POLISHING TiN FOR NANOTUBE SYNTHESIS

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Abstract

Carbon nanotubes have excellent mechanical and electrical properties for applications requiring the smallest probe tips in scanning probe microscopy or electron discharge. Large quantities of aligned multi-walled nanotubes are often synthesized on flat substrates made of quartz, but electrically conductive substrates are preferable for field emission applications. Polished substrates made from compacted titanium nitride (TiN), a conductive ceramic traditionally used for coating cutting tools, were previously used to produce excellent field emitters. However, nanotubes could not be synthesized on surfaces sputtered with TiN, suggesting that the topography of polished surfaces might play some role in enabling nanotube synthesis. To test this hypothesis, we synthesized nanotubes on three sets of TiN substrates that were polished with three processes to obtain different surface roughness parameters. Although nanotubes were successfully synthesized on all TiN substrates, the vertical alignment was inferior to those typically synthesized on quartz substrates. The highest degree of alignment was observed on the roughest samples. This paper describes the polishing processes, characterizes the surface topography, and shows nanotubes synthesized on polished TiN surfaces.

Keywords: titanium nitride, polishing, nanotubes, field emission

Introduction

Carbon nanotubes, first identified in 1991 [1], are a hexagonal lattice of carbon atoms similar to a graphene sheet rolled upon itself to form long narrow tubes. The ends of nanotubes are typically closed by a geodesic arrangement of carbon atoms, similar to one-half of another carbon nanostructure called a “buckyball”. Nanotubes are synthesized in inert atmospheres using CVD, pulsed laser vaporization and electric arc discharge [2].

Depending on the synthesis technique, the resulting nanotubes will either be composed of a single layer of atoms or concentric layers of atoms. Nanotubes with a single layer are referred to as single walled nanotubes (SWNTs), and those with multiple layers are referred to as multi-walled nanotubes (MWNTs). SWNTs are usually less than 2 nm in diameter, and MWNTs are typically less than 100 nm in diameter. While SWNTs may be conductors or semiconductors depending on their arrangement of atoms, MWNTs are excellent conductors and are considered ideal electron emitters for many applications. Their small tip diameters enhance the electric field, and in a sealed gas environment they were shown to be robust electrodes [3]. Current applications include flat panel displays, actuators, gas sensors, nano-diodes and transistors, and atomic force microscopy (AFM) probes [4].

Rao et al. have developed a CVD technique to grow aligned MWNTs on several substrate materials at 675°C in a xylene-argon-hydrogen mixture [5]. The aligned nanotubes shown in Fig 1 were synthesized on a quartz substrate using this process. In field emission applications, a conductive substrate is necessary, and so Rao et al. later synthesized nanotubes on polished titanium nitride (TiN), which is a conductive ceramic [6]. Experiments demonstrated that MWNTs on polished TiN substrates were superb field emitters [6]. However, later experiments

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using substrates with sputtered TiN did not successfully grow MWNTs. This suggests that the topography of polished TiN surfaces, which are rougher than sputtered TiN surfaces [7], are more amenable to nanotube growth. The surface parameters of these polished TiN surfaces and any relation to successful synthesis of MWNTs were not known. This paper investigates the 3D surface topography resulting from polishing compacted TiN and its affect on MWNT growth.

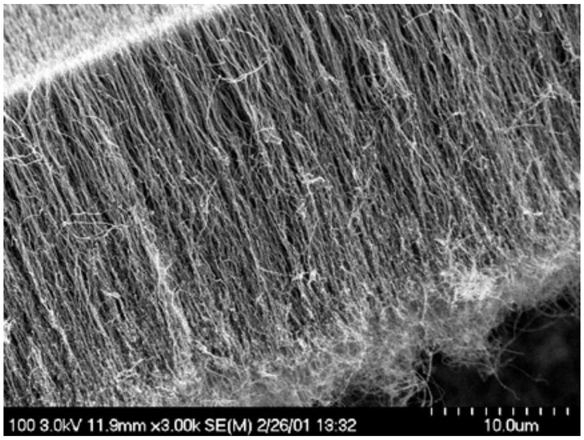

Fig 1: Aligned nanotubes on quartz substrate

Polishing Procedures

We begin with commercially available TiN discs (99.5% pure) used as sputtering targets for coating other surfaces. The targets were either 3.18 mm (0.125 inches) or 6.35 mm (0.25 inches) thick. These targets are formed from TiN powder with particles less than 44 microns in diameter. The powder is pressed and sintered to form a solid approximately 70% dense, with a structure as shown in the scanning electron microscope (SEM) image in Fig 2. 5mm square samples were produced by cutting the targets using wire EDM or a diamond cutoff saw.

