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Citation for published version (APA):

DOI:
10.1063/1.4931706

Document status and date:
Published: 24/09/2015

Document Version:
Publisher’s PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:
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Citation: Applied Physics Letters 107, 123112 (2015); doi: 10.1063/1.4931706
View online: http://dx.doi.org/10.1063/1.4931706
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Low-frequency noise characterization of single CuO nanowire gas sensor devices

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(Received 23 July 2015; accepted 14 September 2015; published online 24 September 2015)

Low-frequency noise properties of single CuO nanowire devices were investigated under gas sensor operation conditions in dry and humid synthetic air at 350 °C. A 1/f noise spectrum was found with the normalized power spectral density of current fluctuations typically a factor of 2 higher for humid compared to dry atmosphere. A core-shell nanowire model is proposed to treat the noise as parallel combination of gas-independent bulk and gas-dependent surface noise components. The observed increase in 1/f noise in the presence of water vapor is explained in terms of Hooge’s mobility fluctuation model, where the increased surface noise component is attributed to carrier scattering at potential fluctuations due to hydroxyl groups at the nanowire surface.

Low-frequency conductance fluctuations of metal oxide nanowires have been studied for the case of SnO2 nanowires and ZnO nanowires. However, metal oxide nanowire devices under gas sensor operation conditions have received little attention so far. In this letter, we report on 1/f noise measurements of single CuO nanowire devices in dry synthetic air and in the presence of water vapor; the latter was chosen as target gas due to its importance for gas sensing applications in ambient atmosphere. Measurement results at a typical operation temperature for CuO nanowire gas sensors (350 °C) are compared and analyzed in terms of a core-shell nanowire model, considering Hooge mobility fluctuations.

Increased 1/f noise in the presence of water vapor is attributed to the interaction of H2O molecules with the metal oxide nanowire surface.

CuO nanowires were synthesized by the thermal oxidation method, dispersed on Si/SiO2 substrates, and individually contacted by metal electrodes using an electron beam lithography lift-off process of thermally evaporated Ni and Au layers, similarly as described elsewhere. Thermal annealing at 400 °C for 5 min in ambient atmosphere was performed in order to improve the nanowire-metal contact properties. In Fig. 1, a representative single CuO nanowire device in four-point configuration is shown. In the present study, an electrode width around 500 nm was used, whereas the equidistant contact spacing was between 0.4 and 1.9 μm.

The focused ion beam lift-out technique was used for the preparation of a transmission electron microscopy lamella of a contacted CuO nanowire, which was used for structural characterization of the CuO nanowires and their interface to the Ni/Au metallization. The CuO nanowire exhibited a roughly circular cross-section with faceted surfaces and a twin boundary, which is commonly observed for CuO nanowires. The metal electrodes showed a thickness around 200 nm and polycrystalline structure. The Ni layer between CuO and Au was around 7–10 nm thick and the lattice spacings indicated that it was oxidized to NiO, presumably during the thermal annealing process.

![Image](Image 485x768 to 535x789)

**FIG. 1.** Single CuO nanowire contacted by Ni/Au electrodes in a four-point configuration.

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The CuO nanowire devices were assembled with micro-heaters and tested in an automated gas measurement setup as reported previously\textsuperscript{8} using a constant total gas flow of 1000 sccm. Electrical characterization results of a representative single CuO nanowire device (diameter 143 nm, contact spacing 1.9 \mu m) are shown in Fig. 2. The IV characteristics in 2-point and 4-point measurements were compared at 350 °C in dry synthetic air (see Fig. 2(a)). No distinct difference was found indicating negligible contact resistance contribution for the 2-point measurement. Furthermore, 4-point resistance measurements at various temperatures from room temperature to 350 °C in dry synthetic air were performed. CuO nanowire electrical conductivity was deduced assuming circular nanowire cross-sections, which can be seen in Fig. 2(b). Electrical conductivity increased more than one order of magnitude when comparing room temperature and 350 °C, which was also found in additional measurements on three other CuO nanowire devices. The positive temperature coefficient of conductivity is consistent with literature reports on CuO nanowires measured under low vacuum conditions.\textsuperscript{2,3} CuO nanowires typically exhibit p-type conductivity\textsuperscript{2,3} which was verified in our case by back-gated field effect transistor devices with non-optimized contact technology. Furthermore, the electrical conductivity of CuO is known to be strongly dependent on the surrounding atmosphere in the investigated temperature range.\textsuperscript{22} For the case of dry synthetic air, the ionosorption of oxygen is expected to lead to a surface hole accumulation layer due to negative surface charges, which in turn results in increased electrical conductivity.\textsuperscript{23}

