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INVESTIGATING MECHANICAL PROPERTIES OF SILICON CARBIDE COATED CARBON NANOTUBE COMPOSITE AT ELEVATED TEMPERATURES

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ABSTRACT

Silicon carbide (SiC) coated vertically aligned carbon nanotubes (VACNT) are attractive material for fabricating MEMS devices as an alternative for bulk micromachining of SiC. In order to examine the mechanical properties of SiC-CNT composites at high temperatures, we fabricated VACNT micro-pillars with different amounts of SiC coating and performed high-temperature micro-pillar compression on these samples. The indentation result shows that the coating can improve the elastic modulus up to three orders of magnitude. Samples were tested at room temperature, 300°C, 600°C, and 900°C under compressive load. No significant degradation of the mechanical properties was observed at elevated temperatures, demonstrating the harsh environment potential of this composite.

KEYWORDS

SiC-CNT composite, high-temperature, micro-pillar, compression test

INTRODUCTION

In past decades, there has been a growing need for micro-electromechanical systems (MEMS) specifically tailored for harsh environment applications, such as, oil drilling, combustion control, and space exploration. Silicon (Si), the conventional material for MEMS fabrication, can hardly meet the requirements for harsh environments applications. This is because the mechanical properties of Si degrade significantly at elevated temperatures [1, 2].

Silicon carbide (SiC) has drawn much attention as one of the most representative wide bandgap semiconductors. It is well-known for its applications mainly in the field of power electronics, due to its low on-resistance and higher thermal conductivity compared to traditional Si-based devices [3, 4]. In more recent years, researchers have started to utilize SiC as a sensing material for high-temperature and harsh environment applications thanks to its excellent mechanical properties [1, 2, 5-11]. In 2018, Nguyen et al. reported a highly sensitive SiC pressure sensor for cryogenic and elevated temperatures fabricated with the SiC laser machining technique [8]. In 2021, our group reported the first poly-SiC Pirani gauge for vacuum level sensing, which operates up to 750°C [9]. In 2023, Wu et al. reported a piezoresistive MEMS pressure sensor based on 4H-SiC, which works reliably under high-temperature, corrosive, and radiative environments [10]. In the same year, Xu et al. studied the properties of amorphous SiC (a-SiC) and found it has an ultimate tensile strength of over 10 GPa. With a-SiC, a resonator with a quality factor of over 10^8 was fabricated [11]. Although the field of SiC MEMS is rapidly expanding, insufficient SiC bulk micromachining techniques are impeding its further development. SiC is an extremely chemically inert and mechanically stable material, which is challenging to process. Researchers have encountered various problems during SiC processing, including, but not limited to, low etch rate, low selectivity, micro-masking effect, and non-vertical sidewalls. As a result, the current SiC MEMS devices are mostly limited to structures based on SiC thin film technology, such as in [9, 11], or SiC bulk micromachining with a large etching surface as in [8, 10].

To avoid the challenging SiC bulk micromachining process, we have developed a bottom-up process, which uses the vertically aligned carbon nanotube (VACNT) array filled with low-pressure chemical vapor deposited (LPCVD) a-SiC, as an alternative method for conventional SiC micromachining [12]. With the so-called SiC-CNT composite, a thermal actuator was proven to be able to operate up to 450°C. A major advantage of the SiC-CNT composite is that we can fabricate high aspect-ratio (HAR) micro-structures easily. In our previous study, we found that the electrical behavior of the composite is dominated by CNT instead of a-SiC. The mechanical properties of the composite were once investigated by Poelma et al. with nanoindentation, showing that the mechanical properties of the composite can be tuned using the a-SiC thickness [13]. However, the mechanical performance at high temperatures has not been studied.

In this paper, for the first time, the mechanical property of the SiC-CNT composite is characterized by micro-pillar compression. The measured samples are micro-pillars coated by different thicknesses of a-SiC. For each type of sample, the compressions are performed up to 900°C.

SAMPLE PREPARATION

The fabrication of the test structures involves the growth of the pristine VACNT pillars and then filling them with LPCVD amorphous-SiC (a-SiC). First of all, an oxide layer is grown on the Si (100) wafer as a diffusion barrier. On top of the oxide, a patterned Al_2O_3 (20 nm) and Fe (2 nm) bilayer is fabricated by the lift-off process. Then, the VACNT is grown by a Blackmagic CVD system. The detailed CNT growth recipe can be found in [12]. The VACNT pillar has a nominal height of 20 μm and a diameter of 20 μm (Figure 1a). After the VACNT growth,