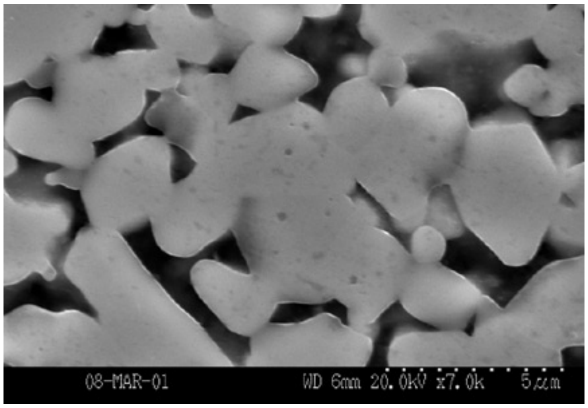

Fig 2: Structure of powder compacted TiN

The samples were labeled and grouped into three sets before grinding and polishing with three different procedures. The procedures were varied for each set to obtain samples with three distinct surface finishes. The duration and the particle size during the final polishing steps were varied. The steps in the finishing procedure for all three sets of samples are shown in Table 1.

Fig 3 is a SEM micrograph of a polished TiN surface viewed at an oblique angle, showing relatively smooth and flat regions interspersed with crevices due to the spacing between particles. It is possible that these crevices, which are not present on sputtered TiN surfaces, may enhance nanotubes growth on polished surfaces.

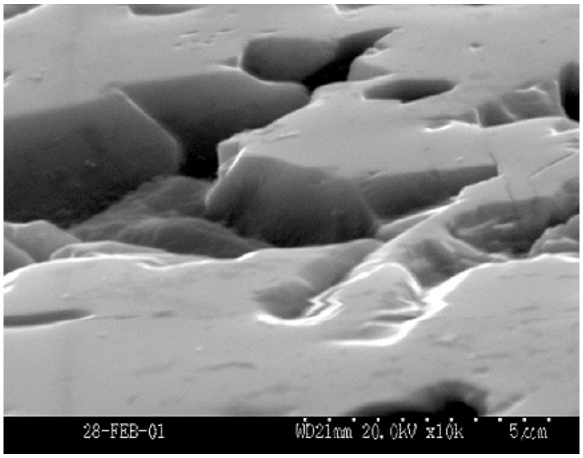

Fig 3: Polished TiN, 75-degree oblique angle

Surface Roughness Measurements

The roughness of the TiN surfaces after polishing was studied with a light microscope, SEM, AFM and a surface profilometer. Light microscope images provide convenient feedback during the polishing process and are easily collected between polishing steps. SEM images give higher resolution and a good indication of feature sizes, but still only provide qualitative information regarding the depth of the features. Atomic force microscope images that show the force on the scanning tip in tapping mode, give quantitative data on specific surface features. The surface profilometer gives quantitative data over a larger area (122 µm x 93µm) and includes surface waviness and roughness. Profilometer measurements in Fig 4 and Fig 5 contrast the surface roughness of samples from Set 1 and Set 2. Roughness parameters as measured with the surface profilometer for the samples from the three sets are shown in Table 2 [8,9].

Table 1: Polishing Procedures for Three Sets of TiN Samples

Step #	Operation	Wheel	Abrasive	Lubricant	t, min.	Force, N
1 (set 1)	Planar grind	MD-Piano 120	Diamond	Water	Plane	120
2	Fine grind 1	MD-Allegro	9 micron DP-suspension	Green/Blue	5	180
3	Fine grind 2	MD-Allegro	3 micron DP-suspension	Green/Blue	10	180
4	Diamond polish	MD-Allegro	1 micron DP-suspension	Green/Blue	8	120
5	Oxide polish	MD-Chem	OP-S or OP-U	-	1	140
1 (set 2)	Planar grind	MD-Piano 120	Diamond	Water	Plane	120
2	Fine grind 1	MD-Allegro	9 micron DP-suspension	Green/Blue	5	180
3	Fine grind 2	MD-Allegro	6 micron DP-suspension	Green/Blue	18	180
1 (set 3)	Planar grind	MD-Piano 120	Diamond	Water	plane	120
2	Fine grind 1	MD-Allegro	9 micron DP-suspension	Green/Blue	5	180
3	Fine grind 2	MD-Allegro	3 micron DP-suspension	Green/Blue	10	180
4	Diamond polish	MD-Allegro	3 micron DP-suspension	Green/Blue	8	150
5	Oxide polish	MD-Chem	OP-S or OP-U	-	1	140

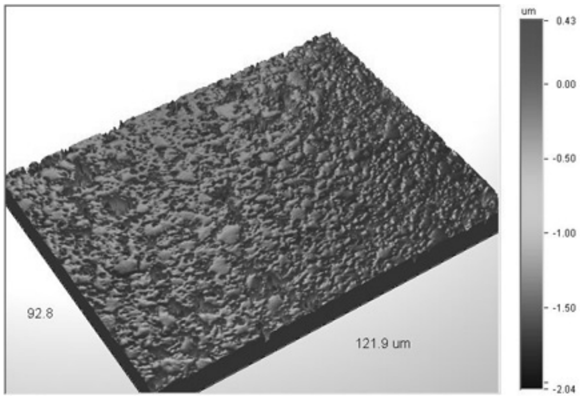

Fig 4: Polished TiN surface, sample set 1.

