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The influence of oxide buffer layers on the formation of catalytic nanoparticles and carbon nanotubes

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The morphology of Ni nanoparticles synthesized on SiO_2 and TiO_2 buffer layers, as well as carbon nanotubes grown on them, was studied. Scanning electron microscopy and transmission electron microscopy analysis revealed that nanoparticles formed on the TiO_2 surface have increased size and low surface density, which leads to the formation of a limited number of carbon nanotube nuclei and reduced homogeneity. In contrast, nanoparticles on the SiO_2 surface have a smaller average diameter, a nearly spherical shape, a uniform distribution, and are characterized by high density. As a result, the synthesized carbon nanotubes are characterized by an ordered structure, a narrow diameter range (5−25 nm), and a high level of crystallinity. These results allow us to recommend the SiO_2 buffer layer as an effective catalyst platform.

Keywords: Carbon nanotubes, buffer layers, nanoparticles, CVD synthesis, morphology, transmission electron microscopy, scanning electron microscopy, crystallinity, amorphous carbon, catalytic particles.

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Large-scale materials and technology research has been conducted in recent years at the nanoscale. Owing to their high mechanical strength [1], unique electrical properties [2,3], high thermal conductivity [4,5], and lightweight [6], carbon nanotubes find application in various fields. They offer wide opportunities in the development of energy storage systems, integrated circuits [7,8], electrochemical capacitors [9], sensors, composites, and thermal interface materials [10–12].

The above applications require the synthesis of high-purity unidirectionally oriented carbon nanotubes (CNTs) with the desired parameters. Owing to its controllability and scalability, catalytic chemical vapor deposition (CVD) is regarded as the standard synthesis method at present. Initial formation of catalytic particles and prevention of their side reaction with the substrate are the prerequisites of efficient CVD. Catalysts are typically deposited in the form of a thin film and break up into nanoparticles upon heating. It was demonstrated that buffer layers provide an opportunity to control the shape and density of catalytic particles [13]. Metal buffer layers turned out to be inefficient [14], but the use of nitride and oxide buffers improves significantly the quality and yield of CNTs [15–17]. For example, significant differences were revealed when the influence of different buffer layers (Al, Al_2O_3, TiN, and TiO_2) on the Fe catalyst was examined [14]. In addition, it was found that the morphology of the buffer layer and the method of its formation affect directly the density and morphology of the catalyst and the formation of CNT arrays [18]. Thus, the choice of effective buffer layer and catalyst materials is crucial for high-quality CNT synthesis.

The present study is focused on the evaluation of efficiency of TiO_2 and SiO_2 buffer layers on single-crystal silicon in the formation of catalytic particles and the synthesis of carbon nanotubes.

An *n*-type Si(110) substrate with a diameter of 7.6 cm and a thickness of 376 μm was prepared for the synthesis of catalytic Ni particles. The substrate was cleaned with acetone and isopropyl alcohol, washed in an ultrasonic bath, and dried in Ar atmosphere.

The TiO_2 buffer layer was formed by atomic layer deposition (ALD, SENTECH Instruments GmbH) with titanium isopropoxide and water used as precursors. Nitrogen was used as the transport gas at a flow rate of 120 cm^3/min. The pressure in the reactor was close to 60 Pa, and the substrate temperature was 200 °C. The deposition process consisted of 200 cycles of 8 s each, resulting in a film thickness of approximately 40 nm. The SiO_2 buffer layer was obtained by thermal oxidation at a temperature of 1000 °C for 2 h in an SNOL-type furnace in air. The approximate thickness of the formed layer was 55 nm. The nickel coating was deposited by electron-beam PVD (EB-PVD) at a pressure of approximately 10^{-6} Torr and a substrate temperature of 20 °C. The emission current was 50 mA, the accelerating voltage was 10 kV, the distance between the substrate and the target was 25 cm, and the deposition time was 40 s. The film growth rate was determined based on the spectroscopic ellipsometry data and was found to be approximately equal to 0.3 nm/s. Prior to the synthesis of carbon nanotubes, the nickel catalyst was activated in an $H_2 : Ar = 1 : 3$ mixture of hydrogen and argon for 10 min. The activation time was chosen with account for the initial Ni layer thickness and the heating temperature, which ensured uniform formation of

