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FTIR SPECTRUM ANALYSIS OF SILICON DOPED WITH ERBIUM

Sharifa B. Utamuradova, Jonibek J. Khamdamov,
Bekzod Sh. Alikulov
Institute of Semiconductor Physics and Microelectronics at the National University of Uzbekistan, Tashkent, Uzbekistan
Khojakbar S. Daliyev
Branch of the Federal State Budgetary Educational Institution of Higher Education "National Research University MPEI",Tashkent, Uzbekistan
E-mail: bekzod.alikulov08199@gmail.com

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Abstract. Semiconductor materials based silicon are a key component of modern microelectronics and optoelectronics. In particular, when Erbium (Er) is introduced into the crystal lattice, a number of important structural changes occur in the silicon structure. In silicon, such changes are particularly well detected by infrared (FTIR) spectroscopy, since this method can accurately record the vibrational modes of bonds such as Si–O–Si, Er–O, Si–C, etc. The formation of new phases in the structure, the degree of oxidation, and the concentration of optically active oxygen are estimated by the location, intensity, and width of the peaks obtained using FTIR. The most important changes were noted around the Si–O–Si assymmetric stretching vibration (ν_{as}) line. While this peak was detected at 1099 cm^{-1} in the sample with erbium atoms introduced, in the original sample it shifted to 1109 cm^{-1}, its intensity also decreased, and the line broadened. These changes are explained by the formation of an oxygen-enriched but highly disordered amorphous SiO_x layer during thermal treatment. As a result, the angle in the Si–O–Si bonds widens, the bond length increases slightly, which leads to a decrease in the vibrational frequency, along with a decrease in bond elasticity. The broadening of the peak indicates an increase in the angle and bond length distribution in the structure.

Keywords: monocrystalline silicon (n-Si); erbium; rare earth element; heat treatment, FTIR spectrometer; diffusion

ИК-ФУРЬЕ СПЕКТРАЛЬНЫЙ АНАЛИЗ КРЕМНИЯ, ЛЕГИРОВАННОГО ЭРБИЕМ

Ш. Б. Утамурадова, Ж. Ж Хамдамов,
Б. Ш. Аликулов
[a]Институт физики полупроводников и микроэлектроники Национального университета Узбекистана, г. Ташкент, Узбекистан
Х. С. Далиев
Филиал Федерального государственного бюджетного образовательного учреждения высшего образования «Национальный исследовательский университет «МЭИ», г. Ташкент, Узбекистан
E-mail: bekzod.alikulov08199@gmail.com

Аннотация: Полупроводниковые материалы на основе кремния являются ключевым компонентом современной микроэлектроники и оптоэлектроники. В частности, при введении эрбия (Er) в кристаллическую решетку происходит ряд важных структурных изменений в структуре кремния. В кремнии такие изменения особенно хорошо обнаруживаются с помощью инфракрасной (ИК) спектроскопии, поскольку этот метод позволяет точно регистрировать колебательные моды связей, таких как Si–O–Si, Er–O, Si–C и т. д. Образование новых фаз в структуре, степень окисления и концентрация оптически активного кислорода оцениваются по положению, интенсивности и ширине пиков, полученных с помощью FTIR. Наиболее важные изменения были отмечены вокруг линии асимметричного валентного колебания Si–O–Si (ν_{as}). В то время как этот пик был обнаружен при 1099 см$^{-1}$ в образце с введенными атомами эрбия, в исходном образце он сместился до 1109 см$^{-1}$, его интенсивность также уменьшилась.Эти изменения объясняются образованием обогащенного кислородом, но сильно разупорядоченного аморфного слоя SiO_x в процессе термической обработки. В результате угол в связях Si–O–Si увеличивается, длина связи несколько увеличивается, что приводит к снижению частоты колебаний и уменьшению эластичности связи. Уширение пика указывает на увеличение распределения углов и длин связей в структуре.

Ключевые слова: монокристаллический кремний (n-Si); эрбий; редкоземельный элемент; термическая обработка, ИК-Фурье-спектрометр; диффузия.

INTRODUCTION

It is known that there are several chemical impurities that have the most serious effect on the defect structure of silicon. These include, first of all, alloying impurities (P, B and As), some transition metals (such as Ni, Fe and Cu), as well as oxygen and carbon. All of these impurities additionally exhibit significant electroactivity in silicon[1,2].

The effect of alloying elements is well known, as they determine the type of conductivity and resistance of a crystal. Oxygen and carbon are the most abundant elements in silicon, and oxygen is one of the main elements in crystals grown by the Chakhralzkiy method and zone melting method, so we will dwell on this in more detail in this section[3,4].

