

Electrical and structural characterization of carbon based films prepared by RF-PECVD and ECR-PECVD techniques for photovoltaic applications

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Carbon based materials, such as amorphous carbon (a-C) and hydrogenated amorphous carbon (a-C:H) as well as diamond like carbon (DLC) with predomination of sp^3 bonds are widely used in electronics and machinery. Among other advantages of these materials, environmental friendly method of preparation is important. In the field of photovoltaics (PV) they can be used as antireflective coating or as emitter layer in amorphous carbon/crystalline silicon (a-C/c-Si) heterojunction for low cost solar cell structure. Diamond-like carbon film was deposited on p-type Si (100) substrates at various deposition conditions by means of Radio Frequency Plasma-Enhanced Chemical Vapor Deposition (RF-PECVD) and Electron Cyclotron Resonance Plasma-Enhanced Chemical Vapor Deposition (ECR-PECVD) techniques. The concentration of chemical elements in films was determined by both, Rutherford backscattering spectrometry (RBS) and elastic recoil detection (ERD) analytical method. RBS and ERD analysis indicate that the films contain carbon, hydrogen and a small amount of oxygen. The current transport mechanisms in prepared samples were investigated using analysis of current-voltage ($I-V$) and capacitance-voltage ($C-V$) measurements.

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1. Introduction

Versatility in industrial applications (from machinery to microelectronics) of carbon-based materials comes from the possibility of influencing their physical properties changing the ratio of graphitic sp^2 bonds (graphite-like) and sp^3 diamond bonds (diamond-like). Each carbon atom has three nearest neighbors in the planar structure and bond is described as sp^2 in the case of graphite. There are many forms of sp^2 carbon with different levels of organization, from micro-crystalline graphite to various forms of disordered carbon. Amorphous carbon (a-C) consists of a mixture of sp^3 , sp^2 and sp^1 bonds. The presence of hydrogen and nitrogen is frequent in the graphite structure. Amorphous layer of a-C or hydrogenated amorphous carbon layer a-C:H which contains a mixture of diamond (sp^3) and graphitic (sp^2) bonds, with a predominance of sp^3 bonds, and significant amounts of hydrogen and other elements, is called DLC (diamond-like carbon) layer. DLC films are characterized by high mechanical strength, chemical inertness, optical transparency and high band gap (depending on the technology and deposition conditions band gap is from the range of 1÷4 eV) [1]. Low-temperature techniques used for preparation makes them economically attractive. Diamond layers have several industrial applications. Doped DLC films are applied in many electronic components operating in extreme conditions, like elevated

temperature, high power, intensity and frequency of radiation. They can be found as part e.g. of the sensors and high-performance semiconductor components. Environmental friendliness and suitable electro-optical properties of these materials predispose them also for PV applications as antireflective layer of solar cells [2]. Photovoltaic effect in the diamond structure is interesting in terms of improving the conversion of solar radiation into the electricity. Solar cells with a-C top emitter layer which forms part of heterostructure a-C/c-Si are an economical alternative to conventional PV homojunction cells [3]. Optical properties of a-C films are closely related to the density of sp^3 bonds. Layer with a higher concentration of sp^3 bonds has a large band gap what results in reduced absorption of sunlight in the visible part of the spectrum. The targeted electro-optical properties of DLC layers are affected by the ratio of graphitic sp^2 and sp^3 diamond bonds as well as by the concentration of hydrogen and oxygen in the layer [4, 5]. The thickness of the DLC films is an important parameter influencing the structural properties (hybridization of carbon orbitals in the structure) [6]. The most common method of preparation of DLC films is plasma assisted chemical vapor deposition (PECVD). As precursors can be used e.g. methane, ethylene, acetylene, and benzene in the gaseous phase [7].

The conversion efficiency of about 6.45 % for PV cells heterostructures which consist of diamond and

crystalline silicon layers (a-C:H/c-Si) was reported in [8]. The basic function of heterojunction a-C/c-Si lies in creating the potential barrier that separates photogenerated electron-hole pairs.

