Plasma deposited polymers as gas sensitive films

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Abstract. The possibility is presented of producing thin plasma polymers with desired properties by using nanofillers. Composite films are synthesized from a mixture of hexamethyldisiloxane (HMDSO) and detonation nanodiamond particles (DNDs). The chemical structure of the composite consists of DNDs distributed in the polymer matrix. The effect of DNDs on the humidity and ammonia sorptive properties of the polymers obtained is studied by measuring the mass changes as a result of gas sorption by using a quartz crystal microbalance (QCM). The results show that, in view of building a sensing element for measuring humidity, ammonia or other gases, it is possible to maximize the sensor sensitivity to a certain gas by using an appropriate concentration of DNDs in HMDSO. Thus, a high degree of sensor sensitivity, together with short response time and minimum hysteresis, can be achieved. Composites of plasma-polymerized HMDSO with DNDs can be used as gas sensitive layers for the development of quartz resonator sensors.

1. Introduction

Since the chemical and physical properties of plasma polymers (PPs), and especially of silicon containing PPs, may be tailored for particular needs, PPs have found a permanent place in electronic sensors [1-5]. Nanotechnology has made it possible to replace classical sensors materials by PPs and fabricate composite films with organic and inorganic materials [6,7]. Nanodiamond structures are of interest due to the combination of the unique properties inherent to diamond with the particles’ specific surface structure. Detonation nanodiamonds (DNDs) with predominant particles’ size of 4 nm can be used as fillers in PPs [6-8]. On the other hand, PPs appear to be the most appropriate technical solution for realization of gas sensors using a quartz crystal microbalance (QCM). These sensor elements combine the specific sensing properties of PPs with the high mass-sensitivity of the acoustic devices [2-5].

This study is an attempt to modulate the structure and properties of plasma polymers by synthesis of DND-based composites from a mixture of hexamethyldisiloxane (HMDSO) and DNDs. The chemical structure of the polymers obtained was established. The effect of DNDs on the humidity and ammonia sorptive properties of the polymers obtained was studied by measuring the mass changes as a result of gas sorption by applying a QCM-technique.

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2. Experimental

The plasma polymerization technology used for obtaining plasma polymerized hexamethyldisiloxane (PPHMDSO) was described previously [4]. The polymerization of the HMDSO (Merck, 99.99%) was performed at 0.08 mA/cm² current density (27.12 MHz) and vacuum of about 133 Pa for 15 min. The composite deposition was carried out in the same equipment as the polymer films. The following procedure was applied: 0.10 g DND powder was added to 100 ml HMDSO and shaken for 15 min in an ultrasonic apparatus; further, the mixture was stirred (275 r.p.m) continuously at room temperature. The plasma conditions were the same – 0.08 mA/cm² current density and vacuum of about 133 Pa for 15 minutes. The films were deposited on KBr as well as on the quartz resonators.

The FTIR absorbance spectra of the plasma polymer films were recorded on a Bruker FTIR spectrometer in the 4000-400 cm⁻¹ spectral region with a resolution of 2 cm⁻¹. The humidity-frequency measurements of the sensor system and the methodology were described in [2], while those of the ammonia-frequency measurements were presented in [9]. All studies were carried out at room temperature (26 °C).

3. Results and discussion

3.1. FTIR study of plasma polymers

The modification of the PPHMDSO structure achieved by adding DNDs filler is seen in the FTIR spectra (figure 1).

The characteristic peaks of sp³ bonded carbon at 1550 cm⁻¹ and sp² bonded carbon at 1160 cm⁻¹ of the DND are easily observed. Thus, the DND-PPHMDSO polymer is characterized by functional groups of the type –OH, >C=O, Si–O–Si, Si–O–C and the formation of new (C-Si-C) bonds and different tetrahedral CH₃ (the bands in the region 2800 – 3000 cm⁻¹). The change observed of the characteristic polymer bands can be explained by penetration of DND particles in the polymer matrix.

3.2. Humidity sorptive properties of the plasma polymer films

Humidity-frequency characteristics (HFCs) of quartz resonators with PPHMDSO and DND-PPHMDSO are shown in figure 2. The two curves were obtained by measuring the frequency shift when increasing the relative humidity (RH) at a constant temperature of 25°C. The sensitivity to humidity of a polymer coated quartz resonator is the frequency change as a function of the percentage change in RH and depends on the chemical composition and structure of the film. This is the slope of the HFCs in figure 2.

