Silicon nitride for third generation photovoltaics

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The photovoltaics is one of the most promising renewable energy technology which can contribute substantially to our future energy needs. According to the prognosis, the photovoltaics could compete with conventional electricity production e.g. the grid parity will be reached before 2030 year. In order to reach this goal the ratio price/power of PV modules should be reduced significantly. The efficiency of solar cells produced today is limited by Shockley-Queisser limit to 31 % for an optimal band gap material of 1.3 eV. The laboratory record of conversion efficiency of silicon solar cell with *PERC* structure equal to 25 % was obtained at the University of New South Wales in Australia. This is probably the efficiency limit for industrial silicon solar cells. The 90 % production of PV modules today is based on the crystalline silicon solar cells called the first generation solar cells. The price of that modules is dominated by the Si wafers and other materials used for the modules encapsulation. The thin films solar cells called the second generation of photovoltaics are less expensive because they do not use the wafers but the price of the thin films is also limited by the cost of materials used for encapsulation. Therefore, there is need to increase considerably the efficiency of solar cells by developing new concepts of third generation solar cells. The efficiency of first and second generations solar cells is mainly limited by two factors:
- photons with smaller energy than energy gap E_g are not absorbed in the base material;
- excited carriers by high energetic photon ($E_{ph} > E_g$) give excess energy to phonons due to thermalisation process.

The aim of new concepts is to increase efficiency by reduction these two losses .
One of the main approaches of new solar cells is a tandem solar cell composed of two or more cells with different bandgaps. The theoretical limit of efficiency depends on the number of cells. In the limit of an infinite number of cells the theoretical efficiency is 86.8 % for the concentrated and 69 % for non-concentrated sun light. For the 3-cells tandem the limit efficiency is 48.6 % and for 2-cells tandem the efficiency limit is 42.5% for the non-concentrated sun light.

The high efficiency is not the only one requirement for the solar cells third generation. They should be based on the thin films and use only abundant and non-toxic materials, as well. One of the best material for that purpose is silicon and new, silicon based materials like silicon quantum superlattices. The Si quantum superlattice is composed of the quantum dots (QDs) embedded in the dielectrics like SiN_x, SiC or SiO_2. One of the main requirement is low barrier height and small distance between dots in order to obtain the small conductivity. The bandgap of the Si quantum superlattice depends on the diameter of the quantum dots. For example for the bandgap 1.7 eV the diameter should be about 2 nm. The optimal bandgaps are in the range 1.7 eV-1.8 eV for top cell on Si bottom cell for 2-bandgaps cells or 1.5 eV and 2.0 eV for the middle and upper cells on Si bottom cell for a 3-bandgaps cell.

In our work the quantum dots silicon superlattice is based on silicon nitride films. The films were deposited by *RF* (13.56 MHz) *plasma enhanced chemical vapor deposition* (*RF PECVD*) using *Oxford Plasma Technology PLASMALAB 100 System* in the Institute of Electron Technology in Warsaw. The multilayer structures consisting of near-stoichiometric silicon nitride SiN_x layers followed by silicon–rich silicon nitride SRN layers were deposited and heated at 1000 and 1100^{o}C in order to obtain the quantum dot superlattices. The method described by Zacharias and his co-workers was used. The idea was later used by Green and

co-workers for the superlattices consisting of silicon dots embedded in different dielectric materials like SiO_2, SiN_x, SiC_x. The scheme of silicon superlattice quantum dots formation is presented in Fig. 1.

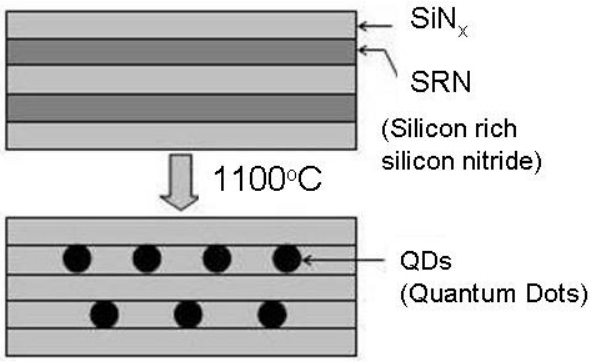

Fig. 1. Scheme of formation of quantum dots (QDs) in silicon nitride multilayer according to Zacharias and Green (M. Lipiński in *Archives of Materials Science and Engineering*, 46 (2010) 69-87).

