Humidity and salt sensor based on CdSSe nanowire chip

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Abstract. The humidity and salt sensitive characteristics of sensor based on polyimide coated CdS$_{1-x}$Se$_x$ semiconductor alloy nanowire chip have been investigated. The composition-graded CdS$_{1-x}$Se$_x$ nanowire chip with large size shows excellent photo-sensitivity and stress sensitivity, synthesized by a simple CVD method and its composition can be gradually tuned from CdSe to CdS. The conductivity of the sensor showed good humidity response characteristics with a maximum responsivity (dI / I) of 85% at 80% RH. In addition, the current decreases linearly with increasing salt concentration, indicating that the chip sensor has good salt responsiveness and the best salt responsiveness is 80%. The RH dependent resistance upon illumination exhibits good linearity (R$^2$=0.9948) to guarantee the high prediction accuracy. In addition to good moisture and salt response characteristics, the sensor also exhibits excellent stability and reproducibility.

1. Introduction

It is significant to monitor and control the humidity in medical preparation, chemical processing, electronics and automotive industry. Therefore, there is a tremendous effort towards building humidity sensors employing different sensing mechanisms which include capacitive$^1$, resistive$^2$, hygrometric$^3$, gravimetric$^4$ and optical$^5$ technologies. One-dimensional semiconductor nanomaterials have been studied extensively and regarded as one of the most promising candidates for realizing ultrasensitive sensors because of their large surface-to-volume ratios, polarized crystal orientation and high carrier mobility. Because of the high gain, long carrier lifetime and good photoconductivity, CdS$_{1-x}$Se$_x$ (x=0-1) nanomaterials are widely investigated to discuss their special photoelectric properties by many researchers until now. Thus, CdS$_{1-x}$Se$_x$ nanomaterials have been used to fabricate photodetectors$^6$, filed-effect transistors$^7$, nano-lasers$^8$, solar cells$^9$ and nano-probes$^{10}$.

Polymer-based films, which exhibit high affinity for water due to the presence of hydropilic functional groups, are widely considered to be potential applications as sensors. In addition, it has the characteristics of low processing cost and high flexibility, which is essential for future wearable and connectable devices$^{11}$. Especially among them, polyimide (PI) is reported to regard as an excellent hygroscopic material by many research groups. As a kind of polymer material containing imide ring ([-CO-NH-CO-]) on the main chain, polyimide (PI) possesses many advantages, such as high temperature resistance, good mechanical properties, stable chemical properties, insulation and so on, which make it be widely applied in microelectronics and other fields.

In this paper, a humidity and salt sensor using ternary alloy CdS$_{1-x}$Se$_x$ nanowire chip and polyimide (PI) has been successfully fabricated. Using a common CVD method, the micro-zone CdSSe nanowire chips are synthesized. Polyimide is applied as a moisture sensitive material on the surface of the
CdSSe nanowire chip, and its volume expands as the humidity increases, resulting in a change in stress on the CdSSe nanowire layer. As the surface stress of the CdSSe nanowire chip increases, its current also increases. The linear relationship between humidity and resistance provides the basis for accurate humidity detection. In addition to this, the PI-coated CdSSe nanowire chip also exhibits a response characteristic to the salt concentration of the surface.

2. Methods
CdS$_{1-x}$Se$_x$ nanowire chip was synthesized by a CVD method. The entire reaction system has been described in detail in a previous paper$^{12}$. First, a CdS powder (Alfa Aesar, 99.995%) and a CdSe powder (Alfa Aesar, 99.995%) were weighed and mixed in a ceramic boat, and the ceramic boat was placed in the center of the tube furnace. The silicon wafer on which the surface-deposited Au catalyst was placed as a growth substrate was placed 10 cm away from the sample in the tube furnace. A high purity Ar (90%) / H$_2$ (10%) mixed gas was introduced into the tube furnace to exclude O$_2$, and the gas flow rate was controlled at 60 sccm for 30 minutes. The tube was then rapidly warmed to 1000 °C in 10 minutes and held at this temperature for 120 minutes while the Ar (90%) / H$_2$ (10%) flow rate was maintained at 20 sccm. After the tube furnace is naturally cooled to room temperature and the silicon substrate is taken out, a CdSSe nanowire with a compositional gradient change can be obtained. Finally, the interdigitated Al electrode was fabricated by vacuum thermal evaporation on the surface of CdSSe chip, and the polyimide (PL) film layer was uniformly coated on the surface of CdSSe nanowire chip by spin coating. The humidity and salt sensor were successfully prepared.

3. Experimental results and discussion

Figure 1(a) shows the CdS$_{1-x}$Se$_x$ nanowire chip obtained by CVD method. The SEM images collected from different representative positions along CdS$_{1-x}$Se$_x$ nanowire chip are shown in figure 1(a), which show that the morphology of the CdS$_{1-x}$Se$_x$ nanostructures gradually changes from nanoribbons to nanowires along the length direction, and the area of nanoribbons is mainly composed of Se and Cd, while the area of nanowires mainly consists of S and Cd. A photo of the prepared humidity and salt sensor is shown in Figure 1(b). As shown in Figure 1(c), the cross-section of a silicon-based nanowire chip sensor confirms that there is sufficient contact between the CdSSe nanowire and the PI, thus ensuring that the stress change from the PI can be fully applied on the CdSSe nanowires.
Figure 2(a) shows the typical I-V curves of the device with various humidity. At 4 V, the current value changes from $7.48 \times 10^{-6}$ to $1.38 \times 10^{-5}$ A when humidity varies from 25% to 80% RH. It is obvious that the current of the device all increases with the increasing humidity, this result shows that the conductivity of the sensor changes with the variation of humidity. The reason is that, when the polyimide absorbs moisture, its volume expands significantly and stresses the CdSSe nanowires in close contact with it, which makes the contact between the CdSSe nanowires more and better. The transport path of carriers in the CdSSe nanowire layer is shortened, so that more carriers are transported from one end of the interdigital electrode to the other, causing an increase in device current. On the other hand, due to the better contact between the CdSSe nanowires, the contact barrier between the nanowires is narrowed and reduced, which promotes the transport efficiency of carriers between the nanowires. Therefore, the current of the device increases as the humidity increases.