Measured current-voltage temperature dependences are suitable tool for the characterization of electrical transport processes in the heterostructures and also provide an indicative overview of the basic PV parameters of the prepared structures [9].

In this paper we have focused our attention on the preparation and study the properties of DLC films prepared by RF-PECVD and ECR-PECVD technology. The structural properties of films were investigated by RBS and ERD measurement. The diode-like behaviour as well as current transport mechanisms of prepared samples were investigated using the analysis of current-voltage (I - V) and capacitance-voltage (C - V) dependences.

2. Experimental

Diamond-like carbon films were deposited on p-type Si(100) substrates having specific resistivity 2-10 Ω cm by radio frequency plasma enhanced chemical vapor deposition (RF-PECVD, 100 W) [10] from gas mixture CH_4 (15 sccm) and Ar (15 sccm) using cathode mode and electron cyclotron resonance plasma enhanced chemical vapor deposition (ECR-PECVD, 400 W) [11] from gas mixture CH_4 (10 sccm) and Ar (10 sccm). Prior to deposition, standard cleaning was carried out to remove impurities from the silicon surface. The substrate holder temperature during deposition was either room temperature (RT) or 200 $^\circ\text{C}$. Samples DLC1-4 were deposited. The conditions were: DLC1 (RT, RF-PECVD, 10 Pa), DLC2 (200 $^\circ\text{C}$, RF-PECVD, 10 Pa), DLC3 (RT, ECR-PECVD, 2 Pa) and DLC4 (200 $^\circ\text{C}$, ECR-PECVD, 2 Pa). The electrodes for DLC/c-Si heterojunctions were evaporated as follows – full area bottom aluminum contact and top gold circular contacts with diameter 0.5 mm defined by metal mask. Concentrations of species in the films were analyzed using RBS and ERD analytical methods. Program SIMNRA was used for simulation of RBS and ERD spectra and concentration of alternative species in the films was calculated. More details one can find in [12]. Current-voltage characteristics were measured in a set-up with Keithley 237 and contact holder with possibility to control the temperature in range 300 K – 480 K. Precision LCR meter Agilent 4284A was used for capacitance-voltage measurements.

3. Results and discussion

The measured and simulated RBS and ERD spectra for samples DLC1, DLC2 and DLC3, DLC4 are shown in Fig. 1. RBS and ERD analysis indicate that the films contain carbon, hydrogen and small amount of oxygen. From the results we can conclude that the concentration of main elements were for sample DLC1: (66, 32, 2) (carbon at.%, hydrogen at.%, oxygen at.%), sample DLC2: (63, 34,

3), DLC3: (65, 31, 4) and for sample DLC4: (65, 30, 5). Oxygen in the samples is residual from the deposition chamber and we suppose the samples not to be influenced by it.

