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STRUCTURAL PROPERTIES OF SILICON DOPED RARE EARTH ELEMENTS YTTERBIUM

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This paper presents the results of a study of the state of ytterbium atoms in silicon, carried out using the methods of Fourier transform infrared spectroscopy (IR) and Raman spectroscopy (RS). Silicon samples doped with ytterbium impurities were analyzed using FSM-2201 and SENTERRA II Bruker spectrometers. Registration and identification of both crystalline and amorphous phase components in the samples was carried out. The results of the study confirm that doping silicon with ytterbium impurities leads to a decrease in the concentration of optically active oxygen N_O^{opt} by 30-40%, depending on the concentration of the introduced impurities. It was also found that an increase in the number of defects leads to a broadening of the amorphous zone. It is assumed that similar dependencies exist for the Si-Yb system; however, to the best of our knowledge, similar results have not been reported previously. It is noted that the relative intensity of the three Raman bands in Si-Yb systems in the LTIOS (*The light and temperature induced ordered state*) state changes, and the relative intensity of Si-Si decreases. This indicates that pendant bonds are mainly formed by the breaking of Si-Si bonds. It was also observed that the light intensity causing this condition is far from that required for laser or solid phase crystallization. Using the Raman spectroscopy method, a structural transformation was discovered, expressed in a densely packed array of nanocrystals with a size of less than 11 lattice parameters. Small clusters were under strong internal stress (up to 3 GPa), which probably prevents the cluster size from increasing beyond the critical value for irreversible crystallization.
Key words: *Silicon; Ytterbium; Rare Earth Elements; Raman; Diffusion; Thermal Coolant; Temperature*
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INTRODUCTION

In recent years, many scientists have shown significant interest in the interaction of rare earth metals (REMs) with a semiconductor surface, in particular, the Si surface [1–3]. This interest is caused by the following factors: 1) as a result of the high chemical activity of rare-earth metals, ordered films can be formed at the rare-earth metal–Si interface with specific physicochemical properties, such as high thermal stability, thermal conductivity and electrical conductivity. These films may be promising in terms of their applications in micro and nanoelectronics; 2) in some cases, a barrier (0.18 eV) is formed at the REM–Si interface [11], which in turn allows the use of such systems to create optoelectronic devices operating in the infrared region. Also interesting is the influence of the degree of filling of the 4f shell during the interaction of rare earth metals and silicon. Many studies have studied the processes of formation of REM–Si interference, including interfaces in Si-Yb structures [4,5]. However, in these works the stages of formation of silicides are not given. In this regard, divalent ytterbium, which is one of the components of these structures, is less chemically active than other rare-earth metals. Thus, we can assume that studying the structures will reveal some new fundamental features of the formation of Si-Yb interfaces. In addition, the Si-Yb system is interesting from a practical point of view, since silicide films are formed under certain conditions, and are promising for use in transistors based on the metal–oxide–semiconductor structure [6].

Amorphous semiconductors exhibit various metastable states under illumination [7-10], which results in a significant change in some properties of the films, which can negatively affect the performance and service life of the device. Therefore, the study of structural changes caused by illumination is of great interest for various technologies based on these silicide films. On the other hand, this should contribute to a better knowledge of the physics of amorphous semiconductors and the kinetics of their crystallization, which are fundamental to the above-mentioned technologies, which have not yet been fully studied. The most studied system is a-Si:H, for which two main metastable effects have been identified upon exposure to illumination. The first of these is the Wronski effect [7,8,10], in which light soaking of a-Si:H leads at relatively low concentrations (10^{16}–10^{17} cm^{-3}) to a medium gap state, associated with the formation of defects and breaking of bonds. Another registered metastable effect is structural transformation [9], and it has been proven that the optical and electrical properties of a-Si have undergone significant changes. These transformations disappear upon thermal annealing below 200°C.

