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DEFECT STRUCTURE OF SILICON DOPED WITH ERBIUM

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The study of thin-film nanocomposites, including crystalline and amorphous silicon nanoparticles embedded in silicon oxide layers, is a key direction in the field of materials for optoelectronics. This study explored the interest in such composites, including erbium silicide ($ErSi_{2-x}$), in the context of their applications in non-volatile memory and photovoltaic devices. Particular attention was paid to the structure and properties of such materials, including the analysis of defects in erbium-doped silicon. The results of the study, based on Raman spectroscopy and X-ray phase analysis, made it possible to identify the characteristics of the composition and structure of the studied samples. The identified data confirmed the presence of crystalline phases of Si and Er in the p-Si-Er composite, and also showed the substitution of Er in the p-Si/SiO_2 structure. Additionally, X-ray microanalysis data confirmed the presence of Si, O and Er in the expected concentrations in the composite film. Further research showed that the introduction of erbium atoms onto the silicon surface leads to minor changes in some signals and the appearance of new vibrations in the Raman spectra of the samples. The decrease in the intensity of the peaks belonging to silicon is associated with the weakening and breaking of some bonds in the structure of the silicon crystal lattice and due to the formation of new bonds in which erbium atoms participate. Thus, the results of this study represent a significant contribution to the understanding of the properties and potential of thin film nanocomposites for applications in optoelectronics, and also enrich our knowledge of the effect of doping on the structure and properties of silicon materials.

Keywords: *Silicon; Erbium; Rare Earth Element; Raman Spectroscopy; Diffusion; Heat Treatment; Temperature; Structure; X-Ray Phase Analysis; Film*
PACS: 71.20. – b, 71.28. + d

INTRODUCTION

Thin-film nanocomposites, consisting of crystalline and amorphous Si nanoparticles embedded in silicon oxide layers, have been extensively studied over the past two decades as suitable materials for nonvolatile memory devices, third-generation photovoltaic devices, and other applications. Continued interest in such composites (including Er-doped ones) remains due to the possibility of manufacturing Si-based light sources for optoelectronic devices [1, 2].

Interest in erbium silicide ($ErSi_{2-x}$) has been growing in recent years, since $ErSi_{2-x}$ exhibits a very low Schottky barrier height on n-type silicon (0.3-0.4 eV) [1, 2]. This unique property leads to promising applications, such as the utilization of $ErSi_{2-x}$ as source and drain contacts in future ultra-scale complementary metal-oxide semiconductor devices, as it can significantly reduce both contact resistance and total series resistance due to its low Schottky contact barrier. Additionally, $ErSi_{2-x}$ finds applications in novel source/drain field-effect transistors featuring a Schottky barrier [3,4].

Despite the low resistivity of $ErSi_{2-x}$, erbium itself can oxidize very quickly due to its high reactivity with oxygen [5]. In many studies on Er silicides reported in the literature, $ErSi_{2-x}$ thin films were typically formed by evaporating erbium onto silicon substrates under ultra-high vacuum conditions, followed by annealing to mitigate oxidation issues.

Silicon doped with rare earth elements has attracted the attention of researchers due to potential issues such as inhomogeneities in impurity distribution, complex diffusion processes, and alterations in its properties resulting from the introduction of rare earth elements into the silicon structure.

This paper examines the issue of the defect structure of silicon doped with erbium. Pristine p-Si, erbium-doped silicon p-Si<Er>, and p-Si-Er composites were studied using Raman spectroscopy and X-ray diffraction.

EXPERIMENTAL PART

For the study, p-Si samples with an initial resistivity of 2.5 Ohm·cm were selected. Prior to alloying, the samples underwent thorough acid-peroxide washing, followed by the removal of oxide layers from their surfaces using an HF solution. After the surfaces of the samples were thoroughly cleaned, films of erbium impurities with special purity (99.999%) were deposited onto the clean Si surfaces using vacuum deposition. Vacuum conditions in the working chamber, with a pressure of approximately $10^{-7}\div10^{-8}$ torr, were maintained by an oil-free vacuum pumping system.

Before diffusion annealing, the samples were placed in evacuated quartz ampoules. Doping of the samples with Er impurities was conducted using the diffusion method at a temperature of 1200°C for 25 hours, followed by rapid and

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slow cooling. To investigate the interaction of impurity atoms in silicon, achieving not only uniform doping of the material but also maximum concentration is crucial. Therefore, we considered the optimal conditions for doping silicon with these impurity atoms.

Raman spectra were acquired using a SENTERRA II Raman spectrometer (Bruker, Germany). This fully automated instrument offers excellent sensitivity and a high resolution of 4.0 cm^{-1}. Senterra calibration was performed automatically and referenced to NIST acetaminophen and silica standards, ensuring a wavelength accuracy of 0.2 cm^{-1}.

