Communication

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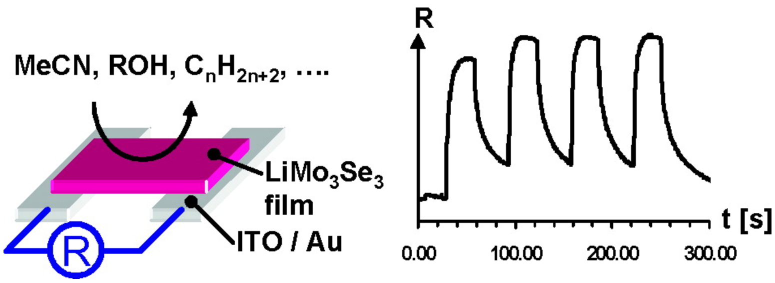

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Chemical Sensing with $LiMo_3Se_3$ Nanowire Films

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Nanowires derived from the Chevrel compound, $LiMo_3Se_3$,[1,2] are remarkable in terms of their structural, chemical, and electrical properties. As condensation polymers of stacked triangular Mo_3Se_3 units (Figure 1a), the nanowires have a diameter of only 0.85 nm (from crystal data).[3] That is, they are smaller than single- (1−2 nm) and multiwalled (2−25 nm) carbon nanotubes.[4] DiSalvo's group discovered in 1985 that $LiMo_3Se_3$ can be exfoliated in polar organic solvents to form dispersions that contain $LiMo_3Se_3$ as nanowire bundles.[1] The fact that the nanowires remain metallic in the exfoliated state[5,6] was exploited for the fabrication of electrically conducting films and nanowire−nanoparticle composites.[7−10] We recently found that thin films of the $LiMo_3Se_3$ nanowires respond to molecular vapors with a decrease of their electrical conductivity. This observation is remarkable considering that as metallic conductors with three conduction channels,[11] $LiMo_3Se_3$ nanowires should only be mildly sensitive to the adsorption of molecules. To better understand this phenomenon and to evaluate the potential of the metallic nanowires as chemical sensors, we have systematically studied the conductivity of $LiMo_3Se_3$ nanowire films in the presence of chemical vapors. We present here initial results from this investigation.

To fabricate the sensors, a solution of the nanowires was deposited onto a homemade electrode array of patterned thin (100 nm) films of indium tin oxide (or gold) on borosilicate glass (Figure 1d). After evaporation of the solvent (water or DMSO), a porous network forms (Figure 1e) that contains nanowire bundles of mean 4−6 nm diameter and with an average length of 10 μm. High-resolution TEMs confirm that the bundles are crystalline and contain several $LiMo_3Se_3$ strands. Assuming that the strands are packed hexagonally like in the solid state (Figure 1c), each of the 4−6 nm thick bundles is calculated to contain 7−37 molecular wires. Room temperature measurements of the lateral resistance of the nanowire films using both a four- and a two-probe configuration reveal resistivities of the films of (3−4) × 10^{-3} Ωcm, which agrees well with previous measurements.[8,10]

When a nanowire film is exposed to molecular vapors of organic solvents, the resistance of the film increases, as shown in Figure 2 (see ref 23). The observed relative resistance changes, $\Delta R/R_0$ ($\Delta R = R - R_0$), are always positive; their magnitude is on the order of 1−70%; they occur within seconds of the exposure, and they are entirely reversible. To determine the nature of the analyte−nanowire interactions that lead to the observed resistance changes, we systematically studied the reaction of the sensors to analytes of variable molecular sizes, polarities, and with different functional groups. It can be seen (lower part in Figure 2) that the strongest responses are caused by analytes with electron pair donors, which suggests that coordinative interactions between analytes and nanowires play a role in the sensor response. In the case of DMSO and methanol, coordinative interactions are also supported by the finding that residual bands of these molecules can be detected in the infrared spectra of the nanowires even after prolonged drying in vacuum (see Supporting Information). For these "sticky" solvents, it usually takes several injection/evacuation cycles before the resistance response becomes stable. Aliphatic hydrocarbons and chlorinated solvents (chloroform), on the other hand, can be easily removed in vacuum. The fact that these noncoordinating solvents still produce a measurable resistance increase of the films suggests that van der Waals and dipolar interactions between analytes and the nanowires also play a role in the sensing process.