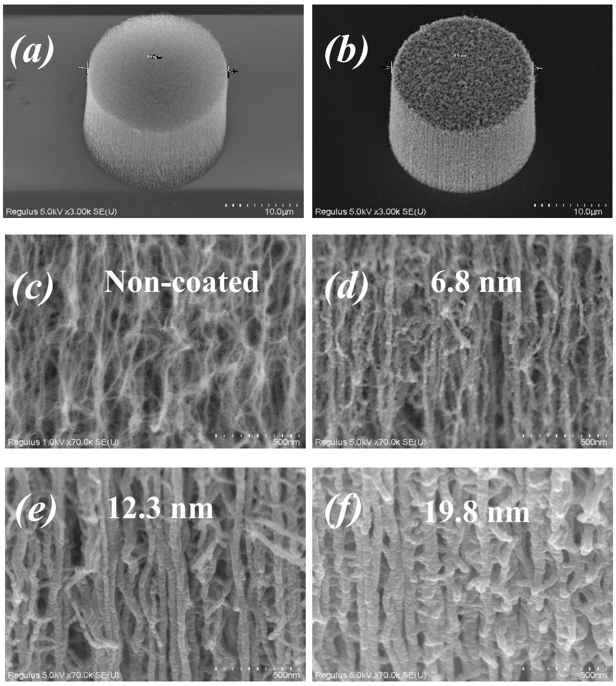

Figure 1. The SEM images of VACNT pillars (a) before and (b) after being coated with a-SiC, and zoom-in views for surfaces of different coating thickness: (c) non-coated, (d) 6.8 nm, (e) 12.3nm, and (f) 19.8 nm.

the wafer with CNT is coated with LPCVD a-SiC, and the filled pillar is shown in Figure 1b. The pillars have different coating thicknesses by applying varied deposition time (non-coated, 6.8 nm, 12.3 nm, and 19.8 nm), and the coated surface is demonstrated in Figure 1c-1f. The thickness of a-SiC was measured by performing ellipsometry on Si dummy wafer.

TEST SETUP

High-temperature pillar compression experiments were performed on an InSEM-HT System equipped with an InForce 50 actuator from KLA Corporation (Milpitas,

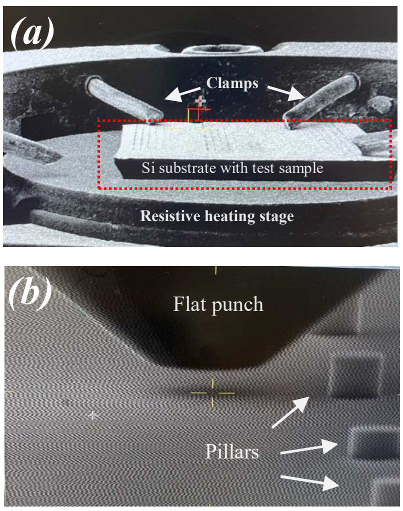

Figure 2. (a) Heating stage with the sample loaded, where the pillars are fabricated on Si substrate; (b) The tip used to apply the force was a boron carbide (B_4C) flat punch from Synton-MDP (Nidau, Switzerland).

CA, USA). The device is intrinsically load-controlled and capable of applying up to 50 mN of force at a maximum travel of 20 µm. The experiments were performed in a pseudo-displacement-controlled manner, where a feedback loop was used to change the applied force to obtain a constant deformation strain rate. The tip used to apply the force was a 40 µm diameter boron carbide (B_4C) flat punch from Synton-MDP (Nidau, Switzerland). The system uses resistive heating on both the punch and the sample. Thereby, the sample is clamped onto a resistive heating plate (see Figure 2a). The sample temperature is measured in a slotted plate between the sample and the heating plate. The tip temperature is measured on the shaft of the actuator, just behind the actual tip. The experiments were run under ultra-high vacuum conditions inside the chamber of a Vega 3 SEM from TESCAN ORSAY HOLDING (Brno, Czech Republic). The SEM was used for in-situ positioning and imaging of the tests. Moreover, some tests were performed with the electron beam off to check for potential influences of the electron bombardment on the mechanical behavior, however, no significant difference was observed.

RESULTS AND DISCUSSIONS

Compression experiments were performed at room temperature, 300°C, 600°C, and 900°C. The loading was performed at 100 nm/s, resulting in a strain rate of 5×10^{-3} s^{-1}. For each type of pillar and set of parameters, at least three tests up to 20 % strain and one test up to 50 % strain were performed (unless the pillars fractured before achieving these strains).

The heating stage showed a misalignment of ca. 2.3° compared to being perfectly perpendicular to the indenter-axis; this error can be seen by the upwards curvature of the stress-strain curve until the entire pillar surface is loaded, and therefore, the measured stiffness is equal to the elastic modulus of the pillar (see Figure 3).

