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Room temperature nitrogen dioxide chemresistor using ultrathin vanadyl-phthalocyanine film as active layer

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ABSTRACT

A room temperature nitrogen dioxide (NO_2) chemresistor using 1.8 nm ultrathin vanadyl-phthalocyanine (VOPc) film as active layer has been prepared by Weak Epitaxy Growth (WEG) method. Its gas sensing properties to NO_2 have been compared with a 7 nm polycrystalline VOPc chemresistor. The ultrathin film device shows stronger response and better recovery character. Further results reveal that the two-dimensional transport film provides an effective charge transfer system after NO_2 adsorption and it gets rid of bulk diffusion at the same time. Kelvin probe force microscopy (KPFM) results suggest that grain boundaries are easily doped by analyte but is slow in desorption compared with crystal grains. The ultrathin film device shows advanced sensing mechanism compared with the polycrystalline film.

1. Introduction

The nitrogen dioxide (NO_2) detection has been becoming a research focus due to the combustion exhaust pollution in recent years. Both organic and inorganic semiconductor materials have been extensively studied for NO_2 sensing [1–3]. But most of these devices operate at elevated temperature to gain satisfied sensitivity and recovery time [4]. This requires long-term operation of batteries and also limits their application in explosive and severe situations. So low power consumption, room temperature operating sensing devices are greatly desired.

Metal phthalocyanines (MPcs), which have been reported as sensitive to NO_2 in ppb levels at above 100 °C, are a class of promising materials for oxidative and reductive gas sensing [5–7]. By annealing the lead phthalocyanine film in the air over 3 h, good-response character to 10 ppm NO_2 gas can be obtained due to film morphology change [8,9]. But the harsh process operating at temperature near material sublimation temperature may also cause unexpected reaction or irreversible changes to the sensing layer which makes the devices not reproducible [10]. Newton et al. improved the copper phthalocyanine (CuPc) film's response by heavily NO_2 doping of the sensing layer to avoid the bulk penetration and leave the analyte sensing dominated by the faster surface adsorption/desorption process [11]. In previous work, sensing layers with thickness of 0.5–1 μm are mostly adopted to gain large surface area and detectable conductance. But the slow penetration of analyte into the bulk film at room temperature will always hinder the recovery process. The Langmuir–Blodgett (LB) films of MPc derivatives offers the chance to obtain sensing layers of molecular dimensions. The ultrathin layers fabricated by LB method with large surface to volume ratio give promise for molecular reception and discrimination [12]. The homogeneity of LB films decreases the number of strongly efficient adsorption sites which lead to fast response and thin layers help to reduce slow diffusion [13].

So a thin and homogeneous film with detectable conductance is desired for room temperature sensing. Here, we introduce a 1.8 nm ultrathin vanadyl-phthalocyanine (VOPc) film as sensing layer deposited by Weak Epitaxy Growth (WEG) method, which is a feasible approach to obtain highly ordered films [14]. The NO_2 response of ultrathin film has been investigated at room temperature. By comparing with 7 nm polycrystalline VOPc film (thinnest detectable polycrystalline film in our facility), the ultrathin film device shows stronger relative response and better recovery property at room temperature. Further experiments showed that the film continuity and surface potential distribution may greatly influence the analyte bulk penetration and surface active sites, respectively. And it shows that the two-dimensional transport in WEG film provides a promising way for room temperature gas sensing.

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2. Experimental

2.1. Fabrication of the organic films

The VOPc samples were purchased from Aldrich Company (USA), and the *para*-sexiphenyl (*p*-6P) sample was synthesized according to the method described before [15]. All the materials were purified twice by thermal gradient sublimation before experiments. The SiO_2 substrates used were thermally oxidized on heavily n-doped silicon and then polished. The *p*-6P films were sublimed onto SiO_2 surface at the substrate temperature of 180 °C. A quartz crystal microbalance was used to control the film thickness at 6 nm. VOPc was sublimed subsequently onto the *p*-6P film with a variety of thickness, 1.8 nm, 3 nm, 4.4 nm and 5.7 nm, to generate Weak Epitaxy Growth film as reported [16]. VOPc was also directly sublimed onto SiO_2 at the same substrate temperature to obtain 7 nm polycrystalline films for contrast.

2.2. Characterization of organic films

2.2.1. Atomic force microscopy (AFM) measurements

The morphologies of the organic thin films were characterized by SPI 3800N instrument (Seiko Instruments Inc.) by tapping mode. Topographical and phase images were obtained simultaneously. The scanner used was 100 μm and a commercially available SiN_4 cantilever with a spring constant of 3 N/m was used in all experiments.

2.2.2. KPFM measurements

The surface potential of 7 nm polycrystalline VOPc film, 1.8 nm ultrathin WEG film and 6 nm *p*-6P film have been characterized by Kelvin probe force microscopy in air. The scanner used was 150 μm and the cantilever was an Rh-coated rectangle Si probe with a spring constant of 1.6 N/m and the resonant frequency of 28.9 kHz. The sample films were evaporated to conductive Si slices and they were electrically connected to the KPFM systems via silver paint. Topographical and surface potential images were recorded simultaneously in lift mode. The *Vac* (ω) of 5 V with frequency of 20 kHz was applied to cantilever. Before each measurement, freshly cleaved highly oriented pyrolytic graphite (HOPG) is used as standard to determine the work function of tip. The work function of HOPG used is 4.475 eV [17].

