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Fabrication of a gas sensor with a piezoelectric PZT film deposited by a novel hydrothermal microwave-assisted annealing

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Abstract

In this article, we use the piezoelectric material of $PbZr_xTi_{(1-x)}O_3$ (PZT) to fabricate a thin film by sol–gel technique. The novel hydrothermal annealing under microwave system substitutes the conventional furnace annealing. The films from various reaction conditions are analyzed by scanning electron microscope and X-ray diffraction. In addition, the PZT film is used to fabricate the gas sensor. The resonant frequency of the developed PZT sensor is about 30 MHz and the sensing limit for organic vapour is estimated to be about 1 ppm.
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Keywords: Sol–gel; Microwave-assisted annealing; Gas sensor; Piezoelectric PZT film

1. Introduction

Quartz crystal resonators have received wide attention for the characterization of small masses due to their stability, simplicity of measurement, high precision, high sensitivity, and ease of analysis. Numerous literatures [1–3] report that the mass change with respect to the frequency shift forms the basic of quartz crystal microbalance (QCM). Any mass added onto or removed from the electrode of QCM will induce a frequency shift (Δf), and this shift is related to the mass change (Δm). The high inherent sensitivity (<l ng/cm^2) derives from the high resolution with which even very small frequency changes can be measured.

Sauerbrey first provided a description and experimental verification on the mass–frequency relationship between rigid foreign layers firmly attached to the quartz crystal resonators in 1959 [3]. The frequency change is directly proportional to the added mass as long as the added mass behaves elastically similar to the quartz itself as shown in below equation

$$\Delta f = \left[\frac{-2f_{\mathrm{ro}}^2}{A\sqrt{\rho_{\mathrm{q}}G_{\mathrm{q}}}}\right]\Delta m_{\mathrm{q}}$$

where Δf is the change of the resonance frequency from the added mass (Δm_{q}), f_{ro} is the resonance frequency of the unloaded resonator, ρ_{q} and G_{q} are the density and shear modulus of the quartz, and A is the surface area of the resonator [3]. From the Sauerbrey equation, it is obvious that the sensitivity is improved when the surface area (A) is decreased and the resonance frequency of the unloaded resonator is increased.

In addition to the conventional quartz crystal for mass sensing, the piezoelectric material such as $PbZr_xTi_{(1-x)}O_3$ (PZT) is also an alternative candidate for the resonator. The ferroelectric and piezoelectric materials for the solid solutions prepared from Pb(Zr, Ti)O_3 have been widely used in microelectronics. The structure and property of PZT can be varied by changing the amounts of titanium and zirconium. The morphotropic phase boundary has been revealed by the discovery of a ferroelectric monoclinic phase in the $PbZr_xTi_{(1-x)}O_3$ ceramic system. A tetragonal-to-monoclinic phase transition is discovered at room

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temperature [4]. Conventionally, the fabrication of non-quartz piezoelectric films is based on the metal organic chemical vapour deposition [3,5–7], physical sputtering [8–12], dense plasma focus [13] or pulsed laser deposition [14–16]. However, it requires high cost for the deposition tool, and very expensive for the precursor or target. The sol–gel method is a very interesting and simple technique for preparing ceramic films, but the method requires a specific temperature for annealing [17–19]. Microwave-assisted heating [20–23] receives much attention due to the high sample throughput, a little amount of reagent volume, reliable temperature and pressure control, and suitable reaction temperature. To the best of our knowledge, no reports exist that describe the annealing of PZT film by utilizing the microwave-assisted annealing.

In this study, we use the piezoelectric material of PZT to fabricate the gas sensor by the simple sol–gel spin coating method. The PZT film after coating is annealed by the hydrothermal microwave-assisted treatment in the home-made apparatus. The morphology of the PZT film is evaluated by the scanning electron microscope (SEM). In addition, the X-ray diffraction (XRD) is used to characterize the film's structure. Finally, the gas sensor with the PZT film is applied to detect the organic vapour.