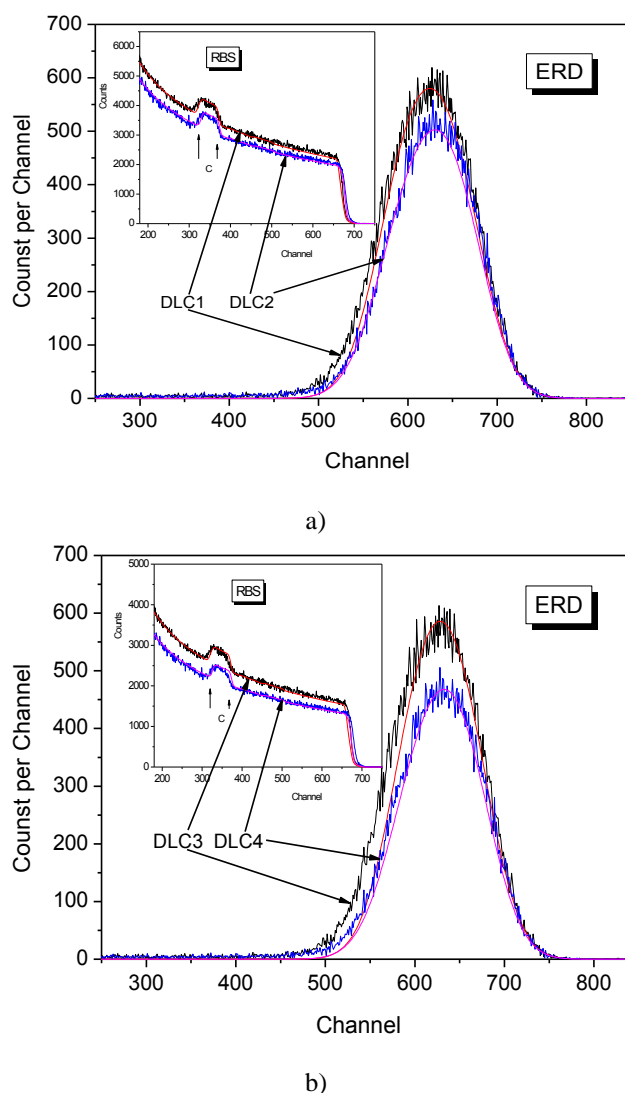


Fig. 1. ERD and RBS spectra of diamond like carbon films for samples a) DLC1, DLC2 and b) DLC3, DLC4. Smooth lines represent simulations

It is generally known [13] that the optical and electrical properties of DLC films are strongly dependent on sp^3 bonds content. The ion density and energy which are related to the plasma density and electron temperature is higher in the ECR plasma discharge than in PECVD plasma discharge. With regard to this fact, it is expected that the technology using ECR plasma discharge results in better film properties. The increasing of the deposition temperature can reduce sp^3 bonding of DLC films and improve their properties. Influence of temperature could be explained by the graphitization at higher deposition temperature, i.e. decreasing sp^3 bonds content.

The capacitance-voltage dependences carried out at 1 MHz shown in Fig. 2 reveal the barrier behavior of prepared DLC/c-Si samples. According to the junction

theory, presence of the depletion region in the structure results in the linear dependence of $1/C^2$ upon the voltage. Such behaviour one can clearly recognize on samples DLC1 and DLC3. Due to the lack of linearity on the $1/C^2$ vs. voltage plots, no depletion region is supposed to be in the case of samples DLC2 and DLC4 what can be the reason of deteriorated diode properties and thus deteriorated PV response of such structures can be expected. Therefore, we have focused our attention on samples DLC1 and DLC3. The slight deviation of $1/C^2$ -V curve from linear trend observed in the low voltage region for sample DLC3 can be attributed to the presence of defect states in the DLC layer. To explain this effect we can take into account similar study done on intrinsic amorphous silicon/crystalline silicon heterojunction [14]. Reverse bias applied at the structure results in the formation of space charge region (SCR) both in c-Si and DLC layers. The emission of electrons from defect states in the DLC caused by the change of Fermi level can result in the formation of positively charged donor like states. While the thickness of DLC layer is around 100 nm, the depletion region can easily spread over the whole thickness at low voltages. Further increase of reverse bias only shifts depletion region into the c-Si part of the junction which results in a deviation of the $1/C^2$ -V curve from the linearity. Due to this effect, the determination of the diffusion voltage using C-V measurements is provided only with high error and higher value of diffuse voltage V_D than it was expected was determined in the case of DLC3. The calculated value in the case of sample DLC3 is too high, $V_D = 3$ V. The negative sign of diffusion voltage compared to expectation observed for sample DLC1 ($V_D = -0.5$ V) is probably the result of charged defect states in the vicinity of the interface. This can be explained by the interaction of plasma with silicon surface, especially ion bombardment during cathode mode RF-PECVD technology.