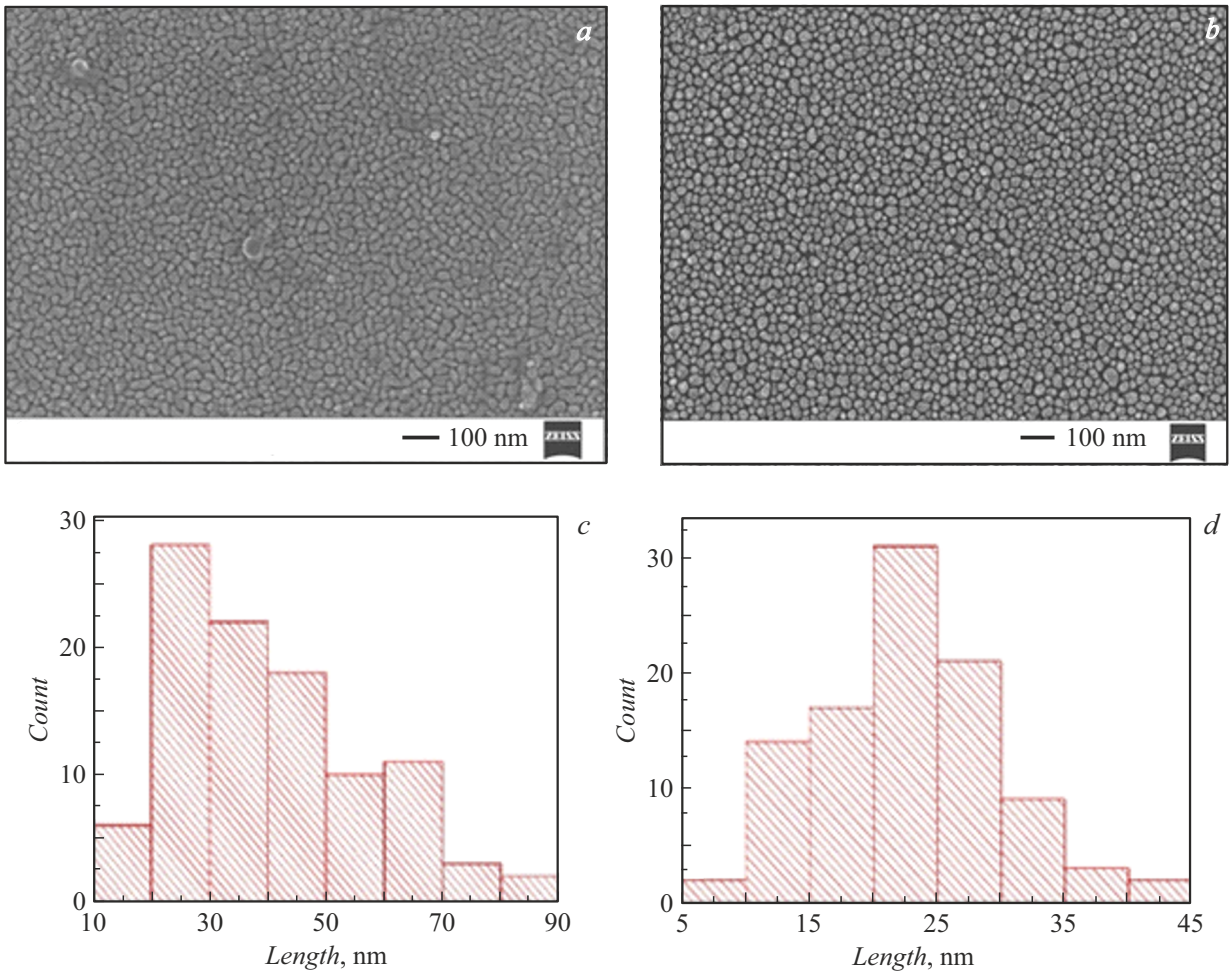

Figure 1. SEM images of Ni catalyst particles formed on the TiO_2/Si (a) and SiO_2/Si (b) samples and statistical histograms of the nanostructure distribution (c, d).

