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Carbon nanofiber growth on thin rhodium layers

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ABSTRACT

A thin layer of carbon nanofibers (CNFs) was synthesized on a thin polycrystalline rhodium (Rh) metal layer by decomposing ethylene in the presence of hydrogen. Interaction of Rh crystals with carbon results in fragmentation and formation of Rh-nanoparticles, facilitating CNF growth. CNFs are immobilized on the surface by an apparently amorphous intermediate layer containing both Rh and C. Maximum CNF growth was achieved at intermediate hydrogen concentrations. A CNF growth mechanism by (sub-) surface diffusion of carbon on Rh is suggested.

Carbon nanofibers/tubes (CNF/Ts) are finding applications in *e.g.* electronic devices, electrochemical capacitors, catalyst support layers in microreactors, additives to polymers and super hydrophobic coatings. Controlled growth of these structures is important to realize application in nanoscale devices. Synthesis of CNF/Ts by catalytic chemical vapor deposition method offers high rate of carbon growth and easy control of the reaction conditions [1]. Fe, Co, Ni are widely studied metals for CNF/T growth, however, the presence of residual ferro-magnetic catalyst particles in the CNF/Ts may be an obstacle for research on the magnetic properties of CNF/Ts, as well as for applications in electronic devices, electrochemical capacitors and catalysts. In addition to ferro-magnetic metals, also Pd, Pt, Ag, Au, Ru, Re, Rh, Ir and Os enable CNF/T growth. So far, exclusively Pd was studied for growing CNF/Ts on thin metal films. In the present work, we report on synthesis CNFs on thin Rh layers, exploring the effect of the conditions on CNF growth.

A 100 nm polycrystalline rhodium layer was deposited at room temperature on a single crystalline silicon wafer (Ø 100 mm) using DC-sputtering technique. Prior to rhodium deposition, a 15 nm thick titanium adhesion layer was sputter deposited on the silicon wafer. CNF formation was carried out at atmospheric pressure in a quartz reactor. The fresh wafers were heated in nitrogen (100 ml/min) from room temperature to 600 °C (6 °C/min), followed by reduction in H_2 (5 vol.%) for 15 min. After flushing with N_2 for 5 min, ethylene was introduced, growing CNFs during 30 min. The concentration of ethylene (10 vol.%) in the feed was kept constant in all experiments, whereas the hydrogen concentration was varied

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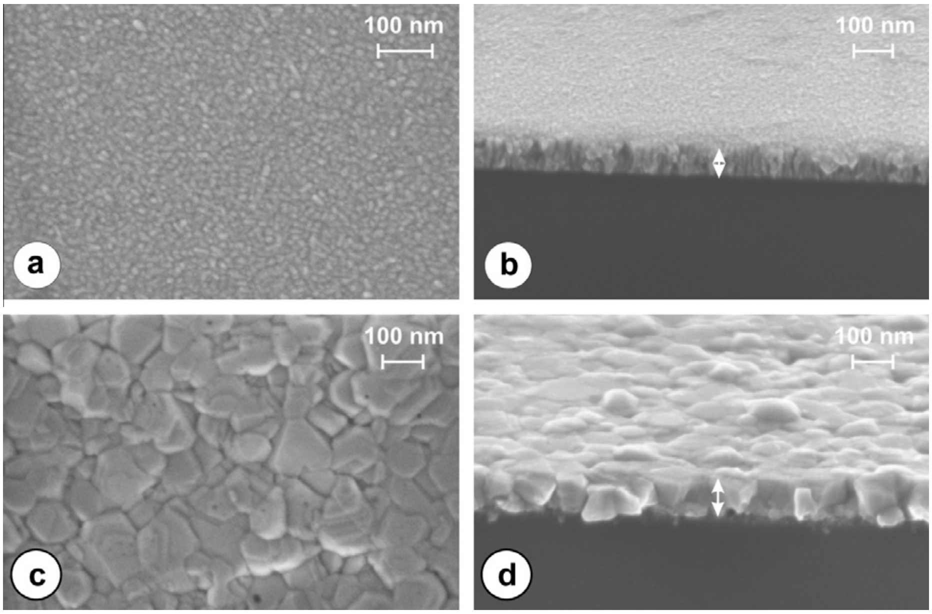

Fig. 1 – (a) and (b) shows the top view and cross-sectional of the as-received thin layer of Rh. (c) and (d) shows the top view and cross-sectional of the Rh layer reduced in 5%H_2/N_2 for 15 min.