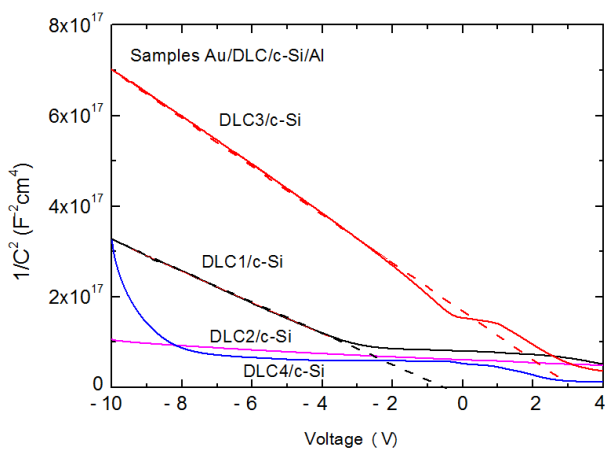


Fig. 2. $1/C^2$ as a function of the applied voltage for DLC/c-Si samples. Linear relationship indicates rectification character of the junction (measurement voltage frequency 1 MHz).

In order to elucidate the current transport mechanisms in heterostructures, the current-voltage dependences at different temperatures for DLC1 and DLC3 samples were measured. The rectification character of PN junction is described by well known Shockley junction equation. In case of sample DLC1, however, the I - V characteristics exhibited significant deviation in comparison to this equation. Measured I - V curves for DLC1 in the low voltage region has hardly identifiable linear area as one can see in Fig. 3. Therefore, it is difficult to determine the diode ideality factor necessary for modeling the characteristics according Shockley equation. Analogous problem was observed by Maeda et al. [15] on amorphous silicon diodes where the nonideality in I - V characteristics was reported to be caused due to an alternation in population of the interfacial states in the presence of an applied voltage.

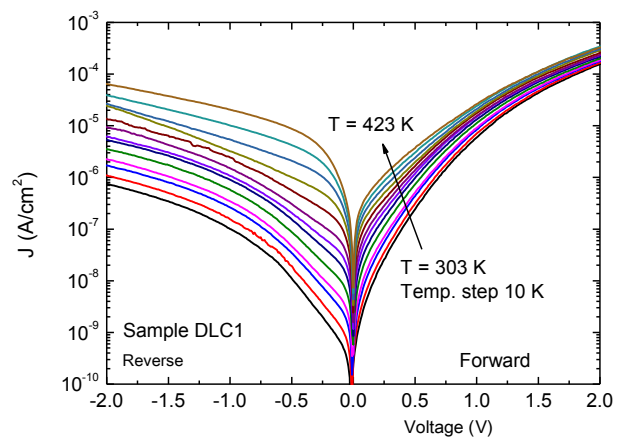


Fig. 3. Current – voltage characteristic measured on sample DLC1 in the temperature range from 303 to 423 K.

I - V characteristics of sample DLC3 measured in the temperature range 303 – 423 K exhibited two exponential regions, first one for voltage $V < 0.25$ V and second one for $V = 0.25 - 0.5$ V under forward bias as it is shown in Fig. 4. An ideality factor n and saturation current density J_S was determined for both regions to provide an analysis of transport mechanism via the structure. Detailed description of the analysis principle can be found elsewhere [16, 17]. The Arrhenius plots of diode exponential factor A , calculated as $A = q/nkT$ and saturation current density J_S for sample DLC3 are depicted in the Fig. 5. Weak temperature dependence of A described by the slope $S = 0.21$ was observed for low voltage region. Such behavior is characteristic for tunneling mechanism. Moreover, while the DLC layer has continuous distribution of defect states in the band gap, we can assume participation of these states on the carrier transport. First, we can discuss the one-step tunneling and multitunneling process described by Riben et al. [18]. These models were applied to explain current transport processes in Ge(n)/GaAs(p) heterostructures. Multitunneling process involves defect states in the

transport mechanism and usually predominates the one-step tunneling. According to the theory, tunneling currents corresponding to these processes should change exponentially with the temperature. This is, however, not our case and exponential change of tunneling current with $1/T$ is observed. Such temperature behavior of saturation current, as it is shown in Fig. 5, is typical for recombination process. It can be assumed the presence of both tunneling and recombination processes in the carrier transport in structure. Possible model to describe such behavior is multitunneling capture–emission process (MTCE) originally proposed for amorphous silicon/crystalline silicon heterojunction by Matsuura et al. [14]. Based on this work and taking in the account the analogy of amorphous silicon/crystalline silicon heterojunction with DLC/crystalline silicon heterojunction, the hole in the valence band of c-Si moves by a multitunneling process from one localized state to another in DLC until the tunnelling rate becomes smaller than the rate for hole release from the state to the valence band of DLC or for recombination of the hole with an electron in the conduction band of DLC. The saturation current activation energy $E_a = 0.41$ eV then define the energy level of the traps which provide the tunneling.

