

STUDY OF Al/a-SiC/c-Si(p)/Al STRUCTURES FOR PV APPLICATION

V. Šály*, J. Huran**, M. Perný*, M. Váry*

*Slovak University of Technology

Faculty of Electrical Engineering and Information Technology

Ilkovičova 3, SK-81219 Bratislava, Slovak Republic

Phone: (421 2) 6029 1746, Fax: (421 2) 6542 0415

**Slovak Academy of Sciences, Institute of Electrical Engineering

Dúbravská cesta 9, SK-841 04 Bratislava, Slovakia

Abstract

Plasma CVD reactor was used to grow a-SiC:H on p-type crystalline silicon substrate. Identification of chemical bonds in the structure of thin amorphous layer by Fourier transform infrared spectroscopy (FTIR) and Raman spectroscopy methods was performed. DC characterization was performed in order to obtain basic electric and PV parameters of prepared sample. AC impedance spectroscopy characterization was performed in order to detect the frequency response of Al-a-SiC/c-Si(p)/Al heterojunction. The analysis of these characteristics, using the impedance spectroscopy method, has allowed the construction of the electrical equivalent circuit (EEC) of the investigated structures. EEC contains series connections of series resistance and parallel combination of thin film capacitance shunted by resistance and constant phase element (CPE) shunted by resistance. The values of the parameters of the circuit elements have been determined at room temperature in the dark and on illuminated samples in the frequency range from 1 Hz to 1 MHz and also at different forward bias voltages. The negative capacitance phenomenon was observed at lower frequencies.

Key words: PECVD, heterojunction, silicon carbide, equivalent AC circuit, complex impedance

1. INTRODUCTION

Slightly doped amorphous silicon carbide layers a-SiC (alternatively modified with other chemical elements, e.g. nitrogen N in our case) which form heterojunction with crystalline silicon are relevant substitute for amorphous silicon (a-Si:H). The conversion efficiency up to 22 % of heterojunction solar cell (a-Si:H/c-Si) was reported and any further substantially increase is not expected (Kanno, H. et al., 2008). In the case of amorphous silicon the problem lies in increased recombination when a thicker layer of a-Si:H is used. Short circuit current I_{sc} of a-Si:H/c-Si solar cell structures is expected to increase when a-Si:H is substituted by a larger band gap material.

The width of the band gap can be controlled in a wide range in the case when carbon is added to the amorphous a-Si:H (resulting in hydrogenated silicon carbide alloy at greater amount of carbon). Increased carbon concentration (x) in a-Si_xC_{1-x}:H_y leads to better light absorption efficiency of heterojunction a-SiC:H/c-Si solar cells (Street, R.A., 2000). Deterioration of electronic properties (mainly electron mobility decrease) due to various kinds of amorphous network structural disorder is a negative accompanying phenomenon related to increasing concentration of carbon. In limit case, when the carbon concentration is closed to 100 %, it leads to creation of amorphous carbon layers or diamond-like carbon films, respectively.

Amorphous alloys of SiC in connection with photovoltaics (PV) are a relatively new subject of investigation. Heterojunction tandem solar design with a-SiC layer on the top (higher band gap) appears to be one of the promising application. Lower processing temperature (around 250 °C) and higher open-circuit voltages are main advantage in comparison to homojunction devices. Higher band gap (1.8 – 2.3 eV) of amorphous SiC layers (compared to a-Si:H) leads to a lower parasitic light absorption (Janz, S., 2006).

An attractive way how to reduce the price of PV element is reduction of silicon consumption, for example by processing of thin-film c-Si solar cell on low cost substrates. The negative accompaniment of this technology is diffusion of impurities from low cost substrate to silicon as a result of high temperature fabrication process. Diffusion barrier which is made from conductive a-SiC layer, is used to prevent diffusion of elements such as Fe, V and Co from low cost substrate. Construction of crystalline thin film solar cells on low cost substrates (silicon carbide technical ceramics) with a-SiC as a diffusion barrier was presented eg. by Janz et al. (Janz, S., 2006).

Passivation layer, as another important element, plays an essential role in the field of photovoltaics. The role of the passivation layer is in the reduction of unsaturated bonds due to hydrogen effusion out of $\text{Si}_x\text{C}_{1-x}$ layer into the multi-crystalline bulk (Janz, S. et al, 2006). There are efforts to replace the traditional passivating layers, such as SiO_2 and SiN_x , by a-SiC (Janz, S., Reber, S. and Glunz, W., 2006) The aim is a more efficient production process involving lower deposition temperatures and high throughput.

One can find other applications of a-SiC:H layers as a barrier layer in silicon hetero-structures (within construction of amorphous silicon solar cells). The role of two a-SiC p-doped layers connected with intrinsic and n-doped layer a-Si:H generates an potential barrier used to separate the charge carriers (<http://www.crystec.com/triasie.htm>, March 2014).

