Semiconductor Physics, Quantum Electronics & Optoelectronics, 2005. V. 8, N 3. P. 16-18.

PACS:78.70.Fy, 78.70.Gg

Spectroscopy of $(Si_2)_{1-x}(ZnS)_x$ solid solutions

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Abstract. Presented are the investigation of $(Si_2)_{1-x}(ZnS)_x$ solid solutions. Morphological, electrical, and optical properties of the solutions are investigated. Chemical components of the solid solutions are homogeneously distributed along the thickness of the layer. The photoluminescence spectra of $(Si_2)_{1-x}(ZnS)_x$ consist of a wide band with the peak within the range of 505 to 520 nm. The Raman scattering shows that approximately 19 % of silicon located directly under the epitaxial film is in amorphous phase.

Keywords: solid solutions, photoluminescence, photoluminescence excitation spectra, Raman scattering.

Manuscript received 25.06.05; accepted for publication 25.10.05.

1. Introduction

Nowadays one of the most topical problems of semiconductor technology and photoelectronics is development of new techniques for growing the epitaxial thin films of semiconductors. The epitaxial thin films of A^2B^6 semiconductor compounds on Si substrates are of especial interest. New materials can be useful in developing perfect and cheap semiconductor devices for modern micro- and optoelectronics. The most acceptable solution of this problem is a gradual transition from the substrate to the film via a solid solution of both components as a buffer layer.

The bandgap of the solid solution varies in the wide range from 1.12 to 3.57 eV. The spectral range of photosensitivity of $(Si_2)_{1-x}(ZnS)_x$ solution ranges from UV to IR. This property of the solution allows us to vary the electrical, photoelectrical, and optical properties of the material.

2. Sample preparation

The samples of the solid solutions of $(Si_2)_{1-x}(ZnS)_x$ ($0.08 \le x \le 0.92$) were grown by the liquid phase epitaxy from a limited amount of tin solution-fusion. The silicon wafers with 20-mm diameter, 350 to 400-μm thickness, and the resistivity $\rho \approx 1.0 \div 10$ Ohm·cm were used as substrates. The wafers were cut from the monocrystalline rod grown by the Czochralsky method. The film ranges in thickness from 5.5 to 6.5 μm.

The samples of the solid solutions of (Si_2)-ZnS with the *n*-type ZnS film were grown on the *p*-type silicon substrate, and the samples of Si-ZnS solid solutions with *n*-type ZnS film were grown on the *n*-type silicon substrates.

The conditions for formation of concentrated and continuous substitutional solid solutions are described by the molecular-statistical and crystallochemical models. These conditions [1, 2] are

$$\Delta z = \sum_{i=1} z_i^m - \sum_{i=1} z_i^n = 0, \qquad (1)$$

$$|\Delta r| = |\sum_{i=1} r_i^m - \sum_{i=1} r_i^n| \le 0.1 \sum_{i=1} r_i^m , \qquad (2)$$

where z_i^m, z_i^n are valences, r_i^m, r_i^n are the valence radii of dissolvent *m* and dissolvable *n*-element, $i = 1, 2, 3, 4$.

The chemical composition of the epitaxial layers of $(Si_2)_{1-x}(ZnS)_x$ was analyzed by the X-ray microanalysis using “Jeol” JSM 5910 LV-Japan.

Photoluminescence (PL) and photoluminescence excitation (PLE) spectra were obtained using the setup СДЛ-2 at 77 K and room temperature. Emission of xenon lamp ДКсШ-150 and N_2 laser ЛГИ-23 ($\lambda = 337$ nm) was used as an excitation source. To compare absolute values of intensities for the PL spectra of the samples, the spectra were obtained under the same conditions.

The spectra of the Raman scattering (RS) were recorded using a double-grating monochromator ДФС-24 at the room temperature. The line 5145 Å of a continuous wave Ar^+ laser was used as an excitation source. The output power of the laser was kept below 100 mW, and laser beam was focused to a spot of 0.5-mm diameter on the sample with the angle of incidence of 45°. The secondary emission was collected in back-scattering geometry.