2. Experimental

The hydrothermal treatment was carried out in a microwave reactor (CEM MARS-5) by immersing the substrate in 30 ml $KOH/Pb(NO_3)_2$ solution of various concentrations. The concentration of KOH was varied from 0.5 M, 1 M to 2 M, and $Pb(NO_3)_2$ was varied from 0.05 M, 0.1 M, 0.15 M and 0.2 M. The substrate with PZT film was put into a Teflon beaker and covered by working solution in the microwave vessel. Prior to microwave heating, the vessel was purged under N_2 atmosphere. The Teflon beaker was drilled by three holes to afford the paths for ions and to prevent the reaction between the PZT films and the precipitation of the solution. For each run, the microwave reactor was sealed and heated to the working temperature of 160 °C in 10 min, and then the system was maintained for 30 min. The system was cooled after the hydrothermal treatment, and the samples were rinsed in boiling deionized water. Finally the sample was dried by a hot plate. The film's quality was analyzed by SEM (HITACHI S-4000) and XRD (Shimadzu XD-5), respectively.

The fabrication procedure for the PZT gas sensor was illustrated in Fig. 1. The 500 nm SiO_2 film and 300 nm Si_3N_4 film were deposited onto Si wafer by the furnace system. The purpose of Si_3N_4 layer was to prevent the possibility of device damage by KOH while at the hydrothermal annealing. The adhesion layer (Cr) and the bottom electrode (Pt) were sequentially deposited on the lithographic pattern of $Si_3N_4/SiO_2/Si$ wafer. Then, the resist was removed by the specific solvents. The sample is annealed by RTA (HEATPLUSE 610) at 650 °C for 5 min. The sol–gel solution of PZT obtained from Alfa Aesar (A Johnson Matthey Company) was spin-coated onto $Pt/Cr/Si_3N_4/SiO_2/Si$ wafer by two steps: 1000 rpm for 10 s, and 3000 rpm for 30 s. The PZT films were subsequently prebaked at 150 °C for 10 min and at 350 °C for 30 min on a hot plate. This pattern was designed by the exposure on photoresist, and etched away by HCl solution. The PZT films then were treated by the specific hydrothermal annealing in the microwave system. Finally, the lift-off process was used to define the top Au electrode by thermal coater. The developed PZT sensors were used to detect the organic vapour of the toluene. The frequency shifts were detect by the frequency counter (Agilent 53132A) and recorded by computer in real-time.

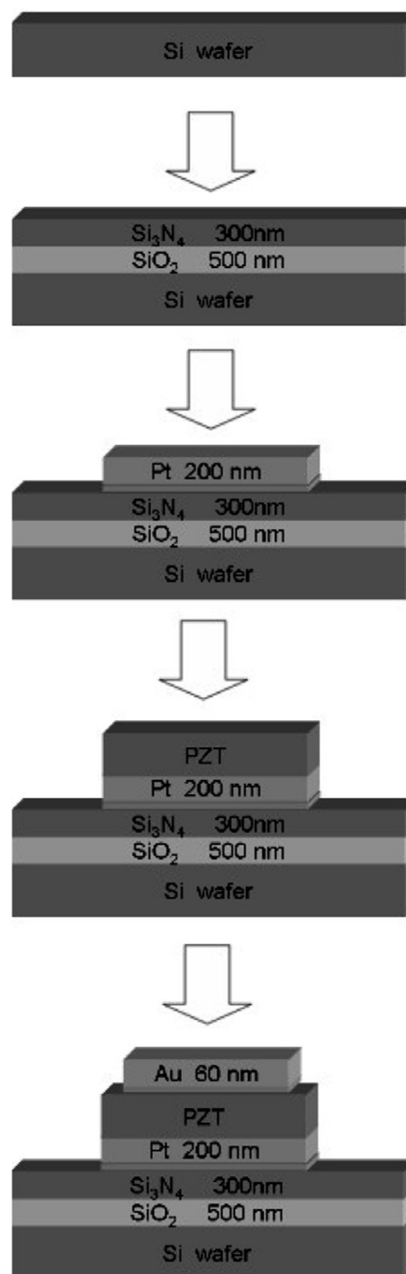

Fig. 1. The fabrication processes for the PZT sensor.

