Photochromic and Field Emission Properties of Ag-TCNQ Micro/Nanostructures

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Abstract. To study the opto/electrical properties of metal organic complex Ag-TCNQ mico/nano structure, they were grown on Si, glass and silver plate substrates by a solution reaction and a vapor-transport reaction, respectively. They were firstly characterized with scanning electron microscopy (SEM), X-ray diffraction (XRD), and Raman spectroscopy. Then Raman observation of single microwire and field emission display of nanowires array were studied experimenterly.

1. Introduction

The morphology, structure and phase control is a long standing problem for understanding the switching effect of charge transfer complex M-TCNQ composed of one metal and organic molecular tetracyanoquinodimethane(TCNQ). Among of them, Ag-TCNQ and Cu-TCNQ are both reported with two phases in form of bulk materials [1,2]. Xiao K et. al have reported the synthesis of Ag-TCNQ phase II as a three dimensional nanowires array by a vapor–solid chemical reaction growth method in the temperature region of 150-180°C at “atmosphere” pressure with the assistance of argon flow[3]. In our previous work, Ag-TCNQ nanostructured arrays were grown on single crystal silicon substrate by a “vacuum” vapor-transport reaction to study the influence of growth conditions on the structure, morphology and field emission properties. And the field emission from Ag-TCNQ nanowires has also been reported by other work[4, 5], but in fact the phase of them is not clear or
doubtful. In our study, the nanowires synthesized at different temperatures are in different phases and the phase change from II to I happens with increasing the reaction temperature[6].

2. Experimental details

Metal organic complex Ag-TCNQ micro/nano structure were grown on Si, glass and silver plate substrates by a solution and a vapor-transport reaction, respectively. They were characterized with X-ray diffraction (XRD), scanning electron microscopy (SEM) and Raman spectroscopy. Then Raman observation of single microwire was carried out to study the photochromic property and a field emission current density-field curve and display image of nanowires array were tested in a two-teminate device by a home-made setup. Raman measurements were carried out on LabRam-1B microscope Raman spectrum instrument (Dilor, France). The source exciting laser wavelength is 632.8 nm and the power is 3 mW. The photochromic measurement was carried out at room temperature in air. Using the CCD system attached to the measurement system, Ag-TCNQ microwires can be easily identified from the as-prepared sample and the light spot was adjusted on one single crystal.

3. Results and discussion

The XRD analysis showed they were crystals in form of phase II and phase I by different method, respectively. The SEM results showed that Ag-TCNQ wire or tube synthesized by the solution reaction was in a micro/nano scale. Ag-TCNQ nanowires by the vapor reaction between Ag droplets and TCNQ molecules were grown vertical to the silver plate substrate, while those were mussy on the glass substrate by the same vapor method. Raman data showed they were both incomplete charge-transfer product. After laser irradiation toward a micro single Ag-TCNQ wire, the dark blue colored wire changed into a yellow one. Moreover, a characteristic peak of neutral TCNQ was observed in the Raman spectrum, but vanished after 30 s or longer laser irradiation. So the single Ag-TCNQ quasi-one-dimensional micro/nano wire displays a reversible photochromic property which can be used to make optical memory elements and optical switches.
Fig. 1. Raman spectra of a single Ag-TCNQ crystal before and after photochromism.

(a): before photochromism
(b): after photochromism

Fig. 2. I-E curve and F-N plot (inset) of field emission for Ag-TCNQ nanowires on Ag plate.

Ag-TCNQ nanowire on Ag plate

d = 250 μm

Applied Field (V/μm)

Current Density (μA/cm²)

Wavenumber (cm⁻¹)

Intensity (a.u.)
Direct experiment for field emission of Ag(TCNQ) nanowires array on Ag plate is carried out here. Results are shown in Fig. 2. It shows the $I$-$E$ curve and its corresponding F-N plots (inset) for field emission from Ag-TCNQ nanowires reacted with 30 nm-thick Ag film on Ag plate. The $I$-$E$ curve has a seemingly feature of the exponential relation. The turn-on field for emission is about 1.50 V/μm, which is much lower than those nanowires on Si substrate. The F-N plot is separated with low and high field regions for the whole emission process, not in complete agreement with the exponential relation especially in the low field region. The slopes and intercepts of these two dotted lines showed that the effective emission area and the work function for the Ag-TCNQ nanowires are not constant under different fields.

As far as the enhancement of field emission from the special structure signed by ITO/Ag/Ag(TCNQ) to ITO/Ag(TCNQ), the contribution of the buffer layer of metal Ag film is considered to be predominant [4]. Here, the as-grown Ag-TCNQ nanowires generating from 30 nm-thick Ag film on Ag plate and under other same conditions have the same morphology and phase structure with that from the buffer layer. XRD results show it belongs to phase I. So the field emission is in the same or alike order.

Further experiment was performed to fabricate field emitter in order to evaluate the properties of Ag-TCNQ nanowires with form of phase I in the device application. The following Fig. 3 showed the photographs of prototype device and lighting display image during the emission at the field of 3.0 V/μm, They suggested a promising reliability in FE device application.

Fig. 3 Photographs of display image from prototype device at the field of 3.0 V/μm
4. Conclusion

Ag-TCNQ single micro/nano wire and nanowires array, in form of phase II and I, were successfully grown on Si wafer and on Ag plate or glass substrate without any template. The reversable photochromic property from micro/nano wires can be used to make optical memory elements and optical switches. Field emission enhancement were gained by adding a μm-thick metal buffer layer between the glass or silver plate substrate and the nanowires. This makes it convenient to further study their fundamental problem and potential application in optical storage, ultrahigh-density nanoscale memory, and logic devices and display devices as well.

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