicon's characteristic one- or two-phonon modes. This peak, like the one identified at 244 cm⁻¹ in our previous analysis, is another vibrational mode of the tungsten silicide (WSi_2) phase formed in the sample. According to the literature, a Raman peak for the WSi_2 phase is also observed in the ~450-460 cm⁻¹ region [9].

In our case, the appearance of this peak at a slightly lower frequency (~429 cm⁻¹) can be explained by **stress** within the silicide phase or its stoichiometry. This result further strengthens our conclusion about the formation of the WSi_2 phase. In studying the results from the Raman spectrometer, we also focus on the third region, the 850-1000 cm⁻¹ range.

Initial p-Si sample. In the 850-1000 cm⁻¹ range of the initial sample's spectrum (Figure 4, a), a strong, broad peak with a distinct structure is observed. Gaussian analysis separates it into two main components: a main peak at ~951 cm⁻¹ (X in the table) and a peak at ~986 cm⁻¹ (L in the table). According to the literature, these peaks correspond to the 2TO(W) and 2TO(L) vibrational modes, respectively. The presence of these complex peaks and their shape is further evidence of the sample's good crystalline quality [7].

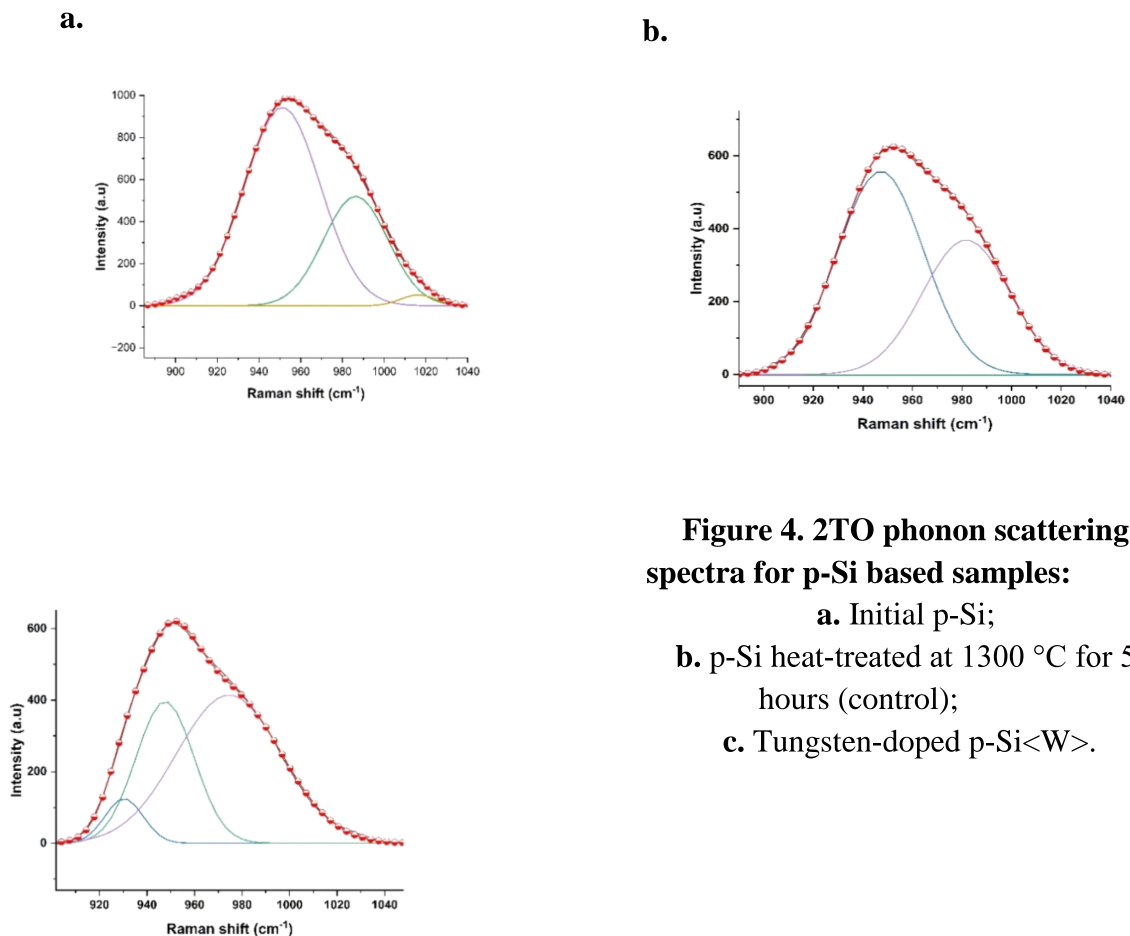

Figure 4. 2TO phonon scattering spectra for p-Si based samples:
a. Initial p-Si;
b. p-Si heat-treated at 1300 °C for 5 hours (control);
c. Tungsten-doped p-Si<W>.

Table 3. Positional parameters of the 2TO phonon modes of the samples.

Initial p-Si			
№	Peak center	Peak height	FWHM
X	951.2017592	943.461	42.9819
L	986.3884147	520.755	36.2679
W	1016.278059	51.8428	19.5605

X	947.1904212	557.443	41.0247
L	0	0	0
W	981.6970444	369.272	41.6404
X	930.339959	124.81	18.8587
L	947.575062	396.366	28.763
W	974.5129583	414.365	51.9684

Heat-treated p-Si sample (control). After heat treatment (Figure 4, b), significant changes also occurred in the spectrum in this region. First, the overall intensity of the spectrum decreased. Second, its shape changed completely: the 2TO(L) peak at ~986 cm^{-1} disappeared (i.e., its intensity was registered in the negative (10^{-4}) range), the intensity of the main peak (~947 cm^{-1}) decreased, and in its place, a new, more symmetrical peak (W in the table) appeared at ~982 cm^{-1}.