Table 1 – Rhodium grain size in fresh sample, pretreated sample and after CNF growth, as determined with SEM and XRD-LB.

Rh–Ti–Si wafer	Particle size window, SEM (nm)	Average particle size, SEM (nm)	Average particle size, XRD-LB (nm)
Fresh	5–20	10	20.4
Pretreated	10–200	90	44.3
CNF grown	5–40	20	36.3

between 0 and 20 vol.% (balance N_2, total flowrate 100 ml/min).

Pretreatment of fresh wafers with H_2 results in significant sintering of Rh grains from ~10 nm to ~85 nm, as can be seen in Fig. 1. XRD analysis of the wafers confirmed this as the intensity of the Rh(111) peak-width decreased significantly (Table 1). The only phase in the layer was metallic Rh according to XRD. Carbon deposition on the Rh surface resulted in the formation of CNFs with metal particles in the tips (Fig. 2), containing exclusively Rh and carbon, according TEM–EDX. This confirms that Rh particles are responsible for the formation of CNFs and no other metals contribute to the growth.

The rate of CNF growth increases with increasing hydrogen concentration (Fig. 3a–d). This behavior is very similar to the effect of H_2 concentration on CNF growth on *e.g.* Ni [2]. The underlying mechanism is probably similar: increasing hydrogen pressure decreases the carbon concentration on the Rh surface due to competitive adsorption of hydrogen and ethylene. Thus, encapsulation of Rh particles with carbon is partly suppressed, retarding deactivation and thus enhancing CNF growth. Further increasing the hydrogen pressure is

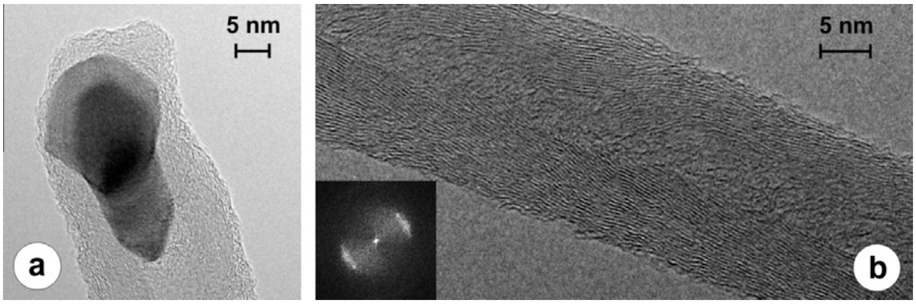

Fig. 2 – CNFs formed at 10%H_2/10%C_2H_4/N_2 (a) HRTEM image of CNF with a Rh metal particle at the tip. (b) TEM image showing the graphene structure of CNF. Insight image shows the diffraction pattern of the fiber.

