

Chemical vapor deposition of carbon layers on Si {001} substrates*

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Chemical vapor deposition of carbon layers was carried out by pyrolysis of acetone in an Ar main gas flow at different temperatures in the range 950- 1200°C, on Si {001} substrates. The morphology of the surfaces of the obtained thin layers was studied by SEM. The layers obtained at high temperature were additionally examined by Raman spectroscopy. The structure of the layers was analyzed by X-ray diffractometry. It was established that their crystalline character becomes more pronounced upon increasing the deposition temperature from 950°C to 1050°C, and even mixed diamond-like and graphite layers appear at 1200°C.

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1. Introduction

Diamond and diamond-like films (DLF) are of great interest, due to their extremely high electrical and chemical resistivity, hardness, thermal conductivity etc.. There are different methods in use for the deposition of such films, and they can be categorized as chemical and physical vapor deposition (CVD and PVD) methods. According to the way of introducing the activating energy into the system, the CVD methods can again be divided into thermal (e.g., hot filament- [1-3] or combustion flame (acetylene etc.)- [4,5]) and plasma- [4,6-9] CVD ones.

Bachmann et al. [4] studied carbon films grown from different C/H, C/H/O, C/H/Cl and C/H/N gas mixtures by CVD, activated by a MW plasma, combustion flame synthesis and a RF plasma torch. They concluded that acetone (CH₃COCH₃) has such C/H/O relationships that it belongs to the non-diamond carbon growth region. In contrast to this conclusion, we reported that the deposition of diamond-like films and micro-crystals by a CVD process with the pyrolysis of acetone vapor in an Ar main gas flow on Si {001} is possible under well-defined conditions [10,11]. The results of depositing carbon films by the thermal pyrolysis of acetone on Si {001} substrates at temperatures in the range 950-1210°C are presented here.

2. Experimental

Si wafers were prepared for the deposition experiments by the procedure described in detail in [11]. The CVD processes of thermal pyrolysis of acetone were carried out in a horizontal-tube quartz reactor. The main gas-flow was pure Ar. The carbon-containing flow was obtained by passing the Ar through liquid acetone at a fixed temperature of 18°C. A main gas-flow of about 300-400 cm³/min and a carbon- containing flow of 45-50 cm³/min were used in the deposition processes. The deposition temperature was set at 950, 1050 and 1200°C. The deposition time was 1-1.5 hours for layers deposited at 950 and 1050°C, and about 1.5-2 hours for those deposited at 1200°C.

The morphology of the layers was examined by scanning electron microscopy (SEM), with a JEOL JSM 6390 microscope.

The X-ray powder diffraction patterns for phase identification were recorded in the angle range $2\theta = 9-123^\circ$, on a Philips PW 1050 diffractometer, equipped with a Cu K_α tube at 18°C. A step-scan mode at steps of 0.03° (2θ) with a counting time of 5 s/step was used for the XRD data collection.

The Raman spectra were measured on a Dilor multichannel spectrometer with entrance slits set to 3.5 cm⁻¹ spectral width. The 514.5 nm line of an Ar/Kr-laser was used for excitation; the absolute accuracy being 0.6 cm⁻¹. The laser beam with a power of 10 mW was focused

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on a spot of about 2 μm diameter on the DLF, using microscope optics.

3. Results

The SEM study of the morphology of the carbon layers reveals a gradual transition from small-sized particles deposited within a framework of rod-like objects, probably nano-rods or nanotubes, with diameters of 30-100 nm (Fig. 1a), through a more compact layer with single rod-like nano-scale objects and undistinguishable surface relief (Fig. 1b), to a more clearly shaped relief with many micro-scale sized crisp-like crystals (Fig. 2). The relief observed in the layers deposited at 1200°C consists of hollows nearly parallel to $\langle 011 \rangle$.

