JOURNAL OF OPTOELECTRONICS AND ADVANCED MARERIALS Vol. 9, No. 5, May 2007, p. 1431 - 1434

Chemical modification of single - crystal silicon surface

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Nanocrystalline silicon layers (3 – 60 nm) have been formed upon single-crystal silicon substrates of very large area (100 cm^2) by stain etching. We studied optical and structural properties of nanocrystalline silicon by photoluminescence, photoluminescence excitation, reflection, scanning tunnel microscopy, scanning electron microscopy and Auger electronic spectroscopy methods. The photoluminescence method has shown that photoluminescence spectra of nanocrystalline silicon of different substrates differ insignificantly (~10%) in intensity. The increase of photoluminescence intensity during prolonged aging in air at room temperature was observed. In the paper it is shown that in the process of formation of nanocrystalline silicon by stain etching, two stages could be defined: the stage of the structure self-organization at nano-level (~35 nm) and the stage of the structure self-organization at micro-level (~60 nm). Latter is observed not only during structure organization, but also during changes of its chemical composition, photoluminescence and antireflection properties.

(Received November 14, 2006; accepted April 12, 2007)

Keywords: Stain etching, Single-crystal silicon, Nanocrystalline silicon

1. Introduction

The development of technology of nanomaterial industry requires new physical and chemical characteristics of these materials. It is possible to mark out three main approaches to creation of nanostructure on solid surface: 1) usage of the precision tool, such as a probe point of atomic force or scanning tunneling microscope; 2) directional chemical synthesis; 3) self-organizing nanostructure. The last introduces the greatest interest due to the relative simplicity and level of investigation of similar processes in the nature. Under self-organizing nanostructures are understood regular superficial, volumetric atomic, molecular, and also clustered structures with nanometric sizes. One of main examples of volumetric nanostructures is nanocrystalline silicon (nc-Si), which nanometric size and order is defined by chemical self-organizing process of etching. nc-Si use in microelectronics is caused by simplicity of management of its electrophysical parameters during manufacturing, that allows to create in single-crystal silicon thick (up to 1 micron) dielectric layers and dividing areas, deep doped layers, and also effectively getter an impurity at planar preservation of the working surface of the plate**.** Special attention is given to development of methods of the control and management of parameters of nanosized materials with the purpose of stabilization of their characteristics**.** Results of researches on control of the sizes of structure (crystallites and pores) at electrochemical and chemical process of etching of a surface [1,2] have shown, that properties of nanocrysalline silicon are bounded up not only with the sizes of crystallites and pores, but also with a chemical composition of nanocrystalline layer. Huge attention is given to research of a photo and electroluminescent properties of nc-Si, that is caused by prospect of creation of light-emitting devices integrated on a uniform silicon plate. It is necessary also to note, that exactly the presence of the large internal surface has allowed the use of this material in such areas as biotechnology, gas detectors etc. [3, 4].

In this paper the study of processes of formation of nanocrystalline layers is carried out at chemical updating of a surface of single-crystal silicon. Their structural, photoluminescent, and antirefletion characteristics are investigated.

2. Experimental procedure

We used boron doped single-crystal silicon square wafers with resistivity of 1 Ohm·cm, with area of 100 cm^2 and thickness of 0.3 μm. The samples were cut perpendicularly to the crystallization direction on the wafer. The surface of the wafers was not polished. Before nc-Si layers formation, all samples were processed in water 50% KOH solution. nc-Si layers were prepared by stain etching in HF:HNO$_3$ solution at the room temperature, natural day-time illumination and time duration from 1 to 20 min. The structure of nc-Si surface was studied using scanning tunnel microscopy (STM) and scanning electron microscopy (SEM). Chemical composition of nc-Si surface was studied by the method of electron Auger spectroscopy (AES) at the LAS-2000 installation intended for surface investigation. The spectra were recorded with energy resolution 3.4 eV. Energy of primary electron beam was 3 keV, and probe current – 5 × 10^{-7} A. The information was taken from the surface of 100×100 μm^2. For investigation of element distribution through the depth of the surface of the samples being investigated the sample was etched with argon ion beam with the energy of 4 keV. The etching rate was 30 Å/min. Photoluminescence (PL) was excited by a xenon-150 lamp with a grating monochromator MDR-23, dispersed by a prism spectrometer IKS-12 and detected by a photomultiplier FEU-79. All spectra were corrected on spectral response. The PL excitation (PLE) spectra were measured at the maximum of PL band. All measurements were performed at 300 K. The reflectance measurements were performed with SPECORD M-40 within the wavelength range of 250-850 nm.