Antireflection coatings for module glasses as a further possible application are known. The resistance against weather conditions as moisture, corrosion, acid surrounding and high-energy radiation makes these materials as a promising alternative to SiN_x and SiO_2 layers (Grunow, P. et al., 2006, Neander, M. et al., 2006) Possible deposition rate of low-temperature deposition of larger areas makes these materials economically attractive.

Controllability of the band gap allows a wide range of applications especially in microelectronics, including thin dielectric layers and semiconductor applications. Optoelectronic applications as another important area include the use of a-SiC photodiodes in optical communications (Louro, P. et al., 2011), optical/image sensors (Magafas., L., 2008) and LED's applications (Kumbhar, A. et al., 2001) Another field of applications a-SiC has found in micro electromechanical systems (Carreno, M.N.P. et al., 2004)

In our work the DC and AC measurements under illumination were performed in order to detect the electronic properties and PV parameters of chosen prepared sample which was prepared in the context of previous research of optimization the technology (Perný, M. et al., 2013, Fahrner, W.R., 2013)

2. EXPERIMENTAL

The heterojunction structures, as shown in Fig. 1, were formed for electrical characterization. The plasma CVD reactor with parallel plate electrodes was used for samples preparation. A p-type silicon wafer with resistivity 6-10 Ωcm and (100) orientation was used as the substrate for the growth of a-SiC layers doped by nitrogen (SiC(N)).

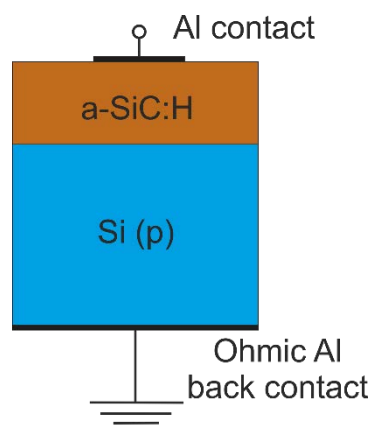


Figure 1: Schematic drawn of studied heterojunction structure

Technological conditions for sample preparation were: gas mixture (SiH_4 -5 sccm, CH_4 -30 sccm, NH_3 -3sccm, H_2 -100 sccm, Ar-10 sccm). The temperature of substrate during the deposition was 300 °C, RF power 100 W and pressure 35 Pa in the chamber. Introduction of the hydrogen to the gas mixture results in the production of samples which can be denoted as a-SiC(N):H films (for simplification further denoted here only as an a-SiC). The circular electrodes of Al (120 nm thick) were formed on the side with SiC film on each sample. The ohmic contact on the opposite back side of samples was created – the whole area Al, app. 250 nm thick. Other technological parameters can be found in (Perný, M. et al., 2013).

The samples formed on Si were annealed in a furnace with forming gas atmosphere (90 % N, 10 % H) for 30 min (heated 100 °C/min from room temperature) at temperature 430 °C and pressure 1 kPa.

DC measurements were performed using Keithley 237 at the temperatures within the interval from 300 K to 400 K and controlled by program DCATS. AC impedance spectroscopy measurement and characterization was performed by SOLARTRON Analytical Module. The measurements were done under illumination within the frequency range from 1 Hz to 1 MHz. Solar simulator ORIEL class AAA was used for the measurement of PV parameters of illuminated sample.

3. RESULTS AND DISCUSSION

3.1 Structural characterization

A very powerful method of quantification and identification of bonds in amorphous layers is the Fourier infrared spectroscopy (FTIR). Fig. 2 shows a characteristic spectrum of a-SiC layers deposited in plasma reactor.

