Towards an optical coupler using fine-wire: a study of the photovoltaic effect of a heterojunction formed in a single fine-wire of tungsten oxides*

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(Received 29 June 2009; revised manuscript received 15 September 2009)

Nanodevices using the photovoltaic effect of a single nanowire have attracted growing interest. In this paper, we consider potential applications of the photovoltaic effect to optical signal coupling and optical power transmission, and report on the realization of a heterojunction formed between WO_2 and WO_3 in a fine-wire having a diameter on the micrometer scale. Using a laser beam of 514.5 nm as a signal source, the WO_2–WO_3 heterojunction yields a maximum output power of up to 37.4 pico watt per heterojunction. Fast responses (less than a second) of both photovoltaic voltage and current are also observed. In addition, we demonstrate that it is a simple and effective way to adapt a commercial Raman spectrometer for the combined functions of fabrication, material characterization and photovoltaic measurement of an optical signal coupler and optical power transmitter based on a fine-wire. Our results show an attractive perspective of developing nanowire or fine-wire elements for coupling optical signals into and for powering a nanoelectronic or nano-optoelectronic integrated circuit that works under the condition of preventing it from directly electrically connecting with the optical coupler.

Keywords: optical coupler, heterojunction, tungsten oxide fine-wire, photovoltaic
PACC: 7830G, 8630J, 7865M

1. Introduction

The photovoltaic effect has already had important applications such as in solar cells and photodetectors. Recently, it has attracted new attention, partly due to a growth of interest in looking for new approaches to improving the efficiency of energy conversion in novel solar cells with low cost. Much effort[1−6] has been devoted to the study of the potential of using nanomaterials for such a purpose, and device structures utilizing nanowires have been shown to have great potential. Significantly, Lieber *et al.* successfully fabricated the first single nanowire solar cell,[7] and demonstrated its application in powering nanoelectronic devices. This achievement shows the attractive perspective of single nanowire photovoltaic devices. Here, we consider another important potential application of photovoltaic nanodevices, i.e. for optical signal coupling and optical power transmission. The conventional optical coupler has important applications such as in optical communication and in the case where devices should work under the condition of preventing them from electrically connecting with the optical coupler. Optical power transmission may find more feasible applications in future integrated circuits of nanodevices, since low power consumption is expected for its operation. With such a nanodevice, one may realize the wireless-powering of nanodevices. In the present study, we fabricate in a single fine-wire a heterojunction formed by two tungsten oxides, i.e. WO_2 and WO_3, and characterize its photovoltaic effect as well. This may serve as an interesting example for the future study of non-coaxial heterojunction-based photovoltaic nanodevices.

Tungsten oxides have many types of structures, such as WO_3,[8,9] WO_2,[10] $W_{18}O_{49}$[9] and $W_{20}O_{58}$.[11] Tungsten oxides are of great interest because of their electrical and optical properties and they are promising materials for photolysis,[12] electrochromic devices[13,14] and sensors.[15,16] In the present study, we are interested in them as semiconductors of a wide energy band gap. Also, it is technically important. In our early study, we have found that nanowires of tungsten oxides have phase transform under laser heating.

*Project supported by the National Natural Science Foundation of China (Grant Nos. U0634002, 50725206 and 50672135), the National Basic Research Program of China (Grant Nos. 2003CB314701, 2007CB935501 and 2008AA03A314), and the Department of Information Industry of Guangdong Province, China.
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This finding leads us to consider the use of laser spot heating to fabricate a heterojunction in a fine-wire of tungsten oxide.

2. Preparation and characterization

Figure 1(a) illustrates a schematic diagram of a nanowire/microwire optical coupler and Figs. 1(b) and 1(c) show the illustration of the experimental set-up we developed for the study of a single wire optical coupler, which is adapted from a commercial Raman spectrometer system (RENISHAW in Via). In this set-up, the laser source of the spectrometer acts as a signal source of an optical coupler, and the heterojunction beneath serves as an optical receiver and electrical signal generator which is based on the photovoltaic effect.