EXPERIMENTAL METHOD

In the research process, n-type silicon (KEF-35) single crystal samples were selected as the basis. For the purpose of comparative analysis, erbium diffusion was performed, a control sample prepared under the same thermal treatment conditions was obtained, and erbium atoms were introduced and prepared into our (KEF-35) silicon single crystal samples taken as the basis.

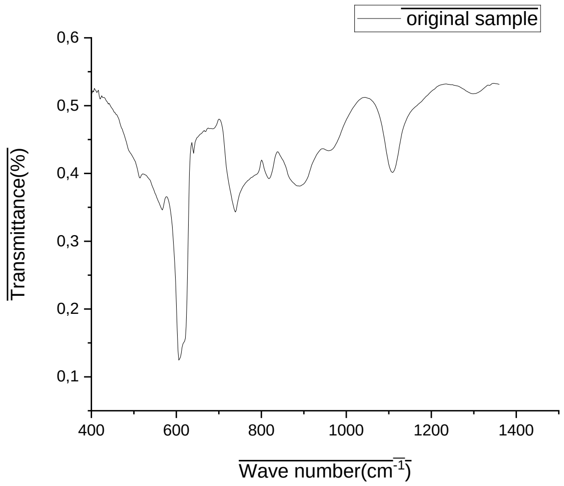

Figure 1. n-Si original initial sample FTIR spectrum

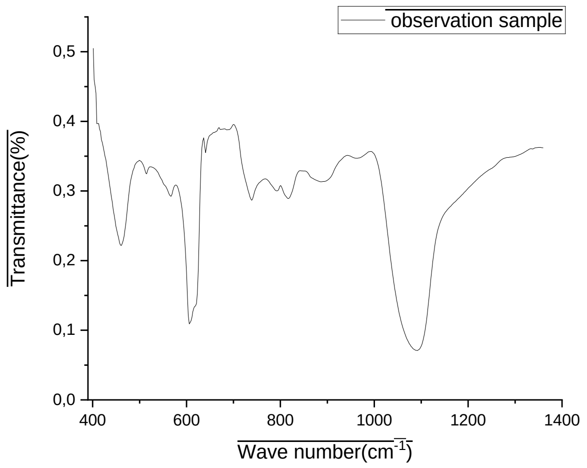

Figure 2. FTIR spectrum of n-Si $_{control}$ sample
n-Si$_{control}$ (heat treated at 1200 °C for 5 hours in a quartz ampoule under vacuum conditions and rapidly cooled after heat treatment)

Analysis of the FTIR spectra showed that in both samples the spectral lines belonging to the main compound complexes were detected around the same wavenumbers. However, the line located at 460.3 cm^{-1} was an exception to this generality, reflecting an important difference between the samples. A clear peak was observed at this wavenumber in the sample thermally treated at 1200 °C for 5 h in a closed atmosphere and in the samples with erbium atoms introduced.

This indicates that the external environment with oxygen is a decisive factor for the formation of complex bonds of the O–Si–O type. The line observed at 460.3 cm^{-1} corresponds to bending vibrations occurring in amorphous oxide layers, as reported in the literature. Also, no significant change in the intensity of the line located at 606 cm^{-1}, which belongs to Si–C complexes, was observed. This indicates that the concentration of carbon atoms and the bonding properties did not change much during the thermal treatment.

In the framework of the study, in order to alloy silicon (Si) crystals with Erbium (Erbium) atoms, high-purity (99.999%) Erbium element was deposited onto the surface of a Si single crystal (Cz-Si) grown by the Czochralski method by thermal sputtering. After that, the prepared samples were subjected to a diffusion process at a temperature of 1200 °C for 5 hours. Diffusion was carried out under two different conditions: under vacuum conditions at a pressure of 10^{-3} Torr, in a quartz ampoule, and in n-Si<Er> samples. In both cases, the samples were rapidly cooled after the diffusion process.

RESULTS AND CONSIDERATIONS

In order to assess the structural changes and bonding state, the infrared transmission (FTIR) spectra of the prepared samples were analyzed. Figure 3 shows the FTIR spectra of the erbium-doped silicon samples. Although the peaks corresponding to the common wavenumbers shown in Figure 1 are not separately marked in the graph, the distinction of other peaks formed is clarified by colored lines:

Black color - specific peaks corresponding to the original sample,

Red color - peaks characteristic of the n-Si$_{control}$ sample thermally treated under vacuum conditions, Blue color - peaks characteristic of the n-Si<Er> sample with Erbium diffusion in a vacuum environment.

