Nanocrystalline Silicon Multilayer Structures for Optoelectronics

Victoria KOVAL, Olexandr BOGDAN, Yuriy YAKYMENKO
Research Institute of Applied Electronics, NTUU "Kyiv Polytechnic Institute", Kyiv, Ukraine
nano_kpi@list.ru

***Abstract* — In this paper multilayer structures, based on nanocrystalline silicon, were synthesized in order to make use of the solar spectrum more efficiently. For this purpose, silicon thin films with structure, that varies from fine- to coarse-grained in the direction from top to bottom layer, were obtained. Nanocrystalline silicon thin films were deposited by electron beam evaporation. The structure of thin film was controlled by means of deposition time and temperature. Analysis of structural studies and transmission spectra has established, that thin silicon film should be deposited at different temperatures in the order of 130, 250 and 350°C. It has been shown, that with increasing one-layer deposition time the significant potential barrier is formed, which leads to growth of rectifying coefficient and photo-emf in multilayer structure. At the same same time, the photocurrent and short-circuit current increases with decreasing thickness of the three-layered structure. The optimal deposition time for solar cells is chosen in view of the magnitude of the filling factor, which significantly affects on the efficiency of solar energy conversion. Obtained structures can be used in photo-and UV sensors, as well as in solar cells.**

***Index Terms* — grain, multilayer structure, nanocrystalline silicon, nanocrystallite, photoconverter**

I. INTRODUCTION

Until recently, silicon thin-film electronics was limited by the use of amorphous silicon, but today the situation has changed rapidly. Instead of amorphous material, its structural modifications have come - protocrystalline (proto-Si), microcrystalline (μc-Si) and nanocrystalline silicon (nc-Si) [1-3]. Amorphous silicon thin film, containing super small crystallites (size of several nanometers or less), that are sometimes difficult to differ conventional methods of materials analysis, is called as protocrystalline silicon [1]. Microcrystalline silicon is characterized by the presence of large grains (size of 100 nm or more) and voids. In addition grains have column form, which in width can reach hundreds of nanometers and several microns in length [2]. But μc-Si thin films have lower absorption coefficient than amorphous silicon. A good alternative to the proto-and microcrystalline silicon is nanocrystalline silicon, which represents the amorphous material with crystallites size of 1 - 50 nm [3].

The application of nanostructured silicon material is caused by several reasons. Firstly, when ordered region (crystallites) appear in the amorphous matrix, the stability of optical characteristics sharply increases during light-soaking. Second, due to the presence of crystallites, the absorption spectrum of nanomaterial significantly expands. The formation of fine-grained structure in amorphous matrix (a few nanometers) enables to absorb efficiently ultraviolet and high-energy visible light, while coarse-grained structure (over 10 nm) absorbs low-energy visible and near infrared radiation [4]. These features of nanocrystalline silicon make it a promising material for manufacturing of thin-film transistors, photosensors, LEDs and solar cells [5-7].

In this paper the synthesis of multilayer structures based on nanocrystalline silicon is proposed in order to use of solar spectrum more efficiently. From this point of view, the gap width has to change from bigger to smaller value in the direction from the top layer to the bottom one. More efficient absorption of solar spectrum takes place in such structures. The upper layer absorbs the high-energy radiation (eg., UV-waves) and transmits the low-energy radiation (eg., visible and IR-waves), one part of which (eg., visible waves) is absorbed by the next layer, and another part (eg., IR-waves) goes further and so on. Application of multilayer structures in photodetectors and solar cells can lead to increased photosensitivity and photo-emf.

The combination of fine and coarse-grained silicon thin films has a significant advantage in comparison with the structures that use entirely different materials (e.g., SiC in α-Si PV-modules or compounds A3B5 in heterostructures for solar cells). All structural modifications of silicon films are similar in terms of lattice parameters, temperature coefficient of expansion and so on, that enable to obtain high-quality multi-layer structure without great efforts.

