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DEPOSITION OF VARIOUS METALS ON VERTICALLY-ALIGNED SINGLE-WALLED CARBON NANOTUBES

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ABSTRACT

Evaporation of different metals (Au, Ti, Al and Pd) onto Vertically-Aligned Single-Walled Carbon Nanotubes (VASWNT) has been studied. Observations through Scanning Electron Microscopy (SEM) showed a clear metal-dependence of the deposition layer structure on top of the VASWNT, reflecting the variation of wettability and cohesive energy of each metal. These characteristics also influence the structures of the metal penetrated through the top surface into VASWNT film, where metal forms particles inside VASWNT film except for Ti. A simple annealing technique to remove metals penetrated in the SWNT films is demonstrated. Some peculiar morphologies found during the processes are also presented.

INTRODUCTION

Single-walled carbon nanotubes (SWNTs) have attracted much attention as promising materials for next-generation thermal and electrical devices due to their extraordinary thermal and electrical properties. Recent development in the alcohol catalytic chemical vapor deposition (ACCVD) method [1] have realized the growth of vertically-aligned SWNT (VASWNT) films [2, 3], which expanded the range of prospective applications. One important example in terms of thermal device applications is to utilize their expected high thermal conductivity to promote heat transfer in order to handle severe thermal management in small-scale electric devices. While detailed heat conduction characteristics of SWNTs are widely discussed [4], they are far from being revealed. Therefore, it is our urgent task to characterize these properties of the VASWNT film.

In the course of characterizing thermal and electrical properties of a VASWNT film, the measurement methods often require deposition of a metal film on top of the VASWNT film as electrodes or as heating sources. However, our first attempt of sample preparation for thermal conductivity measurement [5] resulted in formation of a peculiar metal structure on the surface and suggested that the process may involve certain complexity and this evaporation process need to be studied further first.

In this work, we evaporated several metals onto VASWNT, in order to identify the best experimental condition for the flatness of the metal films and the fundamentals of deposition process, which includes nanotube-metal interaction. We also compared our results with those of the metal evaporation on independent SWNT [6].

EXPERIMENTAL

First, VASWNT films on a quartz substrate were synthesized by using dip-coating method and ACCVD [2, 3]. Secondly, the VASWNT films were placed inside the resistive evaporation equipment (ULVAC VPC-260F) and different metals were evaporated onto the samples. The samples were controlled to keep room temperature or 300˚C during the deposition.

After the evaporation, we annealed the metal deposited films at 440˚C or 600˚C with an intention to improve the flatness of the metal layers. [2, 3]. The annealing process was carried out in 1 atmospheric pressure Ar or in vacuum for 440˚C or 600˚C annealing temperature, respectively. The annealing was done by first inserting the VASWNT-metal samples in the furnace, heating it up to desired temperature, then cooling down the furnace.

In the former case, with 440˚C annealing temperature, the heating rate was in average 40˚C/min until reaching 400˚C. Then the heating rate was reduced to 2˚C/min on heating the sample from 400˚C to 440˚C. As for the latter case with 600˚C annealing temperature, the heating rate was kept almost constant at 30˚C/min until the furnace temperature reaches 600˚C.

RESULTS AND DISCUSSIONS

Room temperature deposition

Figures 1a, 1b, 1c, 1d show SEM photos of the cross-sections of VASWNTs with Au, Ti, Al and Pd deposited on the top surface, respectively. The SEM photos were taken using JEOL JSM-7000F. The nominal deposition thickness and the deposition rate were measured by ULVAC CRTM-6000 thickness meter. For Au (Fig. 1a), the deposition thickness and rate was 150 nm and 0.3 nm/s. For Ti, Al and Pd (Fig. 1b, 1c and 1d), the thickness and rate were nominally 100 nm and 0.2 nm/s. The SEM photos clearly show the differences in the structures of the metal layers among different metals.

