



## Position-selective metal oxide nano-structures using graphene catalyst for gas sensors



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### ABSTRACT

The thermal transport growth of various metal oxide ( $\text{MO}_x$ ) nanostructures using graphene as a catalytic layer was studied. Graphene was synthesized by Cu-catalyzed chemical vapor deposition and transferred onto a  $\text{SiO}_2$ -covered Si substrate using bubble transfer methods. Due to the catalytic activity of the atomic-thick carbon layer, control of the position of the  $\text{MO}_x$  nanostructures as well as the growth parameters, such as nucleation density and growth rate, could be achieved. The position-selective and density-controlled  $\text{MO}_x$  nanostructures were evaluated for hydrogen gas sensor applications, where different responses were obtained with hydrogen molecules.

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### 1. Introduction

Semiconducting metal oxides ( $\text{MO}_x$ ) are functional materials that have advanced applications in many fields, such as optoelectronic devices, catalysts, and sensors, due to their unique properties (optical, electrical, magnetic, etc.), hardness, thermal stability, and chemical resistance [1–3]. As novel applications of  $\text{MO}_x$  nanostructures continue to attract significant interest, new synthesis methods are being developed and new structures are being reported [4–6]. Among the several methods for synthesis of  $\text{MO}_x$  nanostructures, thermal transport is one of the easiest ways to fabricate many kinds of  $\text{MO}_x$  nanostructures, tubes, wires, rods, belts, disks, etc. [7,8].

Many researchers have studied the growth of  $\text{MO}_x$  nanostructures by the thermal transport method using metal catalysts such as Pt, Au, and Ag [9–12]. However, these catalytic metals are not only expensive, but also cause residual contamination after the

growth process. On the other hand, the use metallic element of  $\text{MO}_x$  as a catalyst for growth of the  $\text{MO}_x$  nanostructure can proceed free of contamination issues [13–15]. In this study, the carbo-thermal reduction method ( $\text{MO}_x + \text{graphite (C)} \rightarrow \text{Me} + \text{CO}_2$ ) is used to supply enough metallic element of  $\text{MO}_x$  for thermal transport growth because conventional  $\text{MO}_x$  has a very high decomposition temperature [16–18]. Additionally, to achieve position selectivity, a graphene layer grown by chemical vapor deposition is transferred to the target area of the substrate. Based on density functional theory calculations, the  $\text{sp}^2$ -bonded carbon atoms of graphene can easily from metal-carbide bonds, resulting in preferred nucleation of  $\text{MO}_x$  on the transferred graphene surfaces [19].

To realize this idea experimentally, we focused on several  $\text{MO}_x$  species by considering the stoichiometric ratio between metal and oxygen, the melting temperature, and the type of semiconducting charges: ZnO (n-type,  $T_{\text{melt}} = 1975^\circ\text{C}$ ), SnO (p-type,  $T_{\text{melt}} = 1080^\circ\text{C}$ ),  $\text{SnO}_2$  (n-type,  $T_{\text{melt}} = 1630^\circ\text{C}$ ), and  $\text{WO}_3$  (n-type,  $T_{\text{melt}} = 1473^\circ\text{C}$ ),  $\text{MoO}_3$  (n-type,  $T_{\text{melt}} = 795^\circ\text{C}$ ). The  $\text{MO}_x$  powders were mixed with graphite to obtain sufficient metal flux for thermal transport growth. The crystal structures and morphologies of the  $\text{MO}_x$  nanostructures are investigated by X-ray diffraction (XRD), scanning electron microscope (SEM), and energy dispersive spectroscopic (EDS) analysis. Finally, the  $\text{MO}_x$  nanostructures (n-type ZnO,

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MoO<sub>3</sub>, and p-type SnO decorated SnO<sub>2</sub>) that are automatically connected to each other due to high-density nucleation on the graphene layer, are directly applied as gas sensors, specifically for hydrogen molecules.