3.Results and discussion

3.1. PL and PLE spectr

The researched nc-Si layer had bright emission enough to see it with the eye. The PLE spectra are shown on Fig. 1a. PL spectra are excited by the light within the rang of 280-530 nm and the maximum of excitation is at ~320 nm. PLE as usually has a wide maximum in the visible spectral range and a region of increase of intensity in the near UV range. Fig. 1b shows PL spectra for different samples. As can be seen, each curve is approximately Gaussian with a clear peak at ~640 nm. Comparison of photoluminescence spectra of nc-Si layer of different samples shows that they differ in intensity among themselves insignificantly (only ~10%).

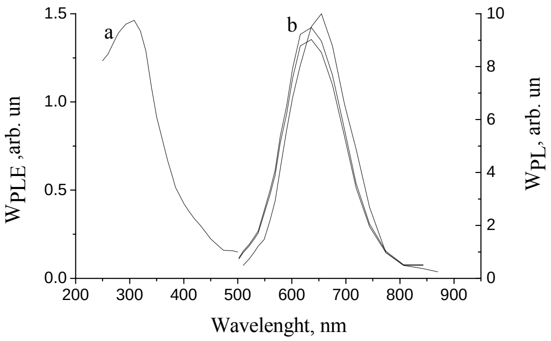

Fig. 1. PLE (a) of nc-Si layers received by stain etching on single-crystal silicon and PL (b) spectra of nc-Si layers for different samples. Excitation wavelength in PL measurements 320 nm.

The main shortcoming for application of nc-Si in optoelectronics is instability of its luminescent properties and degradation of luminescence during aging in air. Since the moment of nc-Si visible luminescence discovery, many works have been done to research PL aging. As for our case, PL intensity of both type samples increased with time (Fig. 2). The changes in PL intensity were estimated via changes of its intensity at the maximum. During one-month aging, PL intensity increased by 1.5 to 2 times due to oxidation process, which is in agreement with the data obtained by different authors [5, 6]. After one-month aging, PL intensity reached its maximum and then remained constant for 12 months. Some deviation of PL intensity from the observed constant value within 5-7 % limits is probably caused by different positions of points for measurements on the sample surface. It should be noted that PL peak position did not change practically during aging.

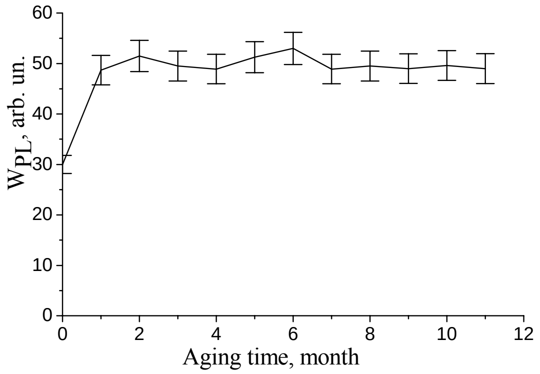

Fig. 2. Dependence of PL intensity on time of aging of nc-Si layers in air, excitation wavelength in PL measurements was 320 nm.

3.2. Structural properties

Study of the morphology of the surface by the SEM and STM has shown that nc-Si has an ordered structure and repeats exactingly the morphology of the surface of single-crystal silicon substrates, forming pores on every single relief piece. The method of STM was used for detailed studying of separate pores of nc-Si. Analysis of the obtained images of the surface shows that nc-Si surface is regularly covered with nano-scale hills up to 20 nm high. However, owing to certain sizes of tips the information of the depth can be incorrect as deep narrow pores can be displayed as shallow holes. Therefore thickness of nc-Si layers has been studied additionally by method of Auger electronic spectroscopy. Dependence of thickness of nc-Si layers (d) from time of chemical etching at a constant concentration of etching solution is resulted on Fig. 3. Thickness of layers was defined as product of speed of layer-by-layer argon ion etching (3 nm/min) and time of etching. Apparently from Fig. 3, thickness of a nc-Si layer grows with increase of time of formation of a layer. At first the ratio is linear, the inclination of a curve depends on concentration of etching solution. At longer period of processing linearity is broken, and the curve leaves on the saturation corresponding to the maximal thickness of a nc-Si layer, equal 60 nanometers. Pore sizes increase up to micrometer sizes and have very large fluctuations. Investigation of structure of obtained samples have shown that it is possible to mark out two stages of surface self-organizing (SO): the stage of structure self-organizing at nano-level (3 ≤ d ≤ 40nm) and the stage of structure self-organizing at micro-level (40 ≤ d ≤ 60nm). During the first stage the nanostructure is formed and developed on initial surface of the silicon substrate. This development takes place due to increase of silicon nanocrystalline layer depth (increase of the nanostructure altitude). At the second stage formed nanostructure starts to etch out heterogeneously due to alternate process – polishing out and as a result both a microrelief of an initial substrate of single-crystal silicon and nanostructure are modified.

