New Materials, Compounds and Applications
Vol.7, No.1, 2023, pp.37-43

Jomard Publishing

RAMAN SPECTROSCOPY OF DEFECTS IN SILICON DOPED WITH CHROMIUM ATOMS

Sh.B. Utamuradova, Sh.Kh. Daliyev, K.M. Fayzullayev*, D.A. Rakhmanov, J.Sh. Zarifbayev

Institute of Semiconductor Physics and Microelectronics, National University of Uzbekistan, Tashkent, Uzbekistan

Abstract. In this work, Raman spectroscopy is used to study the processes of defect formation in single-crystal silicon doped with chromium. It is shown that the doping of silicon with chromium, one of the transition element impurities, leads to the formation of several peaks in the Raman spectra at 308, 398, 521, and 795 cm^{-1}. It has been found that the peaks at 308 and 398 cm^{-1} found in the Raman spectra of the n-Si<Cr> samples are due to chromium silicides $CrSi_2$. It has been studied that the profile analysis of the distribution of chromium in Si samples using a scanning electron microscope (SEM).

Keywords: *Raman scattering of light, silicon, chromium, diffusion, Raman spectroscopy.*

Corresponding Author: *K.M. Fayzullaev,* ***Institute of Semiconductor Physics and Microelectronics at the National University of Uzbekistan 20 Yangi Almazar st., Tashkent, 100057, Uzbekistan, Tel: +998972550805, e-mail: qahramon_fayz@mail.ru***

Received: *28 November 2022;* ***Accepted:*** *16 February 2023;* ***Published:*** *17 April 2023.*

1. Introduction

At present, single-crystal silicon is the main material for semiconductor microelectronics, optoelectronics, and power electronics, the rapid development of which determines the requirements for semiconductor materials (Eymur & Tuğluoğlu, 2021; Daliyev & Saparov, 2021; Utamuradova & Rakhmanov, 2022).

It is known that the technological route for the manufacture of almost any semiconductor device is accompanied by various cycles of low- and high-temperature treatments, which inevitably leads to the formation of various kinds of defects and has a significant effect on the development of the defect structure of silicon and the formation of deep centers (DC) formed by impurities introduced for the purpose of modification of the properties of semiconductor materials (Abdurakhmanov *et al.,* 2019; Utamuradova *et al.,* 2006; Utamuradova *et al.*, 2023). During technological processing of semiconductor wafers in the production of various structures and devices, various interactions of defects occur with each other, which are determined primarily by point defects characterized by maximum mobility in the lattice (Normuradov *et al.,* 2022; Turgunov *et al.,* 2020). Point defects in a crystal are various doping uncontrolled technological impurities that are in both interstitial and substitutional positions, as well as structural lattice defects - Frenkel pairs, vacancies and interstitial atoms. Structural

How to cite (APA):
Utamuradova, Sh.B., Daliyev, Sh.Kh., Fayzullayev, K.M., Rakhmanov, D.A., & Zarifbayev, J.Sh. (2023). Raman spectroscopy of defects in silicon doped with chromium atoms. *New Materials, Compounds and Applications*, *7*(1), 37-43.

lattice defects are defects that always exist in crystals and under conditions of thermodynamic equilibrium, their concentration is equal to the limiting solubility. Therefore, the processes of formation of a defective crystal structure should be related to them. It should be noted that these processes significantly depend on the thermal history of the crystal, on the presence of various uncontrolled (technological) impurity atoms that enter the Si volume during growth from the melt or during certain technological operations and create electrically active or inactive defect states in the silicon lattice.

In recent years, there has been a growing interest in semiconductor materials with special properties. To obtain such materials, doping with unconventional impurities is increasingly being used (Turgunov *et al.,* 2021). In particular, work is being intensified on the preparation and study of the properties of silicon doped with impurities of transition elements, one of which is chromium atoms.