The electrical resistance change of the same single CuO nanowire (diameter 143 nm, contact spacing 1.9 \mu m) during exposure to three pulses of humidity at a temperature of 350 °C is shown in Fig. 3(a). Increased electrical resistance in the presence of water vapor was found, which is in accordance with results on CuO nanowires\textsuperscript{8,24} and thick film\textsuperscript{23} gas sensor devices. The interaction of H\textsubscript{2}O molecules with CuO surfaces is expected to lead to the formation of terminal hydroxyl groups and a decrease of ionosorbed oxygen species.\textsuperscript{23} As a result, band bending, hole concentration, as well as electrical conductivity are decreased at the CuO nanowire surface.

Low-frequency noise characterization of the single CuO nanowires was performed in two-terminal configuration with constant bias using a Keithley 428 current voltage amplifier and a Advantest spectrum analyzer. Power spectra were recorded and averaged after initial temperature/gas flow stabilization of few minutes. The measurements were repeatedly performed showing reproducible behavior, negligible resistance drift, and no memory effects. The normalized noise spectra in dry and humid (50% relative humidity—rH) synthetic air at 350 °C were fitted to $S \propto 1/f^\kappa$ and are shown in Fig. 3(b). In both cases, 1/f noise was found with a characteristic exponent $\kappa$ of 1.15 (dry) and 1.18 (50% rH), respectively, with a standard deviation of 0.02 of the curve fitting parameter. No adsorption-desorption noise resulting in Lorentzian-type spectra\textsuperscript{25} was observed. For different voltage bias conditions corresponding to currents of few nA to around 20 nA, the noise spectral density $S_f$ scaled proportionally with $I^2$, which is expected for resistor-type devices. In the presence of water vapor, an increase of normalized 1/f noise of about a factor of 2 was found.

The normalized low-frequency noise amplitude of single CuO nanowires is comparable to literature reports of devices based on nanomaterials suitable for gas sensing applications, such as Au nanoparticles,\textsuperscript{26} carbon nanotubes,\textsuperscript{27} graphene,\textsuperscript{15} or MoS\textsubscript{2}.\textsuperscript{28} Although a single nanowire configuration was used as a well-defined model system in this study, CuO nanowire arrays might be a promising alternative device architecture for decreasing low-frequency noise, similarly as for silicon parallel nanowire transistor arrays.\textsuperscript{29} Furthermore,
several other techniques have been reported for potential low-frequency noise reduction in the future, such as surface passivation/capping\textsuperscript{30,31} (which is problematic for the gas sensing application) or employing the sensing elements in a suspended configuration.\textsuperscript{32,33}

It is proposed that the electrical resistance and the noise characteristics of the single CuO nanowire may be interpreted in terms of a core-shell model, similar as in Ref. 34 for n-type metal oxide nanowire gas sensors. A comparable model was also reported for ZnO layers, which successfully explained changes in resistance and noise in dark, under illumination and after illumination (persistent photoconductivity).\textsuperscript{35} For p-type CuO nanowires, the surface hole accumulation layer is expected to be influenced by the surrounding gas atmosphere, whereas the bulk remains unaffected. In the following, the length and diameter of the nanowire are denoted by $L$ and $d$, respectively. The surface and bulk parts are considered to be electrically in parallel and have different conductivity and noise. Hence, the total conductance $G$, the resistance $R$, and the total conductance noise $S_G$ of the nanowire core (bulk) and shell (surface) in parallel are

