

Diamond like Carbon Film as Potential Antireflective Coating for Silicon Solar Cells

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In the present study DLC films were deposited on crystalline silicon and quartz substrates from hydrocarbon gases (acetylene (C₂H₂) and methane (CH₄)) by two methods: employing closed drift ion source and radio frequency plasma enhanced chemical vapour deposition (RF PECVD) technique. Optical properties of the formed films were analyzed employing UV/VIS/NIR spectroscopy. It was observed that in both deposition methods the lowest refractive index (at $\lambda = 632.8$ nm), which corresponds to the highest amount of bound hydrogen, is observed when energies per carbon atom are approximately 150 eV (300 eV ion beam energy in a closed drift ion source) and 160 eV (400 V bias voltage in RF PECVD). It is shown that depending on the deposition conditions the region of minimum reflection for the system DLC-crystalline silicon can be varied in a wide range.

Keywords: DLC films, antireflection properties, solar cells.

1. INTRODUCTION

Nowadays, when the global warming is very often discussed as the consequence of unlimited pollution of the plants that are using oil for heat production, the great interest is shown for alternative energy sources, like wind and sun. Due to the growing demand for clean sources of energy, the manufacture of solar cells and photovoltaic arrays is increasing dramatically. High cost is presently the main obstacle for a world-wide increase in the utilization of the electric power provided by photovoltaic cells. For this purpose it is necessary to design photovoltaic cells, which are characterized by high conversion efficiency and low price. One of the crucial problems in solar cells is that a significant part of the incoming radiation is reflected, which limits the efficiency of such devices [1]. As it is known, the reflection losses of incident radiation can be reduced using antireflection coatings [2]. The optimal antireflecting effect is observed when $n_{\text{film}} = (n_{\text{substrate}})^{1/2}$ [3]. For this purpose different type thin film coatings are used. Usually as substrates Si ($n = 3.96$) and GaAs ($n = 3.3$) are used [4]. The criteria for selecting materials and deposition technology for antireflecting coatings are the useful spectral range of transmission, absorption, scattering, internal stress, environmental stability, film homogeneity, reproducibility, thermal stability etc [5]. For this purpose the diamond like carbon films can be used. The advantages of DLC films are their high hardness, chemical and radiation stability as well as deposition at room temperature, possibility to change their optical properties in a wide range by varying the deposition conditions [4]. They can be easily doped by nitrogen [3], silicon [5, 6], silicon oxide [6], boron [7], sulphur [8] during deposition by various methods, such as plasma-enhanced chemical vapour deposition (PECVD) [9, 10],

ion beam deposition [11, 12], microwave deposition [13], pulsed laser deposition (PLD) [14].

In the present work DLC films were formed on crystalline silicon (one of the solar cells materials) and quartz substrates by two different methods: radio frequency plasma enhanced chemical vapour deposition (RF PECVD) and employing closed drift ion source from methane and acetylene gasses respectively. Two methods were compared and the effect of deposition conditions on the antireflecting properties of the DLC films was analyzed.

2. EXPERIMENTAL

In the first experiment hydrogenated DLC films were deposited on monocrystalline Si (100) and quartz substrates at room temperature using a closed drift ion source. Acetylene (C₂H₂) gas has been used as a source of hydrocarbon. The base pressure was $2 \cdot 10^{-4}$ Pa, work pressure $(1 \div 2) \cdot 10^{-2}$ Pa, ion beam energy 300 eV – 700 eV ($E_{\text{ion}} \sim 0.5eU_a$ (U_a – accelerating voltage, e – elementary charge)), deposition time 30–36 minutes (except for the energy of 300 eV the time of deposition was 65 min).

In the second experiment, DLC films were deposited on monocrystalline Si (100) and quartz by RF PECVD in an atmosphere of methane (CH₄) at a pressure of $1 \cdot 10^{-2}$ Pa applying different bias voltages. The bias voltage was varied from 100 V up to 1000 V. The RF power was 40 W – 350 W. The deposition was performed at room temperature, deposition time – 45 minutes.

Before the deposition all the wafers were cleaned chemically.

