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Study of n-diamond and carbon nanowalls structure synthesized by the RF-PECVD

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Abstract. In this work, a hybrid n-diamond-carbon nanowalls structure was synthesized on a 100 mm diameter silicon wafer using RF-PECVD (CCP type). This structure was analyzed by transmission microscopy, electron microscopy and X-ray diffraction. It was found that the addition of carbon monoxide (CO) to a gas mixture of methane (CH₄), argon (Ar), and hydrogen (H₂) leads to the formation of n-diamond nanocrystals in the basal layer. Using plasma surface treatment techniques, the carbon nanowalls were fully removed and the lower layer consisting of n-diamond was studied separately, for which X-ray diffraction results of a separate n-diamond phase were obtained for the first time.

Keywords: n-diamond, carbon nanowalls, X-ray diffraction, allotropic form, hybrid material

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Материалы конференции

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Исследование гибридной структуры n-алмаза и углеродных наностенок, синтезированной методом RF-PECVD

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Аннотация. В данной работе на кремниевой пластине диаметром 100 мм была синтезирована методом RF-PECVD (тип CCP) гибридная структура n-алмаз – углеродные наностенки. Для данной структуры был проведен анализ методами просвечивающей микроскопией, сканирующей микроскопией и рентгеновской дифракцией. Установлено, что добавление угарного газа (CO) в газовую смесь метана (CH₄), аргона (Ar) и водорода (H₂) приводит к образованию частиц n-алмаза в базальном слое. Используя плазмохимическое травление в кислород-содержащей среде, были успешно удалены углеродные наностенки и отдельно изучен нижний слой, состоящий из n-алмаза, для которого впервые были получены результаты рентгеновской дифракции отдельной фазы n-алмаза.

Ключевые слова: n-алмаз, углеродные наностенки, рентгеновская дифракция, аллотропная форма, гибридный материал

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Introduction

Carbon nanowalls (CNWs) are structures consisting of graphite-like two-dimensional sheets oriented almost perpendicular to the substrate surface. The exceptional morphological and structural properties of CNWs, including their vertical orientation, open and ultra-thin edges of graphene sheets, large specific surface area and open areas between graphene sheets, have attracted significant interest. [1]. Due to their important properties, such as high electrical conductivity, thermal conductivity, and chemical stability, CNWs have been successfully applied in nanoelectronics, photoelectronics, and electrochemistry. [2–5].

CNWs are mainly grown using Plasma Enhanced Chemical Vapor Deposition (PECVD) from various types of hydrocarbons with different plasma sources. The interfacial layer formed between a substrate and CNWs, i.e., the basal layer, is an important phase of CNWs synthesis. The basal layer ensures a uniform heat and current distribution within the substrate plane and remains significant for interface resistance and CNW formation. Studying the basal layer has demonstrated that it can be represented by a layer of graphite sheets growing parallel to a substrate, a layer of amorphous carbon, or various carbides formed during interaction with the substrate material. The type of the formed basal layer depends on both the synthesis technique and gas precursors applied during the growth.

Throughout our research, we found that feeding an additional carbon source in the form of carbon monoxide (CO) to a gas mixture (Ar/CH₄/H₂) induces the formation of a unique interface layer consisting of a new-diamond (n-diamond, FCC-carbon). A new diamond crystalline phase (carbon γ phase) was first produced during the low-temperature annealing of a carbon film exposed to Ar ions during deposition [6]. Various methods have been developed to generate nano-sized n-diamond crystallites, including hydrothermal synthesis [7], hydrogen plasma treatment of a diamond surface [8], microwave plasma enhanced chemical vapor deposition (MW-PECVD) [9] and other.

There is no detailed study of the n-diamond structure using X-ray diffraction in the scientific papers due to the small size of nanoscale crystallites and by-products arising during synthesis. Therefore, most of the data on the n-diamond structure has been obtained based on electron diffraction results from TEM studies, which is insufficient to determine the exact structure of the n-diamond. Thus, the n-diamond crystalline structure remains uncertain and requires further scientific investigation [10].