The measurements were corrected for the compliance

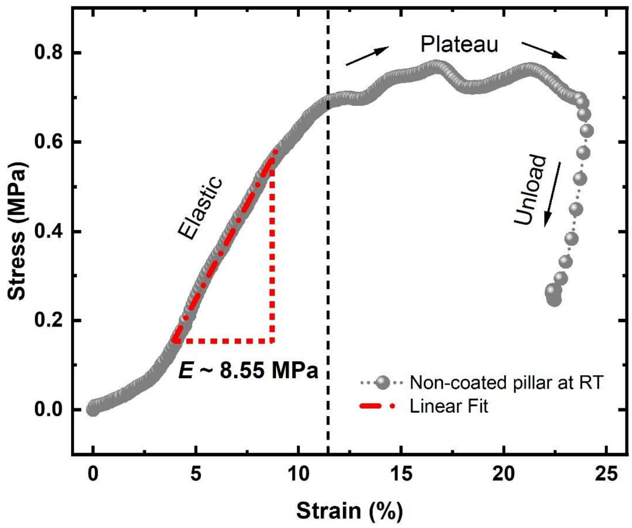

Figure 3. The typical stress-strain curve of a non-coated VACNT pillar. Initially, an elastic regime can be observed (E ~ 8.55 MPa). Then, buckling occurs, where the curve features a wavy plateau.