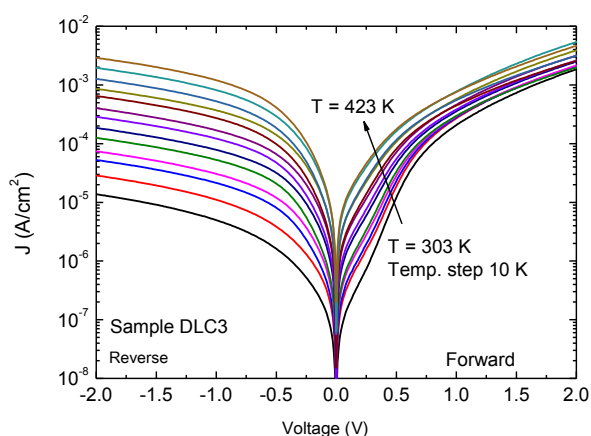


Fig. 4. Current – voltage characteristic measured on sample DLC3 in the temperature range from 303 to 423 K.

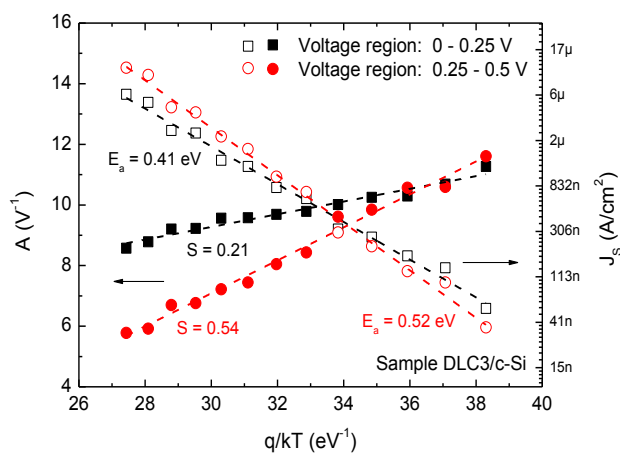


Fig. 5. Arrhenius plot of exponential factor A and saturation current density J_0 for sample DLC3.

Analyzing the high voltage region ($V = 0.25 - 0.5$ V) of the I - V curve simpler explanation can be given. Higher slope of A observed for this voltage region indicates the presence of recombination in the SCR. The saturation current activation energy $E_a = 0.52$ eV is close to the half of crystalline silicon band gap value which indicates that recombination take place in silicon part of the heterojunction. The recombination in SCR can be caused due to the presence of defect states on the silicon surface. While the recombination is undesirable process which deteriorates the performance of the solar cell, for photovoltaic application purpose the next step will be necessary – to improve the quality of the heterojunction interface.

4. Conclusion

We have investigated the structural and electrical properties of DLC films prepared by radio frequency PECVD and electron cyclotron resonance PECVD technology. RBS and ERD analysis indicated that the films contain carbon, hydrogen and a small amount of oxygen. C - V and I - V measurements were employed to describe the current transport in prepared DLC/c-Si samples. Analysis has shown the diode-like behavior of I - V characteristic for samples prepared at room temperature. Temperature dependent current-voltage measurements were conducted to indicate the current transport mechanisms in DLC/c-Si structure and to reveal the conditions and processes in the structure, showing the best properties for sample prepared with ECR-PECVD technique at room temperature. I - V characteristics of sample prepared by ECR-PECVD technique were analyzed and described by multitunneling capture–emission process for voltage below 0.25 V and recombination in space charge region of silicon for voltage in the range 0.25 – 0.5 V. The presence of the SCR recombination indicates defect states in the vicinity of the interface.

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