Ultrasonic nanowelding of carbon nanotubes to metal electrodes

This article has been downloaded from IOPscience. Please scroll down to see the full text article.
2006 Nanotechnology 17 2192
(http://iopscience.iop.org/0957-4484/17/9/019)

The Table of Contents and more related content is available

Download details:
IP Address: 202.120.54.134
The article was downloaded on 10/04/2010 at 13:27

Please note that terms and conditions apply.
Ultrasonic nanowelding of carbon nanotubes to metal electrodes

Changxin Chen, Lijun Yan, Eric Siu-Wai Kong and Yafei Zhang

National Key Laboratory of Nano/Micro Fabrication Technology, Key Laboratory for Thin Film and Microfabrication of Ministry of Education, Institute of Micro and Nano Science and Technology, Shanghai Jiao Tong University, Shanghai 200030, People’s Republic of China

E-mail: chen.c.x@263.net

Received 16 December 2005, in final form 16 February 2006
Published 31 March 2006
Online at stacks.iop.org/Nano/17/2192

Abstract

A simple ultrasonic nanowelding technique has been developed to reliably bond single-wall carbon nanotubes (SWCNTs) onto metal electrodes, by pressing SWCNTs against electrodes under a vibrating force at ultrasonic frequency. The bonds formed have been demonstrated to be mechanically robust. Using this technique, a stable low-Ohmic contact between SWCNTs and metal electrodes was achieved, with resistances in the range of 8–24 kΩ for a 1 μm long metallic SWCNT at room temperature. The performance of carbon nanotube field-effect transistors (FETs) fabricated using this ultrasonic nanowelding method has also been greatly improved. Transconductance as high as 3.6 μS among the solid-state back-gate individual nanotube FETs has been achieved.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Carbon nanotubes (CNTs) exhibit a great prospect as a nanoscale building block for future nanoelectronics due to their unique one-dimensional nanostructure and properties [1]. To explore their potential in various domains, an essential prerequisite is to build reliable interconnections between the CNTs and the external electrical circuits and mechanical systems. To address this need, various chemical and physical processes have been explored to build such interconnections. For example, Burghard et al reported ‘controlled adsorption of CNTs on chemically modified electrodes’ for interconnection of CNTs [2, 3]. However, a stronger bonding instead of a weak chemical adsorption is mandatory for constructing reliable nanodevices. Ruoff et al showed that a focused electron beam in a scanning electron microscope (SEM) can be used to deposit a small amount of hydrocarbon contamination so as to attach nanotubes on an AFM tip [4, 5]. Such a ‘spot welding’ technique has also been used for connecting CNTs and a polysilicon surface electrically and mechanically [6]. Madsen et al presented an in situ method for highly conductive attachment of multi-wall carbon nanotubes (MWCNTs) onto microelectrodes by depositing a gold–carbon composite using a focused electron beam system [7]. Though robust contacts can be obtained by the above methods, limited access to a focused electron beam system and the small-scale spot-treatment nature prevent their large-scale industrial applications. To meet the needs of future large-scale applications, simpler, less capital intensive and more scalable processes are highly desirable.

In this paper, a simple ultrasonic nanowelding process is developed to fabricate reliable bonding between single-wall carbon nanotubes (SWCNTs) and metal electrodes. Contacts formed by the present process are found to have low contact resistance, good long-term stability and mechanical strength. The performance of the CNT field-effect transistors (FETs) fabricated by this method has been demonstrated to have greatly improved.

2. Experimental details

Single-wall carbon nanotubes (SWCNTs) with an average diameter of 1.6 nm synthesized by an arc discharge process were used in this present work. SWCNTs were purified and subjected to chain-scission in a 3:1 mixture of concentrated sulfuric acid and nitric acid at 80 °C for 30 min in a reflux system. The undried SWCNTs were filtrated with isopropanol to remove the water in the sample. Then the SWCNTs were ultrasonicated in isopropanol and centrifuged at 15 000 rpm for
2.5 h to further separate large SWCNT bundles from single SWCNTs. The obtained supernatants at concentrations of several \( \mu g \) ml\(^{-1} \) were ultrasonically treated for about 20 h to sufficiently disperse SWCNTs. Parallel titanium electrode pairs were patterned by optical lithography on n-type silicon wafer, which was thermally coated with a 150 nm thick silicon dioxide layer. The electrode pairs were 300 nm thick, 40 \( \mu m \) wide, 40 \( \mu m \) long, and were separated by a gap of 1 \( \mu m \). SWCNTs were deposited onto the electrodes by simply performing an unassisted deposition of SWCNTs in suspension, or by an AC electric-field assisted alignment process [8, 9]. A droplet of the SWNT suspension was introduced onto the patterned wafers. After the deposition or electric field alignment process, SWNTs were laid over the electrode pair. The number of SWNTs bridging the electrode pair can be readily controlled by varying the concentration of the suspension or the parameters of applied AC electric field such as the bias magnitude and frequency. The as-prepared samples were then ready for ultrasonic bonding.

