The Properties of Nanosized Silicon Prepared by Plasmochemical and Electrolytic (HCl : HF : C₂H₅OH) Techniques

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Abstract The structural and optical properties of nanostructured silicon obtained by plasmachemical and electrolytic techniques are presented. For electrolytic etching of silicon electrolyte the chlorine acid was added to standard HF:C₂H₅OH electrolyte. It was found that adding of HCl to the electrolyte slows the process of electrochemical etching thus creating conditions for efficient etching and formation of Si-O and Si-H bonds on the formed nanosilicon surface. In the present study the nanosilicon samples were obtained in ultra-high frequency plasmochemical system by means of recondensation of ultradispersed silicon powder in nitrogen flux heated to mean temperature of 3500 K. Morphology of films was found to consist of quantum nanowires of a mean diameter of 2 nm. Results indicating stability of nanosized silicon (NanoSi) under intense laser irradiation are presented. It is demonstrated that substantial increase of NanoSi photoluminescence signal can be attributed to their specific structure, as well as to the SiO₂ thin film formed on the nanocrystalline surface.

Keywords Nanostructured Silicon, Photoluminescence, Infrared Spectroscopy

1. Introduction

Nanosized silicon (NanoSi) is of considerable interest due to its application as a material for visible light emitters built up into the silicon matrix. It is established that radiation of silicon nanocrystals shifted to visible light due to quantum size effects can provide an input into NanoSi total photoluminescence (PL). An input of possible silicon/adsorbate irradiation into the PL should also be taken into account [1]. It was suggested earlier that appearance of PL signal in the red region can be attributed to complexes consisting of the localized hole and the oxygen ion not involved in the formation of bridging bonds [2]. Wide potential application of NanoSi in optoelectronics motivates

big attention to NanoSi PL issue.

Results of investigation of the structure of NanoSi, of which optical properties were not substantially changed for a rather long period of time, are presented below. Upon fabrication of such samples an electrolyte, to which the chlorine acid (HCl) of a certain concentration has been added, was used. The PL spectra of fabricated NanoSi, as well as the degradation of PL signal, including that caused by laser irradiation of different power, have been investigated. Alongside, the high resolution transmission electron microscopy (HR-TEM) images and Fourier-transform infrared (FTIR) spectra were also registered which allowed to control the structure and the properties of NanoSi surface states. Additionally the structural and optical properties of nanostructured silicon prepared by plasmachemical technique are also presented.

2. Materials and Methods

Single crystal boron doped p-Si(100) with specific conductance of 0,5 Ohm x cm was used as a material for NanoSi layer fabrication. NanoSi samples were made by the procedure of electrolytic anodization. The sample current density and anodization time were 20 mA x cm² and 10 min, respectively. Samples 1-5 were prepared by adding of HCl into the standard electrolyte in the quantities of 0, 2, 10, 20, 40 ml by 100 ml of solution, respectively. Further, the samples were rinsed in ethanol and dried in the flux of dried air.

The spectral dependences of PL were obtained with the double monochromator DFS-24 with FEU-79 registering device upon initial argon laser excitation at wavelengths of 457,9, 488 and 514,5 nm. The laser irradiation power was in the range of 0,5 to 20 mW with the beam focused to a spot of 1.5 mm², while the mean scanning time was about 3 min. The optical spectra were registered with the aid of fast-scanning Fourier-transform spectrometer IFS-113v (Bruker) in the wavenumber range of 300—15000 cm⁻¹ with

the spectral resolution not higher than 0.5 cm^{-1} .

The main techniques of preparation of nanocrystalline silicon are based on silane decomposition and electrochemical etching. Advantage of using silane as a material for plasmachemical process is its high volatility allowing to avoid considerable energy consumption for material evaporation in reactor. However, due to high fire risk of silane its utilization is restricted for safety reasons. Alternatively, Marsen and Sattler [3] discuss the possibility of magnetron sputtering for the formation of one-dimensional silicon clusters on the surface of highly oriented pyrolytic graphite (HOPG). The main idea of the work bases on the general concept of crystallography that the features of external forms of the natural objects are determined by the features of their internal structure. The latter allows the authors to correlate the existence of silicon wires or tubes with the possibility of existence of low symmetry allotropic modifications of silicon. Hence, one can not exclude the possibility of existence of other forms of nanocrystalline silicon objects.

The processes based on recondensation of silicon are safe and ecological friendly, relatively simple in what relates to preparation and dosing of primary products, and, moreover, use widely available nitrogen as a plasma gas. At the same time, recondensation of silicon in nitrogen ambient has a disadvantage of formation of silicon nitride. To estimate the possibility of silicon nitride formation as well as to determine the optimal conditions for production of silicon nanoparticles the thermodynamics calculations for Si-N_2 system at a different content ratio of silicon and nitrogen in $500 - 3500 \text{ K}$ temperature range have been done. Calculations were done by minimization of Gibbs energy using the program "Terra" developed by B.G. Trusov of Moscow State Technical University named after N.E. Bauman, as well as other program codes.