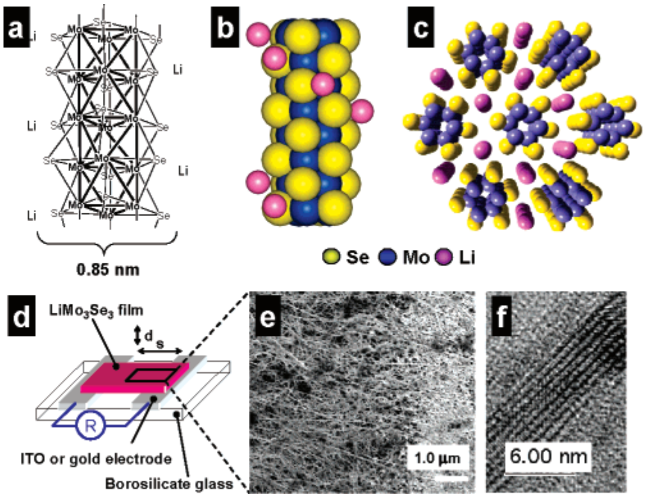

Figure 1. (a) Schematic structure of $LiMo_3Se_3$ nanowires, (b) space filling model of a single nanowire (Li in estimated positions) and (c) of a nanowire bundle, (d) schematic drawing of the sensor (*d*, film thickness: 10−150 nm; *s*, electrode separation: 0.51−1.27 mm), (e) SEM image of nanowire film and electrode, and (f) HRTEM image of a single nanowire bundle.

In addition to the nature of the analytes, the response of the $LiMo_3Se_3$ nanowire films is also a strong function of the analyte partial pressure (Figure 3a and b). While for acetonitrile the response increases linearly in the measured pressure interval, other solvents, such as DMSO and methanol, produce a nonlinear response (see Supporting Information). The smallest pressures that give a measurable response (based on the 3σ criterion[12]) are 2 mTorr (2.6 ppm) for DMSO, 400 mTorr (520 ppm) for MeCN, and 100 mTorr (130 ppm) for MeOH. These detection limits are comparable to sensors based on organic films,[13,14] but are not as low as those of sensors based on individual carbon nanotubes[15] and silicon nanowires.[16] The physical dimensions of the nanowire films also affect the sensitivity of the sensor. Figure 3a shows that the magnitude of the response increases with the electrode separation (conductance path length), and Figure 3c reveals an inverse relationship between response and film thickness (determined by AFM). Increasingly thick films also lead to longer response times of the sensor (see Figure 3d), suggesting that the response is limited by analyte diffusion into the film. Together, these observations clearly show that the resistance changes are due to processes in the film and not at the film−electrode interface.

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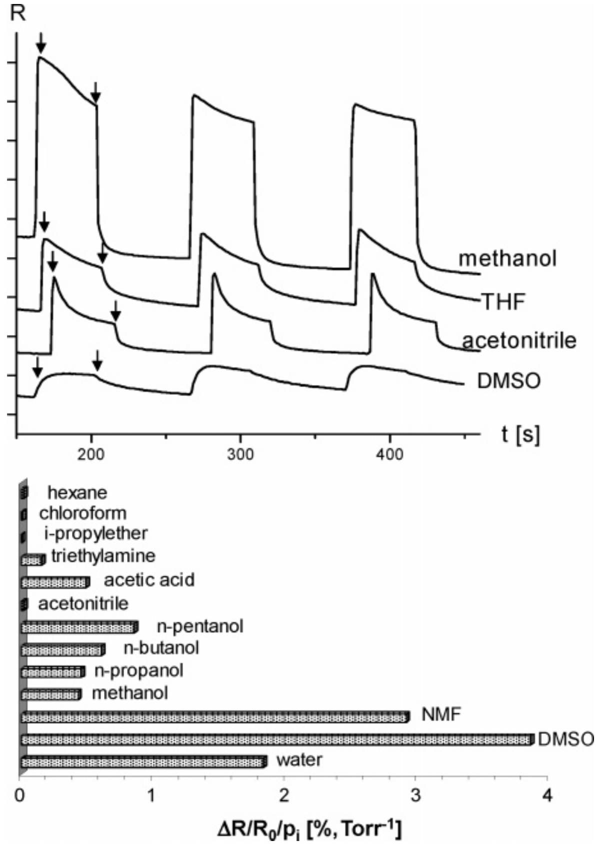