The optical properties of the films were investigated using optical spectrometer Avantes that is composed of deuterium halogen light source (AvaLight DHc) and spectrometer (Avaspec-2048). The transmission of the films (deposited on quartz substrates) was analyzed in the wavelength region from 250 nm to 1000 nm and antireflecting properties of the films (deposited on crystalline

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silicon and quartz) were analyzed in the region from 225 nm to 800 nm. The reflectance was measured normal to the surface. The absorption coefficient was calculated evaluating reflection and transmission of the films using equation:

$$\alpha = \frac{1}{t} \ln \left(\frac{1-R}{T} \right), \quad (1)$$

where t is the film thickness in cm, R is the reflectance, and T is the transmittance.

Laser ellipsometer Gaertner 117 operating with a He-Ne laser ($\lambda = 632.8$ nm) was used for the estimation of the thickness and refractive index of the films.

3. RESULTS AND DISCUSSIONS

3.1. DLC films formed using a closed drift ion source

The refractive index determined with a laser ellipsometer as a function of ion beam energy is shown in Fig. 1. One can see that the refractive index varies in the range of 2.53–2.71, and the thickness (defined by laser ellipsometer as well) varies in a narrow interval of 160 nm–178 nm (Table 1).

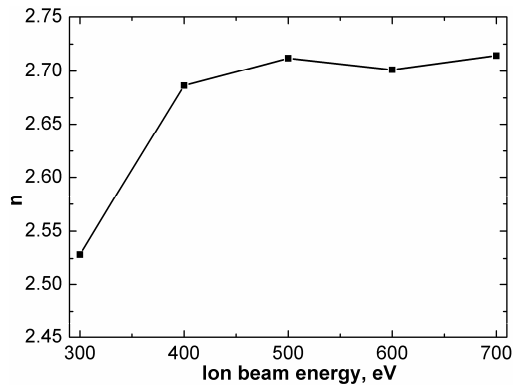


Fig. 1. Refractive index dependence on ion beam energy

Table 1. Thickness of the films determined for different ion energies

Ion beam energy, eV	Thickness, nm
300	178
400	170
500	160
600	170
700	170

The index of refraction has been found to be dependent on the preparation conditions and hydrogen content in the films. It is known that refractive index is affected by the hydrogen content in the DLC films and generally increases with decreasing concentration of bound hydrogen. A higher index of refraction usually indicates DLC with stronger crosslinking, higher hardness, and better wear resistance [15]. The lowest refractive index and highest thickness of the film was observed for the film grown at ion beam energy of 300 eV. Such ion beam energy corresponds to the energy of ~ 150 eV per carbon atom, while the optimal energy per carbon atom in terms of

sp^3/sp^2 ratio is 100 eV [16]. According to the previous statement, we suppose that this sample has the highest concentration of bound hydrogen.

To evaluate the absorption and reflection properties of the films, UV-VIS-NIR spectroscopic analysis was employed. The absorption coefficient was calculated from the transmittance measurements (using DLC on quartz) taking into account the reflectance of the films. The dependence of the absorption coefficient on ion beam energy in the photon energy range from 1.25 eV to 4 eV is shown in Fig. 2. One can see, that the absorption coefficient is highest at low ion energy (300 eV) and lowest at 500 eV. For the other ion beam energies employed during deposition the absorption coefficient stays almost the same. These two mentioned energies defined from the absorption coefficient measurements were also noticed as critical points in the refractive index dependence. One can see in Fig. 1 that these two energies correspond to the critical points: 300 eV corresponds to the film with the lowest refractive index and highest thickness (178 nm), 500 eV – to the film with the highest refractive index and lowest thickness (160 nm). As it was mentioned in [17] for the closed drift ion source, the ion/neutral atoms ratio in this energy region is a function of applied ion beam energy. In higher energy region the ion/neutral atoms ratio is stable. These facts are important because the higher ion/neutral atom ratio provides the higher sp^3/sp^2 ratio in the DLC film [16].

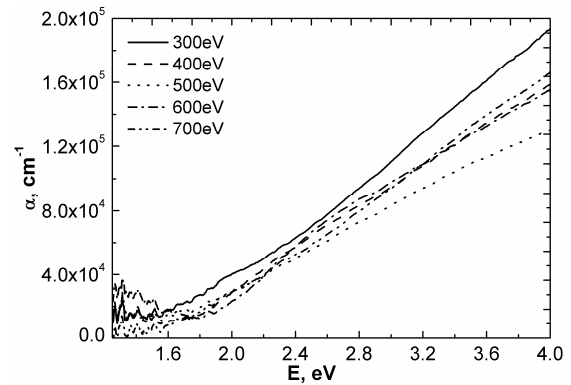


Fig. 2. Absorption coefficient of DLC films versus photon energy for different ion beam energy, employed in the deposition

The reflection coefficient dependence on wavelength of these films in the range from 225 nm to 800 nm is shown in Fig. 3.