3. Results and Discussion

During the measurements it was found that PL intensity of the samples prepared with the added HCl by about two orders of magnitude is higher compared to those prepared without adding of HCl to the electrolyte. The PL maximum is observed at $1.85\text{--}1.9 \text{ eV}$. The shape of spectral curves of the samples 2-4 could be represented by summing of four Gaussians. The change of maxima positions of these Gaussians upon HCl concentration change in the electrolyte is shown in Fig. 1. It should be noted that the long wavenumber peak input into the total PL spectrum dramatically decreases from sample 2 to sample 4, whereas the intensity of samples 3 and 4 increases by a factor of 2 with HCl content increase.

In the spectra of low-temperature NanoSi samples PL there is a quite well resolved fine structure consisting of a set of low intensity peaks separated by $20\text{--}21 \text{ eV}$. The peak separation allows estimating the NanoSi diameter [4], as well as their mean shape, or an array of quantum wires or

quantum dots. Taking into account previous calculation results [5,6], one can conclude that the NanoSi layer under consideration is an array of quantum wires with mean diameter of about 2 nm . Detail analysis of low-temperature PL of the samples prepared with HCl added to electrolyte is presented in [7]. The NanoSi PL spectra did not depend on the laser irradiation wavelength used: 457.9 , 488 and 514.5 nm .

Figure 1. Dependence of Gaussian maxima position modeling the PL spectra shape of samples 1-4 upon HCl content in the electrolyte: 1 — 0; 2 — 2 ml; 3 — 10 ml; 4 — 20 ml.

Results on degradation of PL signal as a function of incident laser irradiation intensity are as follows. PL signal intensity and peak shape of sample 5 did not change during continuous laser irradiation for at least one hour at pump-up intensity of $0.5\text{--}100 \text{ mW}$. The PL intensity for sample 4 exponentially decreased, and the rate of signal intensity variation increased with the increase of laser power. Each sample after being exposed to laser irradiation for 1 hour was afterwards kept in a dark for another 1 hour. Then the PL spectra from the same spot of the samples were measured again. It turned out that the PL intensity for sample 5 was recovered to its initial value. More complicated situation took place for samples 3 and 4: they degraded more rapidly under laser irradiation. The PL properties of sample 4 could not be totally recovered, whereas for samples 2 and 3 the degradation process was of irreversible character. The PL degradation in the green and red part of the luminescence spectrum was of different character. The most dramatic PL peak shape change were observed at higher energy side. On the contrary, the low energy part of PL peak did not undergo such a change. Degradation rate for sample 2 was considerably higher. It is reasonable to connect the time dependence of PL signal under intense laser irradiation with thermal processes occurring in the irradiated region of the sample. This assumption is corroborated with the fact that no change was observed in the spectra of low-temperature PL even if the irradiation time was 60 min at laser power of 100 mW .

Absorption spectra of samples 1 to 5 in the 2000 to 2400

cm⁻¹.wavenumber range are shown in Fig. 2. It is seen that for sample 1 (curve 1) there is strong absorbance attributed to bonds like SiH (2090 cm⁻¹), SiH₂ (2114 cm⁻¹) and SiH₃ (2140 cm⁻¹), whereas for sample 5 the main absorbance is due to atomic vibrations at bonds SiH(O₃) (2254 cm⁻¹) and SiH(SiO₂) (2196 cm⁻¹). For samples 2-5 absorbance on SiH(O₃) bonds increases with increasing the HCl content in the etching electrolyte. These observations are in good agreement with the PL results. It should be noted, however, that such dependence is non-monotonic: One can see a sharp absorbance increase for sample 4 compared to sample 3. Additionally, for samples 2 and 3 there is almost no an absorption band attributed to SiH(SiO₂) bonds. The latter can be related to the fact that there is a thin stoichiometric SiO₂ layer on the surface of NanoSi samples 4 and 5.

Figure 2. FTIR spectra of samples 1-5 (curves 1-5) in the indicated wavenumber region.