The experiments were conducted using a laser with a wavelength of λ_0 = 532 nm, a maximum power of P_{max} = 25 mW, and an acquisition time of 100 s, with the addition of two spectra. This device allows for spectra acquisition in the range from 50 to 4265 cm^{-1}.

The Raman spectra were processed to facilitate comparison of intensity ratios between samples. Prior to normalizing the spectra to the peak at 521 cm^{-1}, corresponding to the most intense peak in the spectral region from 4265 to 50 cm^{-1}, a baseline subtraction was performed for each spectrum.

Raman spectra of samples (4 in total) were obtained at room temperature. The acquisition time for the Raman spectrum was about 120 s. The same laser beam that was used to measure Raman scattering was used to study structural changes. Measurements with increasing laser power density were carried out in order to determine the threshold above which irreversible changes occur. The sample temperature was increased by 20°C under the influence of a laser beam. This temperature increase was estimated using the Stokes/anti-Stokes intensity coefficient formula.

X-ray phase analysis was conducted using a MiniFlex II diffractometer (Rigaku, Japan) equipped with CuKα radiation. Diffraction patterns of the compounds were captured in the angle range of 2θ = 3-60°. The resulting diffraction pattern was analyzed to identify characteristic signals for the resulting p-Si-Er composites, and the presence of elements was determined based on literature data on the phases and the ICDD card database for known compounds. The obtained results enabled us to draw conclusions about the qualitative composition of the samples. X-ray diffraction spectra were recorded at intervals of 0.02° in two-theta, with an exposure time of 2 s at each point.

RESULTS AND DISCUSSION

Figure 1 shows the Raman spectra of both the p-Si type silicon itself and the resulting p-Si-Er composites. The Raman spectrum of the initial sample exhibits peaks at 304 and 521 cm^{-1}, characteristic of cubic silicon, along with a broad peak in the range of 920–1005 cm^{-1} [8–12].

The cubic structure of silicon allows the presence of one first-order Raman-active phonon corresponding to a wave number of 520 ± 1 cm^{-1}, as well as additional peaks with lower intensity [6-11]. According to [13, 14], the vibration at 304 cm^{-1} detected in the Raman spectra of silicon is attributed to the longitudinal acoustic mode. The broad peak in the range of 900–1100 cm^{-1} arises from the scattering of several transverse optical phonons and their overtone state [8,9,10]. Upon studying the broad peak in the range of 920–1005 cm^{-1} as presented in Fig. 1, three vibrations were detected at 944, 948, and 976 cm^{-1}, consistent with theoretical calculations [10].

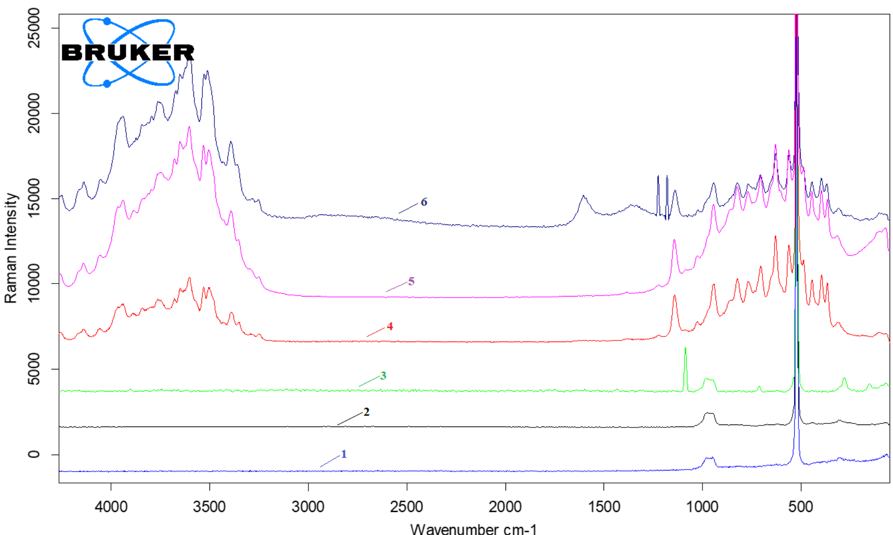

Figure 1. Raman spectra of the obtained composites: silicon (p-Si) with erbium (Er)
Sample 1 represents the original p-Si; Sample 2 denotes doped p-Si<Er> (slow cooling); Sample 3 corresponds to doped p-Si<Er, Cr> (fast cooling); Sample 4 represents the resulting composite p-Si-Er-Cr (slow cooling); Samples 5 and 6 denote p-Si-Er (slow cooling) and p-Si-Er (fast cooling) respectively

Further doping of p-Si silicon wafers with erbium results in minor changes and the emergence of new vibrations in the Raman spectra. The intensity of the main silicon peak at 521 cm^{-1} decreases by a factor of 1.5, while its width at half maximum remains virtually unchanged at approximately 4.0 cm^{-1}. This decrease in peak intensity is likely attributed to the weakening and breaking of bonds in the silicon crystal lattice due to the introduction of erbium atoms.