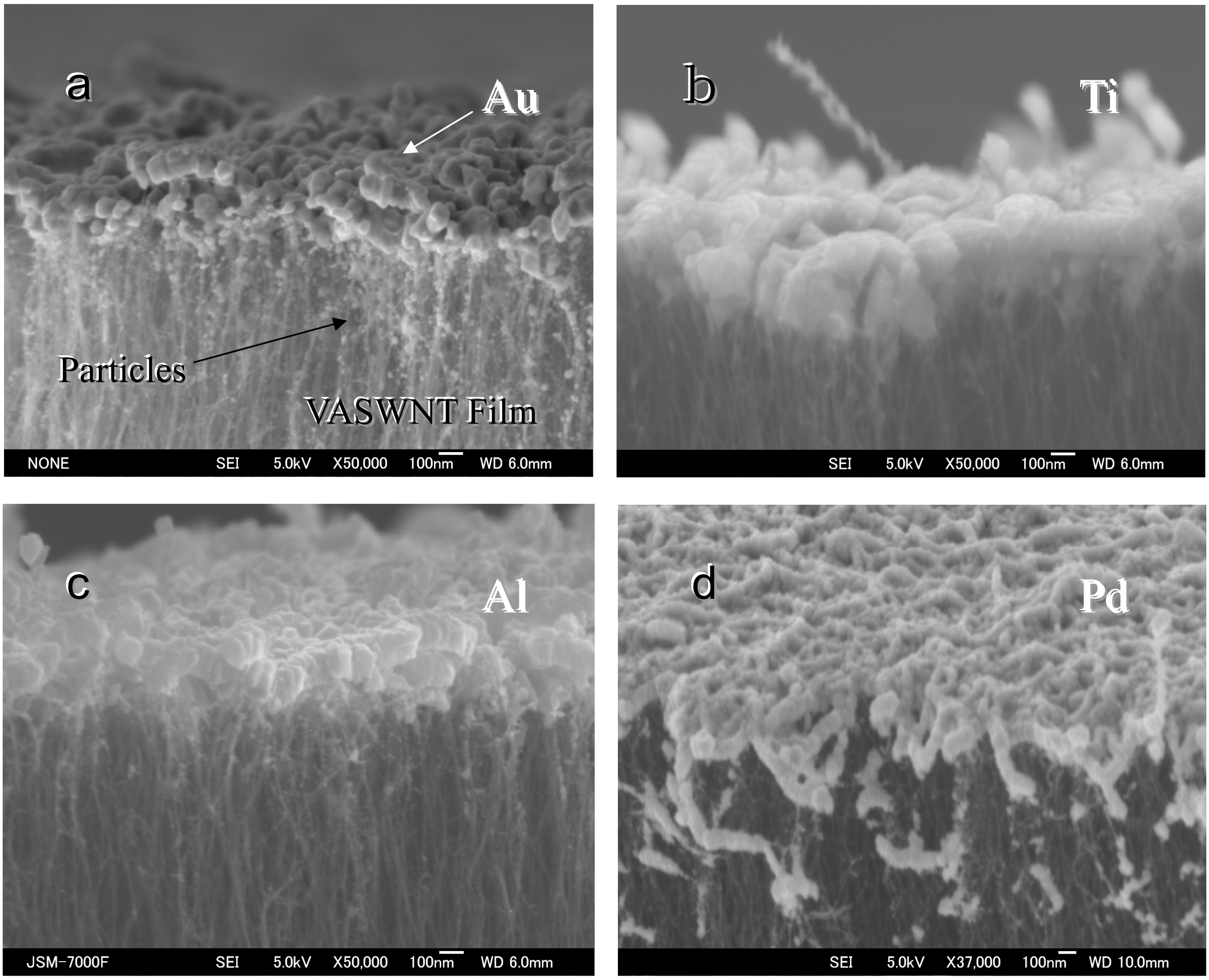

Fig. 1. Images of evaporated metals onto VASWNT films: (a) Au nominally 150 nm thick, rate 0.3 nm/s, (b) Ti nominally 100 nm thick, rate 0.2 nm/s, (c) Al nominally 100nm thick, rate 0.2 nm/s, (d) Pd nominally 100nm thick, rate 0.2 nm/s. These depositions are done under room temperature condition.

