Influence of the rapid thermal annealing on the properties of a-C:H/c-Si structures

S Georgiev 1, A Szekeres 1, E Vlaikova 1,3, G Beshkov 1, D Sueva 2 and E Manolov 1

1 Georgi Nadjakov Institute of Solid State Physics, Bulgarian Academy of Sciences, 72 Tzarigradsko Chaussee, 1784 Sofia, Bulgaria
2 Faculty of Physics, St. Kl. Ohridski University of Sofia, 5 J. Bourchier Blvd., 1164 Sofia, Bulgaria

E-mail: vlaikova@issp.bas.bg

Abstract. The influence of rapid thermal annealing (RTA) on the properties of a-C:H/c-Si (p-type) structures was investigated. The carbon layers were deposited by plasma enhanced CVD at substrate temperature of 340 °C from methanol (CH₃OH) vapor. The C-V and I-V measurements of the a-C:H/Si structures showed that a p-n junction is formed on the silicon surface after RTA and the structures behave as a Schottky diode. The formation of a thin SiC interlayer by 1000 and 1200 °C RTA was proven by the corresponding optical constants obtained from the ellipsometric measurements after RTA and subsequent carbon removal in HF acid.

1. Introduction
Amorphous hydrogenated carbon (a-C:H) deposited by RF-plasma enhanced chemical vapour deposition (PECVD) is a promising material for flat panel displays, metal-semiconductor-metal switches [1] and interlayer dielectric applications. A heterostructure of a-C:H/c-Si has been investigated in [2-5] that is suitable for solar cell applications [6]. The a-C:H layers with a small trap density of states at the a-C:H/Si interface can be used as gate dielectrics in MIS transistors [7]. A study of the material properties of amorphous hydrogenated carbon films obtained by plasma chemical vapor deposition from different saturated and unsaturated hydrocarbon source gases [8] has shown that unsaturated hydrocarbons (acetylene and ethylene) yield films with higher density, lower hydrogen content, and higher refractive index than saturated hydrocarbons. Using CH₃OH/H₂/H₂O mixtures at a substrate temperature of 700 °C [9], diamond-like layers with a well defined 1332 cm⁻¹ diamond Raman peak have been formed.

In this work we studied the properties of an a-C:H /c-Si structure subjected to rapid thermal annealing (RTA) in the temperature range of 800 ÷ 1200 °C. By means of a 5-min annealing, a thin interfacial SiC layer was created, which influences the properties of the structure. By etching away the carbon top layer, it became possible to obtain a SiC/c-Si (p-type) heterostructure with a thin silicon carbide layer.

3 To whom any correspondence should be addressed.
2. Experimental details
Amorphous hydrogenated carbon (a-C:H) films with thickness of 108 nm were deposited on p-type crystalline Si by HF (27 MHz) plasma decomposition of methanol (CH₃OH) vapors at substrate temperature 340 °C and pressure 10 Pa in a planar plasma reactor. The duration of the deposition was 30 min; during deposition the DC self-bias voltage of the HF electrode was maintained in the range 650-750 V.

The samples were submitted to RTA treatment for 5 min in vacuum at a residual pressure of 6×10⁻³ Pa. The RTA temperature was 800, 1000 and 1200°C and was detected by a pyrometer. These temperatures were reached after 2 s and at the end of the annealing they dropped down within 4-5 s.

After annealing, some of the samples underwent an etching procedure using diluted HF (5%) acid to remove the carbon layer from the surface. This procedure aimed to detect a SiC underlayer if such was formed between the film and the substrate. The etched samples were measured by ellipsometry on a Rudolph 436 ellipsometer in the range 280-820 nm and at incidence angle of 50°. The optical constants of the films were calculated by solving the inverse problem of ellipsometry [10]. The film thickness and the optical constants were obtained with an accuracy of ±0.2 nm and ±0.005, respectively.

The a-C:H/Si structures were investigated at room temperature by capacitance-voltage (C-V) measurements at 100 kHz, and by current-voltage (I-V) measurements. For this purpose, Al dots with diameter 5×10⁻² cm were evaporated on the film surface, while continuous Al layer was deposited onto the Si back-side.

3. Results and discussion
Figure 1 shows the C-V dependence of the Al/a-C:H/Si structure with an as-deposited a-C:H film, which is typical for a metal-insulator-semiconductor (MIS) structure. In the accumulation regime at negative voltages below −3 V, the capacitance drops due to the increasing leakage current through the structure. In the positive voltages range the capacitance reaches a minimum saturation value $C_{\text{min}}$, clearly showing an inversion region in the p-Si substrate. Using this $C_{\text{min}}$ value, the doping concentration of the Si substrate was found to be equal to 7.6×10¹⁴ cm⁻³ [11].