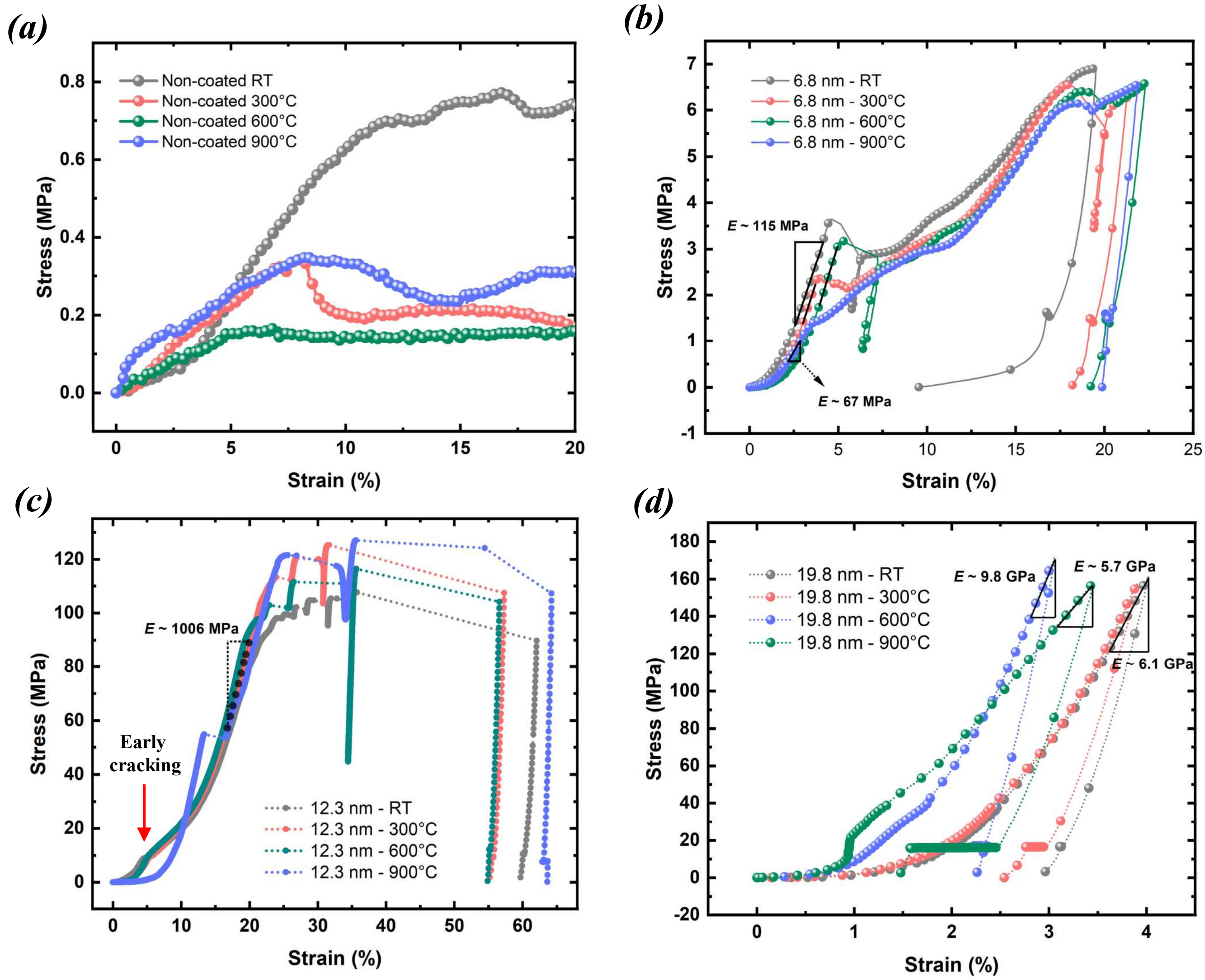

Fig. 4. (a) The stress-strain curve of non-coated VACNT pillars at RT, 300°C, 600°C, and 900°C. The stress-strain curves of VACNT pillars at RT, 300°C, 600°C, and 900°C with a SiC coating thickness of (b) 6.8, (c) 12.3, and (d) 19.8 nm.

of the substrate according to the Sneddon formula for a cylinder being pressed elastically into a flat surface, as shown below [14]:

$$h_{si} = \frac{P \cdot (1-\nu^2)}{E \cdot d}$$

where h_{si} is the sink in depth, P is the applied load, ν is the substrate's Poisson's ratio, E is the substrate's elastic modulus and d is the pillar's diameter.

Intrinsic VACNT

Figure 3 shows the typical stress-strain curve of a non-coated CNT pillar under the uniaxial compression. After the contact establishment, the first section of the curve (where the strain is less than 11.5%) reveals a linear elastic behavior. The linear fitting of this section indicates that the Young's modulus of non-coated VACNT is ~8.55 MPa. With increasing strain, the sample reaches the yield point and the stress-strain curve enters a wavy plateau stage. The plateau section corresponds to the plastic collapse and the formation of buckles in the intrinsic VACNT pillars, which is a unique mechanical response with intrinsic VACNT pillars [13, 15].

The miro-pillar compression results at elevated temperatures are given in Figure 4a. At higher temperatures, the non-coated pillar follows a similar mechanical response compared to room temperature, however, with lower strength. The fluctuating curve after the elastic response indicates that the buckling also happens at high temperatures. However, the yield point took place at lower stress, and this implies a mechanical degradation of pure CNT at high temperatures. This might be caused by the increase in dislocation movement of atoms at high temperatures, resulting in an easier deformation.

VACNT coated with a-SiC

Figure 4b demonstrates the stress-strain curves of CNT pillars coated with 6.8 nm a-SiC at different temperatures. Obviously, in the linear elastic range the strength of the material is enhanced by the filler. At room temperature, a distinct first cracking event (triggered by the misalignment) resulting in a load drop can be observed after the elastic regime at about 5% of strain. This, however, can not be observed at 900°C, which suggests no cracking happened anymore.

Figure 4c shows the stress-strain curves of CNT pillars coated with 12.3 nm a-SiC at different temperatures. An early cracking event could be seen at around 4% of strain from room temperature to 600°C. After early cracking, the stress increases rapidly and smoothly. At strains > 20 %, repeated small cracking events occur until the samples fail with a major crack at > 35% strain. At 900°C, the pillar experiences a load drop before the yield point,

The micro-compression results of CNT pillars with the thickest coating are given in Figure 4d. The mechanical strength of the pillar demonstrates a further improvement compared to the thinner coating. The pillars do not yield even when the maximum load of the indenter is applied. Only some plastic deformation is seen due to the misalignment angle leading to the pillar not being loaded homogeneously at such low strains. The difference in Young's modulus at different temperatures could be a result of drift effect, and the Young's modulus is likely to underestimated due to the misalignment at these low strains.

Within this limited deformation extent, no significant differences in the probed temperature range are evident. As can be seen from the elastic regime, the Young's modulus of SiC-CNT composite coated by 19.8 nm thick SiC has increased around 3 orders of magnitude compared to non-coated CNT pillars.

CONCLUSION

In this paper, we have fabricated and characterized micro-pillars based on SiC-CNT composite. The mechanical property of the SiC-CNT composite was studied by micro-compression up to 900°C. The result shows that the strength of the SiC-CNT composite generally increases with the coating thickness of LPCVD a-SiC. For the thickest coating (19.8 nm), the Young's modulus enhances 3 orders of magnitude compared to the original VACNT. The stress-strain curves of the tested pillars at elevated temperatures follow a similar behavior as at room temperature. This implies that the mechanical behavior of the SiC-CNT composite does not degrade significantly at high temperatures.

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