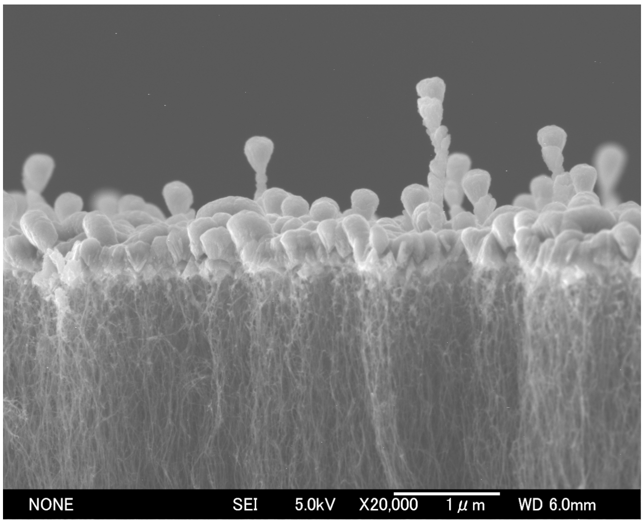

Fig. 2. Image of Ti evaporated onto VASWNT film, nominally 280 nm thick, at room temperature condition.

Formations of grains were clearly observed for Au (Fig. 1a) and Al (Fig. 1c). This reflects strong cohesion between metal-metal and/or relatively poorer affinity between metals and top surface of VASWNT. Grains of the Au appear to be more isolated and closer to spheres compared with those of Al. On the other hand, formation of grains was less distinct for Ti (Fig. 1b) and Pd (Fig. 1d), which suggests better interfacial affinity than the former two cases. The above observations suggest the order of affinity; Ti, Pd > Al >Au.

Figure 2 shows Ti deposited onto a VASWNT film. Here, the thickness of the Ti layer was nominally 280 nm and the deposition was done at room temperature condition. In the figure, mushroom like structures can be observed on the top surface of the metal layer. The structures grow vertically from the top surface presumably being guided by SWNT bundles on the top surface. The figure also shows that ripening of metal structure on the top edge of the vertically grown metal structures. Note that the size of the structure is much larger than that of the grains seen in any cases in Fig. 1. While further investigation is needed to understand the details of the structure formation including the ripening mechanism, the current observation suggests a high affinity of Ti on SWNT bundles.

As seen in Fig. 1a, metal particles were clearly observed inside the VASWNT film in case of Au deposition. This is an evidence of metal evaporants penetrating into the VASWNT films. Similarly, metal particles were observed inside VASWNT films in cases of Al (Fig. 1c) and Pd (Fig. 1d), though the particle sizes were smaller than those of Au. On the other hand, the metal particles were not visible inside the VASWNT film for Ti (Fig. 1b, Fig. 2). However, this may not mean the absence of metal inside the VASWNT. Considering the high wettability of Ti on SWNTs seen in the Ti layers on top surfaces of VASWNTs (Fig. 1b, Fig. 2), it should be more natural to state that metal were not observed inside the

