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Deposition and Properties of Thin PECVD Carbon Films After Rapid Thermal Annealing

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Abstract In this work the properties of PECVD-carbon films before and after Rapid Thermal Annealing (RTA) are presented. The thickness of the investigated films is in the range 50 – 6000 Å. The layers are annealed at 1400°C for different times of 1 s to 3 min in vacuum 5×10^{-5} Torr. Raman investigation has been performed before and after annealing.

1. INTRODUCTION

PECVD processes have been widely used as deposition methods for different semiconductor and dielectric layers which find application as active or passive elements in modern microelectron technology.

Specific construction designs in these systems are used for deposition of carbon, diamond-like and diamond layers [1-7] which are applied in the realization of different types of electron elements [8-10], working in extreme conditions (temperature, vibration, radiation etc.)

The purpose of this paper is to point out some of the peculiarities of the deposition system as well as to investigate the influence of rapid thermal annealing on some characteristics of the layers (Raman spectra/shifts and resistance).

2. EXPERIMENTAL DETAILS AND RESULTS

(100) P-type Si wafers with resistivity 40 – 60 Ωcm have been used in our experiments. Before the deposition of the layers, the substrates have been treated in boiling $H_2SO_4 : H_2O_2$ (1:1) for 30 min, etched for 30 s in $HF : H_2O$ (1:10) and rinsed in running deionized water for 30 min. The carbon layers have been deposited in PECVD reactor (its schematic diagram is shown on Fig.1). The substrates (3) are placed in the discharge chamber (1) on the lower electrode with diameter 13 cm. It is heated by the heater (9) up to temperature 450°C. The surrounding wall is cooled down by water stream. The high frequency is supplied to the upper electrode (2) by high frequency generator (13.56 MHz) with power 60W. The working pressure in the discharge chamber is 26 Pa. CH_3OH , C_2H_5OH and $3HC - CO - CH_3$ have been used as supply sources for C. In order to increase the deposition rate, the discharge space has been divided in two parts by special electrode (7) in the middle of which there is an inlet (9) with diameter 10mm, through which the two parts of the discharge chamber are connected. The substrate is placed against the inlet, in front of the lower electrode, which is isolated

from the ground (the side wall of the reactor) and d.c. negative voltage is applied to it. In this way, negative ions have been intensively extracted from the plasma including carbon and oxygen radicals. This leads to the increase of the deposition rate. Table 1 shows the deposition rate of carbon from different carbon sources with and without the use of the special electrode.

Figure 1: Schematic diagram of the PECVD reactor. 1 - Discharge chamber; 2 - H.F. Electrode; 3 - Sample; 4 - Teflon isolation; 5 - Flowmeter; 6 - Needle valves; 7 - Special electrode; 8 - Inlet ($\Phi 10$) in the special electrode; 9 - Heater.

C source	Deposition Rate (μ/h)	
	without special electrode	with special electrode
CH_3OH	0.06	0.15
$2CH_3OH$	0.11	0.30
$3CH - CO - CH_3$	0.15	0.45

Table 1: Deposition rate of C for different carbon sources.

From the data shown in the table it is clear that the use of the special electrode leads to the increasing of the deposition rate about 3 times.

Our Raman investigations of thin layers ($100 - 300 \text{ \AA}$) show the presence of peaks in the range 970 cm^{-1} and $800 - 850 \text{ cm}^{-1}$, which is an indication that in the initial stage of the phase formation, α and β SiC layers are obtained. Fig.2 shows the Raman spectrum of a layer deposited at pressure of 25 Pa in the discharge chamber, substrate temperature during the deposition 450°C , power 120 W and source CH_3OH and H_2 - 80% (volume). With the increasing of the thickness of the layer ($d = 1000 \text{ \AA}$), diamond layers are obtained. The Raman spectrum of carbon layer with thickness $6000 \text{ \AA}$ is shown on Fig.3.

Figure 2: Raman spectrum of a layer obtained under the following conditions: pressure 25 Pa, substrate temperature 450°C, power 120 W.

Figure 3: Raman spectrum of carbon layer with thickness 6000 Å.

After the deposition of the layers under the specified conditions, the wafers are subjected to rapid thermal annealing at 1400°C for time 1 s - 3 min in vacuum 5×10^{-5} Torr. The Raman spectrum (Fig.3) of thick carbon layer (6000 Å) before the process of Rapid Thermal Annealing, shows a clear peak with maximum at 1510 cm⁻¹. After annealing for 1s, there is no change in the spectrum of the layer, but after annealing for 3 s, two well defined peaks with maximum at 1400 and 1510 cm⁻¹ are revealed. The peaks become more well defined increasing the annealing time. Fig. 4 shows the Raman spectrum of a layer annealed for 3 s and Fig. 5 - after annealing for 10 s. Increasing the annealing time, the two peaks become better defined and practically after times greater than 3 min no more changes appear. Fig.6 shows the Raman spectrum of a layer after 3 min annealing and two clear peaks are registered at 1335 and 1580 cm⁻¹.

Figure 4: Raman spectrum of carbon layer after annealing for 3 s.

Figure 5: Raman spectrum of carbon layer after annealing for 10 s.

Figure 6: Raman spectrum of carbon layer after annealing for 3 min $d = 6000 \text{ \AA}$.

The measurements of the resistivity of the layers show that for annealing times 1-3 s a sharp increase in the resistivity is registered reaching values of $10^7 \Omega$. For annealing times 10-50 s a strong decrease of the resistivity is obtained up to 400Ω , and after annealing for 1-3 min it reaches a value of 200Ω which remains unchanged independently of the annealing time. These results may be due to different phase transitions in the structure of the carbon layers with a very high resistivity for the short annealing times (1-3 s) and reaching the graphite structure for annealing times greater than 1 min.

3. CONCLUSIONS

It has been established that the deposition rate of carbon layers in PECVD reactor is increased about 3 times when a special electrode with an inlet of 1 cm in the middle is used.

The rapid Thermal Annealing leads to the appearance of two peaks in the range $1335 - 1580 \text{ cm}^{-1}$ in the Raman spectra and drastically increases the resistivity of the layers for annealing times 1-3 s.

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