STUDY OF NANOCRYSTALLINE SILICON THIN FILMS FOR APPLICATION IN SOLAR CELLS

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Abstract

Nanotechnological approaches are widely used to improve efficiency and stability of thin-film solar cells. It is assumed that the presence in thickness of amorphous matrix the ordered regions (grains or crystallites) will significantly reduce the Staebler-Wronski effect. In the paper nanocrystalline silicon thin films have been synthesized and investigated their structural, electrical and optical properties. The presence of nanocrystallites in amorphous matrix was determined by transmittance electron microscopy and atomic force microscopy. The technological conditions for appearance nanocrystallites in silicon thin film were found. Study of electrical and optical properties showed that application of nanocrystalline silicon thin films in solar cells are very promising. In particular, we measured the optical absorption spectra to determine the band gap of the material. In the paper the sensitivity of the nanocrystalline material to the visible and ultraviolet radiation was investigated. It was shown that the photosensitivity of the films, containing nanocrystallites, significantly increased in comparison with amorphous silicon. The coefficient of the integral photosensitivity of this material is about 1 mA/lm. Also, it was observed increased sensitivity to UV radiation due to the presence in their composition of small crystallites (1-2 nm). Obtained thin films were applied in silicon solar cells. Photovoltaic effect was observed in heterostructure, formed by nanocrystalline silicon thin film, deposited on silicon substrate of opposite conductivity. Efficiency and stability of nanocrystalline silicon solar cells were measured and the possible ways of increase these values were discussed.

Keywords: nanocrystalline silicon, photovoltaic effect, solar cell

1. INTRODUCTION

Thin film solar cells are rapidly developing and very promising direction in photovoltaics. In a new report on the status and forecast of the global market of thin-film solar cells, published by Wintergreen Research Inc. (USA), indicated the increase of photovoltaic industry turnover from 2.9 billion dollars in 2010 to 44 billion in 2017 [1].

One of the main reasons for the rapid development of thin-film technology is the ability to significantly reduce the cost of solar energy reaching grid parity level. Thin-film solar cells are quite promising in construction of nonvolatile buildings, thanks to the possibility of deposition such PV-modules on almost any surface. And one more indisputable advantage of these panels is a relatively high efficiency at low light levels (for example, on a cloudy day or in regions with few sunny days in a year).

Today, the most part of the world thin-film PV-market falls on amorphous silicon solar cells (about 80%). But solar cells based on amorphous silicon thin films have a significant drawback - high level of degradation under exposed to intense radiation [2].

Therefore, intensive work to find the ways to improve of efficiency and stability in thin-film silicon solar cells continue in many scientific research centers. To this end, we propose to use silicon thin films of nanocrystalline structure.

2. EXPERIMENTAL PART

Nanocrystalline silicon thin films were deposited by two vacuum methods: electron-beam evaporation (EPV) and high-frequency magnetron sputtering (RF MR) in argon environment at a frequency of 27 MHz. To
improve chemical purity of obtained films the prior sputtering of Ti was carried out in a vacuum chamber, which led to reduce the pressure of the residual gases by order of magnitude. The production technology of experimental samples consisted of the following steps: the chemical cleaning of substrates, the deposition of thin film, the deposition of contact pads and the cutting wafers into individual samples.

As substrates we used the following materials: single crystal silicon of p- and n-type conductivity for study the structural, electrical and photosensitive properties of nanocrystalline material and heterojunctions on its basis, NaCl for study the structure of films by transmission electron microscopy, quartz for measurement of transmission spectra and absorption spectra. The influence on basic properties of nanocrystalline material was realized by method of production, conductivity type of substrate and deposition temperature.

The study of sample surface at the nanoscale were conducted by atomic force microscopy (AFM) using a microscope NanoScope IIIa Quadrexed Dimension 3000. The presence of nanocrystals in thin films was observed by transmission electron microscopy (TEM) using a microscope JEM-100 CX. Optical properties of silicon films were measured by means of Double Beam Spectrophotometer 4802 UV / VIS UNICO.