Ultrasonic nanowelding was carried out in an FB-128 ultrasonic wire bonder. The structure and the details of how this wire bonder works can be found in [10]. An Al\(_2\)O\(_3\) single crystal with a 50 \( \mu m^2 \) pressing surface and an rms roughness of 0.2 nm was mounted onto the bonder to act as the welding head. Figure 1 shows a schematic diagram of the ultrasonic nanowelding process. A clamping force of 78.4 mN was applied to press the welding head against the nanotube and electrodes. At the same time an ultrasonic vibration with a frequency of 60 kHz was applied to the welding head through an ultrasonic transducer (figure 1(a)). The ultrasonic energy was transferred to the bonding interface through the ultrasonic welding head. Thus the ends of SWCNTs and electrodes were welded together under the combined action of the ultrasonic energy and a clamping force (figure 1(b)). To investigate the effects of ultrasonic energy on the bonding process, a series of different ultrasonic powers was applied. The welding process was carried out at room temperature for a duration of 0.2 s.

3. Results and discussion

Figures 2(a) and (b) show typical scanning electron microscopy (SEM) images of an SWCNT bridging the Ti electrodes before and after ultrasonic nanowelding with an ultrasonic power of 0.07 W, respectively. (c) SEM image of multiple SWCNTs welded onto the electrode with an ultrasonic power of 0.16 W; the marked regions show the weld junctions.

In addition, the ultrasonic nanowelding can also be used for welding bulk quantities of SWCNTs onto metal electrodes. Figure 3 shows SEM images of a 50 \( \mu m^2 \) electrode surface with nanotubes welded onto it. As shown in figure 3(a), the ultrasonic nanowelding produces an apparent directional welding zone due to the directional vibration of the welding
Figure 3. SEM images of the electrode surface after welding of bulk quantities of SWCNTs onto a Ti electrode at an ultrasonic power of 0.21 W. (a) Surface topography of the welded (upside) and non-welded (downside) zone. The arrow represents the direction of the ultrasonic vibration motion. (b), (c) Zoom-in views of a local region (indicated by rectangles) in the unwelded and welded zone, respectively. The arrows in (c) show that some short ends of SWCNTs protrude from the welded substrate.

The mechanism behind the ultrasonic nanowelding is proposed as follows. During the ultrasonic nanowelding, the high-frequency ultrasonic energy softens the metal and causes plastic deformation of the metal under the clamping stress because of the 'acoustic softening effect' [10, 11]. Thus, the nanosized SWNTs with a one-dimensional structure have been shown to be 'embeddable' and weldable into the metal electrodes.

To examine the nature of the welded bonds, micro-area x-ray photoelectron spectroscopy (XPS) and x-ray diffraction (XRD) analysis were used to study the welded zone. The data are shown in figure 3(a). The XPS analysis reveals that the C 1s core level spectrum (figure 4(a), curve 1) of the region shows a single peak at 284.5 eV when the ultrasonic power is lower than 0.14 W. This peak corresponds to the C–C bond of the original SWCNTs. This result indicates that no detectable chemical reaction happens between the nanotube and the metal electrode at low ultrasonic power. When a higher power (>0.14 W) was used, a new peak appeared at around 280.8 eV (figure 4(a), curve 2). This peak can be attributed to the C–Ti bond in titanium carbide (Ti_xC), which indicates that Ti_xC compounds could have been formed in this process. The micro-area XRD analysis result is also in good agreement with this interpretation. An XRD peak at 2θ ≈ 65.2°, which represents a titanium carbide (Ti_xC) phase, was observed when the ultrasonic power was increased to above 0.14 W. When ultrasonic power was increased to 0.19 W, two peaks of Ti_xC phase are observed in the XRD pattern at 2θ ≈ 41.5° and ≈63.7°, as shown in figure 4(b). All these results indicate that when the ultrasonic power is higher than a threshold value SWCNTs do chemically react with the titanium electrode to form titanium carbide at the welding junction. More comprehensive and in-depth study is needed to substantiate this observation.