The vibration intensity at a frequency of 304 cm^{-1} generally increases, and its width at half maximum decreases from 8.2 to 6.1 cm^{-1}. As a result of studying the broad peak appearing in the region of 900–1100 cm^{-1}, three vibrations were also recorded at 946, 952 and 979 cm^{-1} (Fig. 1). The shift of these vibrations towards the lowest wave numbers compared to the original silicon reaches 4 cm^{-1}, with the largest shift observed at 948 cm^{-1}. Also, other signals appear in the Raman spectra of the obtained composites. For example, the wavenumber of 478 cm^{-1} indicates out-of-plane deformation of Si-O, and the peak of 842 cm^{-1} indicates Si-O bending. The wavenumber of 1053 cm^{-1} indicates Si-O-Si stretching. The wavenumber of 614 cm^{-1} indicates Si-Si bonds [19-21]. In Figure 1, four peaks can also be identified at 422 cm^{-1}, 491 cm^{-1}, 875 cm^{-1} and 1046 cm^{-1}. The peak with a wavenumber of 422 cm^{-1} corresponds to the impurity vibrational Er-O bond, the signals for the Si-O bond are at 491 cm^{-1}. The wavenumber at 1046 cm^{-1} indicates asymmetric stretching of Si-O-Si [19-21]. It is assumed that the two signals corresponding to silicon cannot be detected using the Raman spectrum due to the largest Er weight, since it is completely covered by new Er signals.

The change in the Raman spectrum of p-Si-Er in the range of 60–280 cm^{-1} (Fig. 1) is due to the presence of elemental Er and the formation of new bonds between Er-Si [15-17, 22]. In [15], multichannel Raman spectroscopy was used to quantitatively characterize the formation of Pt-Si at the Pt-Si (100) interface, where spectra were obtained from Pt-Si layers up to 10 Å thick and from <40 Å Pt-Si at 140 Å. According to this work, characteristic vibrations for Pt-Si appear at 82–85 and 140 cm^{-1}. These works also report Raman modes near 90 and 140 cm^{-1} from Pt-Si, the latter mode being due to the formation of a disordered mixed phase of Pt and Si.

X-ray phase analysis

X-ray diffraction patterns of erbium films deposited under various conditions are presented in Fig. 2. The lattice constants calculated from the X-ray diffraction patterns of p-Si-Er are Si = 0.5426 nm, Er = 0.3572 and Er = 0.5626 nm, respectively. The arrangement of Si and Er atoms along crystalline orientations is triangular. The side lengths of the triangles are 0.3841 nm for p-Si and 0.3568 nm for Er, so there is a lattice mismatch [25]. It can be assumed that a certain proportion of defects and deformations will be formed during initial deposition due to lattice mismatch.

The obtained X-ray phase analysis data, presented in Figure 2, indicate the presence of both Si and Er in the composition of the studied samples.