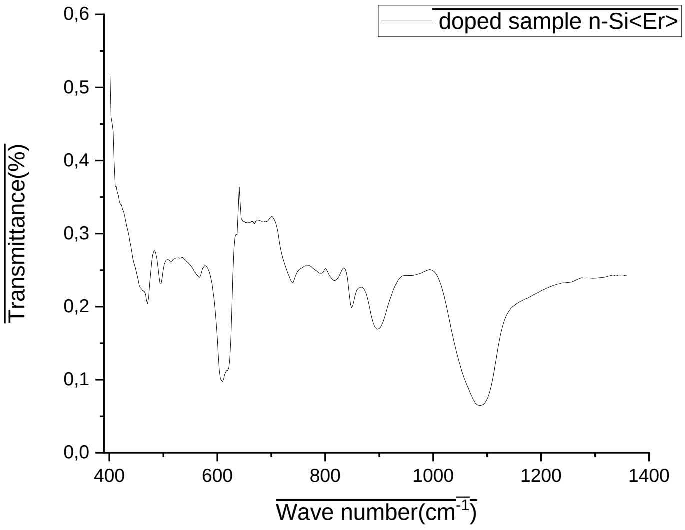

Figure 3. FTIR spectrum of n-Si<Er> (Si sample that doped with Erbium)

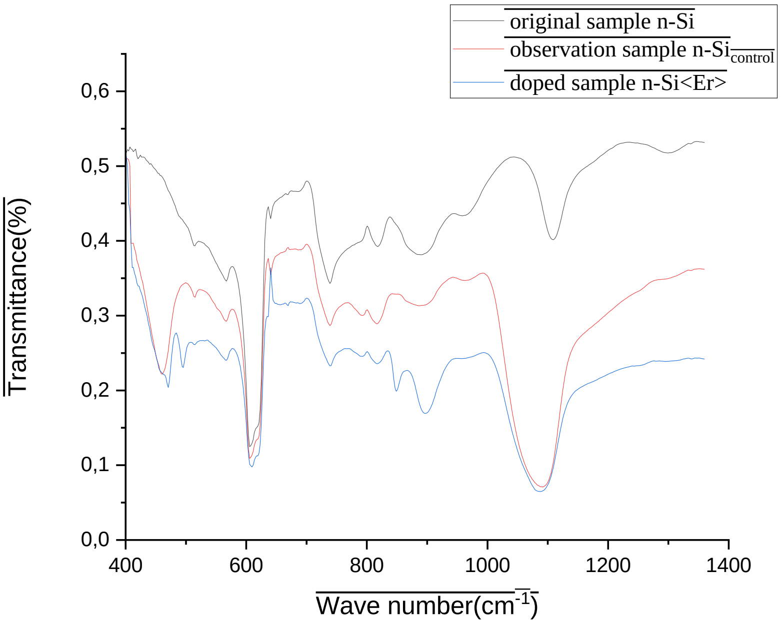

Figure 4. FTIR spectrum of n-Si,n-Si$_{control}$,n-Si<Er> samples

In order to assess the structural changes and bonding state of erbium-doped silicon samples, their infrared transmission spectra (FTIR) were analyzed. The study included n-Si<Er> sample, n-Si $_{control}$ sample, and n-Si starting samples were compared. The main absorption lines in the range of 400–1100 cm^{-1} were identified according to the Er–O, Er–O–Si, and Si–O vibrations reported in the literature[5].

On the other hand, the n-Si<Er> sample diffused in a vacuum environment has a smaller number of peaks, with absorptions at 480, 895, cm^{-1}. These peaks indicate the presence of Er–O bonds and partially developed silicate structures. The lines in the range of 490–540 cm^{-1} correspond to Er–O vibrations belonging to the cubic phase of Er_2O_3, while the lines in the range of 855–900 cm^{-1} correspond to absorptions of Si–O–Er and Si–O–Si bonds [6-9].

Compared with the literature data, it was found that the formation of $Er_2Si_2O_7$ silicate was more complete in the n-Si<Er> sample[10]. In particular, the presence of the main peak around 480 cm^{-1} confirms the free oxidation of Erbium. At the same time, the absorptions in the range of 700–730 cm^{-1} and several broad peaks in the range of 840–1090 cm^{-1} indicate the deep development of silicate complexes in the sample formed in a closed environment[11-15].

In conclusion, based on FTIR spectra, it is revealed that the conditions of the diffusion process significantly affect the bonds and phases formed in the sample. This can lead to increased structural complexity and stability of the surface layer, which is limited to the formation of Er–O clusters and partial silicate structures under vacuum conditions, reflecting the low oxidation state [16].