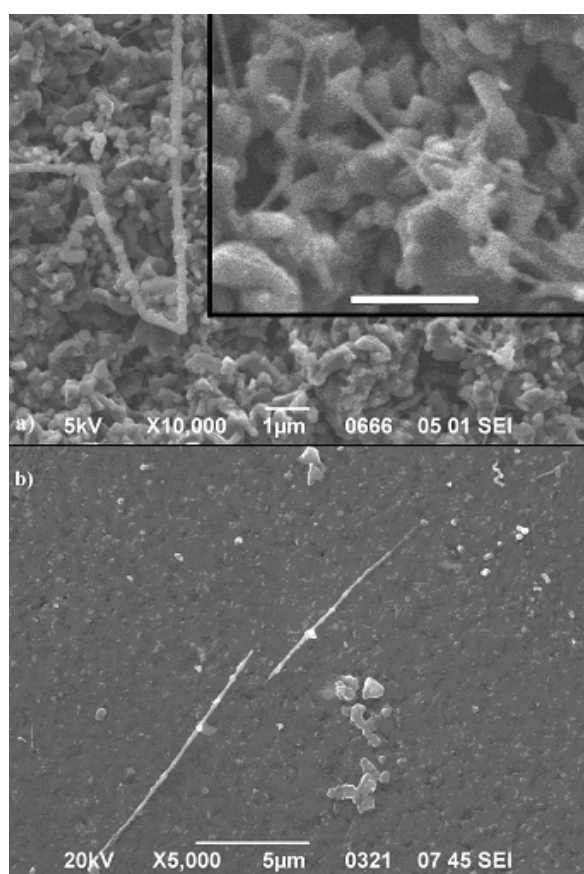


Fig. 1. (a) A secondary electron image (SEI) of a carbon layer deposited at 950°C. The inset presents a magnified part of the same image and the marker represents 1 μm . (b) A SEI of a carbon layer deposited at 1050°C.

The XRD patterns obtained from the carbon layers and the Si substrates are presented in Fig. 3, and reveal several important features. The G(002)- marked peaks correspond to the so-called “graphite” peak from the (002) graphite planes. The Si*(112) peak corresponds to diffraction from the (112) planes in the Si-substrate [12]; the Si (004) peak comes from the Si {001} substrate [13],

and D(111) and D(004) from the diamond-type lattice. The G(002), Si*(112) and Si(004) peaks are observed in the XRD patterns of carbon layers grown at low temperatures (950 and 1050°C), while the D(111), D(004), Si*(112) and Si(004) peaks are observed only in the XRD patterns of layers grown at high temperatures - 1200°C.

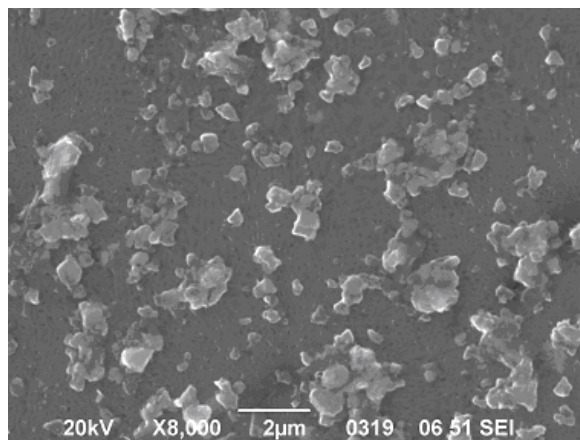


Fig. 2. A SEI of a layer deposited at 1200°C. The $\langle 011 \rangle$ direction is nearly parallel to the frame of the image.

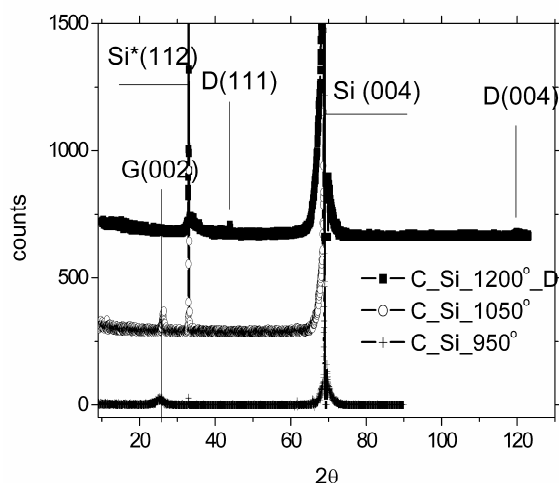


Fig. 3. XRD patterns of carbon layers grown at 950(C_Si_950°), 1050(C_Si_1050°) and 1200°C(C_Si_1200°_D), respectively.

The peaks of the Si substrate become broader with increasing deposition temperature, and a weak amorphous broadening of the Si*(112) peak is observed in the XRD pattern of the high temperature layer.