We have previously studied deep centers formed by chromium atoms in silicon, the behavior of chromium atoms in the silicon lattice under the action of external factors, and the interaction of chromium with uncontrolled impurities by the methods of nonstationary capacitance spectroscopy (Utamuradova *et al.,* 2019).

The purpose of this work was to study the defect structure of silicon doped with chromium using Raman spectroscopy.

Raman spectroscopy, in particular, is one of the most powerful nondestructive analytical methods for analyzing the chemical and phase state of various objects and their structure (Khozhiev, 2020). Raman scattering of light - inelastic scattering of optical radiation by molecules of a substance (solid, liquid or gaseous), accompanied by a noticeable change in the frequency of radiation. In the process of Raman scattering of light, photons of light interact with a molecule and then scatter in all directions. The photons then lose or gain energy, which is then detected and analyzed.

The use of the method of Raman scattering of light (RSL), due to the regularities of changes in the Raman spectra (Parker *et al.,* 1967; Talochkin, 2019; Jafarov *et al*., 2019), provides a wide range of parameters of the object of study. Therefore, Raman spectroscopy is an important nondestructive method for determining the defect structure of single-crystal silicon (Iatsunskyi *et al.,* 2015), which makes it possible to estimate the size of nanocrystals, the ratio of the amorphous and crystalline phases, analyze the composition of crystals, and evaluate deformations and stresses in crystals from the shape and position of the Raman scattering peaks.

2. Materials and methods

For the experiments, we used n-type silicon grown by the Czochralski method with a resistivity of 0.3÷100 Ω ·cm. The original silicon was doped with phosphorus (n-Si). Doping of silicon with chromium was carried out by the diffusion method from the gas phase in evacuated quartz ampoules at temperatures T = 900÷1250 °C for 2÷100 hours, followed by cooling at different rates (Utamuradova *et al.,* 2020).

After diffusion annealing and grinding of the near-surface layer 100 µm thick, enriched with the introduced impurity, in Si<Cr> samples, the resistivity (ρ) was measured using the 4-probe method and the type of conductivity was determined using the thermal probe method (Pavlov, 1987). In according to our previously work (Utamuradova *et al.,* 2022), the presence of chromium in single crystals is confirmed by

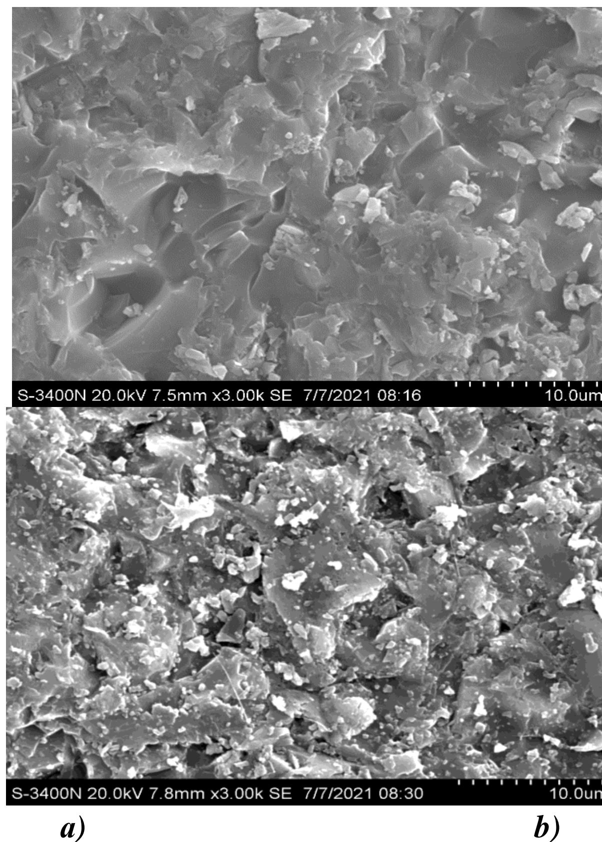
X-ray spectral microanalysis, according to which the chromium content in the samples is 19.62 at. % or 31.12 wt. %.