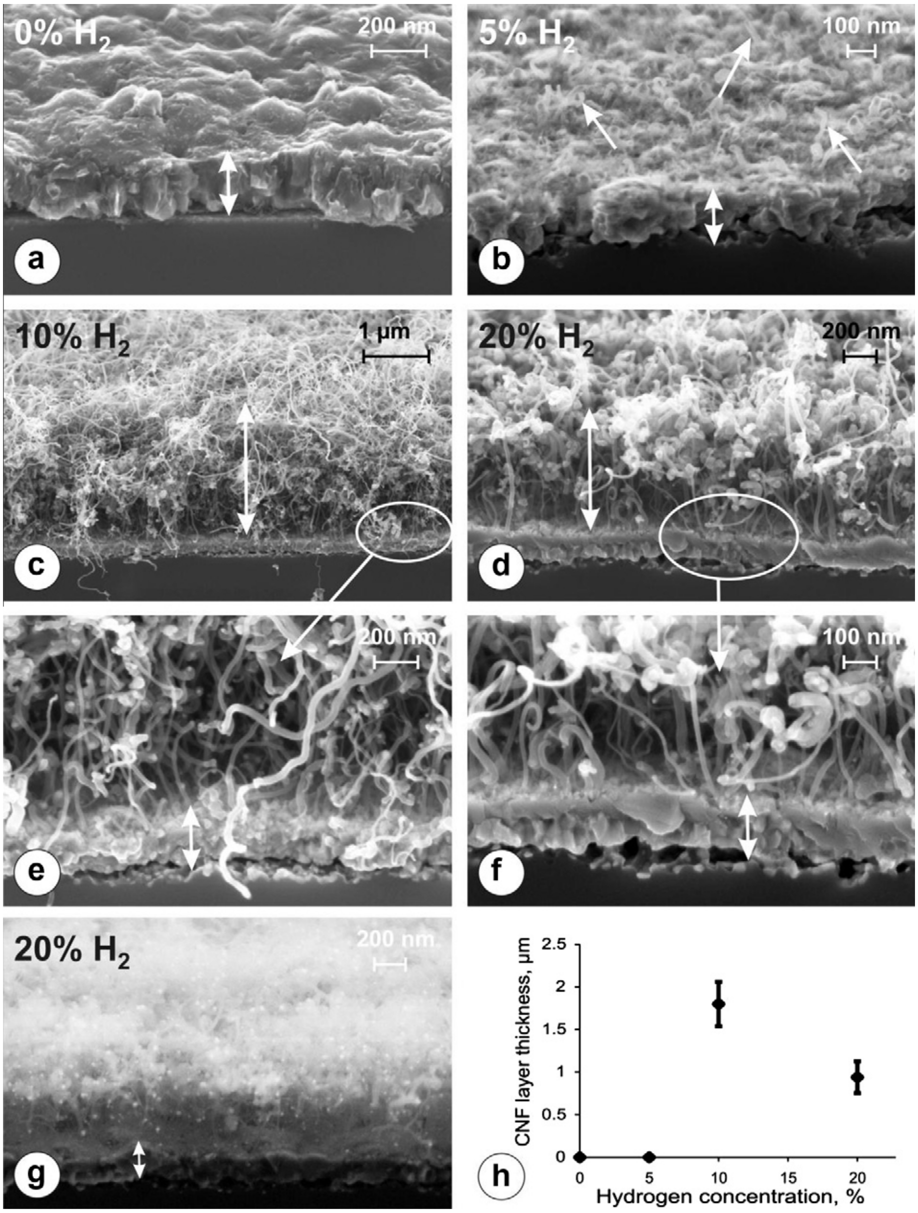

Fig. 3 – (a–g) SEM images at the cross-section of wafers after exposure to ethylene using different hydrogen concentrations. The close-up images (e) and (f) show the continuous layer present under the CNF layer. (g) shows the secondary electron detector image of CNFs formed at 20%H_2. (h) shows the effect of hydrogen addition on the thickness of CNF layer as measured with SEM.

retarding CNF growth because of limiting availability of C on the Rh particles.

The underlayer observed between the CNF-layers and the Si substrate (as indicated with arrows in Fig. 3a, b, e and f) is twice as thick as compared to thickness of the original Rh layer (Fig. 1). At first sight this seems very similar to the attachment of CNFs on Ni surfaces by a micro-porous C layer [2,3]. Exposure to ethylene in the absence of hydrogen results in formation of this underlayer exclusively, *i.e.* no CNFs are formed, and therefore this sample allows detailed characterization of the underlayer. XRD analysis reveals the presence of traces of titanium-silicon carbide and rhodiumsilicide; however, the very low intensity of the diffraction peaks as compared to the Rh signal suggests that the amount is too limited to contribute significantly to the increase in the layer thickness. XPS depth profiling shows that the composition of this layer varies; the top part is rich in carbon and the C/Rh ratio decreases deeper in the layer (Fig. 4). Thus, the underlayer is definitely different from the intermediate micro-porous C layers observed on Ni. Remarkably, SEM (Fig. 3g) is not able to detect any significant texture in the underlayer and therefore the presence of Rh particles of significant size (*e.g.* 10 nm and larger) can be excluded, as such particles would be easily observable in the secondary electron image. Apparently and surprisingly, Rh and carbon are well mixed on the nano level, accounting for the significant increase in thickness.