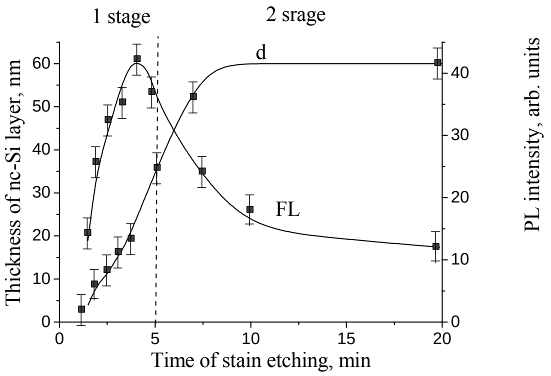

Fig. 3. Dependence of thickness of nc-Si layer and of the photoluminescence intensity of nc-Si layers on etching duration.

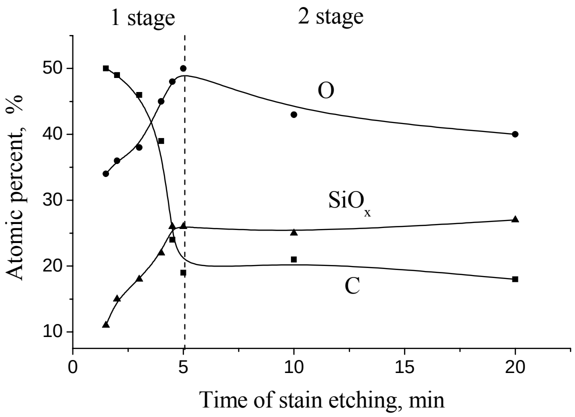

Fig. 4. Dependence of concentration O, C and SiO$_x$ on time of stain etching.

The studyof the chemical composition of nanocrystalline layers under formation has shown, that all generated nc-Si layers represent nanocomposite from nanosize crystals of silicon in an environment of oxide phase SiO$_x$. During the first stage of SO the contents of complex SiO$_x$ on surfaces monotonously increases (Fig. 4). At the end of the first stage the amount of oxide phase reaches the maximal value on a surface and its distribution in depth also stops that correspond to the maximal thickness nc-Si film. At the second stage of SO amount of SiO$_x$ and its distribution in depth does not change. The same character of behaviour of SO is marked for oxygen (Fig. 4). It is necessary to note that as for carbon a completely opposite course is observed. At the first stage of etching the contents of carbon (Fig. 4) on surfaces monotonously decreases up to some critical value, further at the second stage this value does not change. As the contents of complex SiO$_x$ on surfaces and its distribution in depth, as it was already marked, plays an essential role in optical and light-emitting properties of nc-Si, in this work the research of spectra of photoluminescence (FL) of formed nc-Si layers was carried out. Apparently from Fig. 3 FL spectra of nc-Si layers received at etching during 2-8 minutes show a homogeneous red - orange luminescence at room temperature irrespective of the area of an initial substrate. Apparently from Fig. 3, FL intensity changes not monotonously depending on conditions of formation of nc-Si layer : the increase in time of chemical etching from 1 minute up to 5 minutes results in growth of FL intensity, whereas its further growth – in its falling. Observable change of FL intensity depending on modes of etching can be explained on the basis of structural changes which arise during nc-Si formation due to changes of time of formation of nanocrystalline layer and well correlates with the considered stages of self-organizing of a surface at stain etching in a solution of fluoric and nitric acids at room temperature. Thus growth of FL intensity in nc-Si samples generated at change of time of etching from 1,5 up to 5 minutes, occurs at the account of increase of effective radiation area of a surface because the thickness of nanorelief that was formed on the advanced microrelief of an initial plate of silicon increases. The further increase of time of etching at nc-Si formation results in reduction of radiating area of a surface, as an initial microrelief is etching down, and nanopores are etching to micropore.

3.3. Reflection spectra

As it shown by Fathauer [7] changes in etching time can form porous silicon layers with different colour. The as-prepeard stain etched nc-Si samples have grey, darkly grey, brown, dark blue and black under different etching times. Fig. 5 shows the reflectance characteristics of nc-Si etched for different duration. The reflectivity of a single-crystal silicon is presented for comparison. The optimal nc-Si providing the best reflectance is black nc-Si. The stain etching process for such nc-Si formation is characterized by etching time equal to 5 min. As follows from the reflectance characteristics, the duration of the etching affects the location of the minimum of the reflectance.