The relative humidity response of the sensor at 4V is shown in Figure 2(b). It is established as $[I_{\text{various RH}} - I_{\text{RH=25%}}]/I_{\text{RH=25%}}$, where $I_{\text{various RH}}$ is the current measured at different relative humidity, and $I_{\text{RH=25%}}$ is the current at 25% RH. The responsivity increases as the humidity raises, and the maximum responsivity of 85% is obtained at 80% RH.

For predicting the humidity, a standard calibration curve needs to be established firstly, and we found that the resistance changed from CdSSe nanowire chip-based sensor under various humidity is applicable and commodious to be used As a characteristic parameter for predicting the moisture of the surrounding environment as is also shown in figure 2(b). The resistance of the device linearly decreases from $6.68 \times 10^5$ to $3.77 \times 10^5 \Omega$ with the relative humidity increasing from 25% to 80%, which demonstrates that the moisture sensor has excellent humidity-sensing ability. When $R^2$ is equal to 0.9948, the linear fitting of resistance-humidity curve is optimal, and the linear relationship can be used as a calibration curve to predict the RH of moisture when we obtain the resistance of the sensor. It is noteworthy that, compared with most of humidity sensors ever reported in previous papers, our sensors have higher linear relationship, which means better prediction on quantitative analysis for surrounding humidity.
The stability is one of the important parameters to measure the performance of the humidity sensor. As shown in Figure 3, the stability of the sensor's output current over time is measured by detecting the change in the output current of the sensor at 20%-85% RH humidity. It can be found that as the humidity increases, the current increases continuously. For a certain humidity, the current changes by less than 3% in the time range of 1050 seconds, which fully demonstrates that the current of the sensor is stable at different RH levels.

In addition to the humidity sensing characteristics, the CdSSe nanowire chip-based sensor also has good salt response characteristics. Figure 4 (a) shows the salt response process and principle based on the CdSSe nanowire chip sensor. Figure 4(b) is The I-V curve with 80% RH fixed and the sensor at different NaCl concentrations. At 5 V, the resistance increases linearly with the increase of salt content as shown in figure 4(c), which is opposite to the trend of the results of humidity sensing (figure 2(a)). These results demonstrate that the as-prepared sensors have a good response to salt, which is due to that salt has an inhibitory effect on the hygroscopic swelling effect of PI. This can be explained by the schematic shown in figure 4(a). From a macroscopic point of view, in a high-humidity environment,
water molecules quickly diffuse into the polyimide layer and cause the polyimide to expand in volume. If salt is applied to the surface of the device at this time, it adsorbs water molecules from the inside of the polyimide layer and the surrounding environment, and forms an aqueous solution having a higher salt concentration on the outside of the polyimide film. This creates a concentration difference inside and outside the membrane, and the water molecules in the membrane gradually diffuse out of the membrane until the concentration of the solution inside and outside the membrane reaches equilibrium. Therefore, the degree of internal volume expansion of the polyimide film is correspondingly reduced, resulting in a decrease in the pressure applied to the CdSSe nanowire layer, thereby causing a decrease in device current. In addition, by studying the O-H stretching vibration Raman spectra of H$_2$O in NaCl-H$_2$O system, it is found that Na$^+$ in NaCl solution has a damaging effect on hydrogen bonds in H$_2$O$^{14-15}$, while the damages with the increasing concentration gradually increase. Therefore, in a high-humidity environment, the PI film absorbs moisture and swells, while NaCl destroys the formation of hydrogen bonds and limits the absorption of water by PI, resulting in the reduction of the PI expansion rate as well as the decrease of the humidity-sensitive response amplitude. In addition, with the increasing of NaCl on the surface of the PI membrane, the inhibition to humidity response amplitude of the sensors increases. Through the analysis above, it shows that the sensors can be well used for the salt detection. Figure 4(c) shows the corresponding responsivity of the salt sensing at 5 V, defined as $[(I_{\text{salt content}=0 \mu g} - I_{\text{various salt content}})/I_{\text{salt content}=0 \mu g}]$. The maximum responsivity reaches 80% and the change rate is as low as 0.3%/ug, which illustrates the prepared sensors are sensitive to the salt.

4. Conclusion

In this paper, the composition-graded semiconductor CdSSe nanowire-chips were grown, combining the polymer hygroscopic material PI, to successfully prepare relative humidity and salt sensors. Along the length direction of CdSSe chip, the composition can be gradually tuned from CdSe to CdS, with the morphology changing from nanoribbons to nanowires. The prepared sensor has excellent performance in both humidity detection and salt detection, and has the characteristics of high stability and high repeatability. The resistance of the sensor decreases linearly with increasing humidity, and the fitting ($R^2$) of linear relationship for the resistance-humidity curve is 0.9948. The output current increases linearly with increasing relative humidity, with a maximum response of 85% at 80% RH. In addition, the effect of the salt content on the hygroscopically expanded polyimide was investigated. It was found that the sensor output current linearly decreased with the increase of salt, which made it a highly sensitive salt sensor.

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