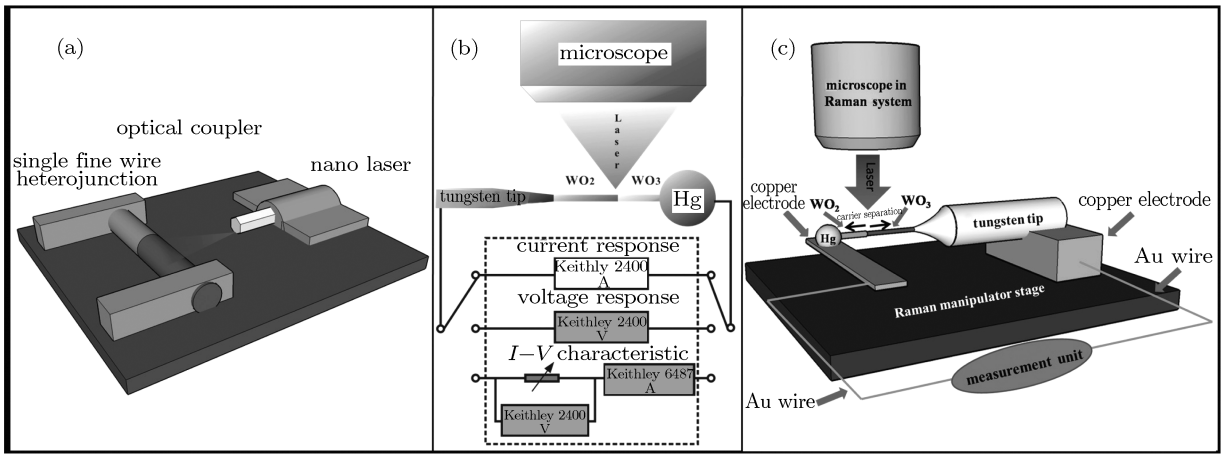


Fig. 1. (a) Illustrations of a nanowire/microwire optical coupler (a), and experimental set-up (b) and (c).

To prepare samples for the experiment, ultra-long WO_2 fine-wires with a length of up to 100 μm and diameter of around 1 μm were synthesized on the ceramic substrate by the simple thermal vapour deposition method, which has been reported by our group elsewhere.[8] In order to measure the electric signal, two electrodes must contact the two ends of the WO_2 fine-wire. With the use of the laser welding method developed by our group and a home-made microassembly system,[17] a single WO_2 fine-wire was first welded on a handleable tungsten tip. In the welding process, helium gas was introduced to prevent the wire from thermally being oxidized. Scanning electron microscopy images of the ultra-long WO_2 fine-wire welded on a tungsten tip are shown in Fig. 2, from which one may see that one end of the fine-wire is melted and attached firmly to the tungsten tip. Then with reference to Fig. 1(c), the tungsten tip was then laid on the top of a copper electrode. On another end of the fine-wire, we used a droplet of liquid mercury to provide a gentle contact to another electrode,[18] because the tungsten fine-wire was fragile.

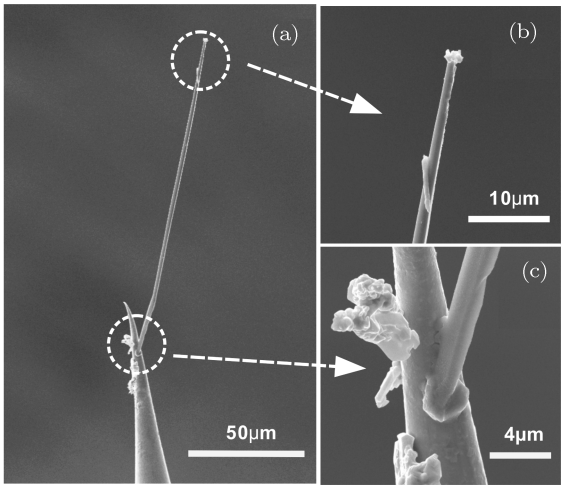


Fig. 2. SEM images of the WO_2 fine-wire welded on a tungsten tip (a), full view of the fine-wire (b), and enlarged SEM images of the join and the end of the wire (c).

Tungsten oxides have many types of structures,

which strongly influence the band structures.[19] Our early study[9] has shown that tungsten oxide nanowires can be oxidized into high-oxygen-content compounds by using laser heating in air. Also, Raman spectroscopy is the most powerful tool to distinguish most of the structures of tungsten oxide.[20] We have fully used these early results and the Raman spectrometer for fabrication of a heterojunction, material analysis and photovoltaic measurement with the use of the combination of its capability of laser heating and Raman spectroscopic analysis. In experiment, the laser beam (514.5 nm) is focused on one region near the end of the WO_2 fine-wire. The heating effect of laser power causes this part of the fine-wire to be thermally oxidized into WO_3. The linear mapping of the Raman spectrum may then be carried out along the axis of the fine-wire to examine the resulting heterojunction structure. Then the fine-wire is moved to penetrate into the liquid mercury droplet. The photovoltaic effect is excited by the same laser source (514.5 nm). The electrical signals are measured by a Keithley 2400 and 6487.