II. EXPERIMENTAL PART

Nanocrystalline silicon thin films were deposited by electron beam evaporation. The modification of film's structure and properties was carried out by means of the following process parameters: deposition temperature (100-350°C) and deposition time (2-5 min). Deposition rate is about 7 ... 10 nm / min.

Nanocrystalline silicon films were deposited layer by layer on a substrate during single technological cycle. Three-layered structure has been chosen for the study. Each layer of such structure has equal thickness, but was obtained at different temperatures (130, 250 та 350°C). In this paper, we studied the effect of deposition time on properties of three-layered structure and compared it with the corresponding one-layered structure.

Thin films were deposited on silicon substrates for investigation of electrical, photo-sensitive and photovoltaic characteristics and on quartz substrates - for transmission spectra measurements. Schematic representation of the layered structure is shown in Fig. I.

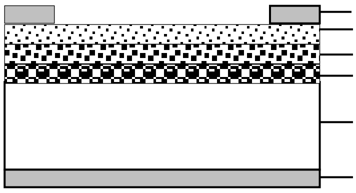


Fig.I. Structure of experimental samples.

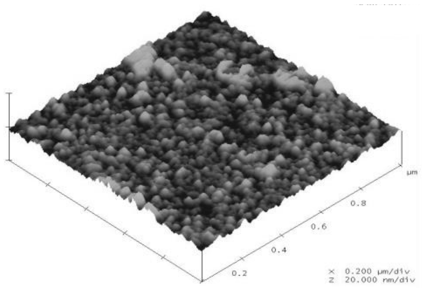
The study of film's structure was conducted by atomic force microscopy (AFM) using a microscope NanoScope IIIa Quadrexed Dimension 3000. Optical spectra of silicon films were measured by means of Double Beam Spectrophotometer 4802 UV / VIS UNICO. Electrical and photosensitive properties were investigated by measurement of dark and light current-voltage characteristics, as well as lux-voltage characteristics using visible light lamps of Phillips Spotone. Sensitivity to UV radiation was measured at wavelength of 350 nm using the UV-lamp Spectrum 5-A4/M. The photovoltaic characteristics of experimental samples were studied by irradiation with simulated sunlight spectrum AM1, 5.

III.RESULTS AND DISCUSSION

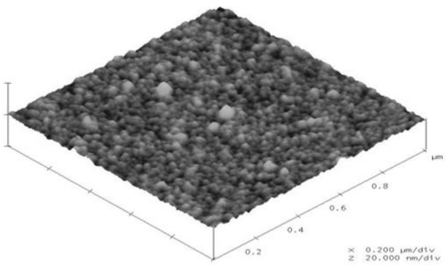
To establish the deposition sequence of silicon layers, synthesized at different temperatures, the surface morphology of silicon films was investigated. According to AFM-images, presented in Fig.II, with increasing deposition temperature from 130 to 300 °C, the structure of silicon film goes from coarse- to fine-grained.

In nucleation theory two mode of grain appearance are known - the regime of full and partial condensation. In the regime of full condensation with increasing substrate temperature the surface mobility of adsorbed atoms increases and their lifetime decreases, which leads to an increase in the radius of the critical nucleus, resulting in appear a coarse-grained structure of the film. At the relatively high deposition temperature adsorbed atoms re-evaporate, the capture area around each nucleus decreases, the maximum possible number of nuclei on the substrate surface increases, and therefore the film of fine-grain structure is formed (regime of partial condensation). Obviously, the results of structural studies, presented in Fig. II, can be explained by the regime of partial condensation.

