



Preparation and characterization of graphene-based vanadium oxide composite semiconducting films with horizontally aligned nanowire arrays



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ABSTRACT

Highly oriented crystalline hybrid thin films primarily consisting of Magnéli-phase VO₂ and conductive graphene nanoplatelets are fabricated by a sol–gel process via dipping pyrolysis. A combination of chemical, microstructural, and electrical analyses reveals that graphene oxide (GO)-templated vanadium oxide (VO_x) nanocomposite films exhibit a vertically stacked multi-lamellar nanostructure consisting of horizontally aligned vanadium oxide nanowire (VNW) arrays along the (*hk*0) set of planes on a GO template, with an average crystallite size of 41.4 Å and a crystallographic tensile strain of 0.83%. In addition, GO-derived VO_x composite semiconducting films, which have an sp³/sp² bonding ratio of 0.862, display thermally induced electrical switching properties in the temperature range of –20 °C to 140 °C, with a transition temperature of approximately 65 °C. We ascribe these results to the use of GO sheets, which serve as a morphological growth template as well as an electrochemically tunable platform for enhancing the charge-carrier mobility. Moreover, the experimental studies demonstrate that graphene-based Magnéli-phase VO_x composite semiconducting films can be used in advanced thermo-sensitive smart sensing/switching applications because of their outstanding thermo-electrodynamic properties and high surface charge density induced by the planar-type VNWs.

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1. Introduction

Graphene oxide (GO) nanosheets with abundant oxygen-containing functional groups (i.e., hydroxyl, epoxide, carbonyl, and carboxyl acid groups) on the basal planes and edges have been adopted as starting materials for the development of graphene-based conductive composite materials (GCMs) using solution processes [1,2]. Various types of solution-based GO-derived graphene nanocomposites such as graphene polymers, graphene-metal nanoparticles, graphene-metal oxides, and graphene-carbon nanotubes have been explored to develop highly active hybrid materials [3–7]. Among the numerous graphene-related composites, low-dimensional GCMs synthesized using semiconducting hosts including TiO₂ [8–12], SnO₂ [13–16], Fe₂O₃ [17], MnO₂ [18–23], Cu₂O [24,25], RuO₂ [26], NiO [27], and CdS [28–30], have recently received widespread attention as state-of-the-art multifunctional semiconductors because of their remarkable optical, chemical, and electrical properties. Most of the previous studies indicate that graphene-related compounds incorporated into semiconductors alter their charge-carrier transport characteristics, leading to a drastic improvement in some of the related properties of the host materials. Although a considerable amount of effort has been devoted to investigating material

properties of the low-dimensional GCM hybrids, highly stable and electrically conductive GCMs with well-defined nanostructures can be further developed using unexplored hosting materials (e.g., Magnéli-phase vanadium oxides or VO_x) for possible use in thermo-sensitive electronic applications.

Based on the critical reviews available in the literature, Magnéli-phase VO_x corresponding to the general stoichiometric formula V_nO_{2n-1} (3 ≤ n ≤ 9), (e.g., VO₂, V₂O₃, and V₃O₅), have been used in a wide range of GCM applications, primarily focusing on the electrodynamic properties due to a first-order structural transformation in the crystal lattice at the transition temperature [31–34]. We sought to adjust the electro-dynamic properties across the insulator to metal transitions in Magnéli-phase VO_x for thermo-sensitive smart sensor applications. We noted that the phase transition temperature, maximum electrical resistivity, and magnitude of the resistivity variation can be altered by modifying the microstructural characteristics as well as by adding doping elements. We recognized that the GO-derived graphene materials are ideally suited for use as a controllable structural modifier and an n-type dopant for fabricating low-dimensional graphene/Magnéli-phase VO_x composites with desirable electro-dynamical characteristics. Recently, a small number of studies on randomly oriented vanadium pentoxide (V₂O₅) nanowires grown on reduced graphene oxide (rGO) have reported highly conductive graphene–V₂O₅ composites fabricated using a green

