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A betavoltaic microcell based on Au/s-SWCNTs/Ti Schottky junction

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ABSTRACT

This paper reports a new type betavoltaic (BV) microcell based on intrinsic p-type semiconductive single-walled carbon nanotubes (s-SWCNTs). Our device composes of Au and Ti asymmetrical electrode pairs with s-SWCNTs laid over them forming Schottky junction with Ti and ohmic contact with Au. SWCNT bundles were self-assembled between Au and Ti electrodes by Dieletrophoretic (DEP) technique, and metallic SWCNTs (m-SWCNTs) were selectively eliminated by current-induced electrical breakdown method. 3.3 mCi/cm^2 thin-film radioisotope ^{63}Ni serves as beta particles source, with 100-year half-time and low toxicity. Test results show that SWCNTs BV microcell has the open circuit voltage (V_{OC}) of 26 mV, short circuit current density (J_{SC}) of 2.19 μA/cm^2 and energy conversion efficiency (η) of 5.20%.

1. Introduction

BV cell has been investigated for years due to their high energy density, uninterrupted energy supply and durability in extreme environments. It might become an alternative of widely used solar cell in many areas, such as wireless sensor nodes [1,2], astronautics [3] and so on. Similar to well-known photovoltaic effect which is the foundation of solar cells, the electron voltaic effect [4] discovered in 1951 brought us a new manner of energy conversion directly from radiation energy to electricity. One of the most attractive advantages of BV technique is the prolonged and continuous energy supply benefiting by the long half-time of special radioisotopes, such that ^{63}Ni we used has a half-time more than 100 years. Besides long half-time, ^{63}Ni is a proper choice of beta particles source for other reasons. ^{63}Ni is less toxic than many other radioisotopes and easy to prepare and fabricate, for example, by electroplating. In addition, it is safe for people and it hardly induces defects in most semiconductive materials because of the temperate radioactivity. Consequently, longevity plus low toxicity, easy preparation and adequate but moderate energy density decides that ^{63}Ni will become a prominent candidate of radioisotope chosen to power BV cells. Since the first Si BV battery was reported by Rappaport in 1954 [5], a series of semiconductive materials have been utilized to make betavoltaic cells, such as GaAs, SiC, porous silicon, and GaN [6–9]. However, most of these microcells are limited to the low current density and energy conversion efficiency.

Because the high aspect ratio and large surface area of carbon nanotubes can enhance electron hole pairs (EHPs) dissociation and charge carrier transportation, they may offer innovative opportunities to make radioisotope power generators efficient. Owing to the unique one-dimensional structure and different chirality, single-walled carbon nanotubes (SWCNTs) have many valuable electrical properties. The electrical conductivity of SWCNT is decided by the chirality, i.e., we can acquire both semiconductive and metallic nanotubes by tuning the diameter with only one sort of material. Compared to traditional materials, SWCNT has greatly low carrier recombination, high carrier mobility and low carrier scattering [10,11], which influence positively on the behavior of devices constructed on SWCNTs. In the field of photovoltaics and solar energy harvesting, carbon nanotube has been widely studied, and hundreds of papers have been published on this topic. Among these papers, the Schottky junction formed between metal and SWCNT is the interest of many researchers for the reason that the rectifying behavior of the depletion region formed at the SWCNT-metal interface can dissociate EHPs and convert solar energy to electricity. Metals with different work functions have been tried in the structure of "Metal/SWCNT/Metal" including Pd/SWCNT/Al [12–14], Pd/SWCNT/Hf [15], Pd/SWCNT/Sc [16], etc. However, few researches have focused on combining the BV technique with SWCNT/metal structure.

This paper proposes our BV microcell with Si-based Micro Electro Mechanical Systems (MEMS) fabrication method, and implements "Au/s-SWCNTs/Ti" structure to play the role of energy conversion from radiation energy to electricity. Detailed design and fabrication process are presented, and the test results are discussed in the following section. It is proved that BV SWCNT microcell is a promising method, and we believe that the performance of the BV microcell would be largely enhanced if the number of SWCNT

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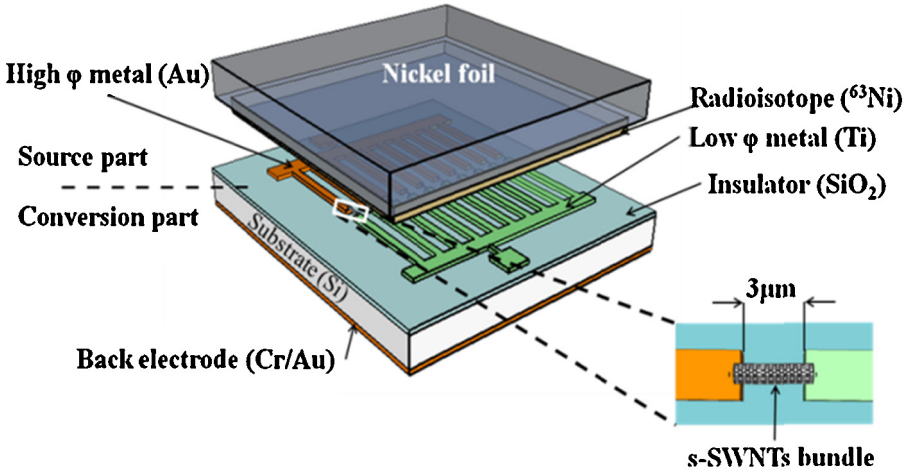

Fig. 1. A three-dimension schematic view of the single-walled carbon nanotubes (SWCNTs) betavoltaic (BV) microcell.

bundles in forming the Schottky contact with metal electrodes could be increased in the next-stage fabrication method.

