Electrical and field emission properties of single crystalline MoV_2O_8 nanowires

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Single crystalline molybdenum vanadate nanowires (MoV_2O_8) were grown on silicon substrates by a simple thermal annealing of spin coated film in the air. The nanowires grown by this method have an average diameter of 100 nm and length between 1- 5μm. The nanowires show decent field emission current densities with a turn-on field of ~1.9 V/μm and good emission stability. The four terminal electrical resistivity of a single nanowire was measured to be 70 Ωcm. Thus, we expect that MoV_2O_8 will be useful as material for future field emitters.

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1. Introduction

Field emission is technologically important for vacuum microelectronic devices such as field emission displays, x-ray source, microwave devices, etc [1-5]. FE emitters based on 1D metal oxides such as ZnO, CuO, WO3 and MoO3 [6-9] have gained great attraction owing to the feasibility in precise structural control during the growth process and hence, a more predictable current-voltage characteristic. Metal vanadates, such as copper vanadates, bismuth vanadates, and zinc vanadates, have recently attracted great scientific attention because of their unique properties such as high mechanical strength, electronic properties, photonic efficiency, and chemical stability [10-14]. Of these metal vanadates, 1D nanostructures of MoV_2O_8 with good conductance are considered to be ideal field emission electron sources. However, there is limited work on this material In our previous report we have studied its electrochemical properties. In this work we have grown high quality single crystalline MoV_2O_8 nanowires on the p-type Si wafers. The direct growth of nanowires on the p-type Si substrate offers a much better electron transport capability by providing a direct conduction path, which is very helpful to lower the contact resistance between nanowires and substrates for enhancing FE of nanowires. We have studied the electrical measurement of individual nanowire and field-emission properties of as grown nanowires. The high field emission current density achieved makes the MoV_2O_8 nanowires a promising candidate for high the current field emitter of flat panel displays and high brightness electron sources.

2. Experimental

We synthesized MoV_2O_8 nanowires via a spin coated solution method following our reported recipe. All chemicals used in this experiment which include, Ammonium metavanadate (NH_4VO_3) molybdenum water and hydrochloric acid (HCl) were of analytical grade and purchased from Sigma Aldrich. They were used without further purification. In a typical synthesis of MoV_2O_8 nanowires ammonium metavanadate (0.2 mmol) was dissolved in 4 ml of molybdenum water with continuous stirring. Concentrated HCl (1.5 ml) was added drop wise for complete dissolution of NH_4VO_3. The resultant yellow solution was used for further experimentation. The precursor solution was spin coated on SiO_2 substrates at 2000 rpm for 30 s which have been ultrasonically cleaned in acetone, alcohol and IPA prior to the deposition. The spin coated substrates were placed into the oven at 550 ºC for 2 h.

3. Results and discussion

The FE-SEM analysis (JEOL JSM 7401F) of the synthesized MoV_2O_8 nanowires was carried out and the results are presented in the Fig. 1(a). The results show that the nanowires having an average diameter of 100 nm and length up to tens of micrometers. X-ray diffraction patterns of the MoV_2O_8 nanowires at are shown in Fig. 1(b) The nanowires synthesized at 550 C consists of a well-defined diffraction peak of orthorhombic MoV_2O_8 (JCPDS card 74-0050). The nanowires were further characterized by TEM and HRTEM analysis. The TEM image of the single nanowire is shown in Fig. 2(a). HR-TEM image of a nanowire is shown in Fig. 2(b) in which the lattice fringes are clearly visible. The distance between the neighboring fringes was found to be 4.1 Å which is consistent with the (201) plane of orthorhombic MoV_2O_8.The selective area electron diffraction (SAED) pattern in Fig. 2(c) confirms the single crystalline nature of nanowires. The chemical composition of the MoV_2O_8

nanowires was determined by Energy dispersive X-ray analysis (EDXA). The Fig. 2(d), EDXA spectrum of the MoV_2O_8 nanowires shows that the nanowires contain only, Mo,V and O with no trace of by-products.

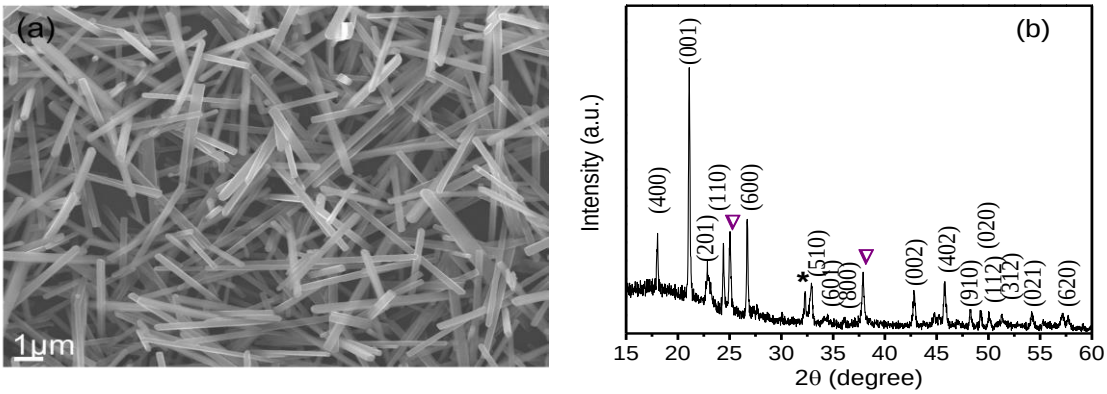

Fig. 1. (a) FE-SEM of nanowires (b) XRD of MoV_2O_8 nanowires,(◊) MoO_3 and (*) Si substrate.