The alternating layers stock comprises films of a near stoichiometric silicon nitride SiN_x layer ($n \approx 1.9$) followed by silicon rich silicon nitride SRN ($n \approx 3.2$). After annealing the silicon quantum dots precipitate in the SRN layers. The description of deposited multilayered structures is presented in Table 1.

Table 1. Multilayer structures composed of *N* - bi-layers: SiN_x/SRN, where SiN_x is a near stoichiometric film and SRN is a silicon rich silicon nitride, *d1* and *d2*- thickness of these layers.

multilayer	*N*	*d1* (SiN_x) [nm]	*d2* (SRN) [nm]
n° 1	50	2	2
n° 2	20	8	5
n° 3	20	3	3

Figure 2 shows the cross-section *HRTEM* images of the multilayer n° 1 consisting of 50-bilayer SiN_x/SRN. Figure 2a shows quantum dots (QDs) at small magnification whereas Fig. 2b presents a high resolution *TEM* image. The estimated size ranges of QDs is about 5 nm. Besides quantum dots of the 5 nm size we have also observed a large twined nanocrystals with 10 nm diameter (Fig. 2c). Although it is an interesting question what is the real size distribution of the new objects, even quantifying the exact average size of the nanoparticles from the *HRTEM* images is an impossible task, because only very small number of nanoparticles give a sufficient good contrast.