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approach (i.e., a hydrothermal method) [35,36]. The graphene-derived V_2O_5 nanowires exhibited improved electrochemical properties that are well suited for electrode materials with high energy and power densities, particularly for lithium-ion batteries and super-capacitance applications. However, there have been relatively few attempts to apply GOs as chemically active growth templates to the formation of well-ordered nanowire arrays using polycrystalline Magnéli-phase VO_x as electrical switching devices. This study was motivated by the need to determine the intrinsic material characteristics of the little-known graphene- V_nO_{2n-1} (G/VO_x) composite semiconductors as part of an effort to exploit low-dimensional GCMs with outstanding thermo-electrodynamic properties.

Herein, we report the synthesis and material characteristics (i.e., chemical, structural, and electrical properties) of G/VO_x composite films with highly horizontally aligned Magnéli-phase VO_x nanowire (VNW) arrays using solution mixing techniques. To fabricate well-aligned composite films, two-dimensional GO platelets were used as morphological molecular templates for the preferentially oriented growth of planar-type VNWs. Subsequently, we investigated the morphological features, crystalline phases, crystallographic orientations, chemical bonding states, and thermally induced electrical hysteresis of the as-prepared G/VO_x composite films by a series of chemical, microstructural, and electrical analyses using field emission scanning electron microscopy (FE-SEM), transmission electron microscopy (TEM), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), Raman spectroscopy, and the four-point probe technique.

2. Experimental details

2.1. Materials

Vanadium (V) oxytriisopropoxide, VTIP or $VO(OPr^i)_3$, was purchased from Sigma-Aldrich Co. LLC as the VO_x precursor. A highly concentrated GO aqueous dispersion with a composition of 79% carbon and 20% oxygen was obtained from Graphene Supermarket in the USA (concentration of 5.0 mg per 1.0 mL) as the GO precursor. The GO was synthesized via a modified Hummers' method and was then homogeneously dissolved in water with a flake thickness of one atomic layer (at least 60%) and a flake size of 0.5–5 μm . Isopropyl alcohol (2-propanol, anhydrous, 99.5%, IPA or $Pr^i(OH)$) was received from Sigma-Aldrich Co. LLC and was used as a diluent solvent. All of the reagents were used as purchased without any further purification.

2.2. Preparation of G/VO_x hybrids

Commercially available $VO(OPr^i)_3$ and GO chemical reagents were used as the starting materials in a hydrolytic sol-gel processing method. First, 76.8 mL of 2-propanol, which is the parent alcohol of vanadium alkoxide, was poured directly into a vial, and then 3.5 mL of as-received $VO(OPr^i)_3$ was carefully added in an inert environment. The $VO(OPr^i)_3/Pr^i(OH)$ solutions were stirred for 10 min, and then 3.5 mL of the GO (i.e., 0.03wt.%) dispersion was introduced to the as-prepared vanadium-containing solution dropwise under constant stirring to avoid precipitate formation in the mixture. The as-obtained solution was vigorously stirred at room temperature for 1 h. During the solution mixing process, the color changed from transparent to dark green. Subsequently, the as-synthesized mixed solution was aged in a cool environment (i.e., 3–5 °C) for 72 h to induce the formation of V_2O_5 nanowire networks based on hydroxylation and condensation processes.

2.3. Fabrication of G/VO_x composite films

The as-prepared G/VO_x hybrid solutions were directly deposited by dip-coating onto the surface of amorphous fused quartz substrates using a computer-controlled precision dip-coater in a hermetic chamber under ambient conditions. The substrates, with sizes of 2 cm \times 2 cm, were pre-cleaned using the conventional RCA cleaning procedure