The samples which were electrochemically etched with HCl containing electrolyte exhibited much more intensive room temperature PL compared to the samples prepared by “traditional technology”, i.e. with no HCl added to electrolyte. Samples 4 and 5 prepared with maximum HCl concentration did not degrade even under intense laser irradiation. The nature of the laser induced PL signal degradation of samples 2 and 3, prepared with lower HCl content, can be reconciled assuming inhomogeneous NanoSi layer structure. This is corroborated with the electron microscopy and low temperature PL data. According to these data, the surface layer consists of nanocrystals with mean size of 1.7-2.0 nm, and of interface layer of either dendrite or porous structure. The thickness of the former layer grows as the HCl concentration in the electrolyte increases. This fact explains the PL signal intensity decrease upon continuous laser irradiation. The difference in the thermal conductivity of NanoSi surface and subsurface layers may be the cause of strong local heating of the sample leading to activation of photoinduced oxidation of Si-Si bonds. Moreover, the temperature jump dramatically enhances efficiency of nonradiative surface recombination. This possibility is also

supported in the literature [8]. It is well known that adding of HCl to normal HF electrolyte can dramatically alter the state of silicon surface [9]. Therefore, as follows from the above results, such a structure must have a higher thermal conductivity coefficient, on the one hand, and has much lower dangling bonds density as a centers of nonradiative recombination, on the other. Additionally, one can also anticipate almost total absence of thermal and photo oxidation of Si bonds on the NanoSi surface. The latter, presumably, explains the PL signal change caused by laser irradiation, as well as the higher PL intensity of the samples, prepared with HCl added electrolyte. This is supported by the previous results [10] indicating that Si nanocrystals, separated by dielectric, exhibit higher PL intensity.

It should be noted, that adding of HCl to the electrolyte slows the process of electrochemical etching. In this regard one should create conditions for efficient etching and formation of Si-O and Si-H bonds on the formed NanoSi surface. If at the sample border, directly contacting the etching interface, the porosity of newly formed layer is not enough, it may prevent formation of stoichiometric SiO₂ layer due to possible lack of oxygen atoms available at the interface. As a consequence, non-stoichiometric SiO_x layer forms which might undergo further oxidation or structural transformation. The latter causes mentioned PL signal degradation after finishing the anodization procedure. Moreover, the centers of nonradiative recombination in the form of Si dangling bonds may be formed. On the other hand, an intensively formed silicon oxide at the etching region may influence the geometry of the sample in the way of formation of porous or dendrite structure, depending on the crystallographic direction in which the Si-O bonds are preferentially formed.

Regarding the nanostructured silicon, obtained by plasmochemical recondensation in nitrogen, the temperature dependences of equilibrium content of Si-N₂ system at silicon to nitrogen different ratio are shown in Figs 3 and 4. The nitrogen content varied from that corresponding to stoichiometric state (Si₃N₄), molar ratio Si/N₂ = 1.5 to that of Si/N₂ = 1/20. It is seen that in all cases the only stable silicon containing phase at a temperature lower than 2000 K is silicon nitride. Condensed silicon is available in equilibrium state at a temperature exceeding the upper limit of thermal stability of silicon nitride and only in liquid state (Note that melting point of silicon is 1688 K). Application of these results to real plasmachemical process with initial temperature of plasma flux of 3000 – 3500 K means that upon condensation of silicon evaporated in the reactor, initially, as the temperature decreases, the particles of liquid silicon form which at a temperature lower than 2000 K can be nitrated forming solid Si₃N₄. Nitration depth and, as a consequence, the concentration of nitrogen is determined by kinetic parameters such as nitration rate and particle exposure time in the reaction zone. To decrease the efficiency of nitride formation one should perform fast forced hardening beginning from 2000 K. The latter can be done either by high efficiency heat exchanger, or by

additional cool gas exposing the corresponding reactor zone.

Figure 3. Temperature dependence of Si-N equilibrium content at molar Si/N₂ ratio of 1.5.

Figure 4. Temperature dependence of Si-N equilibrium content at molar Si/N₂ ratio of 1/20.

According to calculation results, another feature of the system under consideration is that upon its dilution with nitrogen the temperature range of existence of condensed silicon narrows from high temperature side. This is explained by silicon partial pressure decrease with nitrogen content growth and, as a consequence, by more complete silicon evaporation at the same temperature. The latter offers an opportunity to improve the technology of nanocrystalline silicon production by decreasing the amount of silicon powder in the reactor, simultaneously increasing the plasma gas content.

In the systems for plasmachemical nanocrystalline silicon production the silicon powder heating occurs in the plasma zone [11,12]. The particles in reactor move along the gas current lines so that they are trapped in the in-axis region of the discharge and thus undergo thermal treatment. The temperature flow in the system is as follows: Initially the particle temperature grows achieving melting point, then remains constant due to melting, increasing afterwards up to

boiling point and then remaining constant as further heating evaporates the particles until it disappears. Increasing the initial mean diameter of the particles requires increasing of the reactor length in order to completely evaporate the particles. Likewise, as the inlet velocity of the particles increases, the heating in the plasma flux proceeds slower, and the boiling temperature is achieved at longer distance from the inlet point. Therefore, the higher efficiency of silicon particle recondensation in nitrogen plasma flux is achieved at lower particle size and velocity.