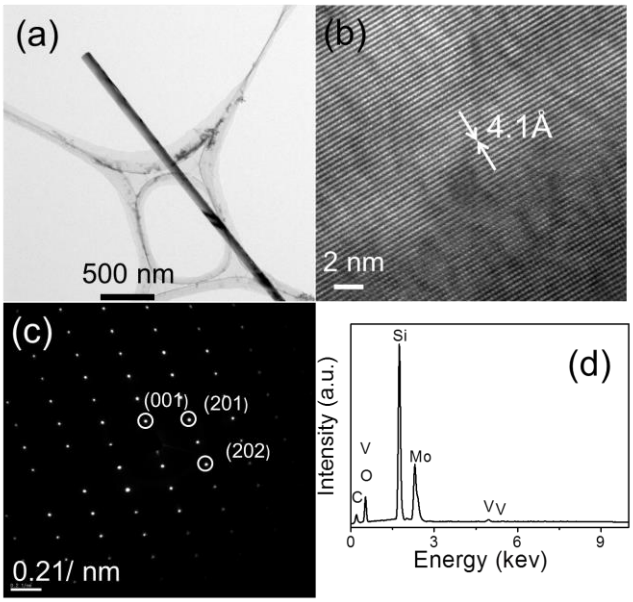

Fig. 2. (a) Low magnification TEM image of nanowires, (b) HR-TEM of nanowire showing high crystallinity (c) corresponding SAED pattern of individual nanowire recorded along [010] zone axis and (d) the EDXA of nanowires show that nanowires are composed of V, Mo and O.

The electron field emission characteristics of MoV_2O_8 nanowires were investigated in a high vacuum chamber with a parallel diode-type configuration at a base pressure of 5×10^{-7} mbar. The field emission current was measured at different voltages using an automatically controlled Keithley 2001 electrometer and DC power supply (HCN, 700-3500). The as-grown nanowires were placed into the vacuum chamber. A stainless-steel probe was used as an anode to induce electrons from the cathode nanowires. The distance between the cathode and anode was 450 µm. A DC voltage sweeping from 40 to 3000 V was applied during the measurements. Fig. 3(a) shows a typical plot of current density versus the electric field for MoV_2O_8 nanowires. The turn-on field is 1.9 V/µm (defined at emission current density of 10 µA/cm^2). The maximum current density for a MoV_2O_8 sample was found to be 800µA/cm^2.

We expect that, direct growth of nanowires on p-type Si substrate facilitates fast transfer of electrons between the nanowires and substrate compared to nanowires grown by hydrothermal or solution methods. The Fig. 3 (b) shows the corresponding Fowler–Nordheim (FN) plot of the field emission property of MoV_2O_8 nanowires. The linearity of the FN curve indicates that the electron emission for MoV_2O_8 nanowires possibly results from a quantum tunneling process [16]. Emission stability of the MoV_2O_8 nanowires was examined by measuring emission over time. No obvious degradation of current density was observed during 1 hour of continuous operation, with the current density at about 40 µA cm^{-2}, as shown in Fig. 3(c). The current fluctuation was within 5%, showing that MoV_2O_8 nanowires provide better emission stability, which is important in practical applications. The electrical transport property of the nanowires was studied on individual nanowire. The nanowires were first removed from the growth substrate by sonication in isopropyl alcohol and deposited onto a silicon substrate capped with a 200 nm silicon dioxide layer. Electron -beam lithography was used to define 4 terminal metal electrode windows, followed by the metal deposition of Ti/Au (5 nm/150 nm) by electron beam evaporation (Fig. 3d, inset). Electrical properties (*I-V*) were measured using four probe station which has Keithley 2612 Source Meter. The typical current-voltage (*I-V*) behavior of individual nanowire is shown in Fig. 3(d). The resistivity (ρ) of nanowire was calculated using the relation $\rho = R*A/l$ where R is the resistance, A is an area of nanowire (width and height) and l is the length of the nanowire between the electrodes. The resistivity of single a nanowire was found to be 70 Ωcm.

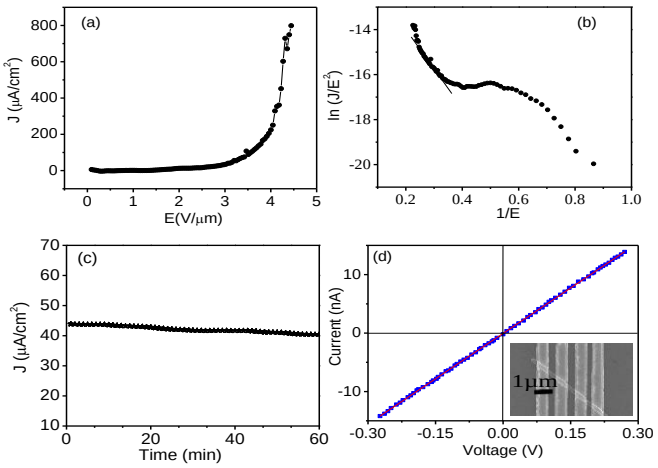

Fig. 3. (a) Field emission current density vs. electrical field from nanowire emitters. (b) Corresponding FN plots of ln (J/E2) vs. 1/E for nanowires. Excellent agreement with the F–N theory of field emission is observed. (c) Stability of the field-emission current from the nanowires over time. (d) The typical characteristics of I–V curve of single nanowire. The bias varies from −0.3 to 0.3 V. Right inset: Scanning electron microscope image of devices.

4. Conclusions

In conclusion, we have successfully grown high quality single crystalline MoV_2O_8 nanowires by the thermal decomposition of spin coated film. Field emission measurements reveal that the turn-on field of the nanowire is 1.9 V/μm. The four terminal electrical resistivity of single nanowires was found to be 70 Ωcm. The experimental results suggest that this facile preparation method could be suitable for the growth of other complex metal-oxide nanowires which can be used in many applications.

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