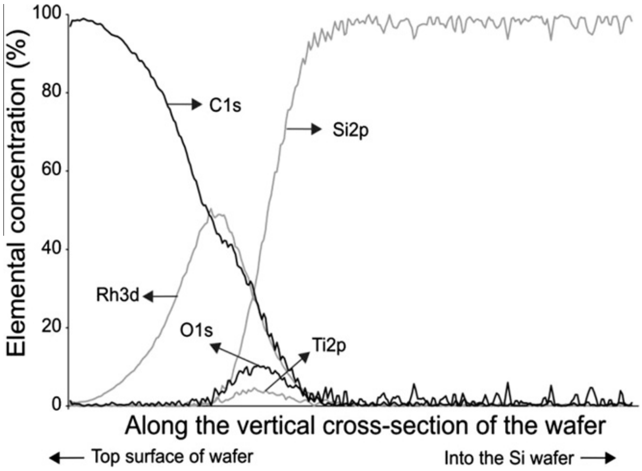

Fig. 4 – Elemental composition as function of the sputter depth according XPS for the sample prepared without H_2 addition.

The average Rh grain size after growing CNFs is clearly smaller than the average grain size in the Rh layer after the pretreatment, as can be seen from Table 1, presenting estimations of crystal sizes based on SEM and X-ray line-broadening. Apparently, deposition of carbon causes fragmentation of Rh grains. Thus, Rh behaves similar to polycrystalline Ni in this respect; fragmentation of large Ni crystals generates Ni nanoparticles, facilitating CNF growth [4,5].

In general, CNF formation is suggested to proceed *via* (i) deposition of carbon on the metal by decomposition of a carbon containing compound, (ii) carbon dissolution and diffusion through the bulk of the metal and (iii) precipitation in the form of graphite at the other side of metal particle [6], although, involvement of surface diffusion can probably not be ruled out. The essential difference between Ni, Co and Fe *versus* precious metals is the fact that the transition metals have reasonable interaction with carbon, or even form stable carbides. In contrast, precious metals interact much weaker with carbon and bulk-carbides are not stable or even nonexistent. However, recent studies in literature suggest that limited dissolution of carbon is possible in metals such as Rh and Pd, especially in the subsurface [7]. Carbon nanostructure formation on other precious metals such as Ru [8], Re [9] and Pd [10] are proposed to proceed by surface diffusion of carbon instead of bulk diffusion.

It is remarkable to observe that deposition of carbon results in fragmentation of the Rh grains in the thin layer, which is a clear indication for significant interaction between Rh and carbon. Also, the shape of Rh particles at the tip of the fiber (Fig. 2a) is very similar to what is usually observed for Ni, including an elongated tail protruding in the fishbone-type fiber (Fig. 2b). Based on these arguments, we conclude that the mechanism for CNF formation on thin Rh layers is partly similar to the case of polycrystalline Ni. On the other hand, CNF growth probably proceeds by (sub-) surface diffusion of carbon instead of bulk diffusion in transition metal particles.

In summary, we have demonstrated synthesis of thin layers of CNFs from a thin layer of Rh metal by catalytic chemical vapor deposition. Interaction of Rh grains with carbon results, surprisingly, in fragmentation of the Rh grains to form nanoparticles, facilitating CNF growth. Rh nanoparticles catalyze the formation of fishbone type CNFs with Rh particles in the tip of the CNFs. Maximum CNF growth is obtained at intermediate hydrogen concentrations, very similar to other metals, *e.g.* Ni. CNFs are immobilized on the surface by an apparently amorphous intermediate layer containing both Rh and C. We suggest that CNF growth mechanism on Rh involves (sub-) surface diffusion of carbon.

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