The G(002) peaks of carbon layers (Fig.4a) grown at low temperatures tend from $2\theta=25.39^\circ$ (for the carbon film deposited at 950°C), through $2\theta=26.26^\circ$ (for the carbon film deposited at 1050°C), to its value of $2\theta=26.54^\circ$ that

corresponds to graphite. The G(002) peak is absent in the XRD pattern of the high temperature film (Fig.4a).

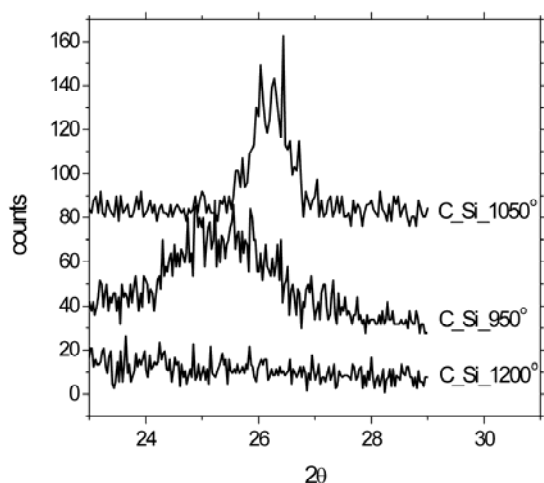


Fig. 4(a) The G(002) peak in the XRD patterns of carbon layers.

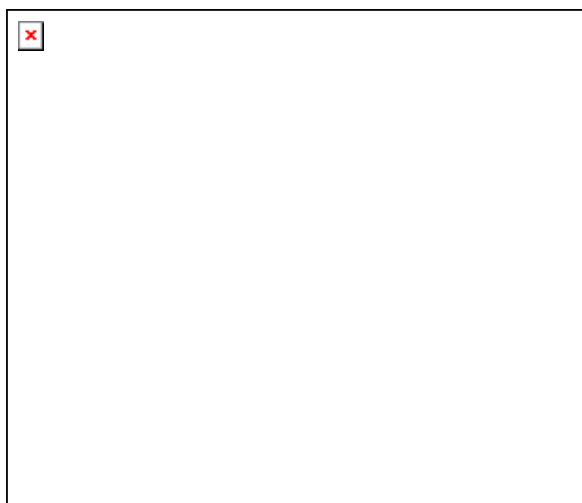


Fig. 4(b) The D(111) at $2\theta=43.88^\circ$ and D(004) at $2\theta=120.03^\circ$ peaks measured in the XRD patterns of carbon layers grown at a temperature of 1200°C.

The diamond D(111) and D(004) peaks were observed at $2\theta=43.9^\circ$ and $2\theta=120.03^\circ$ respectively, at a noise level of about 50% in both cases (Fig.4 b). The intensity ratio of these peaks is about 1. However, it seems that another peak also appeared at about $2\theta=120.5^\circ$ in the XRD pattern of the carbon layer grown at the high (1200°C) temperature. No other diamond reflection was observed.

The Raman spectrum of the high temperature layers (Fig. 5) is very complex. More than 10 different features are observed in the spectrum:

i) peaks: P1 at 1136 cm^{-1} ; P2 at 1153 cm^{-1} ; P3 at 1177 cm^{-1} ; P4 at 1365 cm^{-1} ; P5 at 1488 cm^{-1} ; P6 at 1568 cm^{-1} ;

P7 at 1599 cm^{-1} and a shoulder of a peak P8 at about 1610 cm^{-1} .

ii) bands: B1 at 1300 cm^{-1} ; B2 at 1341 cm^{-1} ; B3 at 1427 cm^{-1} ; B4 at 1585 cm^{-1} .

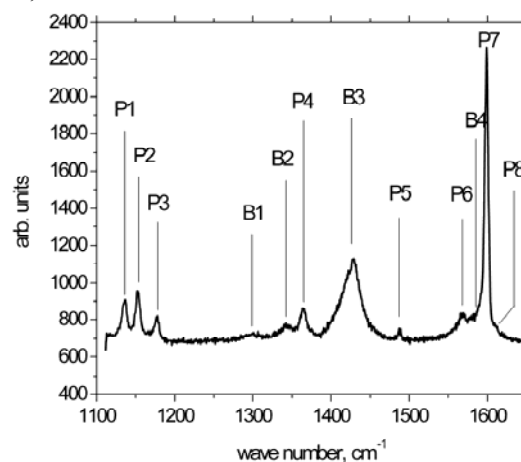


Fig. 5. The Raman spectrum measured on the layer grown at high temperature.