3. RESULTS AND DISCUSSION

3.1. INTERCONNECTION OF STRUCTURE AND OPTICAL PROPERTIES OF SILICON THIN FILMS

Obtained silicon thin films have amorphous or nanocrystalline structure, depending on the technological conditions of synthesis (Fig. 1). As it can be seen from the AFM images, the film surface is uneven and consists of a large number of structural inhomogeneities of different sizes. But in Fig. 1,a the heterogeneities look so blurry and disordered without clear boundaries, therefore can not be classified as nanocrystals. Regarding the nature of the observed structural inhomogeneities in Fig. 1, b, it should be noted that they are usually interpreted as grain of crystalline structure (crystallites). Crystallite size is in the range 10 - 20 nm. However the size of grains, observed in AFM, are somewhat inflated due to the adsorption of gases from the atmosphere and the formation of some shell around of them. In the work another method of structural analysis was used and namely TEM, which gives the opportunity to study the film’s structure in transmission.

![AFM images of amorphous (a) and nanocrystalline (b) silicon thin films](image)

Fig. 1: AFM images of amorphous (a) and nanocrystalline (b) silicon thin films

It was found that the structural heterogeneities, observed in Figure 1,a don't have crystalline structure and this film is really amorphous. At the same time the film, shown in Figure 1, b is characterized by the presence of nanocrystalline structures in the amorphous matrix. Such material is called as nanocrystalline silicon.
The technological modes, in which the nanocrystallites appear in amorphous matrix, were established. In the most cases the silicon films, synthesized by rf magnetron sputtering, have an amorphous structure (Fig. 1,a). This result can be explained from such point of view that the film surface is subject to bombarding of the particles from the plasma environment, which causes additional disordering and amorphization of crystalline formations. In contrast to this, films, synthesized by electron beam evaporation, are characterized by the presence of nanocrystallites in certain technological modes (Fig. 1, b).

The dependence of grain size on the deposition temperature has special behavior. Initially, the film structure goes from fine- to coarse-grained one with increasing temperature (from 100 to 250°C), which is consistent with the theory of nucleation. It is known that the increasing substrate temperature increases the surface mobility of adsorbed atoms and decreases their lifetime, which leads to an increase in the radius of the critical nucleus, resulting in appear a coarse-grained structure of the film. But in high temperature range (300 - 350°C), the formation of many small grains are observed. Observed dependency can be explained by the transition from full to partial condensation at these temperatures. Thus, at the relatively high temperature deposition 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.

Optical properties of the films were investigated based on transmission and absorption spectra. Fig. 2 shows the transmission spectra of silicon films with amorphous and nanocrystalline structures. The peculiarity of the obtained spectra is the appearance of peaks on the edge of the visible and infrared wavelengths. Usually, the appearance of peaks near the edge of intrinsic absorption is associated with impurity or excitonic absorption. In this case, none of these explanations cannot be used. Firstly, these spectra were measured at room temperature, at which the exciton absorption can't observed. Secondly, these samples do not contain target impurities. The oscillation in transparency spectra can be explained by the light absorption in crystallites, energy levels of which there are below the bottom of the conduction band of the amorphous matrix. Taking into account the band model of nanocrystalline silicon, it becomes clear appearance of peaks in the spectra of fine-grained films. The emergence of small grains (2 - 5 nm) creates discrete energy levels near the bottom of the conduction band of the amorphous matrix, which causes additional absorption below the intrinsic absorption edge. The larger crystallites (20 - 30 nm) create so much energy levels in the band gap, that they form quasi continuous energy band. In the latter case, the grains are not seen as quantum dots, but as inclusions of crystalline regions in the amorphous matrix.