$$G = G_s + G_b \Rightarrow R = \frac{1}{G_s + G_b},$$

$$S_G = S_{G_s} + S_{G_b},$$

with the conductance of the gas-sensitive surface layer $G_s$, the conductance of the nanowire bulk $G_b$, the conductance noise of the surface layer $S_{G_b}$, and the conductance noise of the inner part $S_{G_s}$. Noise in nanodevices is either treated in terms of mobility fluctuations\textsuperscript{9,36} as in, e.g., Ref. 28 or as carrier-number fluctuations\textsuperscript{37} especially for the analysis of channels with a gate as in field effect transistors. Here, we discuss CuO nanowire devices without gate and therefore perform the noise analysis within the framework of Hooge’s empirical relation. This treatment also allows the comparison of our results to previous literature reports in terms of a unique material-related noise parameter as proposed in Refs. 38 and 39. $S_{G_s}$ and $S_{G_b}$ are assumed to be uncorrelated 1/f noise sources described by the Hooge parameter $\alpha$ (Refs. 9 and 40) for the nanowire surface ($\alpha_s$) and bulk ($\alpha_b$). Thus, the normalized resistance noise $S_R/R^2$ can be expressed as

$$\frac{S_R}{R^2} = \frac{S_{G_s} + S_{G_b}}{G^2} = \frac{\alpha_s}{N_d} \frac{G_s^2 + \alpha_b}{N_d} \frac{G_b^2}{(G_s + G_b)^2} = \frac{K_s G_s + K_b G_b}{\mu_l^2 (G_s + G_b)^2},$$

where $N_d$ and $N_d$ denote the number of free carriers in the nanowire surface and bulk part, respectively, whereas $\alpha_s/N_s = \alpha_s q \mu_s R_s/L^2$ with the elementary charge $q$, the mobility of the free carriers in the surface layer $\mu_s$, and the resistance $R_s$. The bulk part with $N_b$ and $\mu_b$ is treated similarly, while $\alpha_b q \mu_b$ is replaced by $K_b$. Noise is described in a relative way independent of bias and frequency as $C_{1/f} = fR_s/R^2$. In order to compare results of CuO nanowires with different lengths and diameters (implicitly included in the nanowire’s resistance/conductance), we introduce the parameter $K$ that can be calculated from experimental results as

$$K \left[ \text{cm}^2/\Omega \right] = \frac{L^2 f_{SR} R}{R^2} = \frac{K_s G_s + K_b G_b}{G_s + G_b}.$$

In our measurements, a mixture of the surface and the bulk noise properties ($K_s$ and $K_b$, respectively) is observed experimentally. The $K$-value characterizes the 1/f noise of the material independent of bias, frequency, sample volume, and number of carriers in the device. The benefits of this treatment were explained and different classes for $K$ were proposed in Ref. 39.

For samples with different surface and bulk contributions (for instance, in a core-shell nanowire model), $K$ is an effective value. The surface contribution is only observed with $K = K_s$ if $K_s G_s \gg K_b G_b$ and $G_s \gg G_b$. The bulk is dominant with $K = K_b$ if $K_s G_s \ll K_b G_b$ and $G_s \ll G_b$. The low-frequency noise characteristics of five different single CuO nanowire devices in dry and humid synthetic air are compared in Fig. 4 in a double logarithmic plot of $L^2 C_{1/f}$ versus $R$, similar as previously reported for thin film\textsuperscript{35} and memory devices.\textsuperscript{40} The lowest $K$-value of $3 \times 10^{-22}$ cm$^2$\Omega was found for the CuO nanowire sample with a diameter of 134 nm and a channel length of 0.35 μm. A comparison of $K$-values for different nanodevices and nanomaterials from literature references providing sufficient information about the geometry and bias conditions is given in Table I. The highest $K$-values of around $10^{-21}$ cm$^2$\Omega in the presented CuO nanowires are in the same range as in metals and semiconductors like Au or Si.\textsuperscript{38}

In the case of $K_s = K_b$ (independent of $R_s/R_b$), it would be expected that the values for $L^2 C_{1/f}$ scale with total resistance $R$ for changes in $R_s$ due to dry and humid conditions. In other words, values for $L^2 C_{1/f}$ should lie on a straight line with slope one (in the following termed iso $K$-line) in a log-log plot with $R$ in the horizontal axis (see solid lines in Fig. 4). Deviations from the iso $K$-line occur for $K_s \neq K_b$.

$$K = \frac{K_s}{1 + \frac{G_b}{G_s}} + \frac{K_b}{1 + \frac{G_s}{G_b}} = \frac{K_s}{R_s + R_b} + \frac{K_b}{R_s + R_b}.$$

The five different single CuO nanowires consistently show an increase in effective $K$ in the presence of water vapor.
This work has been partly performed within the project "MSP—Multi Sensor Platform for Smart Building Management" (FP7-ICT-2013-10 Collaborative Project, No. 611887).