Optical transmission spectra of silicon films, deposited at different temperatures, are consistent with structural studies (Fig. III). For example, silicon films, synthesized at high temperatures (300 and 350 °C), are characterized by maximum transparency in the red and infrared range and minimal transparency in the blue and ultraviolet range, indicating a more efficient absorption of high-energy radiation. Such transmission spectra indicate the presence of crystalline phases in the amorphous matrix.



a)



b)

Fig.II. AFM- images of nc-Si thin films, deposited at 130°c(a) та 300°c(б)

Indeed, according to the known dependence of nanocrystal band gap from it's size, follows, that smaller crystals are characterized by higher band gap. The presence of such crystalline grains in the amorphous matrix enhances the absorption spectrum of the material in the high-energy region.

Silicon thin films, obtained at 180 and 250 °C, effectively absorb low-energy visible light (for example, red radiation) that is the evidence of coarse-grained phase.

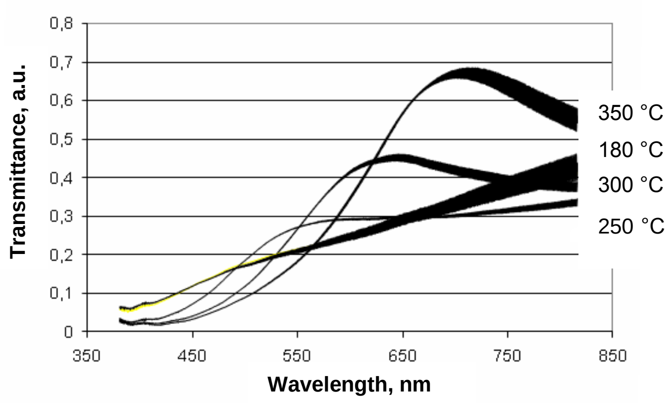


Fig.III. Transmission spectra of nc-Si thin films, deposited at different temperatures

Obviously, the combination of films, containing crystallites of different sizes, in one structure is very promising in terms of a more complete coverage of the solar spectrum. It was asked to change deposition temperature in the sequence 130, 250 and 350°C.

For obtained three-layered structures, the grain size dependence on one-layer deposition time is observed. Thus, the analysis of AFM images of samples with deposition time 2 and 3.5 min, in the contrast enhancement regime, showed the appearance of coarse-grained phase at higher deposition time (Fig. IV). Such modification of film's nanostructure with increasing deposition time, apparently, is due to a greater probability of growth than emergence of new crystallites.

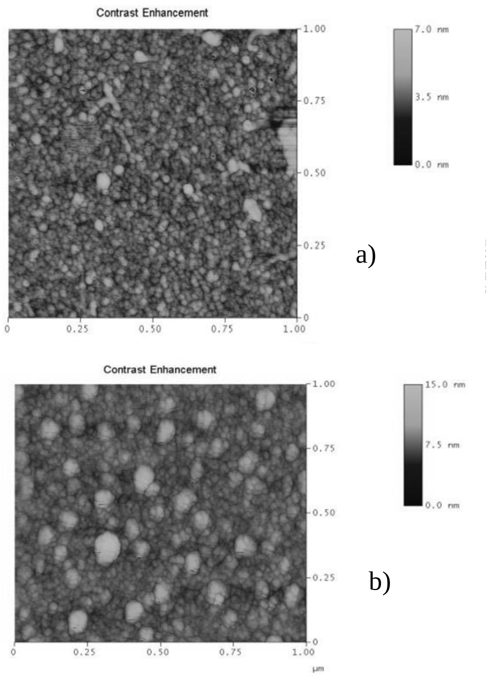


Fig.IV. AFM-images of three-layered structures with one-layer deposition time 2 (a) and 3.5 (b) min

In order to investigate the basic properties of multilayer structures, these films were deposited on single-crystal silicon substrates. Due to differences in band gap and doping level of nc-Si thin films and c-Si, at the their interface the heterojunction is formed. The properties of three-layered structures are compared with the properties of one-layered structure, synthesized at 350 °C during 5 min.