3. Results and discussion

Fig. 1 (raster images) shows the results of chemical composition analysis of surface and spalling the epitaxial layers of $(Si_2)_{1-x}(ZnS)_x$ sample. There are no macroscopic defects and metallic inclusions in the obtained epilayers. The components of the films are homogeneously distributed.

The PL spectrum of the sample is presented in Fig. 2. It consists of a wide band distributed through the visible range with the peak in the range of 505 to 520 nm. It is hard to identify the nature of the band because of its large halfwidth and absence of any structure. The band with the peak at 505 to 520 nm can be associated with emission of ZnS, ZnO, and the solid solutions of $(ZnS)_x(ZnO)_{x-1}$ [3-14]. As for ZnS this band originated from interpoint oxygen of the lattice or from a fraction of ZnO in ZnS [3], or from emission of self-activated ZnS and modification of sublattice of sulphur [4, 5].

As for ZnO, one thinks that the vacancies of Zn [6] or chemisorbed oxygen [7, 8], or non-identified donor-acceptor pairs are centers of green luminescence [9,10].

At present the most widely used is the model based on the data of comprehensive study of EPR and behavior of the green luminescence band with variation of the temperature, influence of magnetic field and uniaxial strain in the direction perpendicular to C axis of the crystal [11]. According to this model, the appearance of green luminescence is caused by radiative transitions in the bivalent copper atoms Cu^{2+} substituting the zinc atoms and always present in small quantities in ZnO. It follows from this model [11-14] that when a crystallophosphor is excited, the hole is caught by one of four oxygen ligands surrounding Cu^{2+}-center. As a result, the excited state of the center is formed. Transition to the ground state is accompanied by the green luminescence.

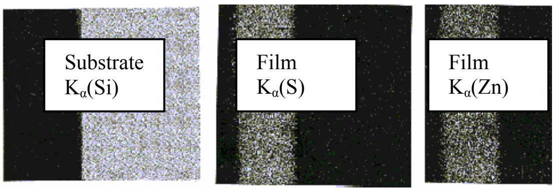

Fig. 1. The raster images of epitaxial layers of solid solutions $(Si_2)_{1-x}(ZnS)_x$.

It can be seen from Fig. 2 that PL spectra of all the samples have the same spectral composition but differ in intensity. The most intense is the PL spectrum of the sample Si_2-ZnS (the film of *n*-type ZnS was grown on *p*-type Si) suggesting that the obtained film possesses the more perfect structure.

In Fig. 3, the PL(curve 1) and PLE (curve 2) spectra of this band are presented. As seen from Fig. 3, two bands with $\lambda_{max} = 347$ nm (3.57 eV) and 376 nm (3.30 eV) and weak inflection in the area 335 nm marked by an arrow are observed in the excitation spectrum. Inflection in the area 335 nm corresponds to the bandgap of ZnS with lower symmetry [14]. The bands with the peaks of 3.57 and 3.30 eV correspond to the bandgap of ZnO (from about 3.35 to 3.25 eV [14]) overlapping with impurity-defect bands of ZnS and ZnO. The analysis of the PLE spectra allows us to conclude that radiative recombination takes place mostly with the participation of impurity-defect levels of material while the role of transitions with the band participation is inconsiderable. In summary, we can conclude that the obtained film probably consists of the solution $(Si_2)_{1-x}[(ZnS)_y(ZnO)_{y-1}]_x$ with highly a disordered structure containing minor amount of the impurities caused by the technological process. A low intensity of luminescence in the studied samples is caused by a small thickness of the epitaxial film, i.e., ZnS, and also by inhomogeneity and defects of the film of variable band structure.

The Raman spectrum of the solid solutions $(Si_2)_{1-x}(ZnS)_x$ obtained on the *p*-type silicon substrate is presented in Fig. 4. As seen from the figure, the lines of ZnS (e.g., 350 cm^{-1}[14]) are absent, but the lines of the silicon substrate are present. Absence of the Raman signal from the ZnS compound can be explained by inhomogeneity and defects of the film. It is confirmed by a very broad wing of the Releigh scattering. This inhomogeneity and disordered structure of the film leads