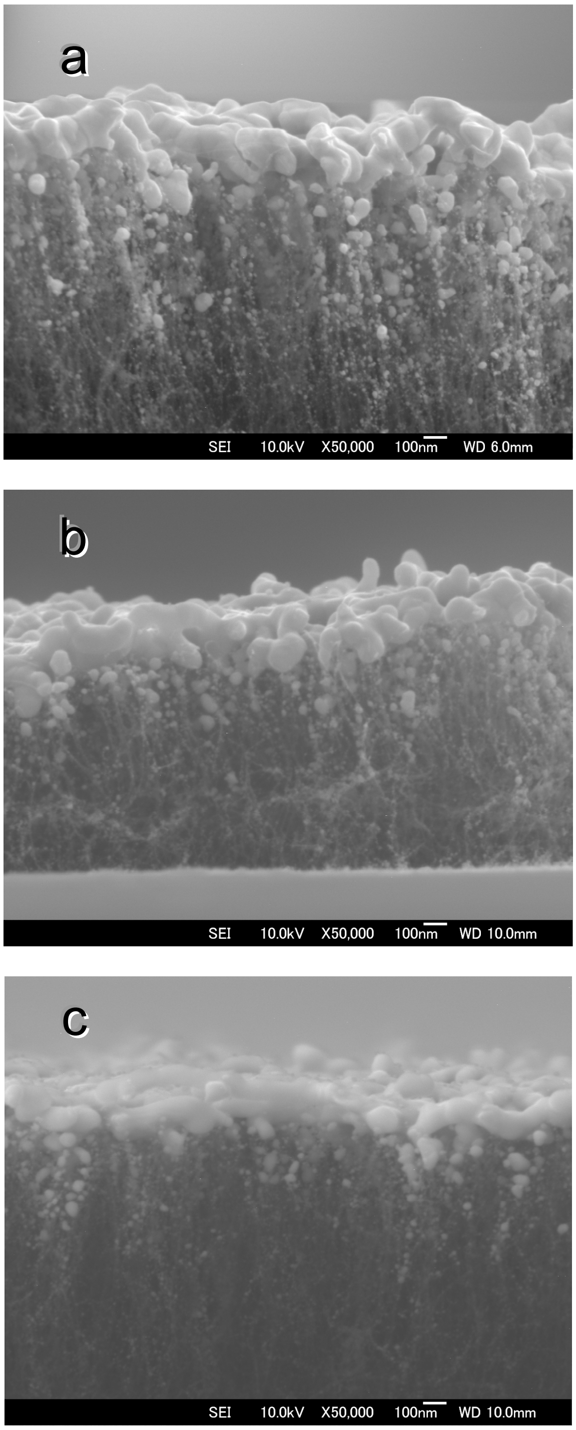

Fig. 3. Images of Au evaporated metals onto VASWNT films with the temperature controlled condition, or the annealing: (a) deposition done on the Fig. 1a VASWNT film temperature controlled to keep 300˚C. (b) Annealed Fig. 1a under 440˚C Ar 1atm pressure, (c) Annealed Fig. 1a under 600˚C vacuum.

VASWNT in a particle form because Ti has wetted the carbon nanotube bundles. The current result suggests that the binding energies between metal and SWNT bundles are, $E_{Ti} > E_{Pd} > E_{Al} > E_{Au}$ as suggested by Zhang et al (6). The agreement with the work on individual SWNT (6) implies that the metal deposition on a film of bundled SWNTs is characterized by interaction properties of metal and an individual SWNT.

From the above mentioned grain size of the metal layers and the affinity of the carbon nanotube bundles to the metals, Ti is the best metal for flat metal surfaces on top of VASWNT films. However, further investigation is still needed for our aim to fabricate electrically and thermally low resistive boundary between VASWNT film and the metal part.

High temperature deposition and annealing

On further pursuing our aim of achieving metal deposition layers with sufficient flatness and contact to VASWNTs, the deposition or the annealing were performed under high temperature ranging from 300˚C-600˚C. By choosing the metal with poorest affinity to VASWNT i.e. Au, we have tested two different methods of temperature control. One is to carry out the deposition under high temperature by heating up the sample holder during the evaporation and the other is to anneal the sample at high temperature after performing the deposition at room temperature.

Fig. 3a shows the result of Au deposition on a VASWNT film with temperature controlled at 300˚C. Compared with the case with room temperature deposition (Fig. 1a), the top surface is flatter with less spherical grains. Fig. 3b shows the consequence of 440˚C annealing applied to the Au layer on a VASWNT film deposited at room temperature. Fig. 3c shows the results of 600˚C annealing applied to Au on VASWNT film deposited at room temperature.