The analysis of electrical characteristics showed that the obtained experimental samples are inherent the rectifying properties (Fig. V). This indicates on the formation of a significant potential barrier for charge carriers in the boundary areas. The significant dependence of straightening on the thickness of structure was found. It was shown, that for the most thin layered structures the rectifying properties does not observed at all (one-layer deposition time is 2 min). With increasing of one-layer deposition time the rectification coefficient is rapidly growing , reaching 2700 at 1 V, that is 6 times larger than the coefficient for single-layer structure (Table I).

This result is explained by the fact, that during small deposition time the transition regions between thin layers occupy the most part of multilayer structure. Therefore, characteristics of such structure is mainly governed by the properties of transition regions, than the properties of the films. Increased rectifying properties of thick three-layered structure in comparison with one-layered one, can be explained by the appearance of larger potential barrier in the near-boundary region.

The study of the optical characteristics showed, that obtained experimental samples are characterised of significant sensitivity to visible and ultraviolet light (Fig. VI, Table I). Moreover, it was found that coefficient of sensitivity is depend on morphology and thickness of silicon film. Indeed, abnormally large photo- and UV sensitivity is observed in thin film structures. Primarily, this is due to a significant difference in size of crystallites under the transition from top to bottom film, that is reflected in expanding of absorption spectrum in the structure.

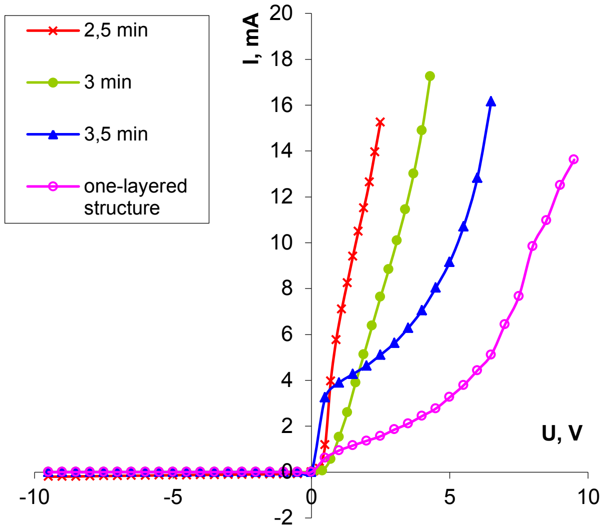


Fig.V. comparison of I-V-characteristics of one- and three-layered structures

According to the structural analysis (Fig. II, b), with increasing deposition time the larger grains are formed in multilayer structure. This means that the absorption spectrum of thick multilayer structures is shifted to low-energy range of radiation. In addition, for thick structures the decrease of photosensitivity is caused due to absorption of radiation in the upper layers.

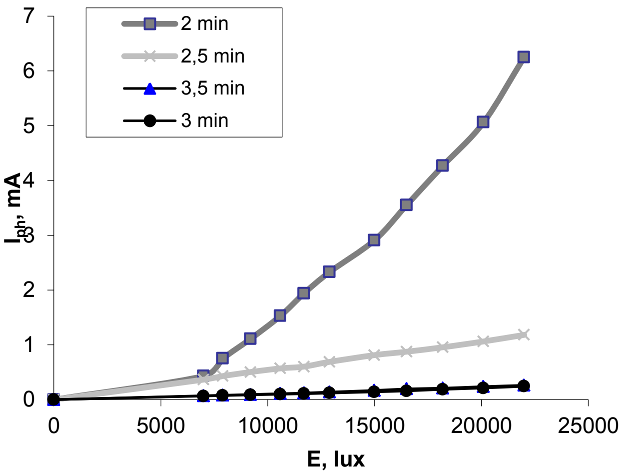


Fig.VI. Influence of one-layer deposition time on lux-ampere characteristics of three-layered structures

As a result, a small part of the radiation reaches to the lower layers and they do not actually participate in the process of absorption.

Comparison of photosensitivity coefficients showed, that even for thick three-layered structures, the photosensitivity is 2.5 times higher than for one-layered one, despite the losses of the absorption in the upper layers. At the same time thin three-layered structures provide the growth of photosensitivity by 2 orders of magnitude compared to the single-layer structure (Table I).