3. Results and discussion

Fig. 2 shows the SEM micrographs for the PZT thin films at various recipes of the hydrothermal annealing. Fig. 2a is the morphology of the PZT film without microwave annealing at the solution concentration of 0.5 M KOH + 0.05 M $Pb(NO_3)_2$, and some significant cracks are appeared on the surface. These cracks mean the film's quality is challenged without the microwave hydrothermal annealing. Fig. 2b–d represents the PZT films after annealing under the same 0.5 M KOH solution, but the concentration of $Pb(NO_3)_2$ is 0.1 M, 0.15 M and 0.2 M, respectively. The morphology for these conditions is very rough for the PZT films. Only few dispersive regions exhibit PZT nucleation and growth. When the PZT films are treated by 1 M KOH + 0.05 M $Pb(NO_3)_2$ (in Fig. 2e) and 1 M KOH + 0.1 M $Pb(NO_3)_2$ (in Fig. 2f) solution, the surface coverage of the film has the higher extent of nucleation and growth. However, these films are still rough and can not be used for the sensor. In Fig. 2g and h, although there are also several cracks, the roughness of the film seems to be better at the concentration of 1 M KOH + 0.15 M $Pb(NO_3)_2$ or 1 M KOH + 0.2 M $Pb(NO_3)_2$. As increasing the solution concentration to 2 M KOH + 0.05 M $Pb(NO_3)_2$ and 2 M KOH + 0.1 M $Pb(NO_3)_2$, illustrated in Fig. 2i and j, the film is still not fully coverage with the nucleation and growth. As to the solution of 2 M KOH + 0.15 M $Pb(NO_3)_2$ and 2 M KOH + 0.2 M $Pb(NO_3)_2$ in Fig. 2k and l, the quality of these films become acceptable than other conditions. Therefore, the reagent concentration of 2 M KOH + 0.2 M $Pb(NO_3)_2$ is used to fabricate the sensor.

XRD patterns of the samples treated by microwave hydrothermal annealing are demonstrated in Fig. 3. These patterns are all analyzed by JCPDS (Joint of committee on powder diffraction standards) data base. Only the amorphous structure is observed in the as-deposited PZT films without the microwave hydrothermal treatment. When