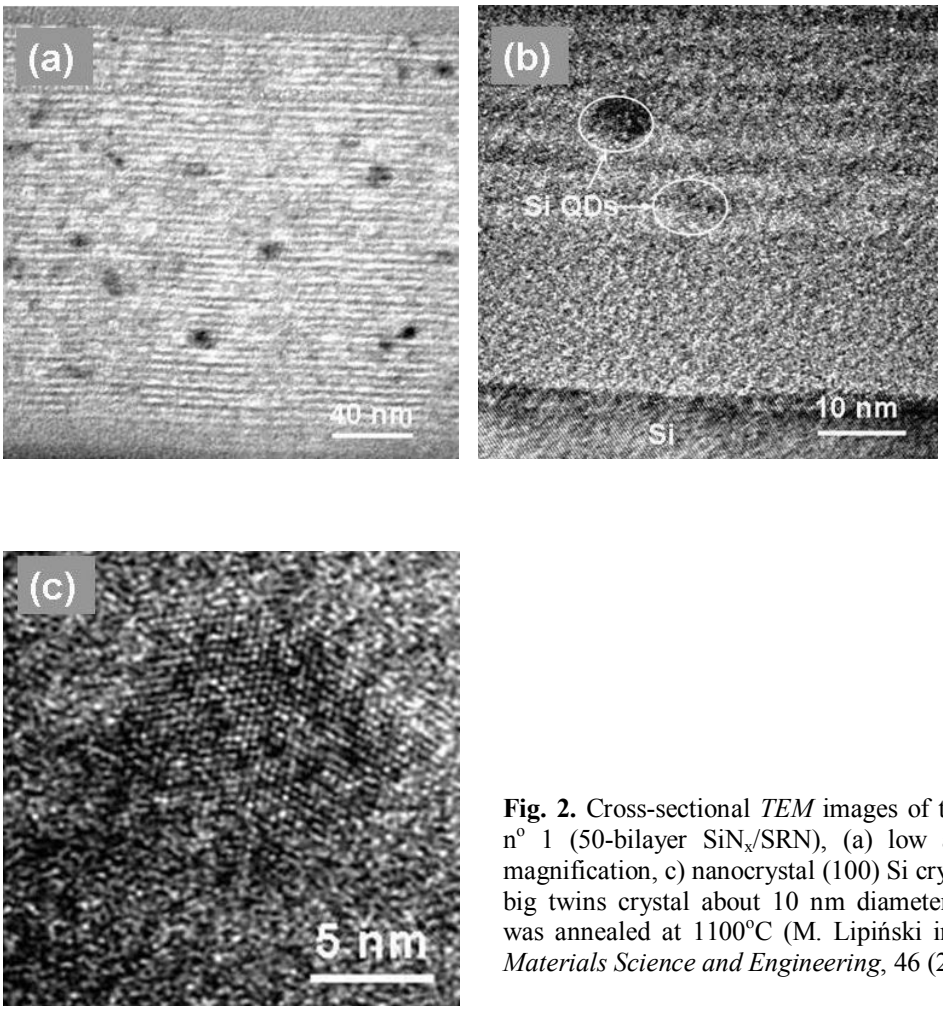

Fig. 2. Cross-sectional *TEM* images of the multilayer n^o 1 (50-bilayer SiN_x/SRN), (a) low and (b) high magnification, c) nanocrystal (100) Si crystal planes of big twins crystal about 10 nm diameter The sample was annealed at 1100^{o}C (M. Lipiński in *Archives of Materials Science and Engineering*, 46 (2010) 69-87).

Figure 3 shows the multilayer n^o 3 consisting of 20-bilayers: SiN_x/SRN. It displays that the shape of the nanocrystals is not spherical**.**

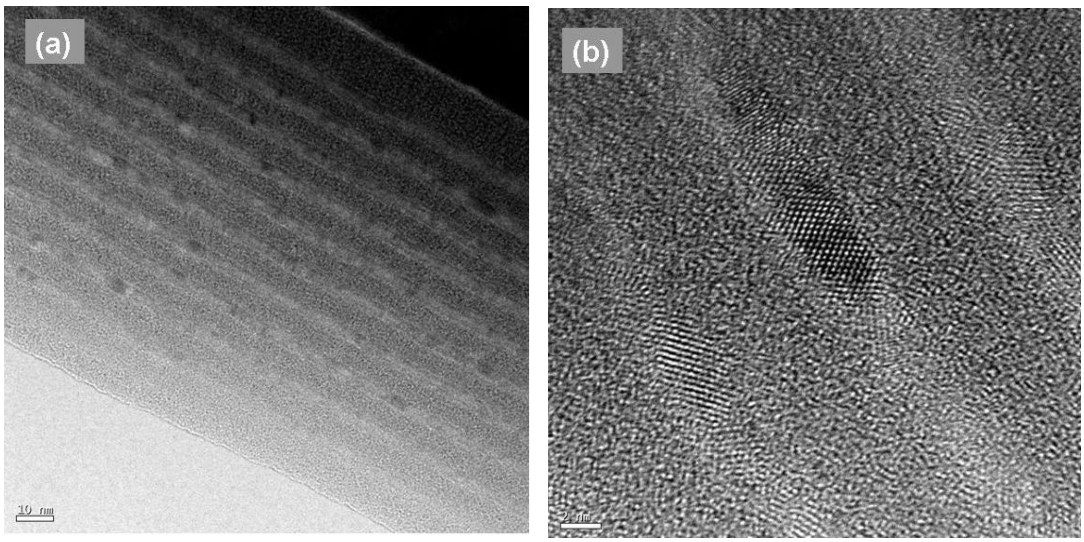

Fig. 3. Cross-sectional TEM images of the multilayer n^o 3, (a) low and (b) high magnification. The sample was annealed at 1100^{o}C (M. Lipiński in *Archives of Materials Science and Engineering*, 46 (2010) 69-87).

Figure 4 shows the post-anneal grazing incidence X-ray diffraction (*GIXD*) spectra of the multilayer n^{o} 3 annealed at 1000^{o}C (a) and at 1100^{o}C (b). It is indicated that sample annealed at 1100^{o}C contains nanocrystals.

