SURFACE PROPERTIES OF ALUMINIUM OXIDE SUPPORT LAYER USED FOR VERTICALLY ALIGNED SINGLE-WALLED CARBON NANOTUBE GROWTH

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Surface properties of aluminum oxide support layer used for vertically aligned single-walled carbon nanotube growth

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INTRODUCTION

During the last two decades, carbon nanotubes (CNTs) have received much attention from both the scientific and industrial communities due to their structural properties and the unique morphology. There also has been growing interest in densely packed or vertically aligned single-walled CNT (VA-SWCNT) because of their suitability in high potential applications such as supercapacitors, electrodes for lithium-ion batteries, and nanotube-polymer composites [1, 2]. Well aligned CNT arrays on the substrates offer morphology advantages for those applications compared to those with random and entangled form of CNT that required modification or adjustment [3]. Regardless of the growth method, CNT formation strongly depends on catalytic activity and catalyst lifetime [4, 5]. A lot of literature has been discussing the function and advantages of catalyst-support material, especially the metal oxide layer. Among them, aluminum oxide (Al-O), including alumina (Al_2O_3) is said to have appropriate surface condition (physically and/or chemically) to support metal catalyst nanoparticles for well-organized CNT growth. In this paper, we report the surface properties of Al films oxidized under various experimental conditions. The samples were analyzed by X-ray photoelectron spectroscopy (XPS), atomic force microscopy (AFM), and spectroscopic ellipsometry (SE).

EXPERIMENTAL

First, Si (100) wafer with thermal oxide layer (400 nm) was used as substrate. The Al thin films of 20 nm nominal thickness were deposited using electron beam physical vapor deposition (EBPVD) at 10^{-4} Pa [6]. For the formation of thermally-oxidized Al-O, deposited Al was first naturally-oxidized at room temperature for 2 hours. Then, the substrate was subsequently transferred to chemical vapor deposition (CVD) reactor used for CNT growth, and thermally oxidized at 400 °C in static air for 10 min. All Al-O films were characterized by tapping mode AFM (Seiko Instruments Inc.) and XPS (Fison Instruments S-PROBE ESCA).

XPS measurements were performed with Al Kα (1486.6 eV) as the X-ray source and the samples were analyzed at 90 ° take-off angle to the surface. The photoelectron binding energy (BE) was calibrated using C 1s narrow spectrum, at 284.6 eV, and chamber pressure during the measurement was 10^{-7} Pa. For comparison and clarity, Al-T sample coated with 0.5 nm Co (Co/Al-T) was also characterized. Detailed surface chemical states of Co/Al-T were investigated by means of XPS analysis.

RESULTS AND DISCUSSION

From different Al-O films, thermally-oxidized Al-O has the most appropriate surface properties to support Co catalyst during alcohol catalytic CVD. The results suggested that low Al metal (or high Al oxide) composition ratio ($I_{metal}/I_{oxide} < 0.2$) and high surface roughness (> 3 nm) of Al-O layers are essential for VA-SWCNT growth. Effective contact area and diffusion behavior of Co catalyst is strongly correlates to the surface roughness of support layer. And, significant variations in CNT growth results are also suggested to be due to the alteration of Co catalyst electronic structure caused by different Al-O surface chemical states. From XPS *ex-situ* measurements, the entire EB-deposited Al metal was completely-oxidized, Co transformed into small particles and partial reduction of Co oxide might have been occurred. Although Co could be re-oxidized due to atmospheric oxygen before XPS measurement, relative relation of Co oxidation states reveals the role of Co oxide as catalyst. Both Co oxide and metallic states are possibly essential for ethanol decomposition and CNT nucleation. Approximation of Al, C, and O compositions showed that the as-prepared Al-O surface is an electron-acceptor-dominated surface where the formation of active catalyst could be enhanced.
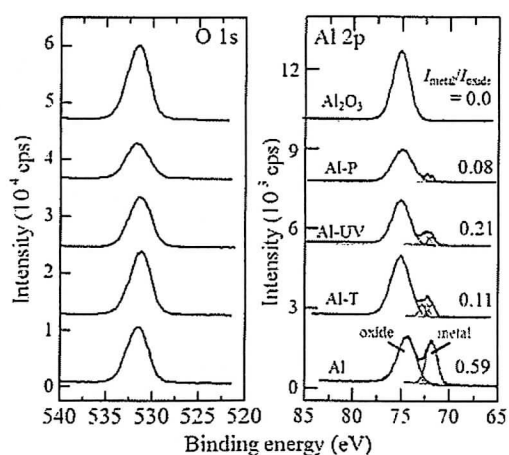

Figure: XPS analysis of 20 nm as-deposited Al films, oxidized samples from different oxidation methods, and as-deposited alumina.

CONCLUSION

Thermally-oxidized Al-O has the most appropriate surface properties to support Co catalyst during ACCVD. Effective contact area and diffusion behavior of Co catalyst is strongly correlates to the surface roughness of support layer. And, significant variations in CNT growth results are also suggested to be due to the alteration of Co catalyst electronic structure caused by different Al-O surface chemical states. Relative relation of Co oxidation states reveals the role of Co oxide as catalyst. Both Co oxide and metallic states are possibly essential for ethanol decomposition and CNT nucleation. Different morphology and surface chemical states of the support layer (in this work, Al-O) may cause variations in CNT growth performance. Oxygen-rich Al-O films could also be essential for VA-SWCNT growth using ethanol-based CVD growth process.

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