The study of n-diamond-CNWs hybrid structure formation is important fundamental research for producing applied micro- and nanodevices, optoelectronic systems, energy storage and conversion systems, various sensors and other tools. Understanding the factors affecting the development of hybrid structures facilitates the control of the synthesis and growth processes, as well as the phase composition.

Materials and Methods

The n-diamond-CNWs hybrid structure was synthesized in the Oxford Instruments Nanofab 1200 Agile reactor. At room temperature, the wafers were placed at a grounded graphite base electrode, which is used with an upper electrode to generate high-frequency capacitively coupled plasma (CCP). The heating to 750 °C was performed in a hydrogen flow at a pressure of 1 Torr, and an average heating rate of 14 °C/min. The depositing phase comprised the feeding of Ar, CH₄, CO, and H₂ process gases (ratio 200:10:7.5:2.5), at a pressure of 250 mTorr and the RF source power of 300 W. Synthesis was performed on a silicon wafer for 3600 seconds without and with feeding carbon monoxide (CO) to a gas mixture.

Scanning electron microscopy (SEM) was performed using FEI Helios, a dual beam FIB-SEM (focused ion beam) system. Images (patterns, micrographs) were acquired using the secondary electron imaging mode while scanning the surface of analyzed objects with an electron beam. Imaging parameters were selected experimentally according to the criteria of sufficient resolution for visualizing relevant characteristics and an acceptable signal-to-noise ratio

The microstructure of the samples was studied by transmission electron microscopy with high resolution (TEM and HRTEM) using a JEOL JEM-2100 Plus microscope at an accelerating voltage of 200 kV. The two-dimensional Fourier transform technique (FFT) was used to obtain diffraction patterns of separate nanoparticles and minimize the noise of high-resolution TEM images.

The samples were analyzed on an X-ray diffractometer using the X-ray diffraction (XRD) technique at a grazing incidence of X-ray radiation to a sample (incident angle $\approx 0.5^\circ$, selected based on the maximum intensity of peaks from CNWs and n-diamond). X-ray diffraction patterns were taken in the scanning mode at an angle of 2θ using $\text{Cu K}\alpha$ radiation ($\lambda = 1.540605 \text{ \AA}$) under the X-ray source parameters of 45 kV and 40 mA. A paraboloidal reflector with a divergence slit of j and an anti-scatter slit of j was set on a primary beam. A parallel plate collimator with a divergence amounting to 0.19° was set on a diffracted beam. The value of Soller slit divergence was equal to 0.04° . A point-linear detector was used as a detector.

Results and Discussion

The phase composition of samples synthesized with and without CO was determined using the X-ray diffraction technique. To analyze the surface layer of the samples, the Grazing Incidence X-ray Diffraction (GIXRD) method was applied. The X-ray diffraction pattern of the sample synthesized without CO (see Fig. 1, blue chart) displays peaks at 2θ angles equal to 25.4° , 43.0° , $45\text{--}46^\circ$, and 78.5° , which refer to CNWs [11]. The lack of (004) reflex at $2\theta \approx 53.3^\circ$ on the diffraction pattern can be explained by a low number of graphene layers in nanowalls along [0001] or their aperiodicity. However, the diffraction pattern of the sample synthesized with CO (Fig. 1, dark-red chart) displays additional peaks at 2θ angles equal to 44.6° , 52.1° , 76.7° , 93.2° , and 98.8° , which were identified as the n-diamond phase according to scientific literature [12].