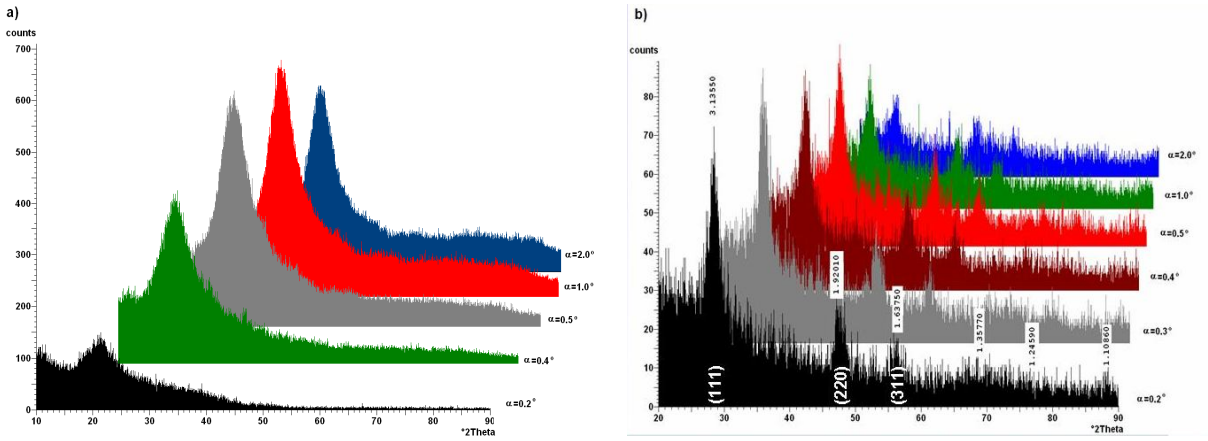

Fig. 4. The X-ray diffraction patterns of multilayer n^{o} 3 obtained by *GIXD* (Grazing incidence X-ray diffraction) method: a) sample heated at 1000^{o}C, b) sample heated at 1100^{o}C with silicon quantum dots (M. Lipiński in *Habilitation monograph*, Krakow, 2011).

Diffraction patterns of multilayer system annealed at 1000^{o}C is the same as-deposited. It shows an amorphous structure of the layer. The diffraction patterns of SiN_x/SRN multi-layer annealed at 1100^{o}C (Fig. 4b) show the broadening of diffraction lines for nano-crystalline phase. These effects indicate the presence of a quantum silicon dots inside SRN layers. The intensity of these peaks decreases with the increase of incident X-ray α angle. For α = 2.0^{o} (2θ) only two distinct reflection peak can be observed. This effect can be connected with much lower concentration of a quantum dots in the direction of substrate.

Figure 5 shows the post-anneal grazing incidence X-ray diffraction (*GIXD*) spectra of multilayer n^{o} 1. An average size of nanoparticles estimated using Scherrer's equation is 4.5 nm.

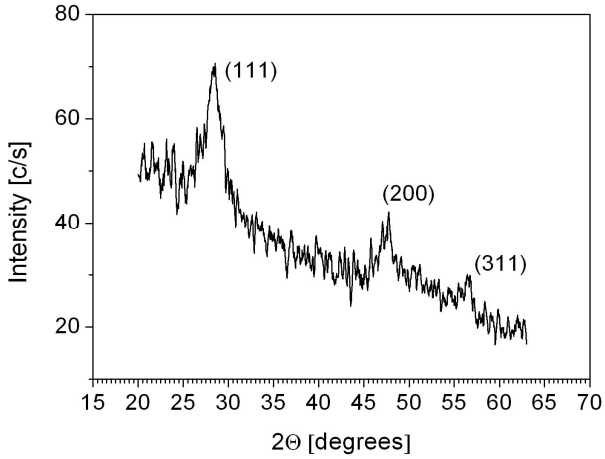

Fig. 5. The X-ray diffraction (*GIXD*) plot for the multilayer n^{o} 2 annealed at 1100^{o}C. The average size of the crystallites is d = 4.5 nm (M. Lipiński in *Archives of Materials Science and Engineering*, 46 (2010) 69-87).

It was shown that the silicon QDots has been formed in the multilayer structures of silicon nitride by annealing at 1100^{o}C. The formation of silicon nanocrystals is verified in the sample heated at 1100^{o}C by *HRTEM* and *GIXD* methods. However, the multilayer structure should be further optimized in order to control the size, the shape and density of the quantum dots in the silicon nitride matrix and to obtain the optimal bandgap of the quantum dot superlattice. The next step of investigation is doping the QDs by phosphorous and boron in order to realize the photovoltaic devices.

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