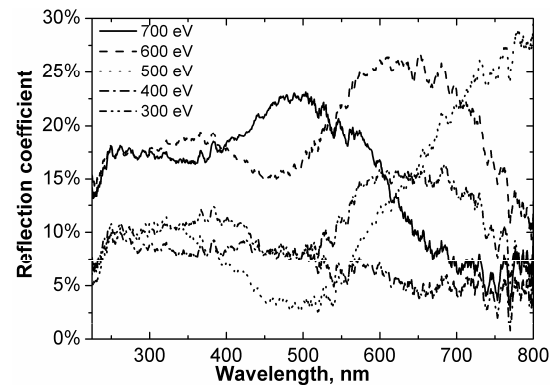


Fig. 3. Reflection coefficient of DLC-quartz versus wavelength for different ion beam energy, employed in the deposition

As expected, the spectra are modulated by the interference fringes, due to presence of the DLC layer. Because of the thinness of the DLC layer, only one minimum in reflectance spectra is observed. It is known that solar radiation has the intensity maximum in the range of visible light around 600 nm [18]. In our case the lowest reflection around 600 nm is observed for the sample formed when ion energy was 400 eV. For the film deposited employing this energy the reflection is almost constant (there is no visible interference fringes in the spectra) all over the measured region and varies between 5 % and 10 %. For the samples formed at ion beam energies of 300 eV, 500 eV and 600 eV one can easily see the reflection bands in the spectra region of 425 nm–525 nm ($\lambda_{min} = 495$ nm), 325 nm–600 nm ($\lambda_{min} = 500$ nm), 375 nm–500 nm ($\lambda_{min} = 470$ nm) respectively. In the case of sample formed at 700 eV it was observed that the reflection coefficient is decreasing in the preferred region of 550 nm–800 nm. The reflectance of the system “substrate-DLC” film varies with the optical thickness ($n \cdot d$, where n is the refractive index of the film, d is the measured thickness of the film) [19]. The shift of minimum reflectance wavelength (λ_{min}) is attributed to the change of optical thickness. Minimum reflectance shifts towards shorter wavelengths when the optical thickness of the layer decreases [20]. In our case the tendency is opposite. When the optical thickness increases, the minimum reflectance shifts to lower wavelengths. This effect can be a consequence of the refractive index condition mismatch (the refractive index of the film must be equal to a square root of the refractive index of the substrate).

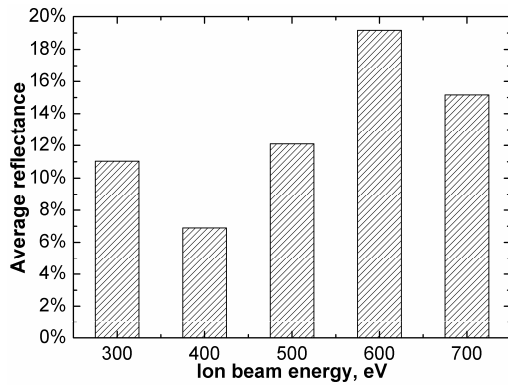


Fig. 4. Average reflectance calculated for different ion beam energy employed during deposition

One of the quantities given for the evaluation of antireflective coating is an average reflectance calculated for polarized or unpolarized light when the light strikes the surface at different angles of incidence [21, 22]. Average reflectance was calculated for all the samples (Fig. 4) in the wavelength region from 225 nm to 800 nm. The average reflectance increases from 6.9 % (400 eV) to 19.1 % (600 eV). It is known [23] that the phase transition of DLC film from diamond-like carbon to graphite-like carbon influences its optical properties. The increase in the graphitic fraction and the clustering of the sp^2 bonded carbon in the film has the effect of reducing the transmittance and increasing the reflectance [23].

3.2. DLC films formed using RF PECVD

Employing RF PECVD the DLC films were formed on silicon and quartz. The refractive index variation on the applied bias voltage is shown in Fig. 5. One can see that refractive index varies in the range 2.13–2.76, and thickness variation is in the region of 240 nm–340 nm (see Table 2).

