1. Introduction

Humidity sensors are widely used in many measurements and control applications, including industrial and agricultural applications, air conditioning systems, food quality monitoring, meteorology and medical equipment. There has been constant pursuit of smaller, cheaper, lighter and better humidity sensing materials in recent years. Therefore, nanometer materials have received great attention for their humidity sensitivity due to their small grain size and large specific surface area, for example, nanocrystalline SnO$_2$/TiO$_2$ bilayered films, ZnO nanorods, carbon nanotube films and so on [1–6]. In the past several years, amorphous carbon (a-C) films have attracted great attention for their potential applications in the field emission, microelectronic devices and hard coating [7–12]. Based on past work, a-C films are expected to be novel sensing materials because of their large sensing area and high chemical inertness and a-C films based gas sensors with high sensitivity and high response rate have been demonstrated as NH$_3$, humidity and ethanol gas sensors [13–15].

Humidity sensors can be classified into four categories: capacitive, resistive, gravimetric and electromagnetic sensors. Among them, the capacitive and resistive types are popular and capacitive sensor designs in particular have attracted major attention. The advantage of the capacitive type humidity sensor over the resistance type sensor is that it uses less power and has much better linearity. In this study, the capacitive humidity sensing properties of a-C film/n-Si (C/Si) heterojunctions are investigated.

2. Experiments

The a-C film was deposited on silicon substrates using direct current magnetron sputtering from a graphite target (The graphite powder was obtained from Qingdao Zhongdong Graphite Company, the purity of the graphite is better than 99.9%). The graphite target is a cold-pressed graphite disk, which was prepared using 76%P–40C pressure system. Firstly, the graphite powder was put into a stainless steel mould at room temperature. After that, the pressure was raised to 25 MPa in 2 min and kept in this state for about 5 min to get the graphite target. (The size of the graphite target was Ø 60.0 mm × 3.5 mm.) The silicon substrates are n-type Si (1 0 0) materials with resistivity in the range of 2–5 Ω cm. Before deposition, the Si substrates were ultrasonically cleaned in acetone and ethanol and then etched in HF solution for 10 min. The deposition took place inside a spherical chamber (SKY Technology Development Co., Ltd., JG560) where the vacuum was about 2.5 × 10$^{-4}$ Pa and the argon pressure was kept at 6.0 Pa and the Si substrates were kept at RT. The size of the C/Si heterojunction was 5.0 mm × 5.0 mm × 0.5 mm. The results of Hall measurements of the a-C films indicated that these films are just like an insulator (resistivity >10$^9$ Ω cm), the carrier concentrations are very small so that they cannot be obtained by current measurement. Measurement of capacitance of the junctions was carried out using two-probe methods using a precision LCR meter (Changzhou Tonghui Electronic Co., Ltd., TH2828). The value of applied voltage during the experiments is 1 V.
The humidity detection experiments were achieved by using supersaturated aqueous solutions of different salts of LiCl, MgCl₂, Mg(NO₃)₂, NaCl, KCl and KNO₃ in closed glass vessels at RT, which yielded sealed atmospheres with RH of 11%, 33%, 54%, 75%, 85% and 95%, respectively [16].

3. Results and discussion

The typical AFM surface image of the α-C film, deposited on Si at 6.0 Pa argon pressure, is shown in Fig. 1. The surface is relatively rough and the average grain size is about 30 nm. The Raman spectra of the α-C films are consistent with the results reported before [14]. One obvious G peak around 1550 cm⁻¹ for the α-C films illustrates the diamond-like carbon characteristics of the films deposited at 6.0 Pa argon pressure.

The change of capacitance of the humidity sensors with frequency was explored in the range of 11–95% RH for C/Si heterojunctions which were deposited for 30 min at an argon pressure of 6.0 Pa, as shown in Fig. 2. The results show that the capacitance increases with increasing RH from 11% to 95% and the capacitance of the heterojunctions increases with decreasing frequency. The capacitance response may be attributed to the rough surface of carbon films and its high surface-to-volume ratio. The specific surface of the carbon films can make a great many of water molecules adsorbed on the surface of the carbon film. With increasing relative humidity the amount of water molecules physisorbed on the carbon film surface increases. The water molecules having a dipole moment can increase the dielectric constant and capacitance of the sensing material. Therefore, the increase in capacitance of the C/Si junction with increasing relative humidity can be attributed to the increase in the amount of physisorbed water having a dipole moment [16,17].

At low frequencies there is plenty of time for water dipoles to orient to a large extent in the material so that the adsorbed water molecules can become more polarized at lower frequencies. With increasing frequency, the adsorbed water molecules become less polarized. Therefore, for a set RH the capacitance of the heterojunctions increase with decreasing frequency [16].

When the frequency was set at 10², 10³, 10⁴, 10⁵ Hz, the humidity sensing properties of the C/Si junction were probed by measuring its junction capacitance at RT at different humidity levels. The capacitance–RH curves of the junction were shown in Fig. 3. The results show a good linear relationship between the capacitance and RH (the R² values of capacitance–RH curves, measured at 10², 10³, 10⁴, 10⁵ Hz, are 0.9887, 0.9470, 0.8484, 0.7881, respectively.). Experimentally, for 1 kHz frequency, when RH changed from 11% to 95%, the junction capacitance showed an increment of ~200%, from ~1000 pF at RH = 11% to ~3200 pF at RH = 95%.

In order to further confirm the influence of RH on the capacitance of the C/Si junction, the C/Si junction was alternately put...
into the two closed glass vessels contained supersaturated aqueous solutions of KNO₃, and MgCl₂, respectively. The capacitance response of the C/Si junction to 33% RH and 95% RH is shown in Fig. 4. When the junction is transferred from 33% to 95% RH, the capacitance of the junction increase by 68% at 1 kHz frequency. The response (recovery) time is defined as the time for reaching 90% of the full capacitance change of the sensor after testing gas is introduced. Seen from the figure, the response time is about 3 min and the recovery time is about 4 min. The results show that these junctions have high sensitivity, and good reproducibility for humidity detection.

4. Conclusions

In summary, a-C films were deposited on Si substrates using direct current magnetron sputtering at RT. An approach to detect various gas humidities at RT was demonstrated based on the change of capacitance of the simple C/Si heterojunctions. The results show that the humidity gas has a large effect on capacitance of the C/Si junctions at RT and the C/Si junction is a potential humidity sensing material with the properties of linear response and good repeatability.

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References


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