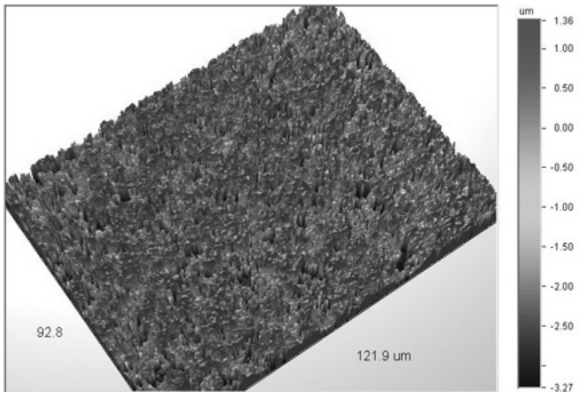

Fig 5: Polished TiN surface, sample set 2

Synthesis of Carbon Nanotubes

Following the polishing process, MWNTs were synthesized on samples from each of the three sets in a 1 m long two-stage reactor [5]. A preheater operating at 200°C heats a mixture of xylene and ferrocene. Argon gas is used to carry this mixture into the reaction chamber, which operates at 675-700°C. After an initial layer of Fe nanoparticles are deposited on the surfaces of the chamber (and any substrates present in the reactor), the nanoparticles catalyze the growth of aligned MWNTs on these surfaces [5].

This technique does not require a separate processing step to seed a catalyst layer on the surface of the substrate since the catalyst is deposited *in-situ* during operation of the reactor. Typical operation times for the reactor are on the order of 2 hours [5,6].

Assessment of Nanotube Alignment

In the case of well-aligned nanotubes (such as Fig 1), a profile image facilitates measurement of the length of nanotubes and density of nanotubes. So after synthesizing nanotubes on the polished surfaces, several cross-sectional cuts were made to achieve a profile view of the aligned nanotubes under the SEM. It is possible to disrupt the alignment of the nanotubes during cutting.

Fig 6 shows aligned nanotubes from a polished TiN substrate from Set 2. For samples in Set 2, typical lengths ranged from 5-10 microns, with knotting in the upper layer. The same style of knotting is observed in the nanotubes synthesized on quarts as shown in Fig 1. On the quartz substrate, nanotube lengths range from 20-100 microns.

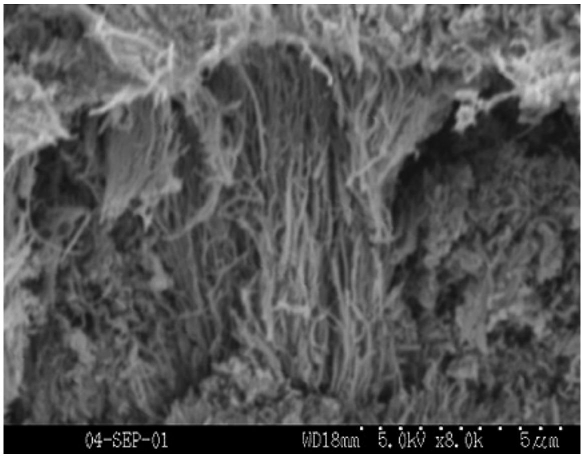

Fig 6. MWNTs on TiN surface, sample set 2

Conclusions

Planar grinding and polishing of TiN is a predictable and repeatable process to achieve smooth surfaces. As indicated by the roughness parameters in Table 2, samples in Set 2 were rougher than samples from Sets 1 and 3. The smoothest TiN surface achieved a "mirror finish" with an Ra of 85 nm, and the roughest surfaces had an Ra of about 400 nm.

MWNTs were synthesized on all polished TiN samples, but none were able to duplicate the same precise alignment observed when synthesizing MWNTs on quartz substrates. The samples that showed some degree of alignment were those in the roughest set (Set 2). Hence, we conclude that some amount of roughness is beneficial when synthesizing MWNTs. This conclusion is in agreement with experimental observations that MWNTs could not be synthesized on smooth TiN sputtered surfaces.

Table 2: Roughness parameters obtained from three different polishing procedures

	Ra	**Rq**	**Rt**	**Rz**	**Rku**	**Rsk**	**Volume**	**Bearing Ratio Htp**
Units	**nm**	**nm**	**nm**	**nm**			**um3**	**Nm**
Set 1	84.48	139.48	2724.64	2211.98	29.81	-3.76	1383.25	2724.64
Set 2	399.78	503.03	4233.09	3769.79	3.97	-0.93	5462.62	4233.09
Set 3	92.47	146.77	3060.34	2355.24	26.56	-3.40	1501.15	3060.34

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