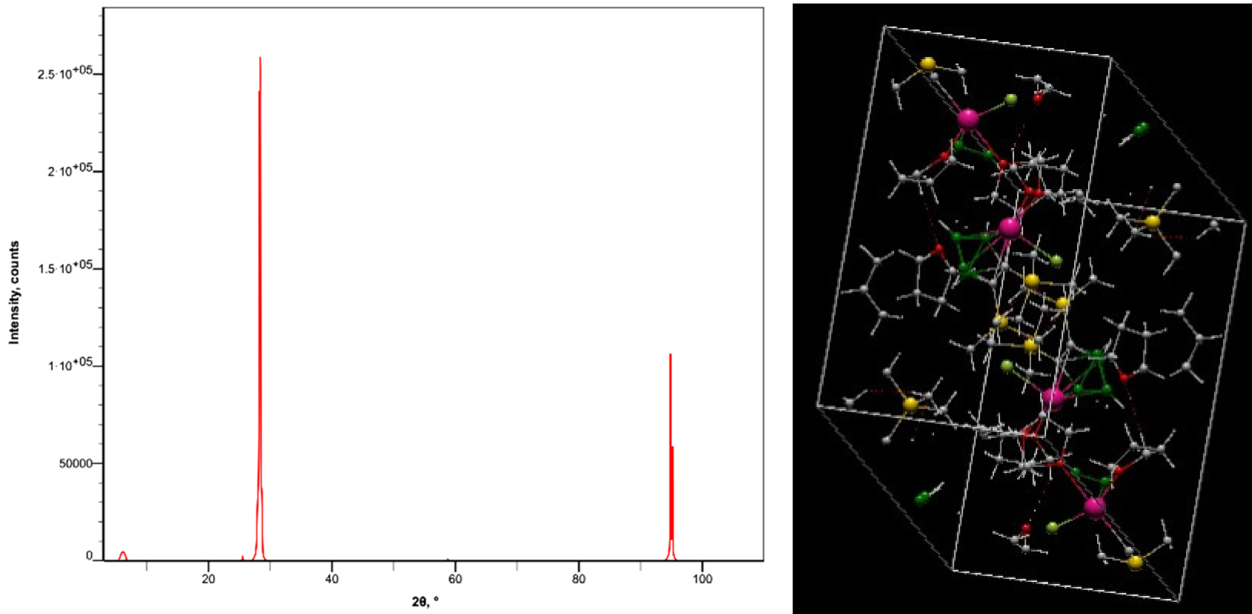

Figure 2. X-ray microanalysis of the resulting p-Si-Er composite

As can be seen from the given X-ray phase analysis data (Fig. 2) of the resulting p-Si-Er composite, the elements Si, O and Er are present in the film in the expected concentrations. This result confirms the substitution of Er in the p-Si/SiO_2 structure. The peak at 28.40 corresponds to Si originating from the glass substrate [23,24]. The present peak at 94.80 is attributed to Er.

Lau et al. [26] studied the effect of the oxide layer impregnated between the metal layer and the Si substrate on the surface morphology of the composite, it is obvious that interfacial contamination is the cause of the formation of surface pores in the silicide layer. These works provide data that the pores consist of $ErSi_{2x}$, therefore the non-planar nature of the $ErSi_{2x}$/Si(111) interfaces in the region of pinholes additionally leads to the formation of polycrystalline $ErSi_{2x}$ on the Si surface [26,27]. Consequently, a large number of Si atoms from the substrate diffuse through the depressions, which contain much faster atomic diffusion paths. Lau et al. [26] and Shen et al. [27] found that the shape of the surface holes is rectangular for Er on Si and triangular for Dy on Si.

CONCLUSIONS

Analysis of the results obtained using Raman spectroscopy shows that the introduction of Er atoms onto the p-Si surface leads to both minor changes in some signals and the appearance of new vibrations in the Raman spectra of the samples. The decrease in the intensity of the peaks belonging to silicon is probably associated with the weakening and breaking of bonds in the structure of the silicon crystal lattice due to Er atoms. The appearance of new vibrations in the range of 60–280 cm^{-1} in the p-Si-Er spectra is associated with the presence of elemental Er and the formation of new Er-Si bonds. The presence of erbium on the p-Si surface is confirmed by X-ray microanalysis data.

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ДЕФЕКТНА СТРУКТУРА КРЕМНІЮ, ЛЕГОВАНОГО ЕРБІЄМ

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Дослідження тонкоплівкових нанокомпозитів, включаючи кристалічні та аморфні наночастинки кремнію, вбудовані в шари оксиду кремнію, є ключовим напрямком у галузі матеріалів для оптоелектроніки. Це дослідження вивчало інтерес до таких композитів, включаючи силіцид ербію ($ErSi_{2-x}$), у контексті їх застосування в енергонезалежній пам'яті та фотоелектричних пристроях. Особливу увагу було приділено структурі та властивостям таких матеріалів, у тому числі аналізу дефектів кремнію, легованого ербієм. Результати дослідження, засновані на спектроскопії комбінаційного розсіювання та рентгенофазовому аналізі, дозволили виявити особливості складу та структури досліджуваних зразків. Ідентифіковані дані підтвердили наявність кристалічних фаз Si та Er в композиті p-Si-Er, а також показали заміщення Er у структурі p-Si/SiO_2. Крім того, дані рентгенівського мікроаналізу підтвердили наявність Si, O та Er в очікуваних концентраціях у композитній плівці. Подальші дослідження показали, що введення атомів ербію на поверхню кремнію призводить до незначних змін деяких сигналів і появи нових коливань у спектрах КРС зразків. Зменшення інтенсивності піків, що належать кремнію, пов'язане з ослабленням і розривом деяких зв'язків у структурі кристалічної решітки кремнію і внаслідок утворення нових зв'язків, в яких беруть участь атоми ербію. Таким чином, результати цього дослідження є значним внеском у розуміння властивостей і потенціалу тонкоплівкових нанокомпозитів для застосування в оптоелектроніці, а також збагачують наші знання про вплив легування на структуру та властивості кремнієвих матеріалів.

Ключові слова: *кремній; ербій; рідкоземельний елемент; раманівська спектроскопія; дифузія; термічна обробка; температура; структура; рентгенівський фазовий аналіз; плівка*