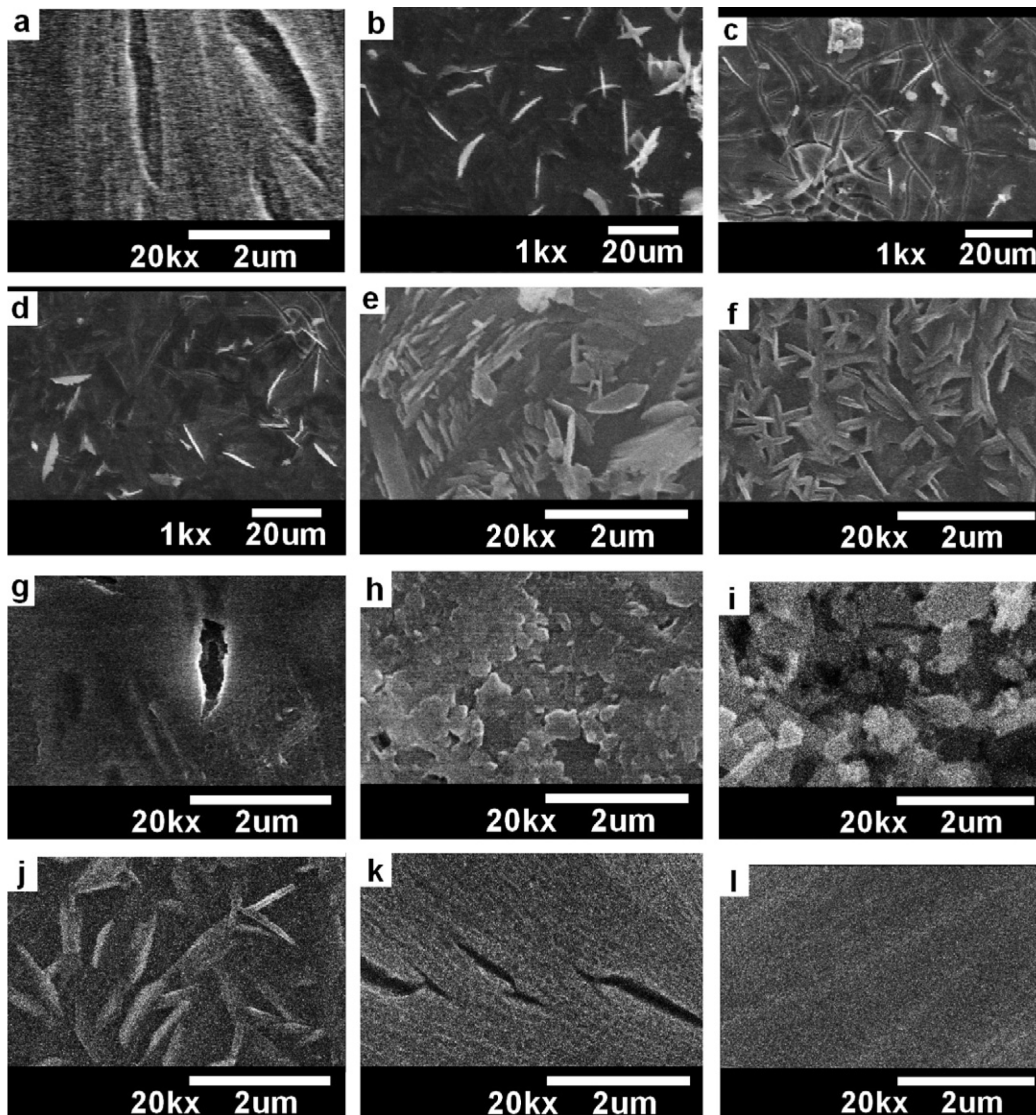

Fig. 2. The SEM images of PZT thin films at various reaction solution concentrations under microwave hydrothermal annealing.

the solutions are reacted under 0.5 M KOH, as illustrated in Fig. 3a, these films still exhibit the amorphous structure. Whereas the weak signal of perovskite phase is observed in the films after typical run of the hydrothermal treatments under 1 M KOH + 0.15 M $Pb(NO_3)_2$ and 1 M KOH + 0.2 M $Pb(NO_3)_2$ solutions, of which shown under Fig. 3b. In contrast, the perovskite phases with a preferred (1 1 1) and (0 0 3) orientations are clearly observed in as-deposited PZT films by the microwave hydrothermal treatment in 2 M KOH + 0.15 M $Pb(NO_3)_2$ solution and 2 M KOH + 0.2 M $Pb(NO_3)_2$ solution, as shown in Fig. 3c. Together with the SEM morphologies in Fig. 2, we can infer that the PZT film has formed the crystallization.