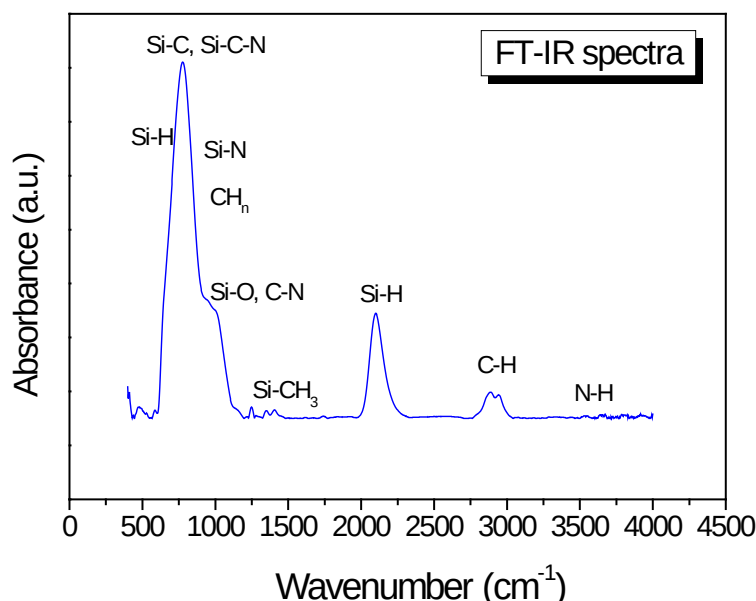


Figure 2: Characteristic FTIR spectra of prepared samples

A database of possible absorption frequencies for a-SiC layers is generally known and can be found eg. in (Bullot, J. et. al., 1987). As one can see in Fig. 2, the dominant absorption band can be found between 740 and 1250 cm^{-1} . We can observe two main Si - C stretching modes, corresponding to wave numbers 609 cm^{-1} and 746 cm^{-1} . Existence of Si-O bonds at wave number around 1108 cm^{-1} is clearly and also observable for all investigated sample (Fraga, M. A., et. al., 2008). CH_3 -Si and some oxygen related vibration modes are observable in the region of 960 cm^{-1} . It is well known that the oxygen incorporation in silicon nitride causes a shift in the absorption band due to Si-N bond stretching near 880 cm^{-1} . In the region from 2000 to 2140 cm^{-1} Si-H related absorption bands can be recognized for all investigated samples. Existence of CH_n bonds at wave number around 2800 cm^{-1} is also clearly visible (Swatowska, B., Stapinski, T., 2010). We can learn from the data that there are still CH_4 and SiH_4 related molecules in the network of the layer as deposited which probably could not be broken in the plasma process.

Fig. 3 shows obtained characteristic Raman spectra of the a-SiC(N) layers on silicon substrates. An essential part of these spectra originates from the silicon substrate, especially the intensity of the lattice vibration at 520 cm^{-1} . The Raman band between 930 cm^{-1} and 990 cm^{-1} is created by acoustical and optical phonon modes of cubic or one of the hexagonal polytypes of SiC. The peak broadening is related to the damping of phonon modes due to the short range ordering of SiC crystallites and the effects of surroundings having Si, as well as C-clusters (Seo, J.K., et. al. 2011). The Raman band between 1300 cm^{-1} and 1700 cm^{-1} is observed and is assigned to diamond like carbon (DLC) (Chen, T., et. al, 2011).

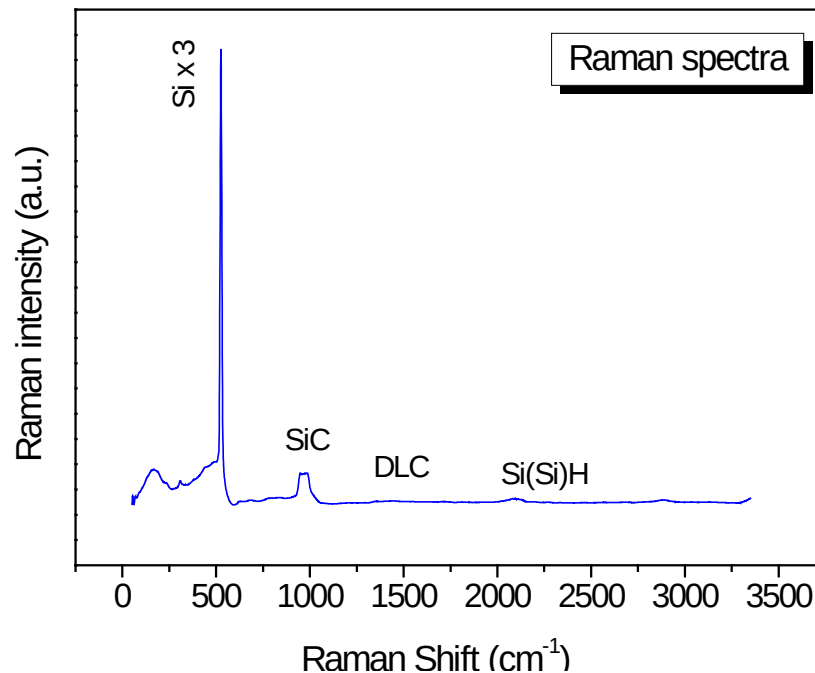


Figure 3: Characteristic Raman spectra of prepared samples

3.2 Electric characterization

The results obtained from dark I-V measurements (presented in (Perný, M. et al., 2013)) indicate the barrier properties of prepared structure and presence of photovoltaic effect was observed under illumination. Basic PV parameters (V_{oc} and FF) were determined as $V_{oc} = 0.292$, $FF = 0.20$. AC impedance spectroscopy characterization was performed by SOLARTRON Analytical Module in order to detect the frequency response of Al-a-SiC/c-Si(p)/Al heterojunctions and identify equivalent circuit of Al-a-SiC/c-Si(p)/Al samples. The measurements were performed at room temperature and on illuminated samples in the frequency range from 1 Hz to 1 MHz and also at different forward bias voltages. Frequency dependences of real and imaginary part of impedance are shown in Fig. 4 and 5.

