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Effect of CuO introduced on activated carbon fibers formed by electroless plating on the NO gas sensing

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ABSTRACT

High-performance gas sensors were fabricated from activated carbon fibers (ACFs) introduced with CuO. The electroless CuO plating of ACFs was carried out to investigate the nitric oxide (NO) gas sensing ability with respect the plating time. The gas sensors were fabricated by dropping a solution (CuO-introduced ACFs + DMF) onto SiO_2/Si wafers patterned with Pt electrodes. The NO gas sensing behavior of the ACF-based gas sensors was determined by resistance measurements. As the plating time increased, the CuO content on the ACF surface increased, and the specific surface area of the ACFs decreased. The gas sensor fabricated from untreated ACFs showed a 4% resistance change upon exposure to NO gas, whereas the sensor with CuO-introduced ACFs showed an approximately 12.5% resistance change. This phenomenon is attributed to the increased number of hole carriers in the ACFs due to CuO, which promotes electron transfer, and benefits the effective detection of NO gas. This method provides as a unique surface treatment strategy to improve the NO gas sensing efficiency.

Introduction

Toxic gases are generated in a variety of industries, and therefore, the detection of these gases is essential. Among these gases, nitric oxide (NO) gas is well-known, typical air pollutant that generates smog and acid rain. Furthermore, NO gas has an influence for environment and human health [1,2]. Thus, the development of a gas sensor to detect harmful gases in necessary. Gas sensors can be used to detect combustible, flammable and toxic gases. Ideal materials for gas sensors should have the following characteristics [3,4]: high sensitivity, high selectivity, fast response time and high recovery. The most important characteristic of a gas sensor is high sensitivity. Many researchers have developed high-performance gas sensor electrodes to achieve high sensitivity.

Gas sensors can be classified according to the operation mechanism, for example, semiconductors, electrochemical, catalytic, and optical gas sensors [3]. Among them, semiconductors are the most common [5]. Metal oxides and carbon nanotubes (CNTs) are examples of semiconductor-type gas sensor materials. Generally, metal oxide semiconductors are used as gas sensor materials due to their high electrical conductivity and rapid response time to target gases [4,5]. However, these sensors are operated at high temperatures over 200 °C [4–6]. CNTs have attracted attention as materials to replace metal oxides because they have the advantage of operating at room temperature [7–9]. However, CNTs are difficult to disperse during the preparation of gas sensors [10,11].

Activated carbon fibers (ACFs) have been examined as gas sensor materials to replace metal oxides and CNTs. ACFs have unique properties, such as a large micropore volumes and excellent adsorption capacities [2,12–16]. However, ACFs have poor electrical interactions between the carbon surface and target gases compared with CNTs, which leads to slow response times and low sensitivity due to the slow movement of electrons in ACFs [17].

Various surface treatments have been investigated to improve the electrical conductivity of ACFs [18–21]. Among them, the electroless plating technique is attractive for its easy operation, eco-friendliness and low cost, and thus, electroless plating has

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been well studied [22–24]. According to previous studies, Cu or CuO was introduced on carbon materials to improve the NO gas removal efficiency [25–28]. The introduction of metal (or metal oxide) on carbon materials can improve the selectivity, sensitivity, and response time.

In this study, we carried out electroless CuO plating to introduce CuO on the ACF surface. Additionally, the NO gas sensing properties were evaluated with respect to the electroless plating time.

Experimental

Electroless copper oxide plating

In this study, pitch-based ACFs (A-10, Osaka Gas, Japan) were used as the NO gas sensor electrode. The ACFs were made into powder by wet-ball-milling treatment. The wet-ball-milling treatment is performed by mixing 5 g of ACFs and balls for 90 s (paint shaker, COAD-1114), and the samples were dried in an oven at 373 K for 12 h. The dried samples were sieved to a size of 45 μm or less. The average length of the obtained sample is about 48.34 μm.

To introduce copper on the surface of the ACFs, surface treatment was carried out in three-steps. The first step was sensitizing. The ACFs were sensitized by immersion in 2 wt.% anhydrous tin(II) chloride (98.0%, Junsei, Japan) solution for 5 min in a bath sonicator at room temperature. Then, the sensitized samples were activated in 0.1 wt.% palladium solution (palladium (II) chloride, Aldrich, USA) for 2 min in a bath sonicator at room temperature. Finally, the palladium-loaded ACFs were submerged in the copper plating solution (copper(II) sulfate pentahydrate, Aldrich, USA) for a designated plating time (5, 10, 15, and 30 s) at 313 K and pH 7.5. The detailed values are presented in Table 1. After copper plating, the resulting sample was washed several times with distilled water to remove residual copper and dried overnight at 373 K. The samples are denoted CuO-5s, CuO-10s, CuO-15s and CuO-30s according to the electroless plating time, and the untreated ACF sample is R-ACFs. The mechanism of sensitizing, activation and electroless plating is shown in Fig. 1.