The study of these samples was carried out by us using Raman spectroscopy on a CARS Raman Spectrometer manufactured by SOLAR TP. The measurements were carried out at room temperature.

3. Results and its discussion

The results of measurements of the resistivity and the type of conductivity in the initial silicon samples and after doping with chromium indicate the donor nature of the levels introduced by chromium into the band gap of silicon. For example, when Cr is introduced into n-Si by diffusion, there is no significant change in the resistivity value.

Fig. 1 shows micrographs of the surfaces of single-crystal silicon wafers before and after doping with Cr. As can be seen, the silicon surface morphology is similar in both cases. It was found that after doping with chromium on the surface of silicon wafers, the density of microparticles increases. These studies were performed on a TESCAN VEGA-3(JINR, Dubna) scanning electron microscope.



a) ***b)***

a - control sample (n-Si), b - silicon doped with chromium (n-Si<Cr>)

Fig.1. Micrographs of the surface of single-crystal silicon

Fig. 2 shows the experimental Raman spectra of single-crystal Si and Si doped with Cr, taken under the same conditions on the CARS Raman Spectrometer. The spectrum shown in Figure 2 has a strong silicon-specific peak at 522 cm^{-1} with a full width at half maximum (FWHM) of 14 cm^{-1}. Silicon has a cubic structure like diamond

(space group O_h^7). The diamond structure of silicon allows the presence of one Raman-active phonon of the first order of symmetry G_{25}, located at the center of the Brillouin zone, corresponding to a wavenumber of ~520 cm^{-1} (LTO) (Temple & Hathaway, 1973).

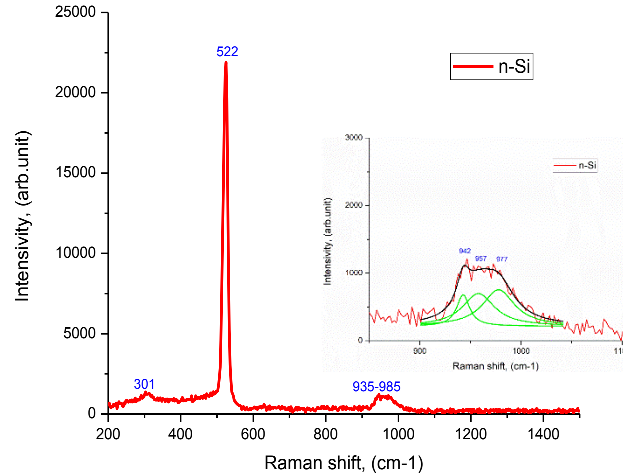


Fig. 2. Raman spectra of control sample (n-Si)

As a result of the long-range translational symmetry of crystalline Si, additional peaks in the range of 100–1100 cm^{-1}, which are much less intense than the LTO first-order peak, can appear in its Raman spectra.

The obtained silicon spectra exhibit a vibration at 301 cm^{-1} (Iatsunskyi *et al.,* 2015; Uchinokura *et al.,* 1974). In many works, this oscillation is attributed to the LA (longitudinal acoustic) mode, but the authors do not provide confirmation of this. In (Graczykowski *et al.,* 2017), it was assumed that a superposition of transverse and longitudinal acoustic modes arises, and the peak is due to overtones TA (2TA(X)) at the critical point X.

In addition, the obtained spectra show a broad peak at 935–985 cm^{-1}. A similar peak between 900–1100 cm^{-1} was found in (Duan Y et al., 2012) for silicon. This vibration is due to the scattering of several transverse optical phonons (2TO) and their overtone state (Smit *et al.,* 2003).