The purpose of this work is to study Si<Yb> and nanofilms of Si-Yb structures. Structural changes were studied using Romanov and infrared spectroscopy.

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MATERIALS AND METHODS

Raman spectra were obtained 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 with a laser with a wavelength λ_0=532 nm, a maximum power P_{max}=25 mW, an acquisition time of 100 s, and the 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 522 cm^{-1}, which corresponded to the most intense peak in the spectral region 4265-50 cm^{-1}, we subtracted the baseline for each spectrum.

Raman spectra of samples (4 in total) were obtained at room temperature. The sample temperature was recorded with an accuracy of -60°C. 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.

Fourier transform infrared (FTIR) spectroscopy is a powerful technique used to analyze the infrared spectrum of a sample. It provides information about the molecular vibrations of a substance, which allows the identification of functional groups and composition of the material.

n-Si samples with an initial resistivity from 0.3 to 100 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 high-purity ytterbium impurities (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 Yb impurities was carried out by the diffusion method at a temperature of 1200°C for 40 hours, followed by rapid cooling. To study the interaction of impurity atoms in silicon, not only uniform doping of the material is necessary, but also a maximum concentration. In this regard, we took into account the optimal conditions for doping silicon with these impurity atoms.

RESULTS AND DISCUSSION

Infrared light passes through or reflects off the sample. Molecules in the sample absorb infrared photons, causing the bonds between atoms to vibrate. The transmitted light hits a detector, which records the light intensity depending on the wave number [20-23].

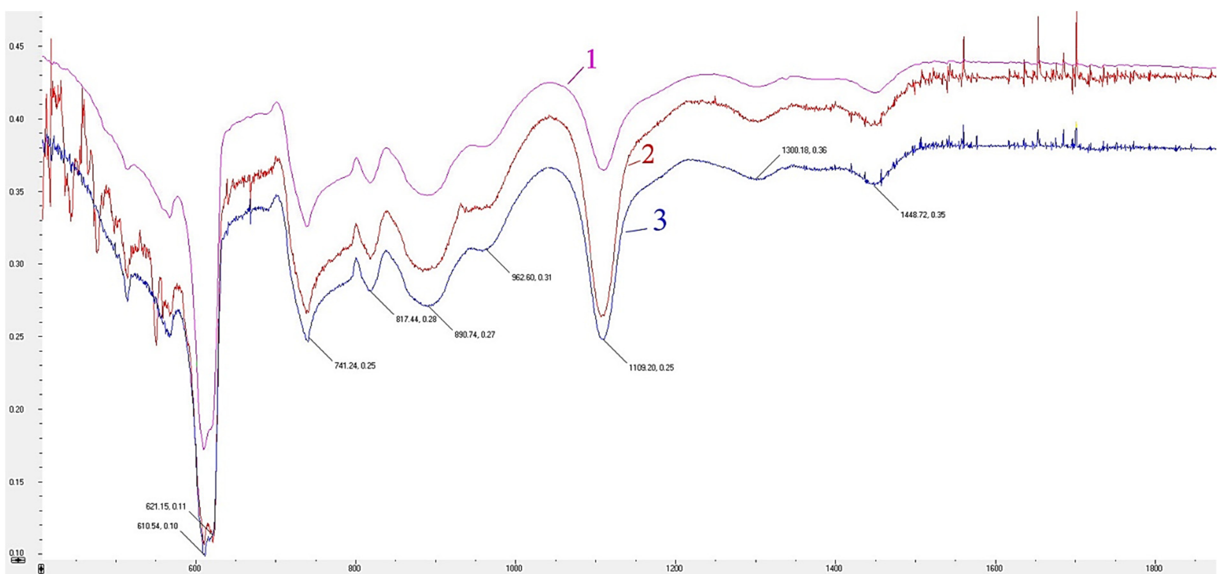

Figure 1. IR spectrum of n-type silicon doped with Yb impurities: 1 - IR spectrum of n-Si<Yb> samples, 2 - IR spectrum of Si original samples, 3 - IR spectrum of Si control samples

Comparing the results obtained, they show that the concentration of optically active oxygen N_O^{opt} decreases significantly after the diffusion of Yb impurities (Fig. 1).