![Figure 1. C-V dependence of Al/a-C:H/Si structure with as-deposited a-C:H film.](image)

After RTA and subsequent metallization, the shape of the C-V curves changes, as enhanced leakage current through the structure is observed. The C-V dependences of the RTA treated structures are presented in figure 2. The arrows indicate the points where the leakage current sharply rises. For 800°C RTA, the C-V curve moves toward more negative voltages in comparison to the C-V curve for RTA treated structures. The arrows show the appearance of intensive leakage current.

![Figure 2. C-V dependences of RTA treated Al/a-C:H/Si structures. The arrows show the appearance of intensive leakage current.](image)
given in figure 1, indicating that during the treatment positively charged traps above the Fermi level are created, most probably due to hydrogen release from the carbon layer. Our ellipsometric studies [12] have established that at temperatures of 1000 and 1200°C the carbon structure undergoes a considerable change, which is attributed to hydrogen loss and/or graphitic transformation in the film. The high leakage current registered in these structures in accumulation regime supports this statement.

In depletion and inversion regimes the reverse current starts to flow at positive applied voltages and the behavior of the structure is similar to the abrupt n+ -p junction (or Schottky diode). Auger electron spectroscopy measurements have proven the penetration of carbon into the silicon substrate during the plasma deposition of DLC layers [7]. Chemical conversion of the Si surface region into a SiC interlayer has been also proven by other researchers [13]. This is why it is reasonable to expect that during RTA some interfacial layer is formed and its composition will strongly differ from that of the deposited carbon film. By analogy to carbonization of Si substrate by rapid thermal chemical vapour deposition in a mixture of propane and H2 [13], one can expect formation of an interlayer between the carbon film and the Si substrate, most probably consisting of silicon carbide.

In order to detect an interlayer, after the RTA procedure, the carbon films were etched away from some samples with a HF etchant and ellipsometric measurements were performed. After the measurements, the samples were metallized and electrical measurements were carried out. The structures are further denoted as Al/SiC/Si. The results are summarized in figures 3 and 4. As is seen in figure 3, the C-V curve of the 1000°C RTA structure (curve 2) is typical for a Schottky diode, as the equilibrium Fermi level is established by electron exchange between the Al top contact and Si substrate. If the formed interlayer is SiC, this means that it is a wide gap semiconductor and does not participate in this process. Therefore it is possible to create an Al/SiC/c-Si (p-type) Schottky heterojunction with thin SiC layer simply by HF etching of RTA treated a-C:H/c-Si structures.

Figure 4 shows the I-V dependences of Al/SiC/Si heterojunctions. The reverse current of Al/SiC/Si is relatively high and in the order of 10⁻⁶ A, while in the forward direction it is relatively low, due to the large serial resistance of the formed interlayer.

In what concerns the ellipsometric data, the analysis showed the presence of a thin interlayer between the carbon film and the Si substrate formed during the RTA treatment, even for samples annealed at 800°C. The thickness and composition of this interlayer depend on the temperature. The values of the refractive index (n) and the extinction coefficient (k) of this interlayer are presented in figures 5 and 6, respectively. According to previous observations [12, 13], the RTA temperature of 800°C is not sufficient for a SiC interlayer to be formed. In this case, a 7.8 nm thick interlayer was detected with optical constants being close to that for silicon (figure 6), which suggests that the layer
consists most probably of hydrogenated silicon with some carbon impurities leading to an increased absorption, as observed. For the higher RTA temperatures (1000 and 1200°C), the thickness of this interfacial layer was found to be 4.6 and 14.3 nm, respectively. The interlayer formed is transparent within the spectral range 500-820 nm and the extinction sharply increases toward the absorption edge, where interband transition of electrons takes place. The corresponding refractive index and extinction coefficient values are similar to those characteristic of SiC thin films [14]. Therefore, we can state that during high temperature annealing carbonization of the Si surface proceeds and, as a consequence, the Si surface layer converts to silicon carbide. As the temperature was raised from 1000°C to 1200°C, the thickness of this SiC interlayer increased, but the similar optical band gap energy ($E_{bg}$) values of 2.9 ± 0.05 eV, deduced from the analysis of the absorption spectra and building Tauc plots [15] suggest that the structure of this SiC interlayer remains the same.

4. Conclusion
The analysis of the C-V and I-V characteristic of RTA treated a-C:H/c-Si structures showed that there exists an interface layer on the silicon formed during annealing and the characteristics are typical for a Schottky heterojunction. It is established that the RTA process at 1000°C (5 minutes) is the optimal one with respect to the electrical properties of these structures. The ellipsometric measurements revealed that RTA at 800°C yields an interlayer consisting most probably of hydrogenated silicon, while at higher RTA temperatures silicon carbide with energy bandgap of 2.9 eV is created.

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