To evaluate the electrical performance of the contact, two-terminal (2t-) resistance tests have been carried out on the nanotube welded across the electrode pairs. To simplify the interpretation of the results, ‘metallic nanotubes’ rather than ‘semiconducting nanotubes’ were used in the two-terminal resistance tests. The metallic and semiconducting nanotubes were identified and differentiated by their non-identical dependences on gate voltages applied to the silicon.
Before welding, the 2t-resistances of these two samples were 49.4 and 55.8 MΩ, respectively. When the ends of the nanotubes lying on the metal electrodes were pressed against the electrodes by a pure clamping force with no ultrasonic power applied, the 2t-resistances of two devices dropped to 8.1 and 10.2 MΩ, respectively. It was demonstrated that the 2t-resistances decreased with the increase of the applied ultrasonic powers. As the ultrasonic power increased to 0.15 W, the 2t-resistances decreased by more than three orders of magnitude, and then saturated at the low values of about 22 and 15 kΩ respectively. In the experiments, the 2t-resistances of 43 samples were measured and statistically analysed. It was found that the obtained lowest resistances for these samples mainly concentrated around 15 kΩ and approximately conformed to the Gauss distribution (inset in figure 5(a)), indicating the formed electrical contacts were reliable. The contacts were also found to be stable in air on a long-term basis and showed little change after storage for three months at room temperature in laboratory atmosphere.

It is considered that the substantial decrease of the 2t-resistance may be caused by the increases in the effective contact area and the formation of conducting carbides at the contact [12]. In addition, possible structure impairments or lattice defects introduced at the ends of the SWCNT by the clamping force and acoustic effect may increase carrier scattering at the junctions, which contributes to break the Bloch symmetry of electrons and thereby to allow easier electrical conduction between both electrodes through the bridging SWCNT [13].

Characteristics of the bonds between semiconducting SWCNTs and metal electrodes, created using this welding technique, have also been studied. Several back-gate CNTFETs were prepared by welding individual semiconducting SWCNTs onto electrodes with ultrasonic power in the range of 0.16–0.19 W. The output and transfer characteristics of a typical CNTFET are shown in figure 5(b). The transistor shows p-type characteristics, with a low threshold voltage of −0.3 V. As shown in figure 5(b), $I_{DSS}–V_{DS}$ curves are highly linear and symmetrical for $−0.5 V < V_{DS} < 0.5 V$. The bonded semiconducting SWCNT exhibits a large ON current $I_{ON, sat} = 18.9 \mu A$ and a high linear ON conductance of $G_{ON} = 0.25 \times 4 e^2/h (R_{ON} = 26.4 \text{k} \Omega)$ at $V_{G} = −9.0 \text{V}$, indicating the low Ohmic electrical contact in the ON state. The obtained CNTFET shows a high transconductance of $g_{m, |V_{ds}|=0.5 \text{V}} = 3.6 \mu \text{S}$ in the linear region of $−4.5 \text{V} < V_{G} < −1.0 \text{V}$ (inset in figure 5(b)), while before the ultrasonic nanowelding it is only of the order of $10^{-9} \text{S}$. This transconductance is the highest among the present solid-state back-gate individual nanotube FETs [9, 14–18], which is a little higher than that of the Ti-contacted top-gated SiO$_2$/SWCNT-FETs ($g_{m, |V_{ds}|=−1 \text{V}} = 3.25 \mu \text{S}$) [19] and is higher by one order of magnitude than that of the Ti-contacted back-gated SiO$_2$/SWCNT-FETs using the annealing method to form low Ohmic contacts ($g_{m, |V_{ds}|=0.8 \text{V}} = 0.2 \mu \text{S}$) [14, 15]. The inverse subthreshold slope ($S$) of our devices is around 180 mV/dec, which is much lower than that of those devices in the same form without ultrasonic nanowelding ($S \sim 400 \text{mV/dec}$) [20] and is identical to that of those devices with bottom gates and Al$_2$O$_3$ dielectrics ($S \sim 180 \text{mV/dec}$) [16]. Therefore, the on–off performance of the devices was well improved after nanowelding. A large on–off current ratio of $10^2–10^3$ has also been

![Figure 5](image-url)