Standard shape, typical for MIS structures, of forward biased frequency dependence of the real part of complex impedance was observed. However, unusual anomaly was observed in the forward biased frequency dependence of imaginary part of complex impedance in Fig. 5. At frequencies up to 50 kHz and DC biases higher than 1000 mV the frequency response of complex impedance related to standard models of capacitive samples is not more valid. The positive values of Z_{imag} were obtained at low frequencies, usually ascribed to inductive character of the impedance. Given the nature of the studied impedance (thin a-SiC layer between two electrodes), the capacitance character of samples and negative phase on the whole frequency range would be expected. Usually such frequency dependence is attributed to the conventional inductance of the system (generally ascribed to the electric conductive interconnections).

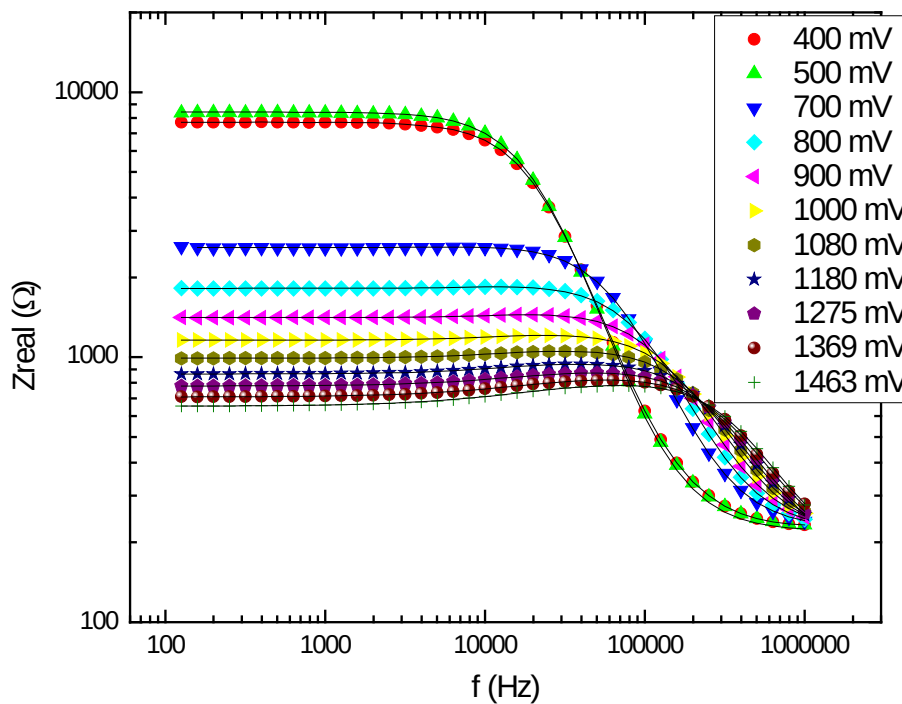


Figure 4: Frequency behavior of the real part of the impedance for the Al/a-SiC/c-Si(p)/Al structure (measured (symbol) and fitted (line)) under illumination at room temperature at different forward bias