Figures 3(a), 3(b) and 3(d) are optical images of the fine-wire taken using the microscope of the Raman spectrometer. As may be seen in Fig. 3(a), the original surface of the WO_2 fine-wire is smooth. Figure 3(b) shows that part of the fine-wire swells up after being thermally oxidized as a result of laser heating. The linear mapping of Raman spectra is carried out along the dashed and solid lines indicated in Fig. 3(b), and the spectra are shown in Fig. 3(c), where a gradual change of spectral shape may be seen from bottom to top of the figure. This spectral evolution shows the corresponding transformation from WO_2 to WO_3 along the fine-wire. In the spectrum at the bottom, the Raman peaks are at 785, 617, 600, 514, 484, 348, 333, 289, 187 and 172 cm^{-1}, indicating that this part of the fine-wire has WO_2 structure; similar to that of WO_2 nanoparticles.[10] In the spectrum at the top, we can see only four Raman peaks at 811, 715, 326 and 274 cm^{-1}, which are similar to the reported Raman spectrum of WO_3.[9,21] Besides, we believe that the spectra between the above two belong to the intermediate structure between WO_2 and WO_3. The above Raman spectroscopic analysis confirms that we have formed a WO_2–WO_3 graded heterojunction in the fine-wire. In addition, Fig. 3(d) shows that the fine-wire penetrated into the mercury droplet, while part of the swelling WO_3 region remains outside the mercury droplet, so that the WO_2–WO_3 heterojunction is exposed.

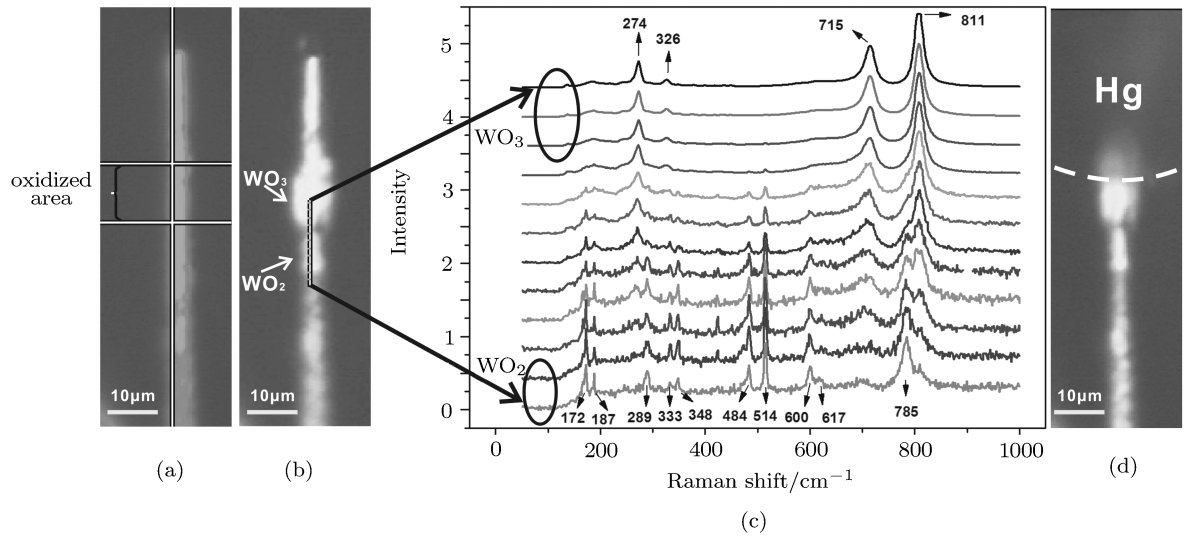


Fig. 3. Optical images of the fine-wire through the microscope in the Raman system. Panel (a) shows the original morphology of the fine-wire. Panel (b) exhibits the morphology after local oxidation and the swelled oxide part, where the white line indicates the Raman linear mapping region. Panel (d) displays the fine-wire penetrating into the mercury droplet and some parts of the WO_3 remaining outside the mercury. Panel (c) indicates the Raman linear mapping spectra, which are accumulated from bottom to top along the white line in panel (b).

