CVD growth control of single-walled carbon nanotubes

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Abstract— Chemical vapor deposition (CVD) of single-walled carbon nanotubes (SWNTs) has been improved in growth controllability for the practical application in electronic and optical devices. Vertically aligned growth of nitrogen-doped and small-diameter SWNTs and horizontally aligned growth on crystal quartz are described. By developing the patterned growth technique, transparent and flexible field effect transistors (FET) are demonstrated using as-grown SWNTs employed as source, drain and gate electrodes as well as channel.

I. Introduction

Recent progress in chemical vapor deposition (CVD) growth of single-walled carbon nanotubes (SWNT) using alcohol as carbon source [1] is discussed. The diameter control, growth alignment control (vertical or horizontal to a substrate) and patterned growth are developed. The diameter was relatively small (around 0.7 nm) within relatively narrow range for our original ACCVD [1] using metal catalysts supported on zeolite particles. However, the diameter is much larger (around 2.1 nm) with wider distribution when we used the vertically aligned condition [2]. The vertically aligned small diameter SWNTs was finally achieved by adding acetonitrile to ethanol. At the same time, SWNT was filled with nitrogen gas and the tube wall was also doped with nitrogen. On the other hand, mechanism of horizontally aligned growth of SWNTs on crystal quartz was revealed that the close-packed atomic structure in *R*-plane was responsible to the alignment. Several techniques were developed for the patterned growth of SWNTs by patterning catalyst on a substrate. Combining these growth controlled techniques, transparent and flexible field effect transistors (FET) are demonstrated using as-grown SWNTs employed as source, drain and gate electrodes as well as channel.

II. Patterned Growth and Small Diameter VA-SWNTs

High-quality VA-SWNT patterns can be grown by conventional technique. Negatively patterned removal of SiO_2 layer by photo-lithography on Si/SiO_2 substrate results the growth of VA-SWNT only from SiO_2 region. The sintering of catalyst metal into Si at high temperature is the reason for the selective growth. The new approach [3] is based on the substrate wettability, which is found to be critical for the yield of SWNTs. On an OH-terminated hydrophilic Si/SiO_2 surface, the growth can be promoted by 10 times, but can be completely suppressed on a CH_3-terminated hydrophobic surface. Selective surface modification is utilized to localize the growth of SWNTs. This new technique has advantages in improved simplicity and potentially better resolution compared to conventional lithography.

Recently, a strikingly small diameter (around 0.7 nm) VA-SWNTs was achieved by mixing acetonitrile to ethanol feedstock as shown in Fig. 1 [4]. With increasing acetonitrile concentration in the feedstock, nitrogen content increased until saturating at approximately one atomic percent. The incorporation of nitrogen correlates with a significant diameter reduction from a mean diameter of 2.1 nm down to 0.7 nm. We found that the majority of nitrogen was in N_2 gas form within the small diameter SWNTs. Only about 0.2 % of N_2 was incorporated to the nanotube walls. The diameter range was also confirmed with UV-Vis-NIR absorption and TEM observation.

III. Horizontally Aligned Growth on Crystal Quartz

We used both R-cut and R-face crystal quartz substrates for the efficient growth of horizontally aligned SWNTs [5]. The R-plane (10-11) is one of the low-index crystallographic planes of crystal quartz. The surface cut from a synthetic quartz block parallel to the R-plane was used as R-cut substrates, and the exposed R-plane was used as R-face substrates. We elucidated that the atomic structure of the R-plane causes the alignment of the SWNTs. While a step-and-

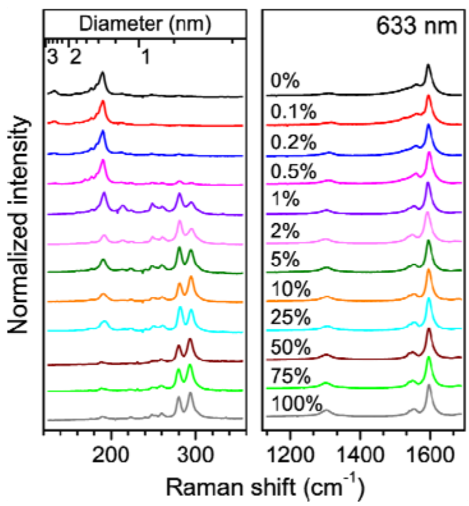

Figure 1. Resonance Raman spectra at 633 nm excitation of VA-SWCNT arrays grown using ethanol-acetonitrile mixture, with different acetonitrile concentrations.