These silicon thin films are characterized by photosensitive properties. The lux-ampere characteristics of silicon films, obtained at different temperatures, are given in fig.3. It was found that film's photosensitivity is determined by its crystallinity degree, and namely: maximum photocurrent correspond to a high degree of
material crystallinity. Also we can see a correlation between nanostructure of film and its photosensitivity at different deposition temperature (Fig.3). It is known that the magnitude of material photosensitivity is determined from lux-ampere characteristic on the base of slope of the curve to the abscissa. At first with increasing the deposition temperature photosensitivity coefficient increases, which corresponds to the process of coarse-grained film formation. At high deposition temperatures the process of fine-grained growth predominantly occurs, which is characterized by small lifetime of nonequilibrium carriers. The small crystallites have a high ratio of surface/volume. Taking into account, that the numerous structural defects are concentrated on crystallite surface, the reason of photocurrent drop at high temperature range becomes apparent. The coefficients of photosensitivity are calculated based on lux-ampere characteristics and shown as a bar chart in Fig.3,b. The maximum value of photosensitivity is 2 mA/lmV that inherent for silicon film, obtained at 180°C.

![Lux-ampere characteristics (a) and coefficients of photosensitivity (b) of silicon thin films in depend on deposition temperature](image)

Fig. 3: Lux-ampere characteristics (a) and coefficients of photosensitivity (b) of silicon thin films in depend on deposition temperature

The investigation of film's sensitivity to UV radiation showed certain special features. In particular, an effective UV absorption is primarily determined by the presence of small crystallites which act as quantum dots, rather than improved transport properties of the material (as in the case of photosensitivity). For obtained silicon thin films the coefficient of UV-sensitivity is 1 - 2 mA/W, but incorporation of some impurities (sensitizers) increases this value up to 12 mA/W.

### 3.2. PHOTOVOLTAIC EFFECT IN HETEROSTRUCTURES BASED ON NANOCRYSTALLINE SILICON THIN FILMS

Because of the difference in bandgap mono-and nanocrystalline silicon, at the interface film - substrate the heterojunction is formed. Moreover, the isotype or anisotype heterojunction are created under deposition the film on silicon substrate of n- or p-type conductivity accordingly. Regardless of the production conditions, photoelectric effect doesn't exhibit in the isotype heterostructures at the time, as anisotype heterostructures are characterized by photo-emf of 120 - 400 mV. This difference is obviously due to the formation of a significant barrier at the interface film - substrate in anisotype heterojunction.

In this paper the investigation of solar cell stability under light soaking were carried out. It was revealed two special features of this material compared with use of amorphous silicon thin films (Fig. 4). The first feature is the rapid stabilization of the photovoltaic parameters under intense illumination (up to 1 hour), which is significantly less than for amorphous solar cells (tens of hours). Second, the degradation of solar cells based
on nanocrystalline silicon thin films was within 1.5 - 10.5%, which is significantly lower than for amorphous silicon one (20 - 30%).

It was also found that the characteristic degradation of solar cells is reduced by about a half, when the structure of nanocrystalline film goes from fine- to coarse-grained, for example: degradation of the open circuit voltage decreases from 6.88 to 4.22% (Fig. 4, a), and the degradation of short circuit current - from 1.54 to 1.4% (Fig. 4, b).

It should be noted, that in this paper nanocrystalline silicon films used as active layer in thin film solar cells without optimization design. Further improvement of solar cell parameters is associated with additional constructive decisions: deposition of some coating, that reduces light reflection losses at up to 30%, as well as the use of buffer layer on the edge of film - substrate, that can increase the open circuit voltage from 370 to 600 mV and short-circuit current from 6 to 30 mA/cm².

4. CONCLUSIONS

In this paper it has been shown the possibility of nanostructured film production by vacuum methods, and determined ways to control of it. The data of AFM and TEM revealed, that more intensive nucleation observed under the following conditions: the method of electron-beam evaporation and high deposition temperature (before starting of partial condensation). Obtained dependencies can be useful in developing of silicon film production technology for device application. On the example of the basic structure, the possibility of using nanocrystalline silicon in thin-film solar cells has been shown. These researches allow to determine the technological modes for the synthesis of stable thin film solar cells based on silicon films.

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LITERATURE