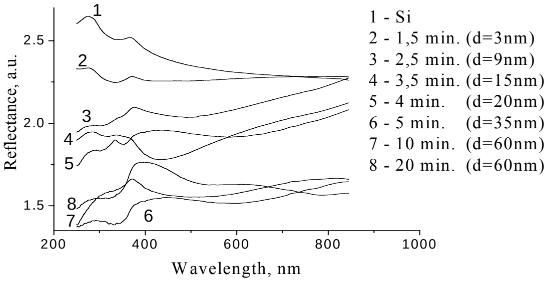

Fig. 5. Reflection spectra of nc-Si layers for different etching duration's.

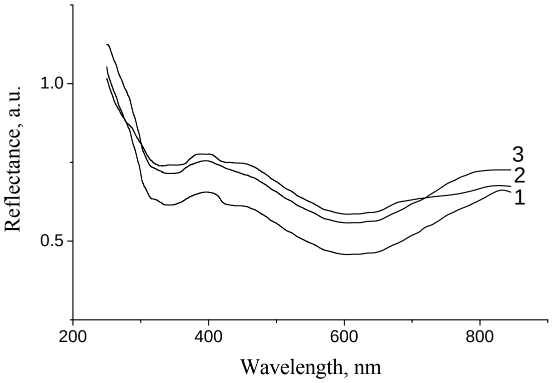

Fig. 6. Degradation of antireflection properties of nc-Si layers on time of aging in air: 1 – newly prepared nc-Si layer, 2 – half year, 3 – year.

It is known, that nc-Si is an object, which at contact to air can essentially change its properties, therefore for effective practical use of nc-Si in quality antireflection covering in work the research of stability of the reflecting characteristics nanocrystalline layer of silicon was carried out during aging on air. The spectra of reflection for samples with nc-Si layer were measured in day after their formation, in half-year and one year of a storage them on air (Fig. 6). As it is visible from a Fig. 6 for all samples in one year after formation of nc-Si layer on them the same laws in spectral dependence of factor of reflection are shown. It is necessary to note, that in the field of lengths of waves 300-700 nm the insignificant deterioration (~10%) antireflection characteristics of nc-Si is observed.

For all samples the correlation between photoluminescent and antireflection properties is observed, therefore, such behavior of antireflection characteristics with increase of thickness of nc-Si layer can be explained as well as in case of changes of photoluminescence properties on the basis of structural changes, which occur as a result of the process of nc-Si formation at various duration of etching. At the first stage during etching time from 1.5 up to 5 minutes, the improvement of antireflection properties is related to the increase of the area of the surface at the expense of increasing height of nanorelief. Further increase of time of nc-Si formation, the area of the surface decreases, as an initial microrelief of a surface is etching out, and nanostructure, that is formed on it, also is etched out, that results in the reduction of antireflection properties.

4. Conclusions

In this work, nc-Si layers (3 – 60 nm) on substrates of very large (100 cm^2) single-crystal silicon have been fabricated by the method of stain etching. It is shown that in the process of chemical modification of the surface of single-crystal silicon by stain etching two stages could be defined: the stage of the structure self-organization at nano-level (<35 nm) and the stage of the structure self-organization at micro-level (~60 nm). The received results allow to draw a conclusion, that process of self-organizing of nanocrystalline silicon by stain etching is shown not only in structure changes, but also in changes of its chemical composition, PL and antireflection properties.

Photoluminescence spectra of nc-Si layers have a characteristic of gaussian-like shape with a maximum at 650 ± 20 nm. These layers have bright PL enough to be observed with a naked eye. It should be noted that PL intensity of nc-Si layers increased significantly during first month aging in air at the room temperature and thereafter is stable for 2 – 12 months. It was found that nc-Si layers with optimal antireflection characteristics were obtained during etching time of 5 min (~35 nm).

It should be noted that nc-Si layers with large area can be used in various very sensitive devices, such as gas detectors, solar cells, biosensors and others.

References

[1] A.G. Cullis , L.T. Canham, P.D.J. Calcott, J. Appl. Phys. **82**(3), 909 (1997).
[2] S. Kalem, M. Rosenbauer, Appl.Phys.Lett. **67**(17), 2551 (1995).
[3] C. Baratto, G. Faglia, E. Comini, G. Sberveglieri, A. Taroni, V. La Ferrara, L. Quercia, G. Di Francia, Sensors and Actuators B: Chemical **77,** 62 (2001).
[4] M.Y. Ghannam, A.A. Abouelsaood, G.F. Nijs, Sol. Energy Mater.Sol. Cells **60**, 105 (2000).
[5] Y. M. Weng, Z. N. Fan, X. F. Zong, Appl. Phys. Lett. **63**(2), 168 (1993).
[6] P. D. Stevens, R. Glosser, Appl. Phys. Lett. **63**(6), 803 (1993).
[7] R. W. Fathauer, T. George, A. Ksendzov, R. P. Vasquer, Appl. Phys. Lett. **60**, 995 (1992).

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