## 2. Experimental methods

**Graphene growth and transfer:** Graphene was grown on commercial Cu foils (Alfa Aesar, item No. 13382, 99.8% purity) by the chemical vapor deposition (CVD) method reported in our previous studies [20]. To transfer the synthesized graphene to the target area of the substrate, we used the bubbling transfer method that utilizes hydrogen bubbles generated at the interface of polymethyl methacrylate (PMMA, spin-coated on graphene at 900 rpm for 60 s and dried under ambient atmosphere for 10 min)/graphene and the Cu cathode surface [21]. Hydrogen bubbles were generated by the electrochemical reaction ( $2\text{H}_2\text{O} (l) + 2e^- \rightarrow \text{H}_2 (g) + 2\text{OH}^- (aq)$ ) by applying 3 V and 30 mA (with a Pt anode) to a 0.5 M NaOH solution [22]. The delaminated PMMA/graphene layer was scooped onto a SiO<sub>2</sub>/Si (100) substrate and cleaned with DI water several times, then dried for 1 h before heating at 180 °C for 30 min to increase the adhesion between graphene and the substrate. Finally, the PMMA layer was removed by using acetone, isopropyl alcohol, and DI water, in sequence.

**Metal oxide growth:** Four different MO<sub>x</sub> powder sources were used for carbo-thermal transport, i.e., ZnO (Sigma-Aldrich, item No. 96479), MoO<sub>3</sub> (Sigma-Aldrich, item No. M0753), WO<sub>3</sub> (Sigma-Aldrich, item No. 550086), and SnO (Sigma-Aldrich, item No. 14527, as sources of SnO and SnO<sub>2</sub>). The MO<sub>x</sub> powder was mixed with graphite powder (99%, Daejung, item No. 4071–1400) in an atomic ratio of 1:2 and placed in the center of quartz tubes with alumina boats. The substrates (half of the SiO<sub>2</sub> surface was covered with graphene) were placed in the end of a furnace 15 cm away from the boat (see Fig. 1a). The vacuum pressure was reduced to 5 mTorr using a mechanical pump, and helium gas (He) was then introduced into the tube at a flow rate of 40 sccm while heating for 1 h until the growth temperature was reached. The alumina boats with the source materials were heated in the center of the furnace as follows: 900–1000 °C (ZnO), 600 °C (MoO<sub>3</sub>), 1000 °C (WO<sub>3</sub>), and 700–900 °C (SnO and SnO<sub>2</sub>). After reaching the growth temperature, O<sub>2</sub> gas was introduced into the chamber for 10 min and the

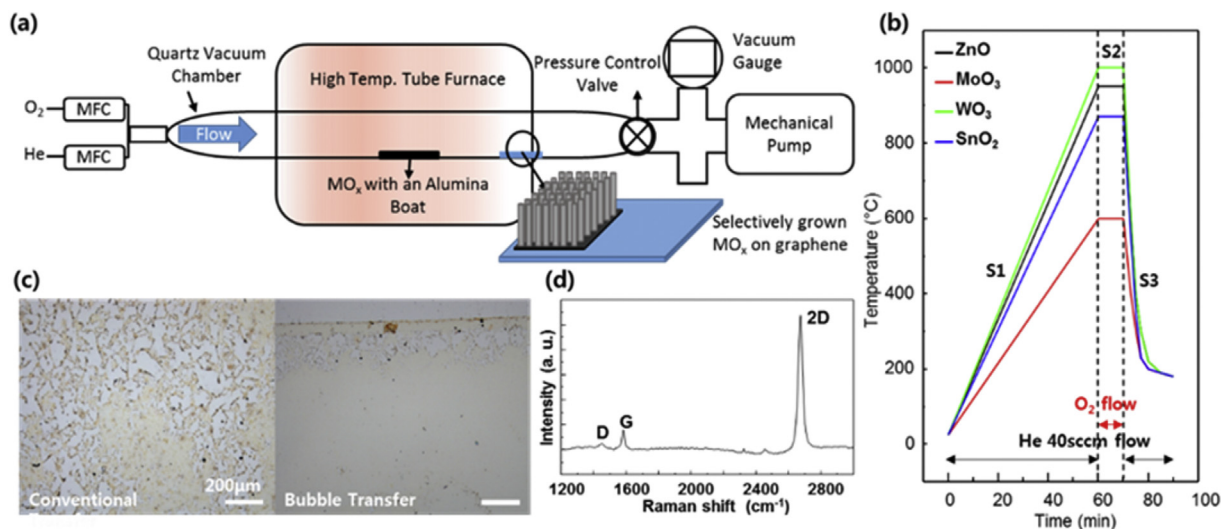
flow rate was controlled within the range of 20 sccm to 200 sccm for growth of the MO<sub>x</sub> nanostructures. After growth, the furnace was cooled to room temperature with He flow at 40 sccm. For the better understanding, we added the time-temperature graph as shown in Fig. 1b.