3. Results and discussion

The current–voltage (I–V) characteristic of the WO_2–WO_3 heterojunction obtained without laser irradiation is shown in Fig. 4. The curve is nonlinear and asymmetrical. We may use the band diagram[22−24] given in the inset of Fig. 4 to explain this characteristic. When the heterojunction is positively biased, i.e. when the WO_3 part is at positive voltage while the WO_2 part is at negative voltage, the positions of E_c and E_v of WO_2 rise and the potential barrier in the WO_2 side reduces. Thus electrons flow from the WO_2 part across the potential barrier and increase as the applied voltage increases exponentially. When the bias voltage is reversed, the positions of E_c and E_v of WO_3 rise, which makes the potential valley in the WO_3 side deeper and the potential barrier in the WO_2 side increase. Both of these can hinder the electrons from coming from the WO_3 part to the WO_2 part, so that a much slower increase in current was observed.

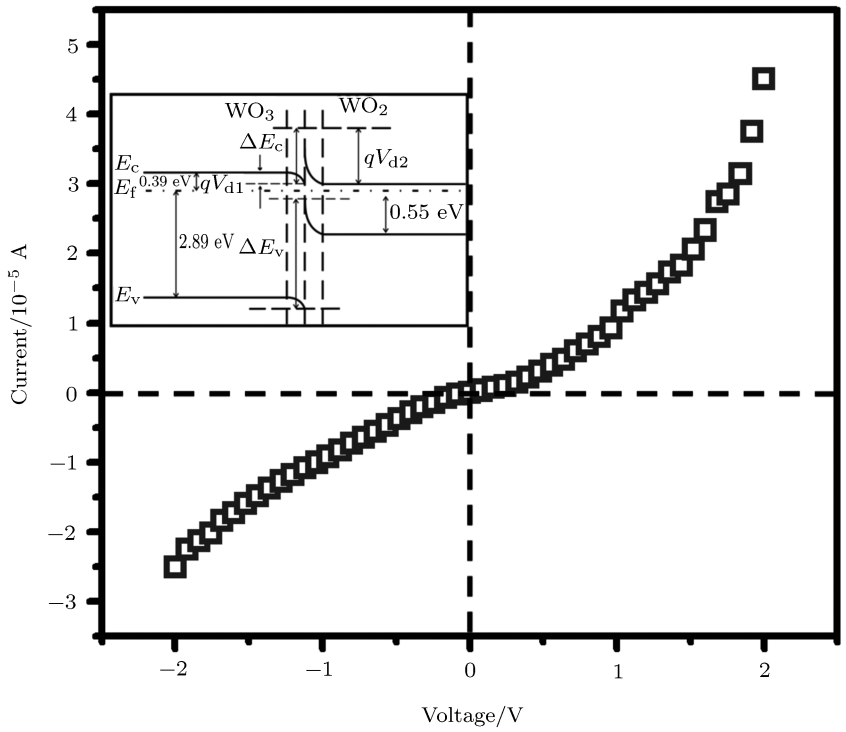


Fig. 4. The I–V curve and the assumed band diagram of the WO_2–WO_3 heterojunction, with the positive voltages applied at the WO_3 part.

In order to investigate the electrical response of the heterojunction to laser beam irradiation, the current and the voltage were measured when the illumination of the laser beam was alternately switched on and off in steps of five seconds. The optical power density used here was about 100 W/cm^2, only 10% of the optical power was used for oxidizing the fine-wire. We checked that the structure transformation did not occur under repeated irradiation at this low power density. As shown in Figs. 5(a) and 5(b), a quick response may be seen from both the current and the voltage to laser irradiation, and the response time is less than one second. In this measurement, no external bias voltage was applied, and the current and the voltage were induced by the laser irradiation. The background current, which appeared without applying external bias voltage and laser irradiation, is around 2 nA (Fig. 5(a)). When the laser beam was on, the current increased to about 40 nA, almost 20 times higher than that when the laser was off (Fig. 5(a)). After turning off the laser, the current reduced to the initial level of the background current immediately. The response has both a fast rising time and a fast falling time, much faster than our digital picoammeter could respond to. These fast changes in current and voltage cannot be ascribed to the thermo effect caused by the laser beam irradiation.

In order to further characterize the photovoltaic effect, a series of output currents and a series of output voltages were measured when the fine-wire was connected to a variable resistor. We placed a tunable load resistor in the circuit and used the fine-wire heterojunction as a power source. Tuning the resistance of the

load resistor, we measured the current and the voltage under the illumination of the laser beam of 514.5 nm on the heterojunction. As shown in Fig. 5(c), the data points form a curve roughly consistent with an exponential relationship. The open-circuit voltage and the short-circuit current are 3 mV and 40 nA, respectively. They may be improved in a later study by reducing the length of the fine-wire; more carriers may undergo recombination in a longer fine-wire. Given that the diameter of the fine-wire is about 1 μm, the short-circuit current density is calculated to be about 4 A·cm^{-2}. Also, the maximum output power is calculated to be 37.4 pico watt (pW). Dividing this value of the maximum output power by the value of the product of the short-circuit current and the open-circuit voltage, we can obtain the fill factor to be 29.5%.