With increasing of deposition time, UV-sensitivity of these structures is more determined by absorption losses in the upper layers than photosensitivity. Therefore, for thick three-layered structure the coefficient of UV-sensitivity is lower than for one-layered structure. However, thin experimental samples showed significant sensitivity to this radiation, exceeding the magnitude of UV sensitivity in one-layered structure by 2-4 times (Table I).

TABLE I. THE BASIC PARAMETERS OF ONE- AND THREE-LAYERED STRUCTURES

One-layer deposition time, min		K_{rec}	K_{ph}, mA/lmV	K_{uv}, mA/W	U_{oc}, mV	I_{sc}, μA
one-layer	5	450	0,04	0,96	227	35
three-layer	2	1	11,7	3,75	-	-
	2,5	14	0,12	2,24	233	295
	3	2500	0,1	0,43	270	100
	3,5	2700	0,1	0,25	270	242

The photovoltaic effect is inherent to the three-layered structures (Fig. VII, Table I). It should be noted that for thin three-layered structure (one-layer deposition time is 2 min) this effect does not take place, because the potential barrier is absent (as shown above). In general, the height of potential barrier determines the magnitude of photo-emf in the structure. So, in thick three-layered structures the rectification coefficient, and hence the open circuit voltage increases significantly compared with one-layered structure (Table I). Further increase of deposition time does not lead to improved photovoltaic characteristics, because serial resistance grows in the structure.

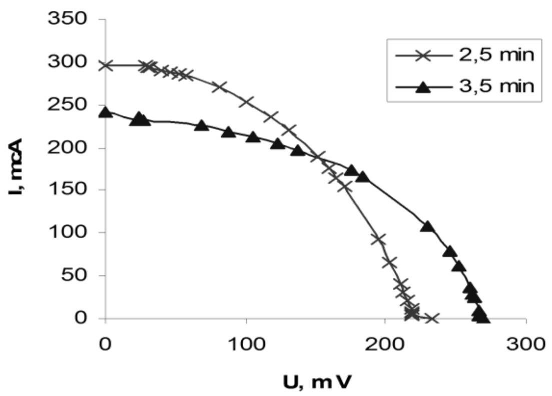


Fig.7. Influence of one-layer deposition time on the photovoltaic characteristics of three-layered structures

It is seen that significant increasing of short-circuit current is main constituent in efficiency of converting solar energy. The presence in three-layered structure the crystallites of different size (from smallest to largest in towards to the substrate), allows them to absorb almost the entire solar spectrum. As a result, total photocurrent through the structure will increase. With increasing deposition time, the short-circuit current is somewhat reduced due to the shift of absorption in direction of low-energy range and the cutting off high-energy radiation.

Thus, on the one hand, long deposition process increases the open circuit voltage, on the other hand, reduces the short-circuit current. To choose the optimal technological conditions for synthesis of three-layered structure with photoelectric effect load characteristics were measured (Fig. VII). As shown in Fig. VII, the layered structure with one-layer deposition time of 3.5 min converts sunlight more efficiently, because it is characterised by larger value of filling factor.

V. CONCLUSION

In this paper, three-layered structures, based on nanocrystalline silicon, were synthesized. It has been shown that multilayer structures are very promising for thin-film photodetectors and solar cells.

It was found, that for the synthesis of efficient sensors of visible or ultraviolet radiation, the one-layer deposition time should not exceed 2 ... 2.5 min.

Synthesis of thin film solar cells of high efficiency requires, obviously, a combination of different deposition time in one structure. So, the upper layers should deposit for a short period of time to expand the absorption spectrum of the structure and, therefore, increase its short-circuit current. The bottom layers have to be obtained longer to generate the greatest possible potential barrier for charge carriers, and thus increase the value of open circuit voltage.

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