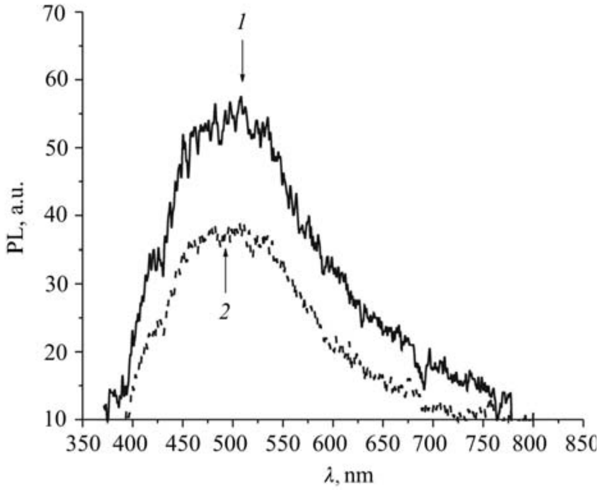

Fig. 2. PL spectra of the samples (Si_2)-ZnS (curve 1) and Si-ZnS (curve 2) at the room temperature.

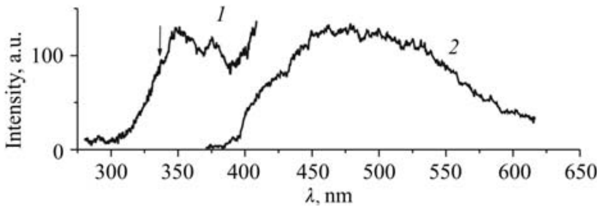

Fig. 3. PLE (curve 1) and PL (curve 2) spectra of the sample Si_2-ZnS ($T = 77$ K).

to degradation of the Raman signal due to broadening the Raman lines. Thus, the Raman signal from ZnS is difficult to distinguish from a background noise. Probably, it can be stated that ZnS film is amorphous which is not surprising taking into account its variable with thickness composition and considerable mechanical strains at the film-substrate interface. But independent confirmation of this conclusion can be obtained only by the X-ray diffraction analysis.

The intensive phonon line 522.1 cm^{-1} indicates that the major part of substrate material is in Si-I phase. At the same time, the presence of the band 455 to 490 cm^{-1} means that part of substrate material is in an amorphous (α-Si) phase [15]. From the ratio of the areas of the peaks 522.1 and 475 cm^{-1} we can find that amorphized is about 19 % of silicon in thin layer that is placed directly under the epitaxial film. Other lines corresponding to another phases of silicon did not appear.

According to [15], the fact that the frequency of the Raman line in silicon corresponds to 522.1 cm^{-1} but not to 520 cm^{-1} means the existence of strains on the surface of silicon. A shift of the Raman line is proportional to the strains on the surface with the coefficient $\varepsilon = -3.2$ cm^{-1}/GPa [15]. Thus, from the shift of the line the value of the surface strains can be determined. It was found as 0.65 GPa. A negative sign of the strain value indicates that radius of the curvature of the surface is also negative.

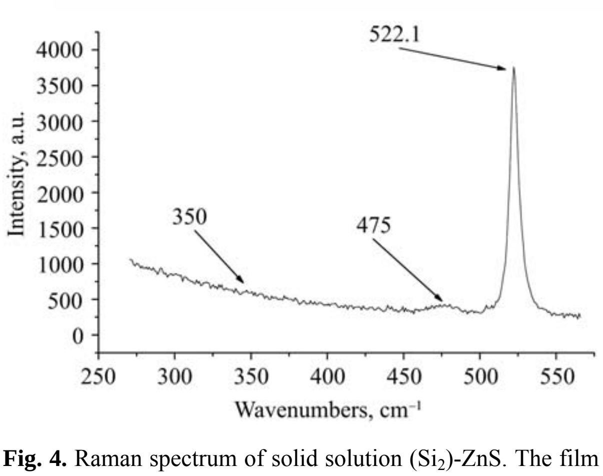

Fig. 4. Raman spectrum of solid solution (Si_2)-ZnS. The film ZnS of *n*-type was grown on the silicon substrate of the *p*-type.

4. Conclusion

Thus, the analysis of the whole set of experimental data reveals that the developed technology allows to synthesize the new epitaxial solid solutions $(Si_2)_{1-x}(ZnS)_x$ which are promising for designing the devices of modern electronics on this basis. The mechanism of formation of such layers is a subject of further studies.

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