**Analysis:** Raman spectra were obtained with a LabRAM HR Evolution–Nicolet iS50 (HORIBA–Thermo, Jobin Yvon) spectrometer using a He–Ne excitation source (532 nm), with a laser beam spot size of 1 μm in diameter, and an accumulation time of 60 s. X-ray diffraction was performed with a Rigaku MiniFlex spectrometer (XRD; 3 kW, Cu-Kα, HD307172) at a scan speed of 2°/min. Scanning electron microscope (SEM) images were acquired and energy dispersive spectroscopic (EDS) analysis was performed by using a JSM-6700F (JEOL) device at 5.0 kV. Hydrogen gas sensing tests were conducted with a Keithley-4200 instrument in the vacuum probe station chamber at room temperature (for ZnO) and at 200 °C (for MoO<sub>3</sub> and SnO<sub>2</sub>). Due to high density of MO<sub>x</sub> nanostructures, direct electrical wiring on the MO<sub>x</sub> surface was done by silver paste (ELCOAT P-100, CANS) without additional process. The distance between electrodes was 0.5 cm. X-ray photoemission spectroscopy (XPS) was carried out in an AXIS Ultra DLD model (KRATOS, U.K.) at the Korea Basic Science Institute. XPS spectra were obtained at a base pressure of  $2.0 \times 10^{-10}$  Torr at 300 K with a monochromatic Al Kα line at 1486.69 eV.

## 3. Results and discussion

To use the high-quality graphene sheet as a catalytic seed layer for the functional MO<sub>x</sub> nanostructures, we did not use the conventional transfer method that employs Cu etchants such as FeCl<sub>3</sub>, Fe(NO<sub>3</sub>)<sub>3</sub>, or (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub>, but the bubble transfer method was used herein as explained in the experimental section. By using bubble transfer, a clean graphene surface without residual carbon and impurities was obtained (see Fig. 1c). The Raman spectrum of bubble-transferred graphene comprises a high-quality monolayer as shown in Fig. 1d (showing a weak D peak (~1350 cm<sup>-1</sup>), which is related to defects, and a strong symmetric 2D peak (2690 cm<sup>-1</sup>) with a 2D/G (1580 cm<sup>-1</sup>) peak ratio of more than 3.0) [21,23].

Fig. 2 shows the MO<sub>x</sub> nanostructures grown on the substrate (half of the SiO<sub>2</sub>/Si surface was covered by graphene) via the carbo-thermal transport method (the O<sub>2</sub> flow rate was fixed at 150 sccm).



**Fig. 1.** (a) Schematic image of graphene synthesized by CVD and MO<sub>x</sub> growth. (b) Time-temperature graph for the MO<sub>x</sub> nanostructure growth. (c) Optical images of graphene on SiO<sub>2</sub>/Si substrate; left: conventional transfer; right: bubble transfer method. (d) Raman spectra of graphene after bubble transfer onto the SiO<sub>2</sub>/Si substrate. (A colour version of this figure can be viewed online.)

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