Table 2. Energy per carbon ion and thickness of the films determined for different ion energies (E_i)

Bias voltage, V	E_i , eV	Thickness, nm
100	40	240
200	80	239
400	160	330
600	240	320
800	320	308
1000	400	290

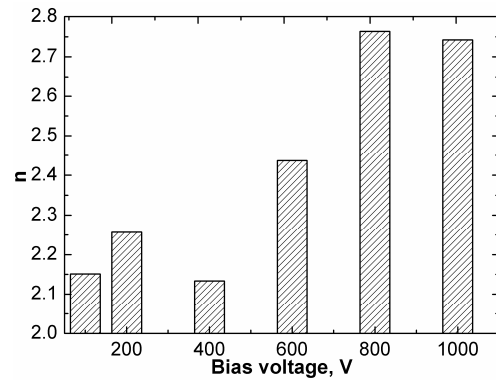


Fig. 5. Refractive index dependence on bias voltage employed during deposition

According to [16] the ion beam energy is directly proportional to bias energy $E_i = kV_b$, where $k \sim 0.4$. In our case the ion energy varies from 40 eV to 400 eV per carbon atom. It is known [16] that refractive index increases with the increase of bias voltage which is connected with the increase of the density of the film (in the region of bias voltages 0 V–600 V for methane). One can see in Fig. 5 that the tendency of the increase of refractive index is present except for the bias voltage of 400 V. Film formed at 400 V (ion energy ~ 160 eV per carbon atom) shows the lowest refractive index which corresponds to the highest amount of bound hydrogen in the film. With increase of bias voltage, the hydrogen content decreases and bonding becomes more sp^2 [16].

The absorption coefficient dependence on photon energy for films formed employing different bias voltages is shown in Fig. 6. One can see that the highest absorption is observed for the sample formed at 800 V and lowest absorption is observed for samples formed at 200 V and 400V. Two energies – 400 V and 800 V – were also distinguished from the refractive index dependence on the bias voltage (Fig. 5). According to the Table 2, one can say that the absorption coefficient is not influenced by the thickness of the film, because the difference of the thickness is too small (22 nm) for the samples formed employing voltages mentioned previously.

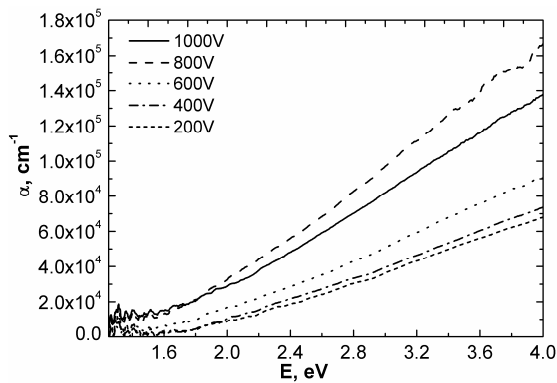


Fig. 6. DLC absorption coefficient versus photon energy for the different bias voltages employed during deposition

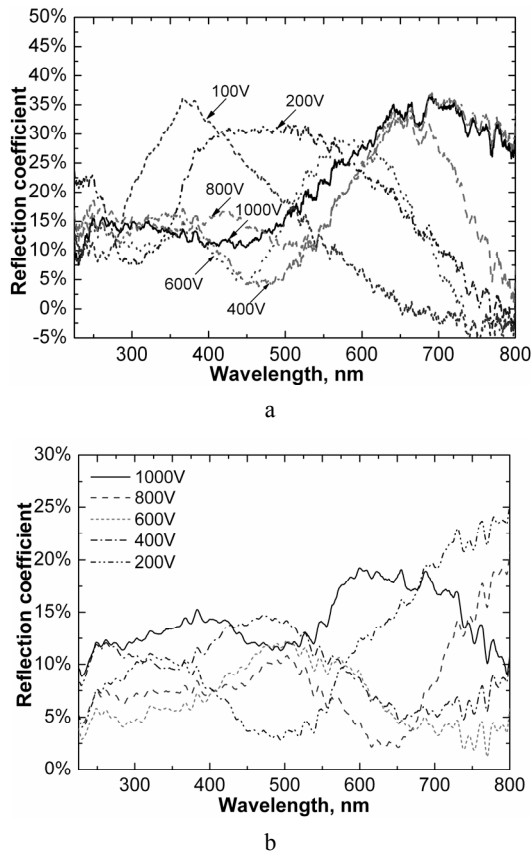


Fig. 7. Reflection coefficient vs. wavelength for DLC films deposited at different bias voltage for films formed on: a – silicon; b – quartz