**Figure 5.** Electrical performance of individual metallic and semiconducting SWCNTs after the ultrasonic nanowelding. (a) Two-terminal (2t-) resistances as a function of the ultrasonic power for two metallic nanotube–Ti contacts. Before the ultrasonic nanowelding, the 2t-resistances of sample 1 and 2 were 49.4 and 55.8 MΩ, respectively; the ultrasonic power of 0 W in the figure represents that the ends of the SWNT were pressed against the electrodes by pure clamping force without ultrasonic power applied. Inset: the statistical analysis and distribution fit of the obtained lowest 2t-resistances for 43 samples after nanowelding. (b) Output characteristic of the CNTFET with an individual semiconducting SWNT as the conduction channel. Inset: transfer characteristic curve.
Figure 6. Characterizations of the mechanical stability of the ultrasonic nanowelding by AFM manipulation. (a) Three-dimensional AFM image of an unwelded SWCNT bridging the electrodes. (b) AFM image of the SWCNT in (a) shifted laterally by the AFM tip. (c) AFM image of a nanowelded SWCNT pushed to fracture by the AFM tip. The SWCNT diameter was measured to be about 1.5 nm by AFM height, which indicated an individual SWCNT instead of a SWCNT bundle. The arrows in (b) and (c) show the travelling paths of the AFM tip.

achieved. For the obvious performance improvements in the CNTFET, the significant decrease in the contact resistance is clearly an important cause. Another possible explanation can be attributed to the change in the transistor configuration from the ‘side-bonded’ nanotube–metal contact to the ‘end-bonded’ nanotube–carbide contact due to the formation of titanium carbides, which enhanced the modulation effect of the gate [14].

Besides the electrical tests, the mechanical integrity of the welded bonds has also been tested by mechanically pushing the hanging middle segment of a welded nanotube with an AFM tip. In the experiment, 20 unwelded and welded samples were tested. In the contact-mode AFM, with the feedback turned off, the cantilever was pressed down onto the substrate, and dragged along the path parallel to the electrode pairs. It was found that when SWCNTs were not welded to the electrodes, SWCNTs were easily shifted and could no longer bridge both electrodes (figures 6(a) and (b)). This observation qualitatively shows that the van der Waals’ forces between the CNTs and substrate underneath are not large enough to resist the movement of the CNTs. In contrast, for the nanowelded samples, the two ends of the 95% SWCNTs remained bonded to the electrodes even after the nanotube had been pushed to fracture (figure 6(c)). This suggests that the bonds bear reasonable mechanical strength. It is observed that segments
of CNTs close to the electrodes are still approximatively perpendicular to the electrodes while segments of CNTs at the fracture surface are strongly bent after the AFM-dragging test, as shown in figure 6(c). This phenomenon can be explained by the existence of the van der Waals force between the CNTs and the substrate, which prevents the lateral movement of the CNTs and causes the CNTs to be dragged along its axis, forming this strained configuration [21].

Finally, it should be mentioned that ultrasonic welding experiments have also been performed, resulting in bonding between SiC or Si nanowire and titanium electrode as well as SWCNT and gold electrode. All these bonds show good electrical contacts. Therefore, the present approach is feasible for wide ranges of one-dimensional nanomaterials and metals.

4. Conclusion

Bonding between the SWCNTs and metal electrodes was realized by a simple ultrasonic nanowelding technique. The bonds formed were measured to be mechanically strong. With this technique, the long-term stable Ohmic contact between SWCNTs and electrodes was achieved and the 2t-resistance was decreased by more than three orders of magnitude. The performance of the CNTFET fabricated by this method was also demonstrated to be greatly improved. This technique does not depend on the specific kind of nanocomponent or metal electrodes. Moreover, it is hopeful that the ultrasonic welding area can be scaled up so that multiple bondings on a substrate can be achieved in one single step, under one single press vibrating at a specific ultrasonic frequency.

Acknowledgments

This work is supported by the National Basic Research Programme of China No 2006CB300406, Shanghai Science and Technology Grant No 05nm0533 and the National Natural Science Foundation of China No 60576064.

References

Corrigendum

Ultrasonic nanowelding of carbon nanotubes to metal electrodes
Changxin Chen, Lijun Yan, Eric Siu-Wai Kong and Yafei Zhang Nanotechnology 17 2192–2197

The authors regret that there were two errors in the final published version of this article. The literal expression ‘a 50 μm² pressing surface’ and ‘a 50 μm² electrode surface’ in the 2nd and 4th paragraphs of the 2nd page should be corrected to ‘a 2500 μm² circular pressing surface’ and ‘a 2500 μm² electrode surface’.