(i.e., 1:1:5 concentrated $NH_4OH/H_2O_2/H_2O$ wash followed by 1:1:6 concentrated $HCl/H_2O_2/H_2O$) before the dip-coating procedure. The freshly surface-modified substrates were withdrawn vertically from the as-synthesized mixed solutions at a hoisting speed of 5.0 mm s^{-1} , and the dipping time was maintained at 3 min. During the process, the entrained fluid films rapidly concentrated on the substrate surface in the form of an aggregated gel by a complex process involving gravitational draining and solvent evaporation. Then, the as-deposited homogeneous wet gel films were dried at 80 °C in the air using a halogen lamp to remove the residual organic components and to facilitate the condensation reaction. The as-obtained dried gel films were post-heat-treated at 500 °C for 2 h under a vacuum of 1.333×10^{-2} Pa at a heating rate of 3.5 °C min^{-1} to reduce (i.e., deoxygenate) the V_2O_5 and GOs to V_nO_{2n-1} Magnéli phases and rGOs within the dried films. After the post-heat-treatment process, all of the samples were cooled naturally at atmospheric temperature and were stored separately in labeled containers.

2.4. Measurement and characterization

The morphology and microstructure of the samples before and after post-heat treatments were investigated by FE-SEM using a JEOL JSM-6700F instrument with a 15-kV accelerating voltage. For FE-SEM analysis, the prepared sample was cut into a small square piece using a cutting tool. Then, the sample was fixed on the specimen holder using a conducting silver paste. After the silver paste was dried at room temperature for 1 h, we observed the surface morphology and the cross-sectional microstructure of the samples. In addition, TEM observations were carried out using a JEOL JEM-3010 apparatus with an accelerating voltage of 300 kV in order to obtain more detailed information about the morphology and microstructure of the VNWs in the post-annealed composite films. The site-specific TEM specimens were prepared by a dual-beam focused-ion beam (FIB/SEM) lift-out method using a FEI Helios Nanolab 650 instrument with a Ga^+ ion beam of 30 kV and a probe current of approximately 10–100 pA. In this method, the surface region of interest on the G/VO_x composite films was covered with protective Pt layers and then the specimen was milled with the focused Ga^+ ion beam. After the precisely-controlled milling process, the thin lamellae between the trenches were lifted out and mounted onto a Cu grid for TEM analysis.

Crystallographic information for the samples, including their crystalline phases, crystal orientation, average size, and lattice strain, was obtained by real-time in-situ glancing incidence XRD (GIXRD) on a Rigaku Smart Lab diffractometer with a high-resolution Bragg-Brentano (θ - 2θ) geometry and monochromatic $Cu-K\alpha$ radiation ($\lambda = 1.5412 \text{ \AA}$) at 45 kV and 200 mA operated at a 1.5° incident angle. The GIXRD patterns were acquired at diffraction angles of 5° to 80° with a scanning speed of 3° min^{-1} and a detection interval of 0.02° in continuous mode. Then, time-resolved in-situ XRD measurements were performed in the temperature range of room temperature (RT) to 700 °C with a rate of 3.5 °C min^{-1} , a temperature interval of 50 °C, and a temperature holding time of 2 min at each temperature step.

XPS surface analyses were conducted to precisely determine the oxidation states of the vanadium ions and to identify individual elements on the sample surface. The XPS spectra were acquired using a Thermo Scientific Theta Probe utilizing monochromatic $Al-K\alpha$ radiation as the excitation source. In this study, the binding energy calibration was conducted on C—C component of C1s peaks of the G/VO_x charged sample in reference to the C1s peaks of a commercial source of GO (i.e., 284.7 eV), and a Shirley function was used to subtract the background signals for a quantitative evaluation of the measured XPS spectra. The calibrated XPS signals for C1s, O1s, and V2p were then fitted using mixed Lorentzian-Gaussian curves with the spectral fitting parameters (i.e., binding energies and the full width at half maximum (FWHM) values) to distinguish the different chemical compounds. Note that the FWHM values for V2p_{3/2} species of V_2O_5 and VO_2 standard samples on our instrument operated at 100 eV pass energy were 1.09 eV and 1.42 eV, respectively. To verify the existence of the GO derivative, Raman spectra were recorded

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