The results show that doping silicon with ytterbium impurities reduces the concentration of optically active oxygen N_O^{opt} by 30-40%, depending on the concentration of the introduced impurities.

To determine the crystallite size using Raman scattering, the bands were selected in accordance with the modified length correlation [18,19]. The Raman intensity can be expressed as

$$I(\omega, L)\alpha \int \exp\left(-\frac{q^2L^2}{8}\right)\frac{d^3q}{[\omega(q)-\omega]^2+\left(\frac{\Gamma_0}{2}\right)^2}. \quad (1)$$

where Γ_0 is the linewidth of the phonon peak of crystalline Si, ω(q) is the phonon dispersion law, the phonon wave vector q is expressed in units of 2π/a, where a is the lattice parameter of crystalline Si, L is the diameter of the crystallites, expressed in units of the lattice parameter. For pure Si, the phonon dispersion equation can be approximated by the equation of the following expression:

$$\omega^2(q,T) = A(T) + [A^2(T) - B(T) \times (1 - \cos \pi q)]^{\frac{1}{2}}. \quad (2)$$

A and B are determined from the phonon dispersion curve

$$A = \frac{(\omega_0(T) + \Delta\omega)^2}{2},$$

$$B = \frac{\frac{(\omega_0(T)+\Delta\omega)^4}{4} - \left((\omega_1(T)+\Delta\omega)^2 - \frac{(\omega_0(T)+\Delta\omega)^2}{2}\right)^2}{2}, \quad (3)$$

where ω_0 and ω1 are the phonon frequencies of the central (q=0) and outer zone (q=1), respectively, and Δω is an additional parameter that we introduce to take into account the magnitude of the internal voltage. Initially, experimental LTIOS spectra in Si were fitted using equation (1) and assuming Δω=0 in equations (3). The change in ω_0 and Γ_0 with temperature changes were previously determined on a crystalline Si sample. The dependence of ω_1 on T was taken to be the same as ω_0. We assume that the shift will occur due to the presence of internal tension and stress, which is not taken into account if Δω=0. The internal stress can be determined by the usual relationship given for crystalline Si [14]:

$$\Delta\omega(cm^{-1}) = 2.3\sigma\ (GPa), \quad (4)$$

It has previously been argued that the difference in Raman phonon bands between crystallites and nanocrystallites mainly concerns their passband, while the Raman frequencies are very similar, a statement supported by attributing the calculated transition to internal voltage [13]. IR (Fig. 1.) and Raman (Fig. 2.) spectra of Si and Si-Yb were obtained for use in the study. The Raman spectrum of amorphous layers consists of several broad bands reflecting a single phonon density of states. When the material is crystalline, the bands become narrower and distinct peaks appear. In the case of Si-Yb, three first-order Raman bands associated with Si–Si appear, and vibrations of the Si-Yb and Yb–Yb bonds also appear. The peak position and intensity of these bands depend on the composition, as well as on other factors, such as heating, etc., which in turn can contribute to a shift in the frequency of the peaks (Fig. 2.).