These changes, as mentioned in our previous analyses, once again confirm the dual effect of the heat treatment. The disappearance of the 2TO(L) peak and the change in the spectrum's shape are related to the recrystallization of the lattice and the change in its internal stress. The appearance of a new peak at ~982 cm^{-1} is of particular interest. This frequency may be characteristic of oxygen-related defects in silicon. It is known that silicon grown by the Czochralski (Cz) method has a high oxygen concentration, and during high-temperature heat treatment, it forms oxygen precipitates with Si-O-Si bonds [10]. The literature reports that the vibrations of these precipitates manifest in this exact region. This reinforces our data that new types of defects appeared in the crystal bulk as a result of the heat treatment.

Tungsten-doped p-Si<W> sample. The spectrum of the tungsten-doped sample (Figure 4, c) is completely different from that of silicon. Instead of the two-component peak from the initial sample, three separate peaks with almost equal intensities (~930, ~948, and ~975 cm^{-1}) were now observed. Peak shifts the positions of the peaks differ sharply from the standard state for silicon. In particular, the shift of the lowest-frequency peak from ~951 cm^{-1} to ~930 cm^{-1} indicates high deformation and stress (strain) introduced into the lattice by the tungsten atoms.

Formation of a new spectrum: This spectrum cannot be considered silicon's intrinsic 2TO scattering spectrum. It is a completely new spectrum, reflecting the new, complex vibrational states that have emerged as a result of the interaction between tungsten and silicon. In our previous analyses, we determined that the tungsten silicide (WSi_2) phase was formed, identified at 244 cm^{-1} and 429 cm^{-1}. Although this high-frequency region is not the area where the main peaks of WSi_2 are located, the presence of this new phase fundamentally alters the electronic and phonon properties of the entire material. Consequently, complex, multi-phonon scattering processes arise, creating the new spectrum we observe. This result indicates that the introduction of W not only generates defects but also modifies the fundamental vibrational properties of the entire material.

CONCLUSION

Raman spectroscopy analysis conclusively confirmed that both doping and the formation of a new phase occurred during the diffusion process. The observation of new, intense peaks at frequencies of ~244 cm^{-1} and ~429 cm^{-1} in the p-Si<W> spectrum indicates the formation of a stable crystalline phase of tungsten silicide (WSi_2) on the silicon surface.

The incorporation of large tungsten atoms and the formation of the WSi_2 phase induced strong compressive mechanical stresses within the silicon crystal lattice. This was confirmed by the shift of the 2TA phonon peak (from ~308 cm^{-1} to ~319 cm^{-1}) and the primary silicon LO peak (from ~523 cm^{-1} to ~524 cm^{-1}) towards higher frequencies in the Raman spectrum. Thus, it was determined that tungsten doping fundamentally alters not only the electrical properties of silicon but also its compositional (oxygen) and fundamental structural characteristics (formation of the WSi_2 phase and lattice stress).

REFERENCES.

1. Kh.S. Daliev, Sh.B. Utamuradova, O.A. Bozorova, and Sh.Kh. Daliev, “Joint effect of Ni and Gf impurity atoms on the silicon solar cell photosensitivity,” Applied Solar Energy (English translation of Geliotekhnika), 41(1), 80–81 (2005).
2. K.S. Daliev, Sh.B. Utamuradova, A. Khaitbaev, J.J. Khamdamov, Sh.B. Norkulov, and M.B. Bekmuratov, “Defective Structure of Silicon Doped with Dysprosium,” East Eur. J. Phys. (2), 283 (2024). https://doi.org/10.26565/2312-4334-2024-2-30
3. X. Kong, Z. Xi, L. Wang, Y. Zhou, Y. Liu, et al., “Recent Progress in Silicon−Based Materials for Performance Enhanced Lithium Ion Batteries,” Molecules, 28(5), 2079 (2023). https://doi.org/10.3390/molecules28052079
4. Jerzy Ruzyllo, Richard E. Novak, “Cleaning technology in semiconductor device manufacturing” ISBN 1-56677-188-9 Printed in the United States of America
5. K. Nakashima “Thermally induced defects in p-type silicon” Journal of Applied Physics (1993)
6. R. Shuker and R. W. Gammon, "Raman-Scattering Selection-Rule Breaking in Amorphous Materials," Physical Review Letters, vol. 25, no. 4, pp. 222–225, 1970
7. P. A. Temple and C. E. Hathaway, "Multiphonon Raman spectrum of silicon," Physical Review B, vol. 7, no. 8, pp. 3685–3697, 1973
8. L. Romano, A. M. Piro, M. G. Grimaldi, and C. Bongiorno, "Raman spectroscopy analysis of defects and strain in ion implanted Si," Journal of Applied Physics, vol. 121, no. 23, 235105, 2017.
9. De Wolf, "Micro-Raman spectroscopy to study local mechanical stress in silicon integrated circuits," Semiconductor Science and Technology, vol. 11, no. 2, pp. 139-154, 1996.
10. G. Milekhin, M. S. A. Guedes, L. A. M. G. G. de Souza, et al., "Structural and vibrational properties of tungsten silicide thin films grown by magnetron sputtering," Journal of Applied Physics, vol. 129, 015301, 2021.