catalytic nanoparticles. The samples were heated in a CVD chamber at a temperature of 700 °C in an atmosphere of H_2 and Ar; after that, CH_4 was supplied, and CNT synthesis was carried out for 30 min at $Ar : H_2 : CH_4 = 5 : 1 : 2$. The thickness of buffer layers measured by spectroscopic ellipsometry (SENTECH SER850) was 40 nm for TiO_2 and 55 nm for SiO_2. According to the results of earlier studies [19], the TiO_2 layer is characterized by an anatase phase with a nanocrystalline structure, while SiO_2 is amorphous. Scanning electron microscopy (SEM; ZEISS Sigma 500), transmission electron microscopy (TEM; HRTEM JEM 3010 URP-JEOL), and Raman spectroscopy (Renishaw RM 100 with a laser wavelength of 785 nm and a laser power of 1 mW) were used for analysis. Since local destruction of the sample surface was observed at higher powers, measurements were carried out at the minimum radiation power.

The morphology of the Ni thin film was investigated by SEM. Figures 1, a, b present the images of Ni particles formed after heating on the TiO_2 and SiO_2 buffer layers. On the TiO_2 surface, they assume the form of islands of varying sizes and irregular shape; on SiO_2, they are near-spherical in shape and have a smaller average diameter and a more uniform distribution. This suggests that the SiO_2 buffer layer is more efficient in forming high-density catalytic particles and distributing them uniformly over the surface. The thermal decomposition of the thin Ni film is associated with minimization of its surface energy, and this process is effected through surface diffusion [19]. SEM images were analyzed using ImageJ. On the TiO_2/Si surface, the average particle size was 40.8 nm at a density of 853 μm^{-2}; on the SiO_2/Si surface, the average size and the density were 22.8 nm and 1090 μm^{-2}, respectively. The histogram did also reveal that particles on the SiO_2/Si surface are significantly smaller and are distributed within a narrower range. The Raman spectra shown in Figs. 2, a, b are indicative of the formation of multi-walled CNTs in both cases. The *RBM* peak was not observed; the *G* peak was observed at 1591 cm^{-1} (TiO_2) and 1574 cm^{-1} (SiO_2), while the *D* peak was identified at 1357 and 1340 cm^{-1}, respectively. Second-order peak G' was also detected in both samples. The D/G ratio was 0.79 for TiO_2 and 0.53 for SiO_2, indicating a higher purity of CNTs synthesized on the SiO_2 buffer layer [20].

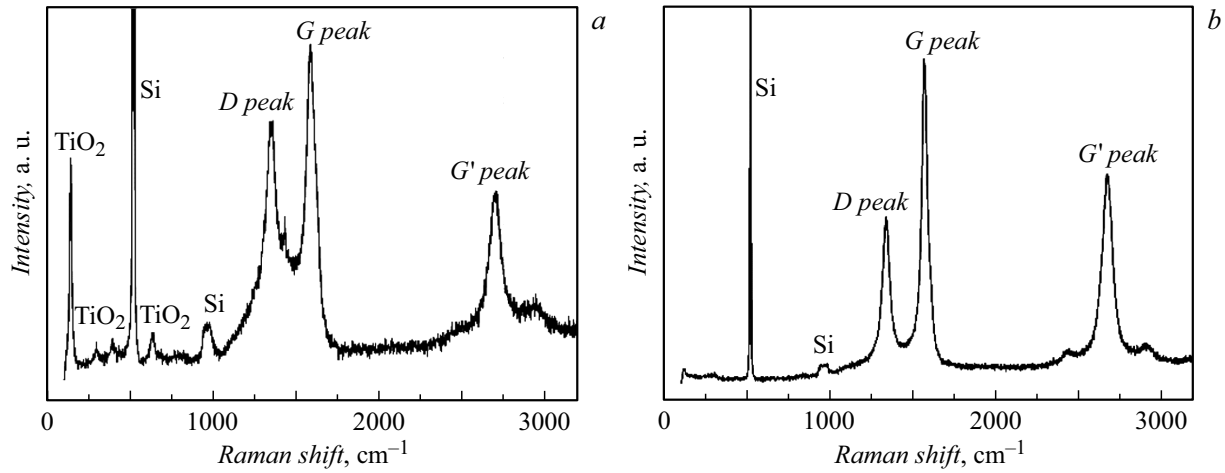

Figure 2. Raman spectra of CNTs grown on the $Ni/TiO_2/Si$ (*a*) and $Ni/SiO_2/Si$ (*b* samples).