As a result of high-temperature Er diffusion and subsequent thermal treatments, significant changes in the optically active oxygen and carbon concentrations were observed in n-Si<Er> samples. The graphical data presented in the figures above serve to analyze the results (Table 1) of the oxygen concentration calculated using the SemiSpec program of the FSM-2201 device based on the absorption intensity in the region of ~1100 cm^{-1} in the FTIR spectrum. It can be noted that Si–O–Si bonds directly affect the electrophysical parameters of the crystal. Therefore, determining the optically active oxygen concentration in the crystal structure is a is one of the important scientific goals of the study. The FTIR absorption spectra of silicon samples with Er diffusion in a closed environment were analyzed. In the control sample with Er added, which was heat treated at 1200 °C for 5 hours and then rapidly cooled, it was observed that the concentration of optically active oxygen decreased by 2.61%. This indicates that Er atoms reacted with interstitial oxygen atoms in the silicon crystal lattice, forming complex bonds such as Er–O or Er–O–Si. As a result, the optical activity of oxygen decreased, resulting in a decrease in intensity in the corresponding areas of the absorption spectrum. This directly confirms the effect of Er diffusion on the optically active state of oxygen[17-19]. In this sample, the concentration of optically active oxygen decreased to 0.061×10 cm^{-3}, i.e., a decrease of 2.61% compared to sample control. This indicates that during the high-temperature thermal treatment and rapid cooling, the oxygen atoms previously bound in the cluster state partially dissolved and returned to the optically active state. As a result, the absorption line in the FTIR spectrum deepened and the O_{opt} value increased. The carbon concentration did not change significantly in this sample.

Table 1: Erbium-doped silicon diffusion regime, O and C concentrations

No.	Sample	Diffusion temperature and environment	Cooling mode	Oxygen and Carbon Concentration
1.	$n-$ Si(original)			$N_{O_2} = 1{,}450 \times 10^{17}\text{см}^{-3}$ $N_C = 2{,}757 \times 10^{17}\text{см}^{-3}$
2.	$n - Si(control)$	$T = 1200$℃ да $t =$ 5соат (closed environment)	Rapidly cooled	$N_{O_2} = 2{,}397 \times 10^{17}\text{см}^{-3}$ $N_C = 2{,}765 \times 10^{17}\text{см}^{-3}$

3.	$n - Si < Er >$	$T = 1200$°C да $t = 5$ соат (closed environment)	Rapidly cooled	$N_{O_2} = 2{,}336 \times 10^{17}$ см$^{-3}$ $N_C = 2{,}783 \times 10^{17}$ см$^{-3}$

Changes are shown for samples in which Er diffusion was performed under vacuum conditions. This sharp decrease indicates that Er atoms strongly combine with interstitial O, forming unique silicate (Er_xSi_yO) structures[20]. This process reduces the number of optically active oxygen in the silicon lattice. Carbon also decreases in a similar direction, indicating the presence of Er–C–O ternary complexes.

This situation may be due to the partial decomposition of Er–O complexes formed at high temperatures, as well as the transition of oxygen from the external environment to the interstitial state. As a result, the kinetic stability of the oxide and silicate phases in the crystal lattice is likely to be disrupted. This leads to the clear appearance of oxygen in the spectrum as an optically active center. The carbon concentration is observed to be partially restored at this stage[21].

These results demonstrate the technological availability of Er in a silicon crystal through a high-temperature Er diffusion process. The diffusion carried out in a confined environment is characterized by interactions and clustering of surface bonding oxygen and carbon atoms, and the formation of active complexes of interstitial oxygen with Erbium atoms is observed.

In the next step, a low-temperature thermal treatment and slow cooling process restores the previously bound or clustered oxygen and carbon atoms to the optically active state[22]. This allows the formation of oxide-silicate complexes in the silicon crystal, internal elastic deformation states, and control of surface and bulk defect electrical properties (e.g., density of recombination centers, carrier mobility, deep level states).

Therefore, it is possible to optimize the parameters of semiconductor structures by controlling the spatial position and distribution of oxygen and carbon elements depending on the temperature, environment, and cooling regime of the Earth's diffusion[23].

CONCLUSIONS

These changes, which were detected by the FTIR spectrometer, were recorded around the Si–O–Si asymmetric stretching vibration (ν_{as}) line. In the sample with erbium atoms, this peak was detected at 1099 cm^{-1}, while in the original sample it shifted to 1109 cm^{-1}, its intensity also decreased, and the line broadened. These changes are explained by the formation of an oxygen-enriched, but highly disordered amorphous SiO_x layer during thermal treatment. As a result, the angle in the Si–O–Si bridge bonds is moderately widened, the bond length is slightly increased, which, along with the decrease in bond elasticity, leads to a decrease in the vibration frequency. The broadening of the peak indicates an increase in the angle and bond length distribution in the structure.

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