ABSTRACT

This paper presents a novel method to achieve large area contact integration for copper(II) oxide (CuO) nanowire array-based hydrogen gas sensors, which provides a simple solution to the ongoing challenge of harvesting nanostructured materials for gas sensing applications. The method presented herein offers six distinct advantages over previous nanostructured gas sensing technologies: (1) convenient electrical access to as-grown, freestanding nanowire arrays, thereby obviating postgrowth thin-film metallization, (2) lithography-free fabrication, (3) usage of large area nanowire arrays to circumvent low yield of single nanowire sensors, (4) reusability of contacts for batch characterization, (5) compatibility with all free-standing arrays grown on electrically conductive substrates, and (6) rapid response and recovery times. The CuO nanowire array-based gas sensors exhibited 5× to 25× increased resistance during operation, and a 20× improvement in recovery time compared to prior works.

KEYWORDS

Hydrogen, gas sensor, contact integration, copper oxide, nanowires

INTRODUCTION

Improved sensitivity continues to drive current gas sensing innovation. Towards this end, metal oxide nanowires have garnered increased attention as promising gas sensing materials owing to their large surface area-to-volume ratio. With this advantage, impinging gas species are provided larger surface area onto which to adsorb and react with the sensing material as compared to simple planar thin films, yielding greater sensitivity. Additionally, metal oxides are known to be cost-effective and stable during operation [1]. The abundance of work in this area using SnO$_2$ [2,3], ZnO [4], TiO$_2$ [5], and WO$_3$ [6] nanowires gives credence to the efficacy of these materials. While the performance of some of these devices is already sufficient for real-world application, much work remains to be done before these devices can be commercialized. Specifically, most nanowire-based gas sensors require laborious and fabrication-intensive patterning of metal contacts before the device is ready for use, which renders the completed device impractical for cost-effective, mass-scale manufacturing [7]. The process of integrating a nanowire into a device typically begins by removing the nanowire from its growth substrate. In the case of single nanowire gas sensor devices, the nanowire...
is then deposited onto the device substrate through a dropcast method before the patterning of metal contacts via electron beam lithography [8-10]. Alternatively, nanowires can be dropcast and randomly aligned onto a pair of pre-patterned comb electrodes [11]. Other groups have grown nanowire arrays from pairs of interdigitating electrodes, with intersecting nanowires forming self-assembled contacts [12-14]. Most of these methods suffer from poor yield or repeatability due to the difficulty of forming ohmic contacts and the variation in electrical properties for each nanowire, and all of these devices require some form of photolithography. These concerns will need to be addressed before nanowire-based gas sensing technology infiltrates the commercial gas sensor market.

Herein, we present a large area contact integration method to enable facile and immediate gas sensing capability of nanowire materials. The purpose of this scheme is to harness the performance of current state-of-the-art nanowire-based gas sensing devices through an assembly methodology that is more amenable to cost-effective mass production. This method involves the introduction of a pair of contact pads pressed atop the vertically-aligned nanowire array, providing convenient, instant electrical contact. As a result, no post-growth metallization is necessary. Furthermore, this method obviates the need for photolithography, a very desirable advantage considering that electron beam lithography—a time consuming and expensive process—is commonly used to precisely pattern contacts with small feature size. Additionally, an inherent benefit of the large area contacts is that the entire nanowire array is used for gas sensing, which should present an improvement in process yield over single nanowire devices. Lastly, the top contact substrate is reusable so that a single substrate can be used to characterize batches of nanowire arrays.

The device scheme is presented in Figure 1. An array of CuO nanowires is electrically accessed by an electrode substrate consisting of two contact pads positioned above the array. Although CuO nanowires were used for this demonstration, it is worth noting that a diverse range of nanowire materials can serve as the sensing material in this device scheme as long as the growth substrate is electrically connected to each individual nanowire, which makes this architecture extremely versatile. The mechanism of resistance change is depicted in the inset of Figure 1. Preadsorbed oxygen ions O\(^{\bullet\bullet}\) and O\(^{2-}\) on the nanowire surface inject electrons into the p-type CuO upon reaction with the reducing H\(_2\) gas, decreasing the majority carrier concentration in the nanowire and therefore increasing its resistance [15]. The change in resistance of the array can be measured between the contact pads due to the current path as depicted in Figure 1(a). A complete circuit is traced from the left contact pad into the nanowires on the left half of the array, through the conductive growth substrate, and up through the nanowires on the right half of the array into the right contact pad. The CuO nanowires used in this demonstration, as shown in the SEM micrograph of Figure 1(b), average 8 \(\mu\)m in length after a 2-hour thermal oxidation.

**FABRICATION**

The fabrication of the CuO nanowire array gas sensor follows a simple process. Electrical connection used to monitor the resistance of the nanowire array is provided by contacts fabricated via the method depicted in Figure 2 (I). A silicon wafer was thermally oxidized, yielding a 300 nm layer of silicon dioxide. Next, the contact pads were formed on the SiO\(_2\) layer. This can be achieved with various materials including metal foils, evaporation or sputtering of metal thin films with a simple shadow mask.
or conductive paste. Each contact spanned an area of 1 cm × 1 cm to ensure sufficient contact between the contacts and the nanowires.