Characterization of the prepared samples

The morphologies of the ACF surfaces were analyzed by scanning electron microscopy (SEM, Hitachi, S-5500). Energy dispersive spectroscopy (EDS) was performed to confirm the presence of copper. The crystalline phases of CuO introduced on the ACFs were determined using X-ray diffraction (XRD, Empyrean). XRD analysis was conducted over a range of 10–80° using a Cu target. Each sample was degassed at 423 K for 6 h, and nitrogen adsorption was carried out at 77 K with an ASAP 2020 (Micromeritics Ins. Corp., USA) to measure textural properties such as the specific surface area (SSA), total pore volume and pore size distribution.

Preparation of the gas sensor

To uniformly disperse the samples in solution, the ACFs (0.1 g) were dispersed in DMF (1 g) and sonicated for 60 min.

Table 1
Preparation conditions for the electroless-plated ACFs.

Sample name	Reaction temperature (°C)	pH	Reaction time (s)
CuO-5s	40	7.5	5
CuO-10s			10
CuO-15s			15
CuO-30s			30

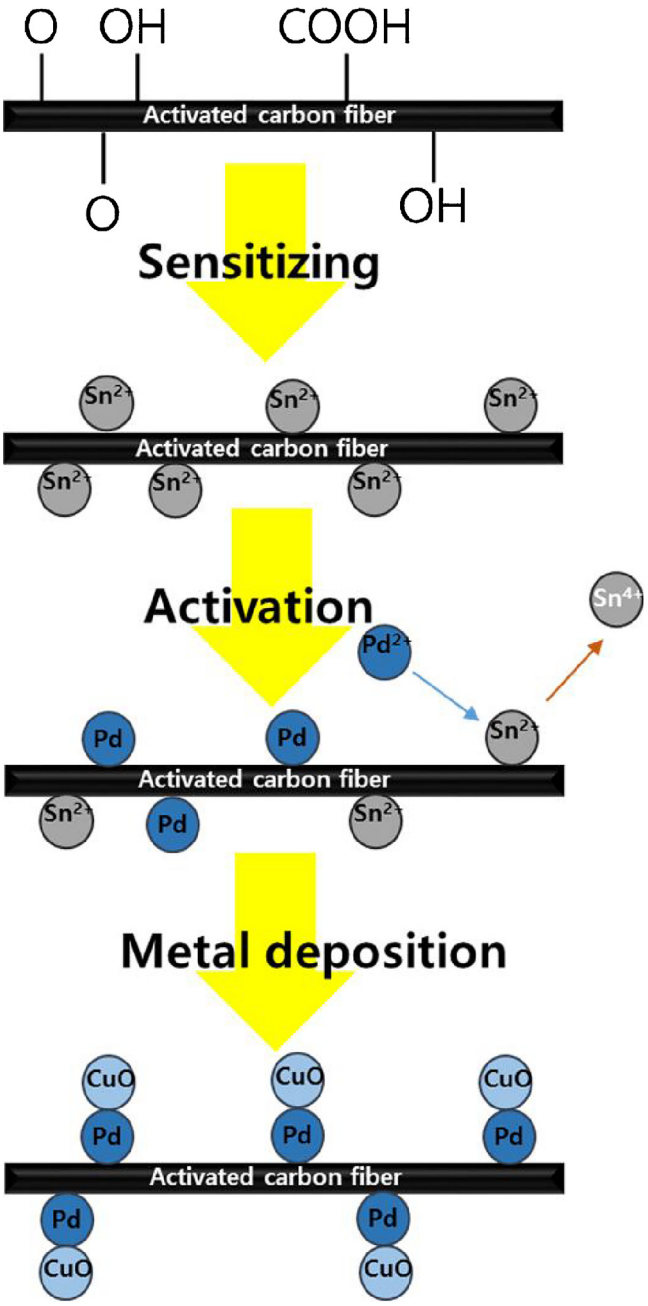

Fig. 1. Mechanism for the electroless copper plating of ACFs.

Subsequently, this dispersed solution (10 μl) was dropped onto an oxidized silicon[1] (320 nm SiO_2) wafer with a micro-pipette (Transferpette® electronic pipette, BrandTech Scientific, Germany) and then dried for 4 h at room temperature. A silver wire (ø 0.1) was attached to the Pt electrode[2] containing the samples using

[1] The silicon wafer was treated as follows. The silicon wafers were washed with acetone, ethanol and distilled water in an ultrasonic bath for 30 min. The dried silicon wafers were then heated at 1173 K for 2 h under N_2 atmosphere to form a SiO_2 film on the surface.

[2] The Pt sputtering conditions were as follows. Before Pt sputtering, Ti was sputtered onto the SiO_2 wafers to prevent the Pt electrode from peeling. The SiO_2 wafers were placed in a sputter-coater chamber (DC magnetic sputtering; Hanbaek Vacuum, Bucheon, Korea), which was then evacuated to 3.5×10^{-3} Pa. The target power was 200 mA and 310 V, and Ti sputtering was performed for 30 s. After Ti sputtering was complete, Pt sputtering was carried out at 20 mA and 315 V for 180 s under the same vacuum condition as Ti sputtering.

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