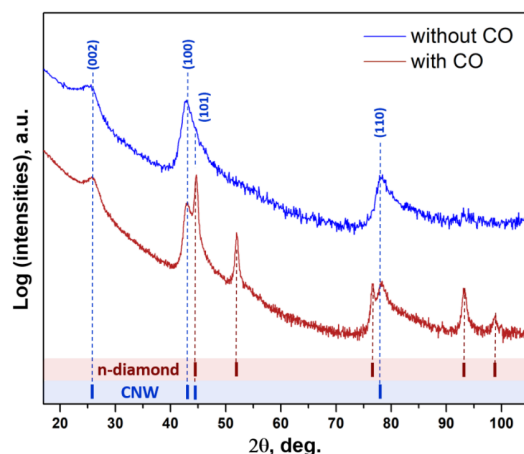


Fig. 1. Grazing incidence X-ray diffraction patterns for the samples synthesized without CO (blue chart) and with CO feeding (red chart). The location of peaks for the CNWs phase and n-diamond phase are marked on a line diagram

Several peaks in the diffraction pattern overlap with each other. Since experimentally obtained X-ray diffraction patterns for the n-diamond phase without overlapping peaks from accompanying phases are not presented in the literature, we removed CNWs from the hybrid structure by treatment in oxygen plasma. The diffraction pattern (Fig. 2) for the range of 2θ angles from 25° to 105° distinctly displays peaks at 2θ angles equal to 44.6° , 51.8° , 76.4° , 93.0° , and 98.5° for the $\text{K}\alpha_1$ position. The value of integral FWHM (integral breadth) for all peaks is ≈ 1.3 , which corresponds to an average size of crystallites equal to $\approx 10 \text{ nm}$ and calculated according to the

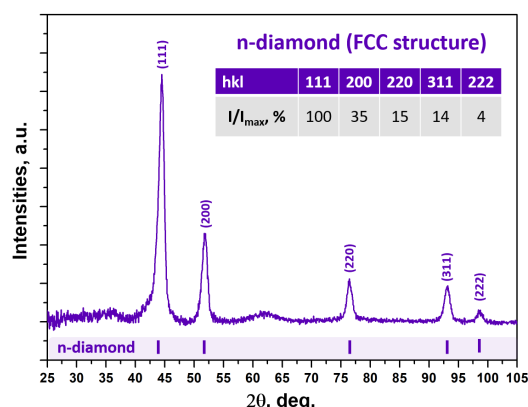


Fig. 2. Experimental X-ray diffraction pattern of a nanocrystalline n-diamond phase indicating the fractional intensity of each peak. The diffraction pattern background was removed

Scherrer formula. The intensity ratio of each peak is given in the insert to Fig. 2. The number of reflexes, their relative position, and intensity ratio substantiate that the n-diamond structure can be described by a crystallographic set $Fm\bar{3}m$, as it was suggested in a series of scientific papers [8].

According to the diffraction pattern interpretation using the $Fm\bar{3}m$ structure, the n-diamond lattice parameter is equal to $a = 3.52\text{\AA}$, which is in agreement with the literature data [6].

A general cross-section view of the sample containing the hybrid structure grown with and without CO for the same synthesis duration of 3600 seconds is shown in Fig. 3, *a*, *b* in SEM images of secondary electrons. It can be seen that at the same synthesis time, adding CO to the reaction mixture leads to the growth of higher CNWs. The increase in CNWs growth rate is associated with a shift in the balance between the process of etching in the oxygen plasma and the deposition towards deposition, which occurs when a small amount of CO is added to the gas mixture.

The morphology and structural differences of the obtained samples samples were also analyzed using the TEM technique. The general view of the CNWs-Si interface for samples grown without CO and with CO feeding is provided in Fig. 3,*c* and Fig. 3,*d*, respectively. The TEM images show

