Organic solar cells based on ZnO nanowires layer

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Abstract- **In our research we are looking for alternative to solar cells based on silicon. We are using zinc oxide (ZnO) which is N type semiconductor instead of silicon. To reach PN junction P type polymer is used. ZnO is in form of well aligned nanowires. Since the distance between nanowires is smaller than the mean free path of electrons almost all emitted electrons are collected. We use vapor-liquid-solid (VLS) method to create ZnO nanowires. Used substrate was sapphire, silicon and silica glass. Small solar cell was manufactured and its open circuit voltage under light was measured.**

I. Introduction

Scientists all around the world are looking for new energy resources or are improving current techniques of conversion to electric energy. Conversion from sunlight is one of promising method. Except sufficient natural conditions, the growing price of silicon is one of its disadvantages. Conventional solar cell uses tree or comb structure of contacts to collect emitted electrons. These structure must be fine enough comparable with mean free path of electron. If not so, emitted electrons recombine inside the semiconductor material and are not generating desired current. One way how to collect all emitted electrons is to make the structure of contact very fine. In our case one of contacts is semiconductor zinc oxide in form of well aligned nanowires. Herewith collecting electrode is inside the structure of solar cell and makes active part of PN junction. In addition the structure of ZnO nanowires is very fine.

Zinc oxide is transparent N type semiconductor material with wide direct band gap 3.4 eV at room temperature. This direct band gap is profitable for use in solar cell applications. Other properties of ZnO favorable for electronic applications include its stability to high-energy radiation and to wet chemical etching. Radiation resistance makes ZnO a suitable candidate for space applications (it corresponds to fact that solar panels are used as a power source) [4].

II. EXPERIMENTS AND RESULTS

There are many methods how to create well aligned structure of zinc oxide nanowires. We used vapor-liquid-solid method (see fig. 1) [1]. This method is very sensitive to the substrate because the principle of this method is based on epitaxial growth. It is necessary to have substrate with internal structure very similar to structure of zinc oxide, low lattice mishmash is required. Such we used silica glass, sapphire and silicon. The experiments were done also with ordinary lab glass, but the result was like expected (in means no structure of zinc oxide was created on it). The lattice mishmash also influences a structure of created nanowires layer. Sapphire as a material with internal structure very similar to one of zinc oxide allows the growth of perpendicular zinc oxide wires. On the other hand on substrate made of silicon and silica glass the wires have disordered structure.

In process of manufacturing of zinc oxide nanowires we put onto glass boat our substrate covered with gold film and near to the substrate we put mixture of ZnO powder and graphite powder (see fig. 4). This boat is given into the furnace with defined heating cycle (maximum temperature is 1100 ÷ 1200 °C). Argon atmosphere was used. ZnO powder is reduced by graphite to Zn vapor and CO/CO_2. The Zn vapor is transported to substrate and creates alloy with gold. When the alloy (droplet) is saturated, Zn oxidizes with oxygen and nucleates under the Zn-Au alloy droplet. Such ZnO nanowire (with Zn-Au alloy tip) is formed. The position where nanowire will appear is selected by the presence of gold clusters. Such we can create pattern of zinc oxide nanowires. The thickness of gold which we use in our experiments is 2.5 nm. All substrates had dimensions 10x10 mm.

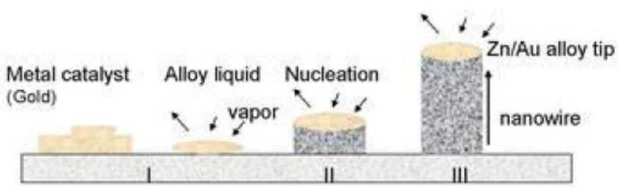

Figure 1. Basic scheme of the VLS process in a tube furnace [2].

When the maximum temperature was kept for the duration of desired time the furnace is turned off and the cooling is provided under the natural cooling. When the temperature inside is near to the room temperature, the boat with our substrate is taken out of the furnace.

The diameter of nanowire grown on silicon and silica glass was similar and was about 100 nm, on sapphire the nanowire was thicker with diameter about 350 nm (see fig. 2). The diameter of nanowire on the substrate depends on the thickness of gold cluster. Thicker gold cluster creates thicker nanowire.

The length of nanowires depends on the time during which the maximum temperature is applied. The type of substrate does not influence the length a lot. The time changed from 35 to 60 minutes and the related length varied from 1 to 15 µm. Also the length of nanowires was not constant on the same substrate. For example on the same substrate a length of nanowires varied from 7 to 13 µm. That is obvious from the position of the substrate on the boat (see fig. 4).