4. Discussion

The observed peaks and bands in the Raman spectrum could be attributed to different bonds/ structures in the high temperature carbon layers:

-the band B2 at 1341 cm^{-1} is probably due to sp^3 -hybridized C-C bonds, and could be considered as evidence for a diamond-type structure [14];

-the band B4 at 1568 cm^{-1} is usually attributed to the so-called "bridged" graphite that corresponds to diamond-like films [15];

-the peak P4 at 1365 cm^{-1} and the band B5 at 1585 cm^{-1} are slightly shifted upwards from the well known D and G bands of graphite, and could be related to "glassy" carbon [15];

-the peak P1 at 1153 cm^{-1} and the peak P5 at 1488 cm^{-1} are situated nearby to the peaks at 1140 and 1488 cm^{-1} attributed to C-H rocking or CH_2 - deformation in H-C=O and CH_2 groups. These residuals, termed as "transpolyacetylene", are situated at the grain boundaries in the nano-diamond films [16-19]. The shoulder observed at 1610 cm^{-1} may be considered as a disorder-induced feature from a graphitic-like sp^2 -bonded site- [16,20]. The strong sharp peak at 1599 cm^{-1} may be considered as due to the so-called dumbbell defect [20]. This consists of an isolated sp^2 bonded pair. Because the defect is localized, rather than extended, its vibrational modes are expected to give rise to fairly sharp Raman peaks, as indeed is observed here [20].

-the peaks P2 at 1136 cm^{-1} and P3 at 1177 cm^{-1} could not be assigned definitely. They are clear and sharp peaks and could hardly be related only to VDOS bands. However, around 1165-1175 cm^{-1} a VDOS-feature of nano-diamond has been reported [16,21,22].

According to the XRD pattern and the Raman spectrum, it seems that a small part of the layers deposited

at 1200°C has a diamond-type structure. A possible explanation of the observed intensity ratio of $I_{D(004)}/I_{D(111)}$, that is 5-7 times higher than the normal value for the diamond-type lattice, is a partial texturization of the carbon layer with diamond-type structure about the $\langle 001 \rangle$ axis. The presence of the D(111) peak also supports these assumptions. The observed weak peak at about $2\theta=120.5^\circ$ in the same XRD pattern (Fig. 4 b) is probably caused by some of the carbon allotropic forms deposited within the layer.

Examination of the morphology of the high-temperature layers revealed a practically continuous layer - see Fig. 2. At the same time, it was established that in the first stages of growth of diamond-like films, the crystal growth took place mainly on high-roughness areas of the polished Si- substrate, and formed a network of micro-scale paths and islands, while the rest of the surface was occupied by SiO₂ and various waste-products of the high temperature pyrolysis of the acetone [14]. Accordingly, it seems that the small fraction of the carbon layer with diamond-type structure crystallizes on the paths/islands, while the diamond-like and glassy-carbon layers are deposited on the rest surface.

The observed appearance and intensification of the Si*(112) peak, as well as the broadening of both Si peaks in specimens of layers deposited at different temperatures, could be explained by the increasing deposition temperature and the duration of the CVD process, as well as by the stress generated at the layer/substrate interface.

5. Conclusions

Deposition of carbon layers with different structures, depending on the process temperature, was achieved by a CVD process of the thermal pyrolysis of acetone. The carbon layers deposited at 950°C consisted of sub-micron sized carbon particles deposited within a framework of rod-like objects, probably nano-rods or nanotubes. The crystalline character of the carbon layers deposited at 1050°C was more strongly pronounced, and a small fraction of crisp-like crystals was observed, probably deposited on the layer during the annealing process. The carbon layers deposited at 1200°C consisted of at least three fractions: I) a small fraction with a diamond-type structure, probably texturized about the $\langle 001 \rangle$ axis; II) a diamond-like film consisting of the so-called "bridged" graphite and III) a glassy-carbon fraction. Some residual quantities of H-C=O and CH₂ groups (probably products of the thermal reduction of acetone) existed in the diamond-like and glassy-carbon layers.

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