From the SEM photos for higher temperature conditions, we see two phenomena. One is that the top surface part becomes flatter. Another is that, inside the VASWNT film, the large particles become more spherical and the small particles disappeared. We think the cause of the latter phenomenon to be following: The smaller particles obtained kinetic energy from high temperature caused by annealing, causing migration. Being larger particles is energetically more stable compared with being smaller particles, this causes merging to the larger particles. This process is the Ostwald ripening process [7].

In the course of testing various annealing conditions, we occasionally found peculiar morphologies such as formation of patches of metal layers shown in Fig. 4. This structure was obtained when annealing the sample with relatively high heating speed. In this case, the annealing process was following: First, the sample was kept outside the heating chamber until the temperature reached 600˚C. Secondly, the sample was inserted into the chamber by magnets. Thirdly, the sample was annealed for 10 minutes. Fig. 4 suggests that SWNTs have been dragged by Au metal condensating at high temperature. This results in rupture of the VASWNT film.

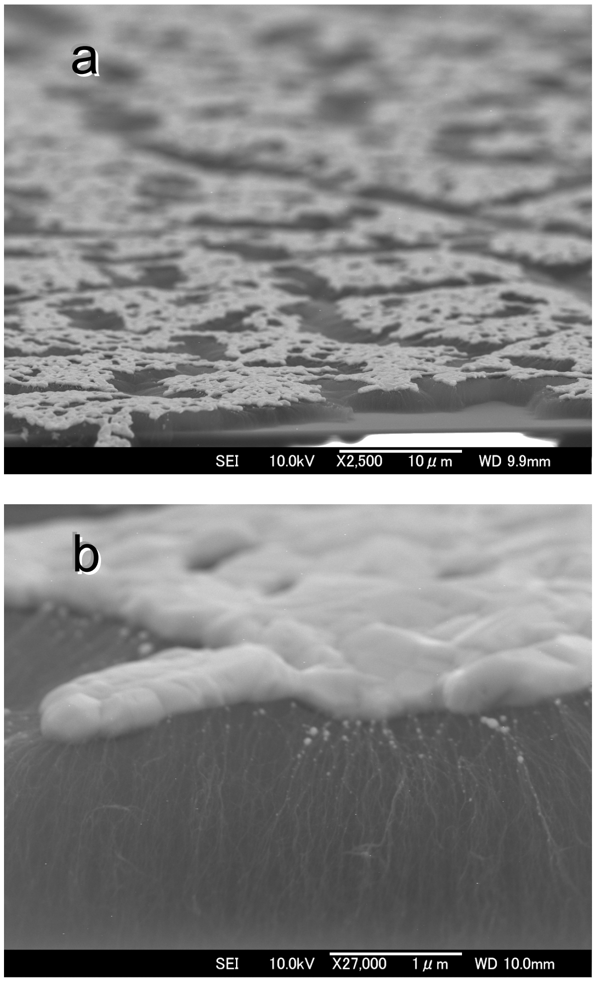

Fig. 4. Some images taken during this research: (a) 600˚C 10 minutes annealing of Au deposited VASWNT film in Ar 1atm pressure. (b) magnified view of Fig. 4a.

CONCLUSIONS

The study reports deposition of various metal (Au, Ti, Al and Pd) on VASWNT films. The structures of the deposited metal on VASWNTs were investigated based on SEM observations. The results showed distinct metal-dependence of the structure of the deposition layer on the top surface, which can be attributed to the variation of wettability and cohesive energy of each metal. Metal evaporants were also found to penetrate into the VASWNT film and form particles in case of Au, Al, Pd. Metal with larger grains and flat surface is identified to be Ti. For the case of Au deposition, annealing process was demonstrated to be effective for further surface flattening and reducing the amount of metal particles inside VASWNT films. Annealing also gave rise to peculiar morphology. Further investigation should be done to achieve best electrically and thermally low resistive surface.

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