2. Design and theory

Our silicon-based device structure consists of a conversion part and a source part (Fig. 1). In the conversion part, Au with a high work function (φ) of 5.47 eV is chosen to form ohmic contact with s-SWCNTs and Ti with a low work function of 4.33 eV is chosen to form Schottky junction with s-SWCNTs. To improve productivity, the front electrodes (both Au and Ti) are patterned into 15 opposite finger pairs which are 30 μm in length, 3 μm in width and 3 μm in the gap of opposed finger pairs. By means of dielectrophoretic (DEP), s-SWCNT bundles are arranged in lines to connect Au finger and Ti finger across the gap. The back electrode is employed as an electrostatically coupled gate to deplete carriers of s-SWCNTs in order to protect s-SWCNTs from damage when high current densities are used to burn off metallic SWCNTs (m-SWCNTs). SiO_2 layer is used to insulate the front electrode from the Si substrate. In the source part, 3.3 mCi/cm^2 ^{63}Ni thin film electroplated on a nickel foil continuously emits beta particles for energy supply. The reasons why ^{63}Ni is chosen as beta particles source are the low toxicity, low radiation, high safety and long half-time.

The difference of work function between the metal electrodes and s-SWCNT is of vital importance in our BV microcell. Band diagram of the Au/s-SWCNTs/Ti structure (Fig. 2) illustrates how the energy conversion is realized. S-SWCNT bundles are innately p-type when exposed in oxygen, and the Fermi level (E_f) of s-SWCNT is higher than the E_f of Au and lower than the E_f of Ti, resulting in the energy band of s-SWCNT bending. Ti and s-SWCNT forms Schottky junction, and the depletion region almost spreads over

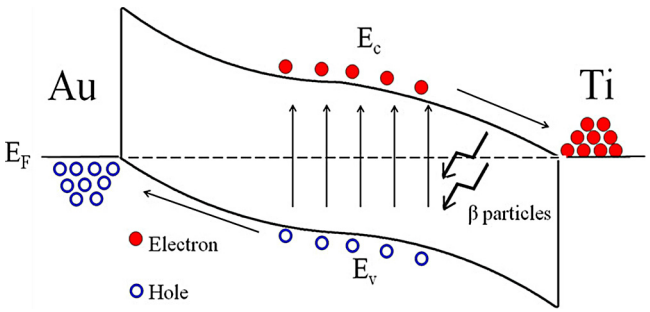

Fig. 2. Band diagram of Au/s-SWCNTs/Ti structure illustrating the energy band bending, electron hole pairs (EHPs) generation and EHPs separation.

the whole s-SWCNT. At the same time, Au and s-SWCNT forms ohmic contact. According to the conventional theory of Schottky barriers, almost all the contact between metal and semiconductor has a Schottky barrier with the Fermi level pinned near the valance band of semiconductor by the interface states, which means that it is normally impossible to form an ohmic contact between Au and a semiconductor. However, unlike the circumstance of traditional planar devices, the "Fermi level pinning effect" does not apply to the contact between the nanotubes and metals. On the contrary, the work function of metals has strong influence on the Schottky barrier height of nanotube-metal junction, just like the ideal Schottky contact. This phenomenon is explained by Léonard and Tersoff [17], and it can support that in our BV microcell Au and s-SWCNT indeed forms ohmic contact.

Therefore, EHPs excited in the depletion region by beta particles will be separated by the built-in electric field, holes collected by Au electrode and electrons collected by Ti electrode, generating electrical potential difference between Au and Ti. Hence, a battery is created, where Au works as the cathode, and Ti works as the anode.

3. Fabrication

The fabrication process (Fig. 3) started with a Si wafer. After 300 nm SiO_2 were thermally grown on both sides of Si wafer, the SiO_2 on the back side was wiped off by buffered hydrofluoric acid (BHF). Then phosphorus ions were implanted to the back surface of Si wafer followed by annealing at 1000 °C. Cr/Au (20 nm/150 nm), as back electrode, were sputtered on the back side of Si wafer and annealed at 320 °C to form ohmic contact (Fig. 3(a), different from the ohmic contact between Au and s-SWCNT). To form front electrode, Cr/Au (20 nm/150 nm) and Ti (150 nm) were respectively sputtered and patterned into finger pairs on Si wafer (Fig. 3(b)). The whole wafer was diced to 5959 μm × 6980 μm dies as samples. In the following process (Fig. 3(c)), s-SWCNTs are self-assembled by DEP technique between Au and Ti electrode finger pairs of each sample. The 3.3 mCi/cm^2 ^{63}Ni thin film was electroplated on a nickel foil to serve as beta radiation source (Fig. 3(d)).

SWCNTs suspension should be prepared before assembling. SWCNTs powder was ultrasonically dispersed in dimethylformamide (DMF) for 2 h obtaining 5 μg/ml suspension. An AC voltage source (V_{PP} = 5 V and f = 5 MHz) loaded between Au and Ti front electrodes was used to generate electric field distributed in the gap of Au and Ti finger pairs so that the SWCNTs in the suspension would automatically arrange themselves in the direction of the electric