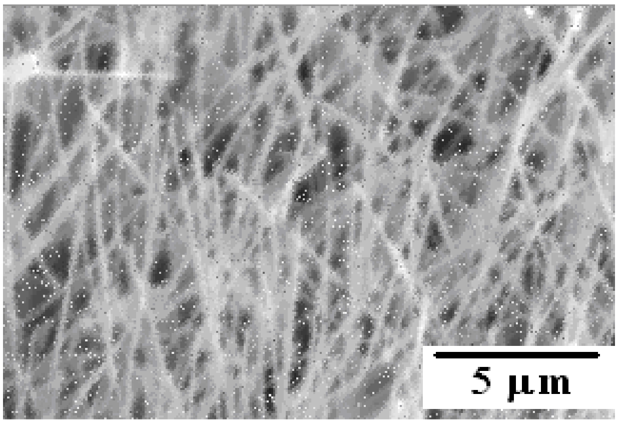

Figure 2. SEM image of structure of ZnO nanowires on silicon substrate.

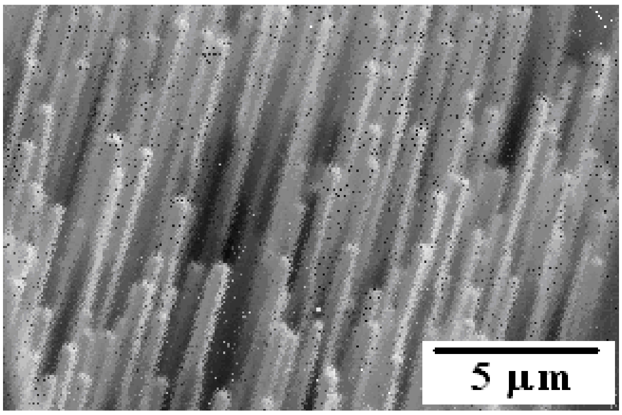

Figure 3. SEM image of structure of ZnO nanowires on sapphire substrate.

The method of VLC growth is very sensitive. The furnace has to have temperature zones to reach temperature gradient to allow vapor of zinc to condensate. The result if layer of ZnO is created or not very depends on the position of our substrate and position of zinc oxide source inside the tube furnace.

Droplet of polymer (P type semiconductor) is applied on the surface of substrate covered with ZnO nanowires and when the polymer is dried polymer and ZnO are contacted with silver varnish. Such created solar cell is on fig. 5.

Used polymer as a P semiconductor was PEDOT (commercial name Clevios P by company H.C. Starck) with chemical name poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) aqueous dispersion. Different concentrations and thickness of polymer was tested. Polymer was dilute with distilled water to reach concentration 1:3, 1:5, 1:8 (polymer : distilled water). Concentrated polymer was applied in different thicknesses. Different thickness was prepared such that we put drop of concentrated polymer on the substrate and we regulated the volume of concentrated polymer with syringe. Such we sucked out concentrated polymer but the diameter of created drop was same. That was very easy way how to control the thickness. When dried the area was same but the thickness of polymer differed.

Figure 4. Boat with mixture of zinc oxide and graphite on the sides, substrate is put in the centre of the boat. White part is reacted ZnO. Situation after heating cycle – substrate is covered with ZnO.

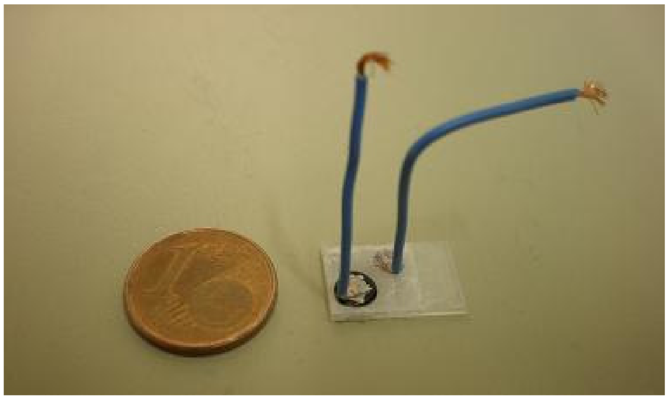

Figure 5. Realization of solar cell.