Figure 5. FTIR spectra of single crystal silicon implanted by nitrogen and oxygen at an energy of 100 and 175 keV, respectively (curve 1), and total doses of 5×10^{16} (curve 2) и $2 \times 10^{17} \text{ cm}^{-2}$ (curve 3).

Figure 6. FTIR spectrum of nitrogen containing nanosilicon.

In the present study the nanosilicon samples were obtained in ultra-high frequency plasmachemical system by means of recondensation of ultradispersed silicon powder in nitrogen flux heated to mean temperature of 3500 K. The properties of synthesized nanoparticles are determined by temperature, particle concentration and the cooling rate. The mixture of powders of obtained nanosilicon and unreacted silicon was subsequently ultrasonically dispersed in an ethanol and then separated by centrifugation. To check the features of synthesis of nanopowder, including silicon nitride, the Fourier-transform infrared (FTIR) spectra (Bruker) of the samples in the wavenumber region of modified vibrational

modes of Si-O, Si-Si, C=O, Si-N, C-N, Si-H, C-H, SiH(O₃), Si(O)(OH)(SiH₃), Si(O)H(OSiH₃), O₂-Si-H(OH), Si-O-Si, C-O, N-O, etc., were measured. The spectra of silicon with implanted oxynitride hidden thin layers [13] are shown in Fig. 5, whereas Fig. 6 shows the FTIR spectra of nitrogen containing nanosilicon. These data can be reconciled assuming that nitrogen integrated into the outer shell of silicon nanoparticles passivates the surface dangling bonds. (The presence of nitrogen is detected by XPS of silicon nanoparticles). The latter is a key point for preparation of nanocrystalline silicon with stable optical and electron properties. The structure of nanoparticles was studied by means of electron diffraction and high-resolution transmission electron microscopy (HR-TEM). It was found that along with spherical particles there were also silicon nanowires and hollow nanospheres (Figs. 7-9). As follows from HR-TEM data analysis the spherical nanoparticles are composed of crystalline silicon with lattice parameters of 0.31 nm and 0.19 nm, which correspond to distance between {111} and {220} atomic planes of fcc silicon. Fig. 9 shows HR-TEM image of peripheral area of a certain spherical hollow Si nanoparticle (the interface border is shown by an arrow). It is seen that at a thickness of c.a. 2 nm the structuring of this border is clearly visible.

Figure 7. HR-TEM image of spherical silicon nanoparticles.

Figure 8. HR-TEM image of silicon nanowires.

Figure 9. HR-TEM image of peripheral region of a single spherical hollow silicon nanoparticle.

Apart from technological relevance in semiconductor nanoscience and technology the particles under consideration may be used in biomedical research and treatment. The reason is that such particles consist of crystalline core and surrounding shell thus exhibiting biological passivity. For instance, the silicon nanocrystals can be used for preparation of anti-cancer substances for photodynamic therapy of cancer [14]. A key point in this case is photoinduced production of singlet oxygen. The latter can be produced via resonance energy exchange between an exciton localized in silicon nanocrystal and oxygen existing on its surface [15].

4. Conclusion

Technological approach for preparation of NanoSilicon, exhibiting an enhanced as well as normal photoluminescence is developed. In case of higher PL activity the surface of the corresponding samples is effectively passivated reducing dangling bond density as a sites for nonradiative recombination. The low-temperature PL spectra feature a set of peaks separated from each other by 20-21 meV with the maximum band being centered around 1.85-1.9 eV. The peak separation allowed to estimate the morphology of the film, which was found to consist of quantum nanowires of a mean diameter of 2 nm. No dependence of PL spectra on the laser irradiation wavelength was observed. FTIR results suggest that the main absorption mechanism is due to SiH(O₃) (2254 cm⁻¹) and SiH(SiO₂) (2196 cm⁻¹) interatomic vibration. On the other hand, for the samples prepared by “standard technology”, i. e. with no HCl added to etching electrolyte, the main absorption occurs on SiH (2090 cm⁻¹), SiH₂ (2114 cm⁻¹) and SiH₃ (2140 cm⁻¹) bonds. For plasmochemically prepared nanosilicon particles in N₂ gas the nitrogen integrated into the outer shell of silicon nanoparticles passivates the surface dangling bonds, which is an important factor for production of nanocrystalline silicon with stable optical and electron properties. It is shown that the higher efficiency of silicon particle recondensation in nitrogen plasma flux is achieved at lower particle size and velocity.

Acknowledgements

The work was partly carried out with the equipment of CKP SOGU "Physics and Technology of Nanostructures" and supported by the Program of Strategic Development of North-Ossetian State University

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