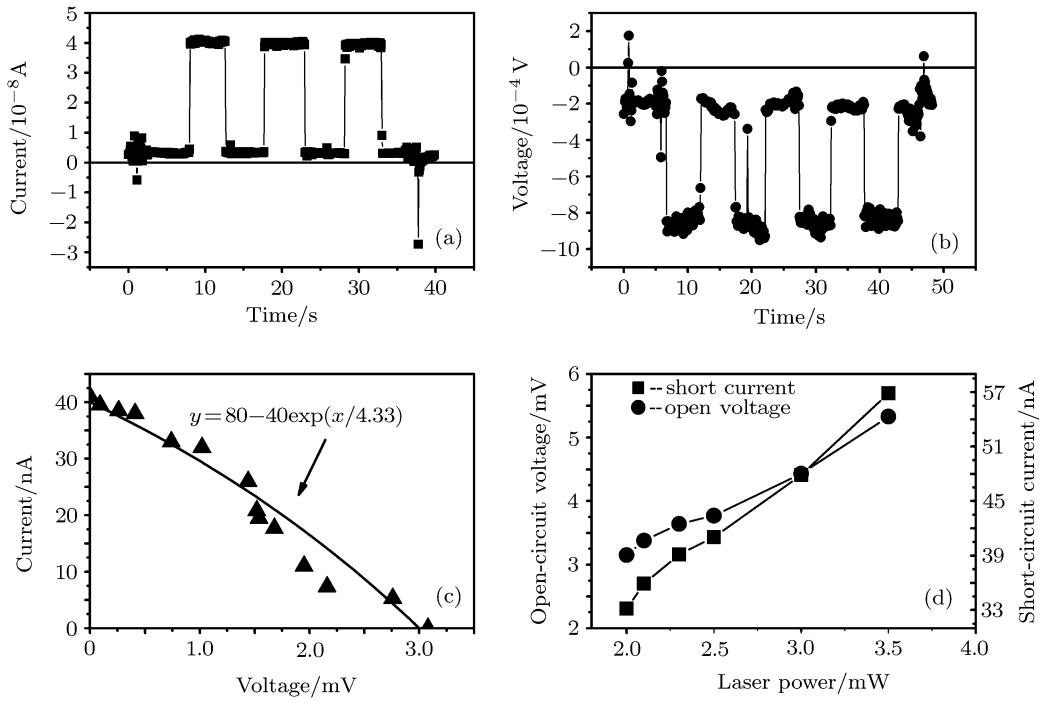


Fig. 5. Responses of current (a) and voltage (b) to laser irradiation, current and voltage obtained with a resistor with tunable resistance (c), and short-circuit current and open voltage versus laser power (d).

In order to determine the short-circuit currents and open-circuit voltages at different levels of radiation, both of them were measured when the laser power changed from 2 mW to 3.5 mW. As shown in Fig. 5(d), they increase as laser power goes up. The relation between laser power and open-circuit voltage is nonlinear when the laser power is below 2.5 mW, and starts to become linear when the laser power is over 2.5 mW. Owing to the limitation of the maximum power of the laser source available in our Raman spectrometer, we could not obtain more data for determining the mathematical relationships showing the dependence of both the open-circuit voltage and the short-circuit current on laser power.

4. Summary

A Raman spectrometer may be adapted for a combination of the fabrication, material characterization and photovoltaic effect measurement of an optical signal coupler and optical power transmitter using a microwire/nanowire of tungsten oxides. Using this, a heterojunction may be prepared in a single fine-wire of tungsten oxides without relying on expensive micro-fabrication facilities. The output current and the output voltage are detected from such a heterojunction under laser irradiation without applying an external bias voltage, and both of them can be switched quickly, showing its potential as an element of a microwire optical coupler. Also, the WO_2–WO_3 heterojunction can yield a maximum output power of up to 37.4 pW per heterojunction for an input laser beam of 514.5 nm, showing its attractive perspective as a microwire element of a future optical power transmitter for wireless powering of a nanoelectronic or nano-optoelectronic integrated circuit. We believe that if a nanowire of tungsten oxides is used, a similar photovoltaic effect should be observed.

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