TABLE I. Comparison of K-values for different nanodevices and nanomaterials. Depending on layer or nanowire (NW) geometry, the 1/f part of the spectra was used to calculate the K-values as follows (volume $V$, length $L$, width $W$, resistivity $\rho$, and sheet resistance $R_s = RW/L$): $K = C_{1/f}V/\rho = C_{1/f}WL/R_s$.

<table>
<thead>
<tr>
<th>Material</th>
<th>K (cm$^2$/Ω)</th>
<th>Comment</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuO-NW</td>
<td>$3 \times 10^{-22}$–$1 \times 10^{-21}$</td>
<td>623 K; dry and humid atmosphere</td>
<td>This work</td>
</tr>
<tr>
<td>Lanthanum strontium manganite-NW</td>
<td>$7 \times 10^{-24}$</td>
<td>Antiferromagnetic phase</td>
<td>41</td>
</tr>
<tr>
<td>$4 \times 10^{-22}$</td>
<td></td>
<td>Ferromagnetic phase</td>
<td></td>
</tr>
<tr>
<td>Au nanoparticles (layer)</td>
<td>$2 \times 10^{-23}$</td>
<td>...</td>
<td>42</td>
</tr>
<tr>
<td>Si-NW(gate all around)</td>
<td>$8 \times 10^{-22}$</td>
<td>$\sim$3000 Si-NWs in parallel</td>
<td>29</td>
</tr>
<tr>
<td>Si-NW</td>
<td>$4 \times 10^{-21}$</td>
<td>200 K</td>
<td>10</td>
</tr>
<tr>
<td>InAs-NW</td>
<td>$1 \times 10^{-19}$</td>
<td>...</td>
<td>43</td>
</tr>
<tr>
<td>$5 \times 10^{-21}$</td>
<td></td>
<td>PMMA passivation</td>
<td></td>
</tr>
<tr>
<td>MoS$_2$</td>
<td>$10^{-20}$</td>
<td>Single layer</td>
<td>28</td>
</tr>
<tr>
<td>Graphene</td>
<td>$10^{-19}$</td>
<td>Single and multilayers</td>
<td>44</td>
</tr>
<tr>
<td>Graphene</td>
<td>$10^{-18}$</td>
<td>Boron nitride capping</td>
<td>31</td>
</tr>
<tr>
<td>Carbon nanotubes (2D network)</td>
<td>$&gt;10^{-18}$</td>
<td>Inhomogeneous current density</td>
<td>27</td>
</tr>
</tbody>
</table>

(see closed symbols in Fig. 4), which can be interpreted by different noise properties of the CuO nanowire surface and bulk. No qualitative differences were observed for CuO nanowires with different contact electrode spacing and diameters ranging from 90 nm to 243 nm. All $L^2 C_{1/f}$ values in humid synthetic air are above the iso-K line drawn through the result in dry conditions (denoted by open symbols in Fig. 4).

It is expected that the overall increase in 1/f noise in the presence of water vapor can be attributed to increased low-frequency noise of the gas-sensitive CuO nanowire surface. In the presented core-shell nanowire model, the higher effective K-values can be interpreted by an increase of $K_s$ due to the interaction with surrounding water vapor molecules. It is assumed that randomly distributed hydroxyl groups at the CuO nanowire surface act as scattering centers and change the band bending resulting in increased 1/f fluctuations compared to the case of only chemisorbed oxygen ions in dry synthetic air. We consider increased noise due to carrier scattering at surface potential fluctuations.

In summary, the low-frequency noise characteristics of single CuO nanowire devices were investigated in dry and humid synthetic air under gas sensor operation conditions. Increased 1/f noise was found in the presence of humidity, which was explained in terms of a core-shell nanowire model. Our results confirm the influence of surrounding gas molecules on the noise properties of single CuO nanowire gas sensor devices, which suggests opportunities for further noise spectroscopy studies in different gaseous environments for the future.