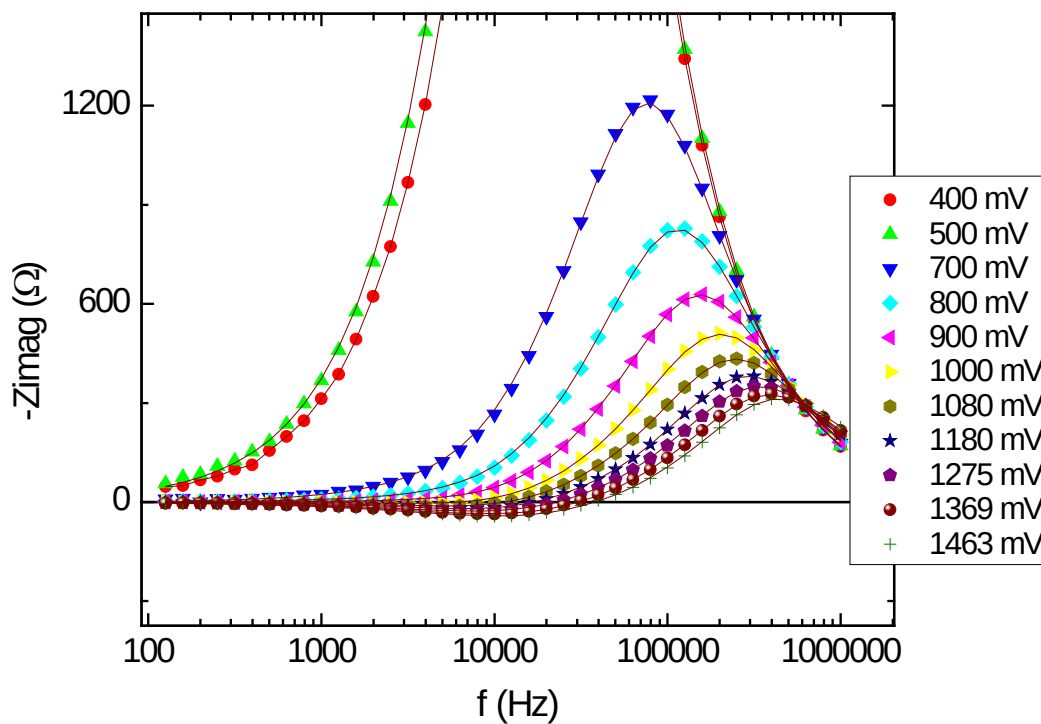


Figure 5: Frequency behavior of the imaginary parts of the impedance for the Al/a-SiC/c-Si(p)/Al structure (measured (symbol) and fitted (line)) under illumination at room temperature at various forward biases

In our case such reasoning would be incorrect for two main reasons. The inductance makes sense when strong magnetic field is applied, which is not the case here. And also, for the case that classical inductance $|Z| = \omega L$ and its influence could be observed, however, it is so at higher frequencies, often about 1 MHz. Therefore, the anomalous behavior in Fig. 5 is not the result of parasitic inductance. Similar explanation can be found in (Magafas, L., 2008).

The measurement of complex impedance quantities was performed and complex capacitance C^* calculated. The real part of complex capacitance C' , for higher forward bias voltages (V), turns to negative values. This effect was also observed and presented either on inorganic (Perera, A.G.U. et al., 1999a) or organic (Pingree, L.S.C et al., 2005) layered structures. The phenomenon can be attributed to the carrier capture and emission from the interface states. The negative capacitance can be attributed to the existence of defect states at the interfaces between crystalline semiconductor and amorphous carbide layer (Perera, A.G.U. et al., 1999b).

According to the theory presented in (Fahrner, W.R. et al., 2006) each energy level E_i in the band gap introduces one C–R time constant. We have searched for the best fitting circuit with regard to the shape of frequency dependence of real and imaginary part of complex impedance Z^* (Fig.4 and 5). It is evident that the simple equivalent circuit with one parallel R_p C_p combination must be modified when one would like to estimate physically relaxation processes in the structure and the contribution of the interfacial states has to be taken into account. They offer an additional conductive path related to the recombination in the junction. Usually the transport processes related to the junction of heterostructures are represented as connection of R and C elements. In our case we introduce constant phase element (CPE), denoted as P here, except of capacitor. The measured network reflects the contribution of the junction expressed by $C1$ parallel to $G2=1/R2$, the interface states expressed by $P1$ parallel to $G3=1/R3$ and series resistance $R1$. We have decided to use series connection of parallel RC elements while in the case when resistor $R3$ is of small values, as it is in the case of lower voltages and shown in Fig. 6, constant phase element $P1$ is actually shunted by parallel resistor $R3$.

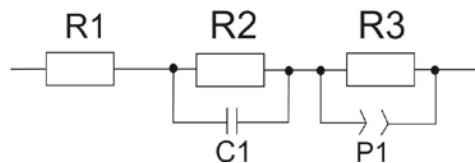


Figure 6: Proposed equivalent circuit of the heterostructure Al-a-SiC/c-Si(p)/Al

A constant phase element also appears currently in modeling the behaviour of the imperfect dielectrics. Constant phase element P in AC equivalent circuit represents different inhomogenities such as blocking effects (interfacial states, porosities, etc.). The electrical impedance of CPE is expressed as

$$Z = \frac{1}{P(i\omega)^n} \quad (1)$$

and its components

$$\text{Re } Z = \frac{c_n}{P\omega^n}, \quad \text{Im } Z = -\frac{s_n}{P\omega^n} \quad (2)$$

where is

$$c_n = \cos\left(\frac{\pi n}{2}\right), \quad s_n = \sin\left(\frac{\pi n}{2}\right) \quad (3)$$

CPE is in fact pure capacitor in the case when $n = 1$ (Kochowski, S. & Nitsch, K., 2002) and pure resistor when $n = 0$. Variation of exponent n on the applied DC voltage is shown in Fig. 7. As can be seen in Fig. 7, CPE behaves like a classical capacitor only when low levels of DC bias are applied – up to about 800 mV.