Open circuit voltage of created solar cell was measured under light intensity 45 000 lx. Spectrum and intensity of light is on the fig. 6 (for comparison sunlight is depictured also). Reached open circuit voltage for each combination of thickness of polymer and concentration of PEDOT polymer is shown in Table I. After measuring open circuit voltage, thickness of polymer and zinc oxide layer was measured with using atomic force microscope. Measured values are in Table II.

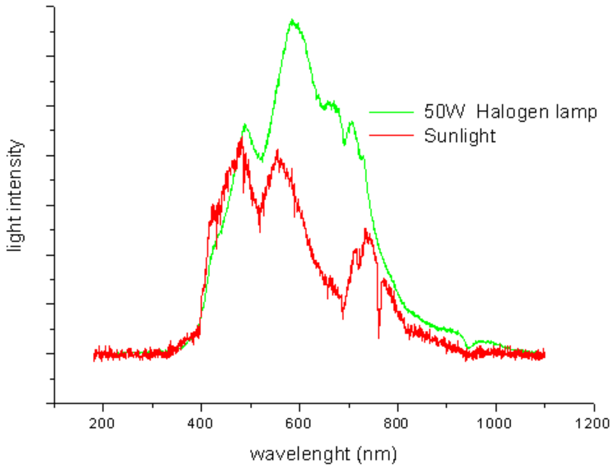

Figure 6. Spectrum and light intensity of halogen lamp and sunlight in the laboratory.

TABLE I
OPEN CIRCUIT VOLTAGE OF SOLAR CELL WITH DIFFERENT THICKNESS OF POLYMER ON SILICON. LIGHT INTENSITY IS 45 000 LX. ALL VALUES ARE IN MILIVOLTS.

	thickness of polymer		
conc.	**high**	**medium**	**low**
1:3	0.8	0.6	0.1
1:5	0.6	0.2	0.2
1:8	0.2		

TABLE II
THICKNESS OF POLYMER AND ZINC OXIDE LAYER ON SILICON

		thickness of polymer		
conc.		**high**	**medium**	**low**
1:3	ZnO	7.05	9.4	12.75
	poly	2.46	1.51	1.36
		high	**medium**	**low**
1:5	ZnO	9.87	13.61	9.58
	poly	3.5	3.18	1.51
		high		
1:8	ZnO	13.95		
	poly	5.08		

As shown in the table I, the highest open circuit voltage on silicon substrate was reached for polymer PEDOT concentration 1:3 (0.8 mV). That is why we decided to apply this concentration in case of using silica glass as a substrate. In case of silica glass we applied 4 types of thickness of polymer PEDOT in concentration 1:3. Thickness of zinc oxide nanowires layer was constant in all surface of our substrate and was 1.22 µm. Results of measured open circuit voltage are in Table III. Highest open circuit voltage was 0.9 mV and this was reached for thickness of polymer 2.3 µm (thickness of zinc oxide nanowires was 1.22 µm). Such we got highest open circuit voltage than in case of silicon substrate. We demonstrated that values gained in case of silicon substrate are not influenced by the material of substrate because we got maximum voltage comparable to one on silicon which is N type semiconductor. Silica glass is insulator.

TABLE III
THICKNESS OF POLYMER AND OPEN CIRCUIT VOLTAGE OF SOLAR CELL CREATED ON SILICA GLASS. LIGHT INTENSITY 45 000 LX. THICKNESS OF ZINC OXIDE 1,22 MICRONS.

	thickness of polymer			
	high	**medium 1**	**medium 2**	**low**
polymer (µm)	3.44	2.3	1.83	0.99
OCV (mV)	0.8	0.9	0.6	0.3

PEDOT polymer was also applied on nanowires on sapphire. There was not measured any voltage. The reason is very simple. The nanowires are perpendicular and there are not in electrical contact.

III. CONCLUSION

Organic solar cell based on layer of zinc oxide nanowires was created. N part of junction was zinc oxide, P part polymer PEDOT. Maximum reached open circuit voltage was 0.9 mV. Base material of substrate does not influence gained voltage, serves only as a substrate for creation of zinc oxide nanowires. It is not supposed to manufacture solar panels with method mentioned above (vapor-liquid-solid method) because this method is limited by material of substrate. Materials which serve as a substrate for creation of zinc oxide nanowires are expensive and the process is energy expensive. But with chemical methods we can create zinc oxide nanowires structure with very cheap way (cheap substrate, cheap chemicals, low temperature) [5, 6]. This method could be very promising for the future. Although the voltage for one cell is not very high, we are able to manufacture huge low cost solar panels which could be embodied to roofing or facade rendering of our houses.

ACKNOWLEDGMENT

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