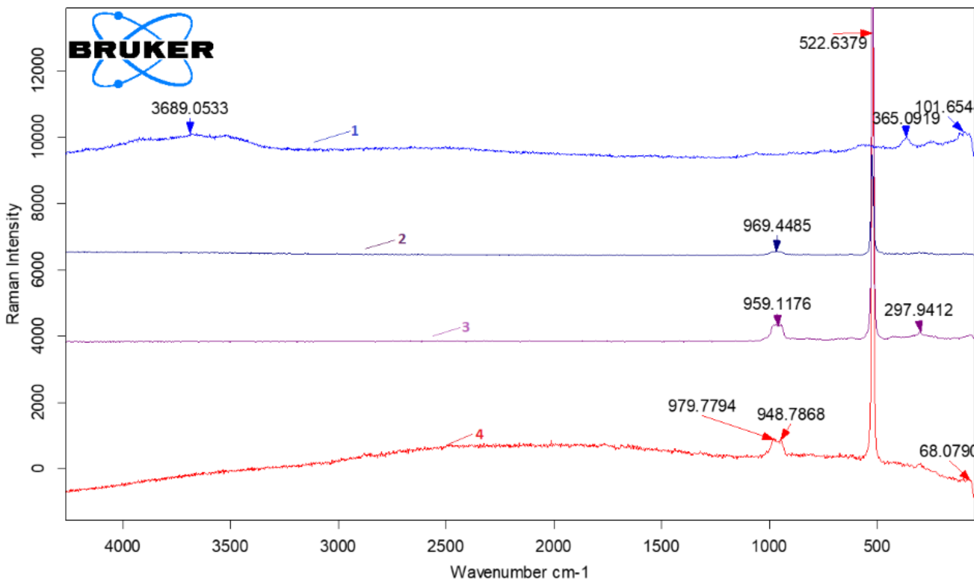

Figure 2. Raman spectrum. (1)-ytterbium (Yb); (2)-KEF-40 (initial); (3)-KEF-40-Si<Yb>; (4)-KEF-100-Si<Yb>

The laser beam and temperature induce an ordered state (hereafter referred to as LTIOS), which is monitored by the Raman spectrum. Further increase in temperature under the influence of light preserves the Raman signature of the nanocrystalline material.

As we already mentioned, LTIOS appears under the light. exposure within a certain temperature range for various compositions of a-Si-Yb alloys. LTIOS is observed at significantly lower laser power densities than those required for laser crystallization.

The size of nanocrystals remains around 8 lattice parameters, reaching a maximum value of 11 lattice parameters. The amount of internal stress varies greatly. When Δω is plotted as a function of T, it can be seen that the internal stress increases in the mid-temperature range and partially relaxes in the temperature range where the amorphous state is visible in the Raman spectra. The presence of large stresses should deform the crystallites, similar to the so-called paracrystallites, the existence of which has been reported by other authors in very thin a-Si layers [15,16]. On the other hand, the Raman spectrum of partially crystallized silicon is usually represented by two bands, one of which corresponds to the TO phonon of nanocrystals, which appears at a lower frequency than one of the large crystals (522 cm^{-1}) and the second, much wider, appearing at lower frequency (969 cm^{-1}) associated with the surrounding amorphous matrix. The volume fraction occupied by nanocrystalline nuclei (Vnc) is proportional to the Raman scattering intensity of the first order TO phonon band.

This can be estimated by the intensity of the TO phonon in the nanocrystalline state, normalized to the sum of the intensities of the TO phonon in the amorphous (969 cm^{-1}) and nanocrystalline state (522 cm^{-1}) where the coefficient of 0.88 is a correction due to the difference in the Raman cross sections of crystalline and amorphous Si [17].

$$V_{nc} = \frac{I_{nc}}{I_{nc} + 0.88 I_a}. \quad (5)$$

This means that the increase in the volume occupied by ordered Si does not arise due to the formation of large crystalline grains, but is a consequence of an increase in the number of crystallites of reduced size. This structure is characterized by tensile stress in grain boundaries, at which expansion of the bond length is energetically more favorable [18]. The activation energy for the transition from amorphous to nanocrystalline can be estimated at 0.15 eV. The size of the nuclei lies in the range of 8–11 lattice parameters, larger than the size of the threshold for the existence of a stable crystalline diamond-like lattice, which was estimated to be about 6 lattice parameters [18]. When the state of the highest order is reached, it is almost completely filled with crystalline grains. Since the grain size was about 8–11 lattice parameters, it is necessary to take into account a large number of nucleation centers. This large accumulation of nucleation may be due to defects in the amorphous material. This suggests that the existence of LTIOS is closely related to the structure of the amorphous layers and, therefore, defects in the amorphous layers may play an important role in this effect. It is also known that the kinetics of crystallization of amorphous Si strongly depends on its structural relaxation state [19]. The Raman spectrum of an amorphous semiconductor provides information about the state of structural relaxation. In particular, for amorphous Si, the TO-Raman bandwidth (969 cm^{-1}) is related to the distortion of the dihedral bond angle *Dq* which can be approximated by the following equation:

$$(\Gamma_{TO})^2 = 32^2 + (6.75Dq)^2. \quad (6)$$

It was found that an increase in the number of defects causes a broadening of the amorphous zone. Similar relationships should exist for Si-Yb, but to our knowledge they have not been previously reported. We noticed that the relative intensity of the three Raman bands in Si-Yb systems in the LTIOS state changes, the relative intensity of Si-Si decreases, which in turn indicates that pendant bonds are mainly formed as a result of the cleavage of the Si-Si bond.

CONCLUSION

The results of the study indicate that doping silicon with ytterbium impurities leads to a decrease in the concentration of optically active oxygen N_O^{opt} by 30-40%, depending on the concentration of the introduced impurities. A reversible ordered state was discovered in n-$Si_{1-x}Y_{bx}$ $(0<x<0.38)$ layers under the influence of a laser beam. The light intensity causing this condition was found to be far from that required for laser or solid-state crystallization. Using the Raman spectroscopy method, a structural transformation was revealed that manifests itself in a close-packed array of nanocrystals with a size of less than 11 lattice parameters. Small clusters were under strong internal stress (up to 3 GPa), which probably prevents the cluster size from increasing beyond the critical value for irreversible crystallization.

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СТРУКТУРНІ ВЛАСТИВОСТІ КРЕМНІЮ ЛЕГОВАНОГО РІДКІСНОЗЕМЕЛЬНИМ ЕЛЕМЕНТОМ ІТЕРБІЄМ

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У даній роботі наведено результати дослідження стану атомів ітербію в кремнії, проведені методами інфрачервоної спектроскопії (ІЧ) та спектроскопії комбінаційного розсіювання (РС). Зразки кремнію, леговані домішками ітербію, аналізували за допомогою спектрометрів FSM-2201 та SENTERRA II Bruker. Проведено реєстрацію та ідентифікацію компонентів як кристалічної, так і аморфної фаз у зразках. Результати дослідження підтверджують, що легування кремнію домішками ітербію призводить до зниження концентрації оптично активного кисню N_O^opt на 30-40 % залежно від концентрації введених домішок. Також встановлено, що збільшення кількості дефектів призводить до розширення аморфної зони. Припускається, що аналогічні залежності існують для системи Si-Yb; однак, наскільки нам відомо, подібні результати раніше не повідомлялися. Відзначено, що відносна інтенсивність трьох раманівських смуг у системах Si-Yb у стані LTIOS (The light and temperature inducted ordered state) змінюється, а відносна інтенсивність Si-Si зменшується. Це вказує на те, що підвішені зв’язки в основному утворюються шляхом розриву зв’язків Si-Si. Було також помічено, що інтенсивність світла, яка викликає цей стан, далека від необхідної для лазерної або твердофазної кристалізації. За допомогою методу раманівської спектроскопії було виявлено структурне перетворення, виражене в щільно упакованому масиві нанокристалів з розміром менше 11 параметрів решітки. Невеликі кластери перебували під сильною внутрішньою напругою (до 3 ГПа), що, ймовірно, запобігає збільшенню розміру кластера понад критичне значення для необоротної кристалізації.

Ключові слова: *кремній; ітербій; рідкоземельні елементи; Раманівські спекри; дифузія; теплоносій; температура*