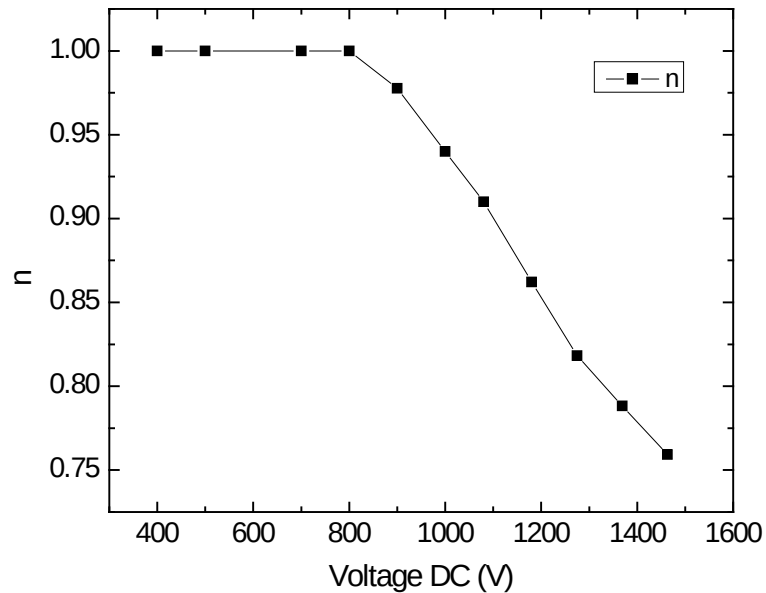


Figure 7: Power law factor n as a function of applied DC bias

The voltage dependence of CPE is presented in Fig. 8. The value of CPE is negative throughout the voltage range. Dependence passes through a maximum as one can notice in Fig. 8.

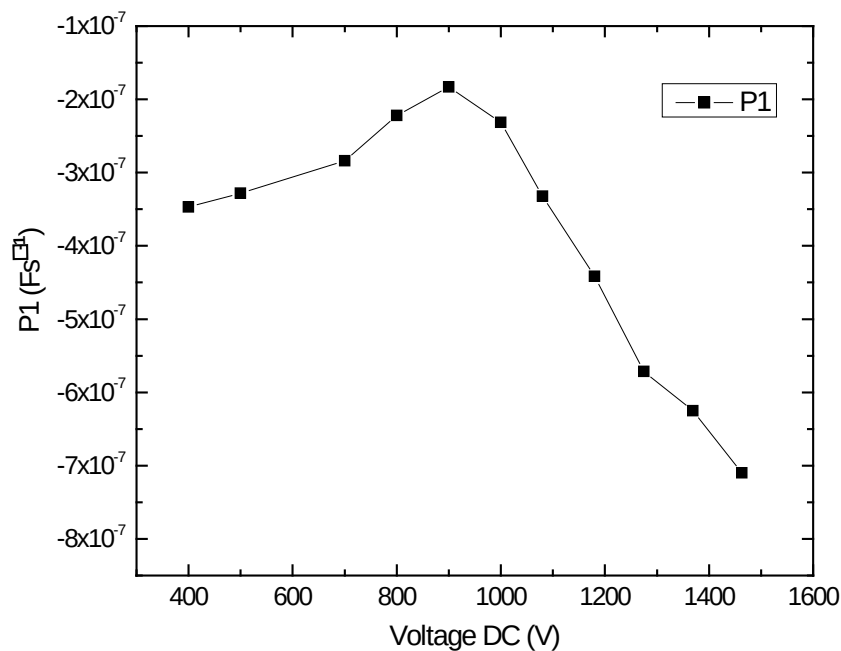


Figure 8: The value of CPE as a function of applied forward DC bias

The EEC parallel capacitance is positive and decreases with increasing bias as can be seen in Fig. 9.