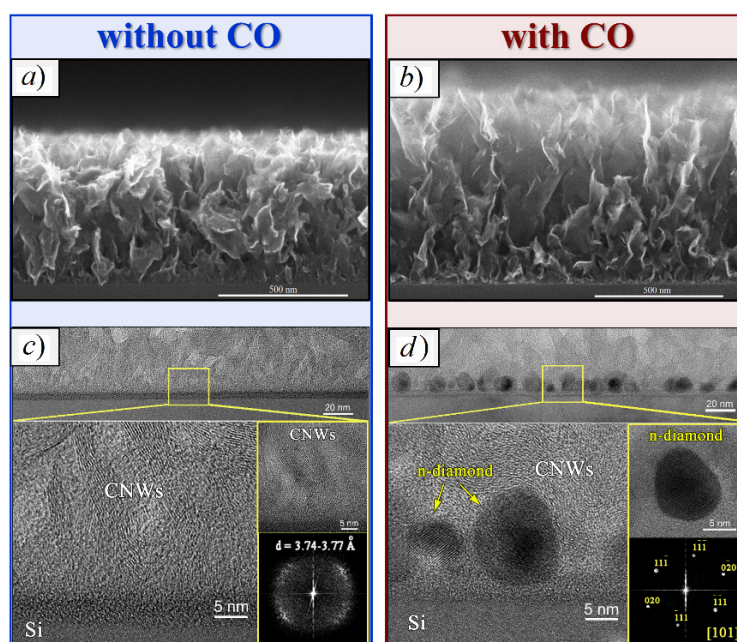


Fig. 3. Cross-sectional (*a*) SEM and (*c*) TEM images of CNWs grown on Si substrate for 3600 seconds without CO. Cross-sectional (*b*) SEM and (*d*) TEM images of CNWs grown on Si substrate for 3600 seconds with CO



a distinctive feature of the sample grown with CO, i.e., the presence of individual nanoparticles formed on the CNWs-Si boundary. According to TEM images, the average size of the particles is 10 nm. The presence of graphene layers of CNWs growing around the observed nanoparticles is also apparent in Fig. 3,*d*. By contrast, in the sample grown without CO, only graphene layers with an interplanar spacing of 3.74–3.77 Å can be visible at the CNWs–Si boundary (Fig. 3 (*c*), insert) corresponding to the interplanar spacing for the (0001) plane of turbostratic graphite [13] and capable of responding to an unformed CNWs structure.

High-resolution TEM images of the CNWs-Si section were taken in several areas of the sample grown with CO to study the nanoparticle's structure. An example of those areas is given in the insert to Fig. 3,*d*, i.e., an enlarged image of a yellow square. Some particles overlapped or were composed of several crystallites, while most of them represented individual monocrystals. To identify the phase, we only used FFT images of monocrystals. Significantly, different allotropes of carbon may exist simultaneously and possess the same value of interplanar d-spacings. Therefore, to ensure precise identification of a phase of carbon nanoparticles under study, we determined interplanar d-spacing and angles between directions in the lattice on FFT images and compared them with values defined for registered allotropes of carbon according to the ICDD database.

A typical HRTEM image of a particle taken for the evaluation and a relevant FFT pattern can be found in the insert to Fig. 3,*d*. The reflection positions on the displayed FFT pattern indicate that this electron diffraction pattern corresponds to the [101] cross-section of the lattice structure [14], and the lattice parameters correspond to the n-diamond phase. By summarizing the electron diffraction data of various individual nanoparticles in the sample, it can be concluded that during synthesis with CO feeding, randomly oriented crystals with an n-diamond structure and lattice are formed. The obtained data are consistent with the results of the investigation by the XRD technique.

Conclusion

The n-diamond-CNWs hybrid structure was successfully synthesized in capacitively coupled plasma discharge using a mixture of carbon monoxide, methane, hydrogen, and argon. The study has demonstrated that feeding CO to the gas mixture is an essential factor in the n-diamond formation. Selective removal of CNWs from the hybrid structure has allowed to experimentally obtain X-ray diffraction patterns for the n-diamond phase, free of overlapping peaks of accompanying phases. The average size of the n-diamond particles was approximately 10 nm at 3600 seconds of synthesis. Having grown the n-diamond-CNWs hybrid structure on 4-inch silicon wafers offers opportunities for large-scale integration and wide practical application.

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