Figure 2. (Top) Resistance/time plots for four analytes (saturated vapor at 30 °C). Arrows mark analyte injection and evacuation of the film. (Bottom) Relative resistance changes (%, Torr^{-1}) for various analytes. NMF is N-methylformamide; DMSO is dimethylsulfoxide.

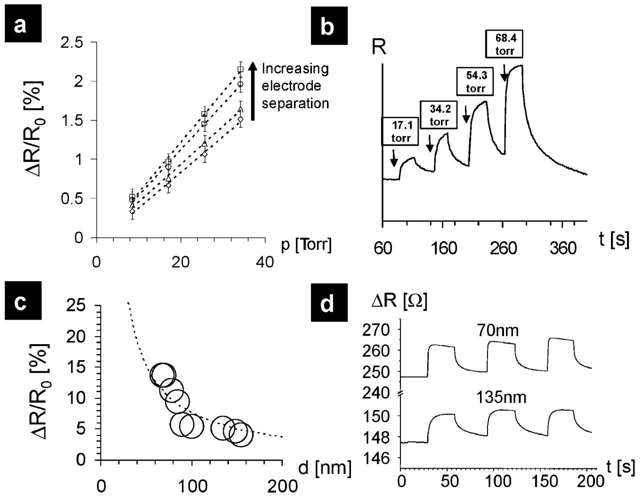

Figure 3. (a) Dependence of sensor response on analyte partial pressure for variable conduction path lengths (0.51−1.27 mm), (b) response profile for MeCN at variable partial pressures, (c) response versus nanowire film thickness (circle sizes represent measurement error; broken line is a fit $f(x) = 770/x$, and (d) response profiles of films with indicated thicknesses.

At present, it is not clear if the observed resistance changes are a result of solvent-induced variations of the electron tunneling barrier across different nanowire bundles[17,18] or if they reflect intrinsic conductivity modulations of the $LiMo_3Se_3$ nanowires. Because $LiMo_3Se_3$ nanowires contain three conduction channels,[11] changes in the band structure of the wires are not expected to drastically affect the conductance. However, it is possible that the conductivity changes are caused by adsorbate-induced variations of the mean free path of the conduction electrons in the wires. Adsorbent-induced scattering of conduction electrons in thin (5 nm) metallic films has been shown to produce resistance increases of up to of 4% of the base resistance.[19−22] The larger resistance changes of the $LiMo_3Se_3$ nanowire films might be a result of the smaller diameter of the wires and the fact that the electrons in the wires are confined in two dimensions and not just in one, as in metallic films.

In conclusion, we have shown that films derived from Chevrel phase $LiMo_3Se_3$ nanowires quantitatively and reversibly respond with their electric conductivity to molecular analytes of variable molecular sizes, functional groups, and polarities. Studies are underway to elucidate the mechanism of the nanowire sensors and to utilize the effects in the quantitative and selective detection of analytes.

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Supporting Information Available: Infrared spectra of nanowires from DMSO and methanol, resistance plots for MeOH and DMSO, response data for different films, and multiple exposures. This material is available free of charge via the Internet at http://pubs.acs.org.

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(23) TEM and SEM images were acquired on Philips CM12 and FEI XL30-SFEG microscopes, respectively. HRTEM images were obtained on a Philips CM200 FEG microscope operated at 200 kV. To evaluate the sensors, nanowire films were placed in a 20 mL chamber and the films were dried in vacuo. After the resistance had stabilized, discrete amounts (0.1−20 mL) of saturated vapors of the analytes in N_2 were injected with a syringe into the test chamber. When the signal had reached maximum intensity, the chamber was evacuated to remove the analyte vapor.

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