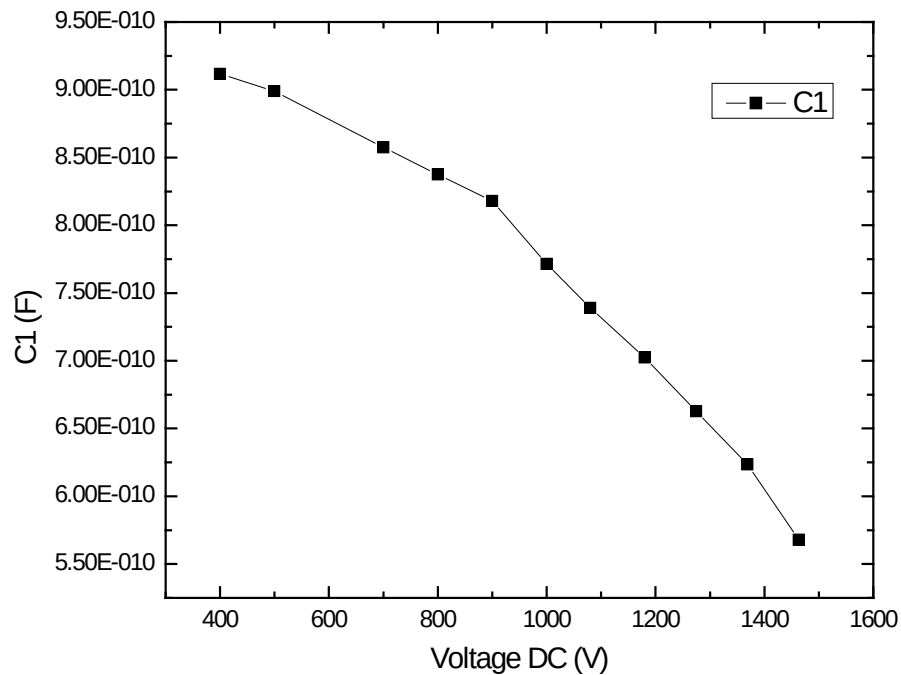


Figure 9: EEC capacitance as a function of forward bias voltage at room temperature under illumination

The parallel resistances R2 and R3 of equivalent AC circuit were estimated under illumination at different bias conditions. The resistances R2 and R3 are dependent on the applied voltage. Decrease of the resistance in the case of R2 and R3 with increasing forward bias is depicted in Fig. 10. Negative resistance was detected in the case of R3 at higher biases what is consistent with the ideas mentioned above. Series resistance R1 is quite high and only a little influenced by voltage bias.

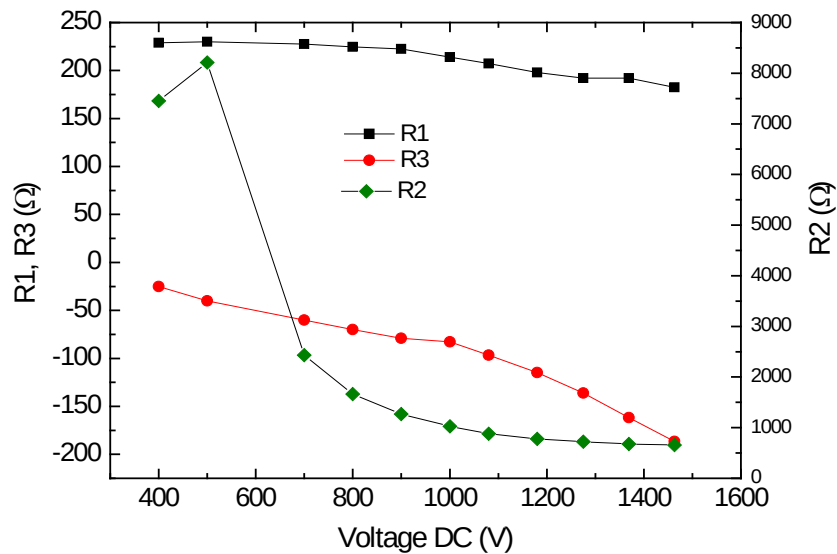


Figure 10: EEC resistances as a function of applied bias under illumination at room temperature (the connecting lines are not a functional equivalent)

4. CONCLUSION

The heterojunction structure Al/a-SiC/c-Si(p)/Al prepared by PECVD method was studied by electrical analyses. Chemical compositions were analyzed by Fourier transform infrared spectroscopy (FTIR) and Raman spectroscopy. The prepared samples show photovoltaic behavior and basic PV parameters were determined under illumination. The impedance spectroscopy (the measurements under illumination) was applied to study electric behaviour, the electric properties and equivalent AC circuit was estimated. Anomalous behaviour of the complex impedance character at lower frequencies and higher forward bias voltages was detected and discussed. The negative capacitance indicates the existence of defect states at the interface between crystalline semiconductor and amorphous layer. The impedance spectroscopy shows to be convenient powerful method to reveal such interesting behaviour and improve the picture about the transport processes in studied structures.

Acknowledgement This paper is result of the project implementation: Finalizing of the National Center for Research and Application of renewable Energy Sources, ITMS: 26240120028, supported by the Research and Development Operational Programme funded by the ERDF.