When the broad peak 935–985 cm^{-1} was decomposed using the Lorentz function, three vibrations were found at 942, 957, and 977 cm^{-1}. As noted in (Hensel *et al.,* 1965), second-order scattering reflects the phonon density of states. The shoulder at 930–940 cm^{-1}, which is defined as a two-phonon overtone at the X point of the band edge, appears in our case at 942 cm^{-1}. The peak at 945–955 cm^{-1}, which is defined as a two-phonon overtone at the W point on the band boundary, appears at 957 cm^{-1}. The peak at 980 cm^{-1}, which corresponds to 2TO-phonon overtone scattering from the critical point L, appears at 977 cm^{-1} (Campbell & Fauchet, 1986). The intensity of the peak at 522 cm^{-1} is 17 times greater than that of the strongest second-order scattering (301 cm^{-1}).

As can be seen from Fig. 3, doping of n-Si samples with chromium atoms leads to a significant change in their Raman spectra. The resulting spectrum contains peaks at 308, 398, 521, and 795 cm^{-1}. The vibration at 521 cm^{-1} can be attributed to silicon. When comparing the Raman spectra of the n-Si and n-Si<Cr> samples, it can be seen that doping with chromium leads to a significant decrease in the intensity of the

fundamental vibration at 522 cm^{-1} (Temple & Hathaway, 1973; Uchinokura *et al.,* 1974).

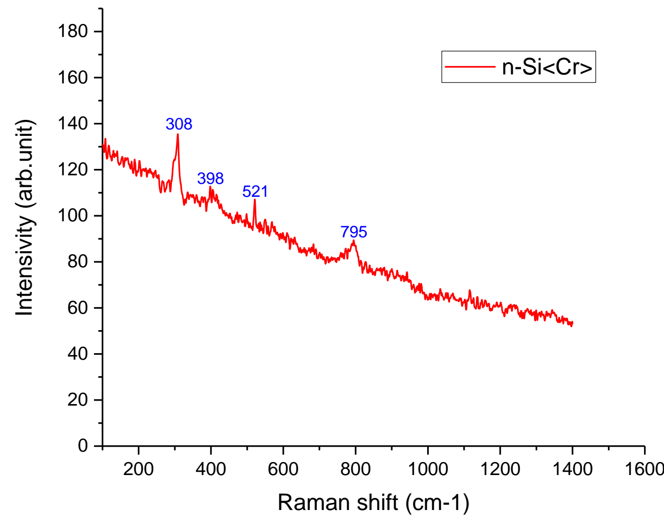


Fig. 3. Raman spectra of single-crystal silicon doped with chromium (n-Si<Cr>)

The most intense peak at 308 cm^{-1} in the Raman spectrum of the n-Si<Cr> single crystal, due to the large shift (7 cm^{-1}) to the high-energy region, can hardly be attributed to the vibration associated with silicon (301 cm^{-1}). According to (Hermet *et al.,* 2015), the characteristic vibrations for $CrSi_2$ in the Raman spectra appear at 233, 251, 301, 307, 357, 399, and 413 cm^{-1}, where the peak at 307 cm^{-1} is the most intense, which is in good agreement with the results obtained in this work (Figure 3). Considering the above, we assume that the Raman peaks at 308 and 398 cm^{-1} found in the spectrum of the n-Si<Cr> samples refer to vibrations associated with the $CrSi_2$ compound. The peak at 795 cm^{-1} is apparently due to the vibration associated with SiO_2 (Borowicz *et al.,* 2012).

4. Conclusion

Thus, an analysis of the results obtained using Raman spectroscopy in studying the processes of defect formation in chromium-doped silicon shows that the introduction of Cr atoms into the Si lattice leads to the transformation of the spectra, the formation of several peaks in the Raman spectra at 308, 398, 521, and 795 cm^{-1}. It has been found that the peaks at 308 and 398 cm^{-1} found in the Raman spectra of the n-Si<Cr> samples are due to chromium silicides $CrSi_2$.

An analysis of micrographs of the surfaces of single-crystal silicon wafers before and after doping with chromium shows that the morphology of the silicon surface in the n-Si and n-Si<Cr> samples is identical, but the density of microparticles increases in the presence of chromium.

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