CuO nanowires were produced by the following method. First, a 25 μm thick copper foil was cleaved into coupons measuring 2 cm × 1 cm. Next, the coupons were tightly wrapped around glass slides and thermally oxidized in ambient conditions at 450°C for 2 hours as seen in Figure 2 (II). At the end of the oxidation, a uniformly dense, 8 μm tall, vertically-aligned CuO nanowire array was evident across the entire foil area, as seen in Figure 3. Uniformity was consistently excellent from sample to sample. Nanowire diameter ranged between 50 to 150 nm.

Once the two components were finished, they were assembled, one atop the other as seen in Figure 2 (III), and secured using heat-resistant tape, readying the gas sensing device for testing.

RESULTS AND DISCUSSION

In order to assess the gas sensing performance of the assembled CuO nanowire array, the device was subjected to five different concentrations of hydrogen gas. To perform this test, the device was placed into a heated, enclosed chamber at 250°C and was allowed to heat up and stabilize at that temperature. The chamber was purged with air before and after each concentration of hydrogen gas was applied to the sensor, and the resulting change in resistance, R/R₀, was recorded during that time. The results of this test are shown in Figure 5.

After the first air purge, a mixture of argon and hydrogen gas yielding a 10% hydrogen concentration was flown through the heated chamber (the first green peak visible in Figure 3), resulting in the blue resistance peak corresponding to that gas concentration. This purge and flow of gases was repeated in succession for increasing concentrations of hydrogen: 15%, 20%, 25%, and 30%. As expected, each increase in concentration yielded a substantial increase in the gas sensor’s resistance, as well as an increase in the rate of resistance increase from its initial resistance value. Remarkably, the recovery time during which the chamber is purged with air is extremely rapid, approximately 30 seconds or less. This compares very favorably to prior reports of hydrogen sensing CuO nanowire devices, which typically feature response times on the order of 10 minutes [16]. One possible explanation for the significantly longer response time recorded in the literature is the quality of electrical contact between the CuO nanowires and electrodes. In their procedure, CuO nanowires were displaced from the growth substrate, suspended in methanol solution, and sprayed onto prefabricated Au/Ta electrodes. Since contact is provided by the nanowires lying physically on top of the electrodes, the electrical contact may have been poor in this case. Additionally, since the nanowires are laid down on the substrate, much of the surface area is lost and unavailable for gas species to adsorb. Both of these factors may have contributed to their much longer response times compared to our results. The resistance change of the gas sensor reached a maximum of 25.5× its original value for hydrogen concentration of 30%. The asymmetry in the rate of rise and fall of each resistance peak is attributed to a limitation in the testing apparatus; air was driven into the gas sensing chamber much more rapidly than hydrogen. Therefore, the rate of resistance increase for each concentration of hydrogen may be even more rapid given greater control of the hydrogen flow rate. The inset of Figure 5 shows the I-V response recorded for the CuO nanowire array gas sensor device. As seen here, the I-V response of the system is ohmic—a critical requirement of high performance gas sensors. This provides confirmation that the placement of the top contact pads onto the CuO nanowire array is an effective method for electrically accessing these nanowires.

Finally, the sensitivity of the CuO NW array to hydrogen gas sensing was determined. Sensitivity S is defined as the ratio of the change of device resistance to the original device resistance before gas flow, or:

\[ S = \frac{R - R_0}{R_0} \]

where \( R \) is the maximum resistance of the CuO nanowire and \( R_0 \) is the original resistance before gas flow.

**Figure 5:** Resistance measured under operation at 250°C, revealing increasing resistance with increasing hydrogen concentration and rapid recovery of initial resistance of less than 30 sec while purging with air. Normalized resistance reached a maximum of 25.5× for 30% hydrogen gas concentration. (Inset) Ohmic I-V response for the entire system.

**Figure 6:** Sensitivity measurements as a function of hydrogen gas concentration. As expected, sensitivity increases with increasing hydrogen concentration, reaching a maximum of 25.5.
gas sensor at a certain hydrogen gas concentration, and $R_0$ is the original resistance of the gas sensor when it has been purged with air. As seen in Figure 6, sensitivity increased with increasing hydrogen gas concentration, reaching a maximum at 25.5x the original gas sensor resistance value in air. The linear trend suggests that gas species entering into the nanowire array can find nanowire surfaces to adsorb onto even as gas concentration increases, a consequence of the large surface area of the nanowire array. In comparison, the literature reports a fourfold increase in resistance for a hydrogen concentration of 6% [16], which is comparable to our data.

It is important to highlight that the overall performance achieved through this top contact scheme compares very favorably to the literature even though this scheme omits several commonly used, time-intensive, and expensive processing steps. This scheme is therefore very promising in continuing the pursuit towards highly sensitive gas sensing devices with potential for mass commercialization. For greater functionality, future work will focus on integrating a microheater into the electrode substrate for localized heating of nanowires during operation.

CONCLUSIONS

In summary, a novel nanowire-based gas sensing architecture is introduced. This architecture eliminates the need for laborious, fabrication-intensive post-processing of nanowire arrays, a recurring issue in the packaging of nanowire-based devices. This architecture enables immediate gas sensing capability through the application of contact pads positioned atop the nanowire array. Gas sensing measurements in the presence of hydrogen showed a sensitivity of up to 25.5x for 30% hydrogen concentration and rapid recovery of initial resistance of less than 30 seconds. This contact scheme shows promise in exploiting the high sensitivity of nanowires while introducing simplicity in the post-processing of as-grown nanowire arrays into completed devices.

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REFERENCES


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