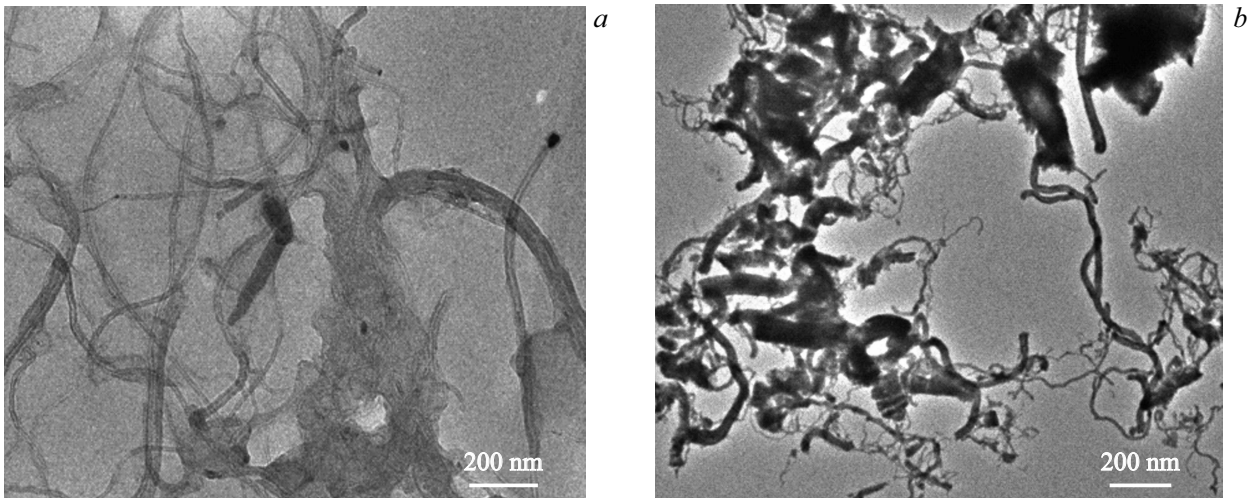

Figure 3. TEM images of multi-walled carbon nanotubes synthesized on the $Ni/SiO_2/Si$ (*a*) and $Ni/TiO_2/Si$ (*b* samples).

The TEM images shown in Fig. 3 reveal that CNTs on the SiO_2 surface have a multi-walled structure with a diameter of 5–25 nm and a length of several tens of micrometers. They are randomly oriented, but have a smooth surface, and Ni particles were found at their ends. A small amount of CNTs with a diameter of 5–40 nm did form (in most cases, together with amorphous carbon) in the sample synthesized on the TiO_2 surface. This is associated with the enlargement of catalytic particles, which leads to suppression of their activity and premature termination of synthesis.

Thus, Ni nanoparticles formed on SiO_2 and TiO_2 buffer layers differ significantly in morphology and density, which has a direct influence on the quality and structure of carbon nanotubes synthesized based on them. Owing to the formation of large nanoparticles with low density, the growth of CNTs with an admixture of amorphous carbon and a less ordered structure was observed on the TiO_2 surface. At the same time, CNTs with a narrow range of diameters and high degrees of crystallinity and purity were obtained on the SiO_2 surface, where nanoparticles with a smaller average diameter, a near-spherical shape, and a high density were formed. The $I_D/I_G = 0.53$ intensity ratio in the Raman spectra verifies the high quality of synthesized CNTs. Therefore, SiO_2 buffer layers may be regarded as an efficient support for controlled growth of high-quality nanocarbon structures.

Conflict of interest

The authors declare that they have no conflict of interest.

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