2.3. Device preparation and sensor test

The schematic device structure is shown in Fig. 2(a) inset. The finger electrodes were fabricated by thermal evaporated Au on top of the organic film through shadow mask in another vacuum chamber. Each device contains 7 pairs of fingers with each finger of 3 mm length and 100 μm distance between each other. All the devices have been stored in air for 48 h before sensor test. The electrical measurement was taken by Keithley2636A double channel source measurement at the voltage of 1 V. Two Mass Flow Controllers (MFCs) (BROOKS 5850S) connected to Dell computer were used to control the flow rate of carrier gas and the standard NO_2 gas to generate diluted NO_2 sample of 10 ppm, 20 ppm and 25 ppm. Air was used as carrier gas and the temperature was stable at 295 K, the relative humidity was 18% during the whole measurement process. The flow rate in the test was fixed at 120 sccm and the gas inlet tubes were made of PTFE to avoid analyte adsorption. The sensor test was realized by exposing the devices to a constant flow of NO_2 gas doses in a homemade PTFE test chamber which was of 50 cm^3 volume inside. Each dose lasted 10 min and carrier gas air was used during the interval. Two devices were tested simultaneously to make sure the experiment repeatability for each sample.

3. Results and discussion

3.1. Surface morphology of sensing layer

The surface morphology of 7 nm polycrystalline film is shown in Fig. 1(a), and the 1.8 nm WEG VOPc film is shown in Fig. 1(b).

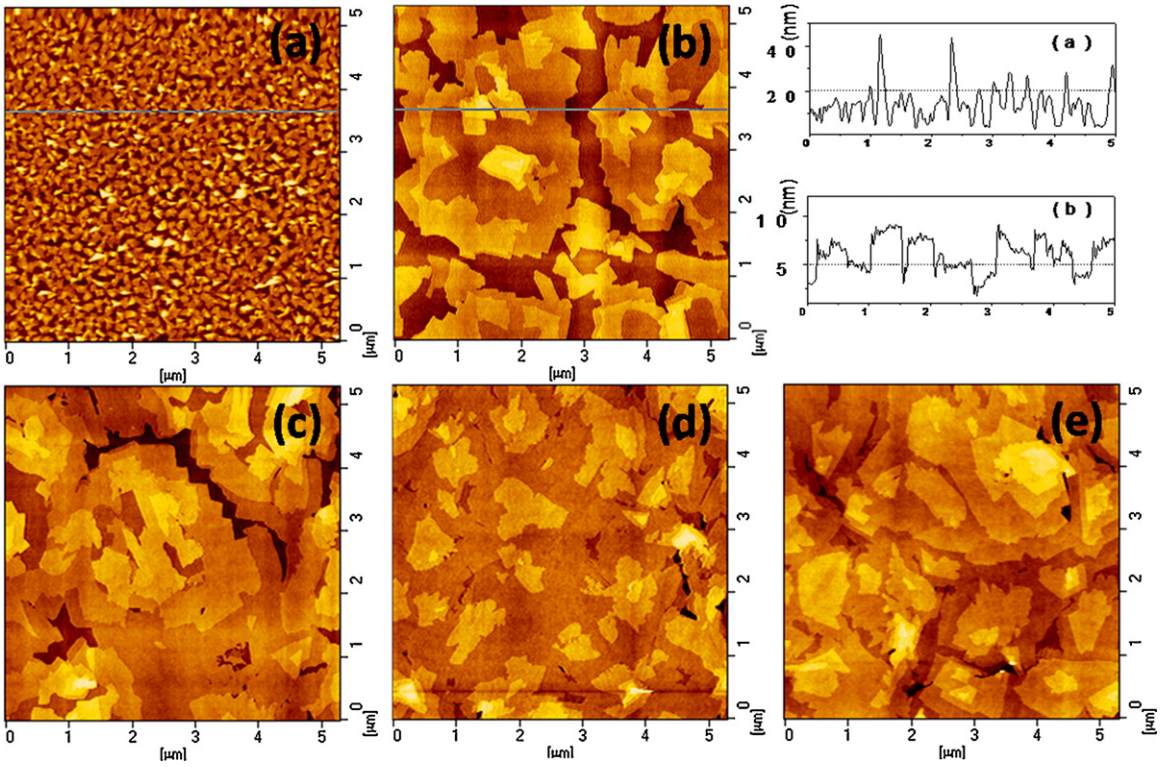

Fig. 1. AFM topography of (a) 7 nm polycrystalline film (b) 1.8 nm WEG VOPc film (c) 3.1 nm WEG VOPc film (d) 4.4 nm WEG VOPc film (e) 5.7 nm WEG VOPc film.