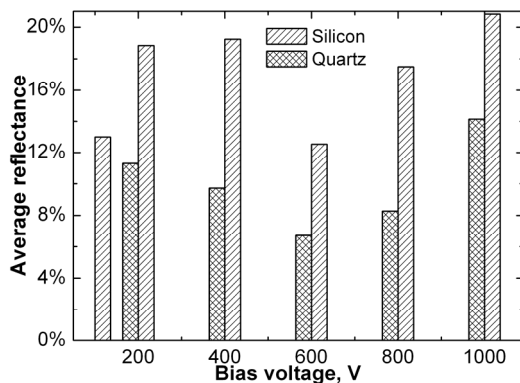


Fig. 8. Average reflectance dependence on bias voltage for films formed on different substrates (silicon and quartz)

Figure 7 shows the reflectance within the wavelength range of 225 nm–800 nm as a function of bias voltage applied during the deposition for both substrates (silicon and quartz). One can see in Fig. 7, a, that it is possible to determine the reflection bands for some of the samples. For the sample formed at 200 V bias voltage the reflection band is situated in a short wavelength region 250 nm–375 nm ($\lambda_{min} = 300$ nm). Other samples formed at 400 V, 600 V and 800 V have the reflection bands in the visible region at 375 nm–575 nm ($\lambda_{min} = 470$ nm), 375 nm–500 nm ($\lambda_{min} = 445$ nm) and 425 nm–575 nm ($\lambda_{min} = 515$ nm) respectively. One can see that the minimum wavelength shifts to longer wavelengths when the optical thickness increases, except for the sample formed at 400 V bias voltage. Analyzing the reflection spectra of the film formed on quartz in Fig. 7, b, one can see that there are two expressed reflection bands: 375 nm–600 nm (200 V ($\lambda_{min} = 492$ nm), 1000 V ($\lambda_{min} = 494$ nm)) and 500 nm–800 nm (400 V ($\lambda_{min} = 695$ nm), 600 V ($\lambda_{min} = 700$ nm), 800 V ($\lambda_{min} = 640$ nm)). The position of minimum reflection shifts to higher wavelengths when the optical path increases (200 V, 400 V, 600 V).

Average reflection of the films formed on different substrates is shown in Fig. 8. The average reflectance of DLC films varies in the range from 12.5 % to 20.8 % for silicon substrate and from 6.7 % to 14.1 % in case of quartz substrate. Despite different substrates, the tendency of average reflectance is similar. It reaches the minimum value at the bias voltage of 600 V. According to previous statements, one could say that there is highest sp^3 amount in the film (formed at 600 V bias voltage), while the highest amount of sp^2 fraction is in the sample formed employing bias voltage of 1000 V (the highest value of average reflection). These results with some uncertainty coincide with the reported results [24]. Analyzing the reflection around 600nm, the results for different substrates are not the same. In case of silicon substrate, the lowest reflection is observed for the sample that was formed with lowest bias voltage applied (100 V). For the quartz substrate lowest reflection in preferred region is observed for sample formed at 800 V and samples formed at 400 V and 600 V shows also quite low reflection (see Fig. 7, b).

CONCLUSIONS

Diamond like carbon films were formed on silicon and quartz substrates employing two methods: closed drift ion beam source deposition and RF PECVD. It was observed in both deposition methods using different gas that the highest amount of bound hydrogen (lowest refractive index) is present in the films that are formed when ion energy is ~ 150 eV–160 eV per carbon atom (close to optimal deposition energy of 100 eV per carbon atom).

We have shown that changing deposition conditions one can obtain films with different antireflection properties (minimum reflection in different wavelength range). For approximately constant thickness of DLC (160 nm–178 nm) changing the ion beam energy in closed drift ion source deposition, the minimum reflection (average reflectance is less than 10 %) was observed for the sample formed at 400 eV (200 eV per carbon atom). For other samples different antireflection regions in the range of

visible light from 425 nm to 600 nm were observed. In case of RF PECVD the broader wavelength region is covered changing deposition conditions (250 nm – 800 nm).

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