The average sensitivities to humidity for the resonators with PPHMDSO and DND-PPHMDSO are 5 Hz/%RH and 1 Hz/%RH, respectively. The results show that the sensitivity to humidity of the QCM with pure polymer is larger than that with DND-PPHMDSO, but a decrease in the response time and a hysteresis effect are observed. Therefore, by varying the DNDs concentration in the mixture one could find a compromise between the sensing element’s sensitivity, response time and hysteresis.
3.3. **Ammonia sorptive properties of the plasma polymer films**

![Graph](graph1.png)  ![Graph](graph2.png)

**Figure 3.** Time-frequency dependence of a resonator with PPHMDSO at 500 ppm NH3.

**Figure 4.** Frequency dependence versus NH3 for a PPHMDSO coated resonator.

The time-frequency characteristics of the sensing elements at a certain ammonia concentration were also studied. Figure 3 shows the dependence for a QCM with PPHMDSO (film thickness of 640 nm) at 500 ppm NH3 concentration.

The ammonia sensitivity of the resonator with PPHMDSO at different concentrations ranging from 10 to 2500 ppm is presented in figure 4. The mass adsorbed was calculated on the basis of the frequency shift measured according to Sauerbrey equation for AT-cut quartz resonators [10] (table 1).

The resonators covered with DND-PPHMDSO have lower sensitivities, compared with those with pure PPHMDSO (table 2), but the response time is shorter.

The results imply that, by choosing an optimum concentration of DNDs in HMDSO for plasma polymerization, it is possible to increase the sensor sensitivity to ammonia vapor or particular gases.

**Table 1.** Dependence of the adsorbed mass versus NH3 concentration.

| Ammonia concentration [ppm] | Adsorbed mass [ng] |
|-----------------------------|-------------------|
| 10                          | 0.44              |
| 50                          | 2.66              |
| 100                         | 4.21              |
| 250                         | 6.86              |
| 500                         | 9.07              |
| 1000                        | 10.85             |
| 2500                        | 11.95             |

**Table 2.** Ammonia sensitivities of resonators with PPHMDSO and DND-PPHMDSO.

| Ammonia concentration [ppm] | Δf [Hz] |
|-----------------------------|--------|
|                            | PPHMDSO | DND-PPHMDSO |
| 10                          | 2       | -           |
| 50                          | 12      | 1.8         |
| 100                         | 19      | 3           |
| 250                         | 31      | 4.9         |

**Conclusions**

A study is presented of composite films produced by plasma polymerization from mixture of DNDs and HMDSO. The chemical structure of the composite consists of DND nanoparticles distributed in the polymer matrix thus creating new bonds. In view of fabricating a sensing element for measuring humidity, ammonia vapor or other gases, it is possible to maximize the sensor sensitivity to a particular gas by using the appropriate concentration of DNDs in HMDSO. Thus, a high degree of sensor sensitivity together with short response time and minimum hysteresis could be achieved. Composites of plasma polymerized HMDSO with DND particles could, therefore, be used as gas sensitive layers for the development of quartz resonator sensors.
References

[1] Saloum S and Alkhaled B 2010 Acta Physica Polonica A 117/3 484
[2] Radeva E and Spassov L 1998 Vacuum 51 217
[3] Avramov I, Rapp M, Krawczak P and Radeva E 2002 IEEE Sensors J. 2/3 150
[4] Tsankov D, Radeva E, Hinrichs K, Roseler A and Korte E.-H. 2005 Thin Solid Films 476 174
[5] Mugumura H, Kase Y, Murata N and Matsumura K 2006 J. Phys. Chem. B 110 26033
[6] Shenderova O A, Zhirnov V V and Brenner D W 2002 Solid State Mater. Sci. 27(3/4) 227
[7] Dolmatov V Yu 2007 Russian Chemical Reviews 70/7 607
[8] Bogatyreva G P, Voloshin M N and Padalko V I 2008 Diamond & Related Materials 17 213
[9] Georgieva V, Stefanov P, Raicheva Z, Atanassov M, Tincheva T, Manolov E and Vergov L 2009 J. Optoelec. Adv. Mater. 11 1363
[10] Sauerbrey G 1959 J. Physik 155 206