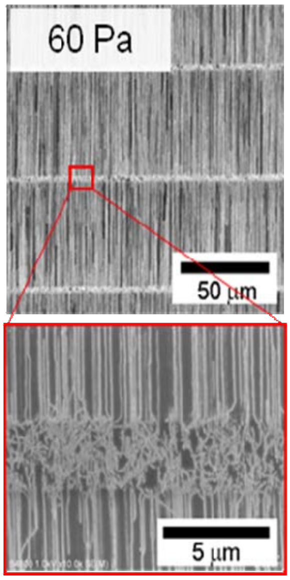

Figure 2. Density controlled CVD growth of horizontally aligned SWNTs on R-cut crystal quarts substrate.

terrace structure clearly appeared on R-face substrates, SWNTs were aligned on the terraced area of the R-plane, regardless of the direction of the step edges. Comparison between R-face and ST-cut substrates suggests that the ST-cut surface can be considered as a collection of tiny r-plane (01-11) domains, which are very similar to the R-plane (10-11). We found the density of horizontally aligned SWNTs depends on partial pressures of carbon source gas [6]. We also examined the time devolution of horizontally aligned SWNT. By extending and broadening the distribution of the incubation time, high-density horizontally aligned SWNTs were achieved as shown in Fig. 2.

IV. All CNT Field Effect Transistor

Carbon nanotube FET is a promising candidate for future electronic devices; however, its fabrication process is still challenging. We have demonstrated CNT-FET using as-grown SWNTs for the channel as well as both source and drain electrodes. The underlying Si substrate was employed as the back-gate electrode. Patterned VA-SWNTs was used for electrodes [7]. The electrodes and channel were grown simultaneously in one CVD process. The resulting FETs exhibited I_{ON}/I_{OFF} ratios exceeding 10^6 and a maximum ON-state current of more than 13 µA.

Finally, we demonstrated polymer-laminated, transparent, all-carbon-nanotube FET, making use of the flexible yet robust nature of SWNTs as shown in Fig. 3. All components of the FET (active channel, electrodes, dielectric layer, and substrate) consist of carbon-based materials. The use of a plastic substrate that is considerably thinner than those used in other flexible CNT-FETs allowed our devices to be highly deformable without degradation of electrical properties [8].

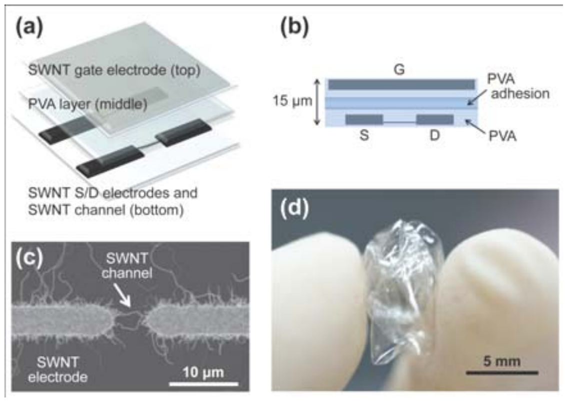

Figure 3. (a) Schematic of the layered structure of fabricated transparent all-CNT-FETs. (b) Schematic cross-section diagram of the device. (c) SEM image of the FET channel region obtained prior to removal from the master Si substrate. (d) Photograph of a crumpled, yet functional, all-CNT-FET device.

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