REFERENCES

- BULLOT, J., et. al., (1987) *Physics of Amorphous Silicon-Carbon Alloys*. Phys. Stat. Sol B 143, p. 345.
- CARREÑO, M.N.P., et. al. (2004) *Self-sustained bridges of a-SiC:H films obtained by PECVD at low temperatures for MEMS applications*. Journal of Non-Crystalline Solids, 338-340, 490-495.
- FAHRNER, W. R. (2013) *Amorphous Silicon / Crystalline Silicon Heterojunction Solar Cells*. Springer, ISBN 978-3-642-37039-7
- FAHRNER, W.R., MUELLER, SCHERFF M. T., KNOENER. D., NEITZERT, HC. (2006) *Interface states heterojunction solar cells*. In: Proceedings of 4th world conference photovoltaic energy conversion, pp 1822–1825.
- FRAGA, M. A., et. al. (2008) *Nitrogen doping of SiC thin films deposited by RF magnetron sputtering*. J Mater Sci: Mater Electron 19:835–840.
- GRUNOW, P., et. al. (2006) *Modelling of the encapsulation factors for photovoltaic modules*. Proc. of the 4th World PVSEC, p. 2152.
- CHEN, T., YANG, D., CARIUS, R., FINGER, F. (2011) *Aluminum doped silicon carbide thin films prepared by hot-wire CVD: influence of the substrate temperature on material properties*. Thin Solid Films, 519, pp. 4516–4518
- JANZ, S., REBER, S., & GLUNZ, W. (2006) *Amorphous SiC: Applications for Silicon Solar Cells*. Proceedings of the 21st EUPVSEC, Dresden, p. 660.
- JANZ, S., REBER, S., et. al. (2006) *Processing of c-Si Thin- Film Solar Cell on Ceramic Substrate with Conductive SiC Diffusion Barrier Layer*. 4th WCPEC, Hawaii, pp.1403-1406.
- KANNO, H., IDE D, TSUNOMURA Y., TAIRA, S., BABA, T., YOSHIMINE, Y., TAGUCHI, M., KINOSHITA, T, SAKATA, H., MARUYAMA, E. (2008) *Over 22 % efficient HIT solar cell*. In: Proceedings of the 23rd European photovoltaic solar energy conference and exhibition, Valencia, Spain, pp 1136–1139
- KOCHOWSKI, S. NITSCH, K. (2002). *Description of the frequency behaviour of metal-SiO₂-GaAs structure characteristics by electrical equivalent circuit with constant phase element*. Thin Solid Films 415: 133–137.
- KUMBHAR, A., et al. (2001) *Photoluminescent, wide-bandgap a-SiC: H alloy films deposited by Cat-CVD using acetylene*. Thin Solid Films, 395(1-2): 244-248.
- LOURO, P., et al. (2011) *Use of a-SiC:H Photodiodes in Optical Communications Applications*. Advances in Photodiodes. Book edited by Gian Franco Dalla Betta, ISBN 978-953-307-163-3,
- MAGAFAS, L. (2008) *Study of optical sensors of the form Al/a-SiC: H/c-Si (n) with high sensitivity*. Journal of Engineering Science and Technology Review.

NEANDER, M., et. al. (2006) *Anti-reflective-coating tuned for higher solar module voltage*. Proc. of the 4th World PVSEC, p. 207

PERERA A. G. U., SHEN, W. Z. ERSHOV, M. LIU, H. C. BUCHANAN, M. AND SCHAFF, W. J. (1999a) *Negative capacitance of GaAs homojunction far-infrared detectors*, Applied Physics Letters 74, 3167; doi: 10.1063/1.124169

PERERA, A. G. U., SHEN, W. Z., ERSHOV, M. LIU, H. C., BUCHANAN, M. AND SCHAFF, W. J. (1999b) *Capacitance Characteristics in InN Thin Films Grown by Reactive Sputtering on GaAs* Applied Physics Letters 74, 3167; doi: 10.1063/1.124169

PERNÝ, M., et. al., (2013) *Optimization of Amorphous Silicon Carbide Thin Films for Heterojunction Solar Cells*. In: 28th European Photovoltaic Solar Energy Conference and Exhibition : Proceedings. Paris, France, 30 September - 4 October 2013. - München : WIP, ISBN 3-936338-33-7. - pp 1915-1918.

PINGREE, L. S. C., SCOTT, B. J., RUSSELL, M. T., MARKS, T. J. AND HERSAM, M. C., (2005) *Negative capacitance in organic light-emitting diodes* Applied Physics Letters 86, 073509; doi: 10.1063/1.1865346

SEO, J.K., JOUNG, Y-H., PARK, Y., CHOI, W.S. (2011) *Substrate temperature effect on the SiC passivation layer synthesized by an RF magnetron sputtering method*. Thin Solid Films 519 6654–6657.

STREET, RA. (2000) *Technology and applications of amorphous silicon*. Springer, New York, Springer Series in Materials Science, Vol. 37

SWATOWSKA, B., STAPINSKI, T. (2010) *Optical and structural characterization of silicon-carbon-nitride thin films for optoelectronics*. Phys. Status Solidi C 7, No. 3–4, 758–761.

Internet: <http://www.crystec.com/triasie.htm> (March 2014)