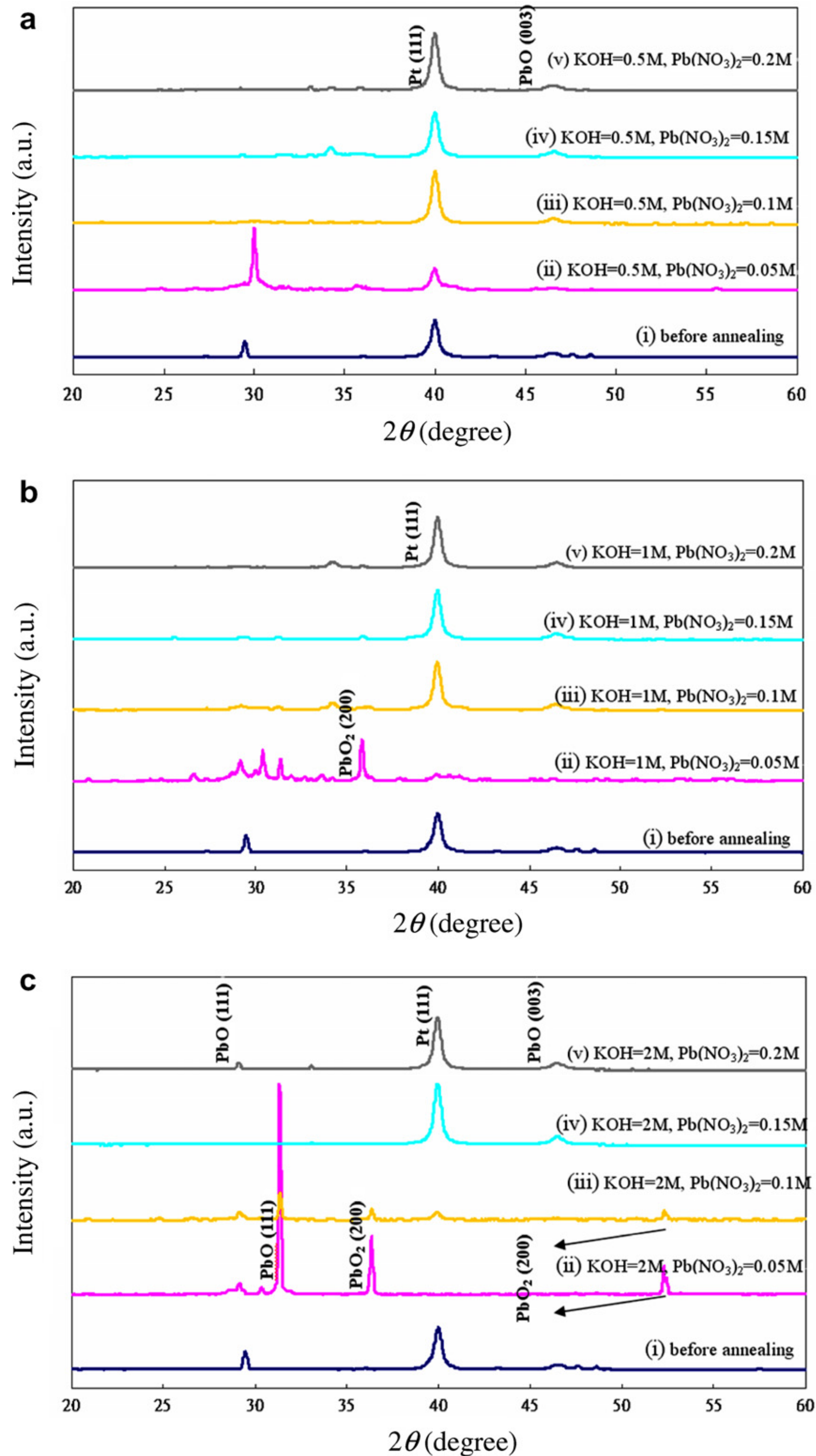

Fig. 3. The XRD patterns of PZT thin films with or without microwave hydrothermal annealing under various $Pb(NO_3)_2$ concentrations and at KOH concentration of (a) 0.5 M, (b) 1 M, and (c) 2 M.

After the success of the PZT film with microwave hydrothermal annealing, the gas sensor based on the PZT film is fabricated as mentioned in Fig. 1. The PZT sensor and the beaker are put in a closed system, the resonant frequency of the sensor will reach the steady state after a couple of minutes. Then, we inject the solvent of interest into the beaker. The solvent gradually vaporizes and reaches the saturation in the closed system. The vapour of interest will diffuse near the sensor surface and adsorb onto the Au electrode. Since this reaction is only a physical adsorption for the solvent, the surface of PZT sensor can be recovered after finishing the sensing process. The saturation effect at various temperatures can control the vapour pressure, and thereby vary the surface solvent concentration.

We plot the frequency shifts and saturated vapour pressures with respect to temperatures for toluene in Fig. 4. The theoretical vapour pressure is also indicated in the figure. The frequency shifts in Fig. 4 for toluene vapour are 6.6 kHz, 11.8 kHz, 15.5 kHz and 18.9 kHz at 30 °C, 40 °C, 50 °C and 60 °C, respectively. As the toluene vapour pressure increases, the deposition of toluene vapour onto the sensor also increases. This observation clearly suggests the signal of PZT sensor is related with the vapour concentration. Therefore, the fabricated PZT sensor can be used to sensing the concentration of organic gases. The resonant frequency of the developed PZT sensor is about 30 MHz and the sensing limit for organic vapour is estimated to be about 1 ppm.

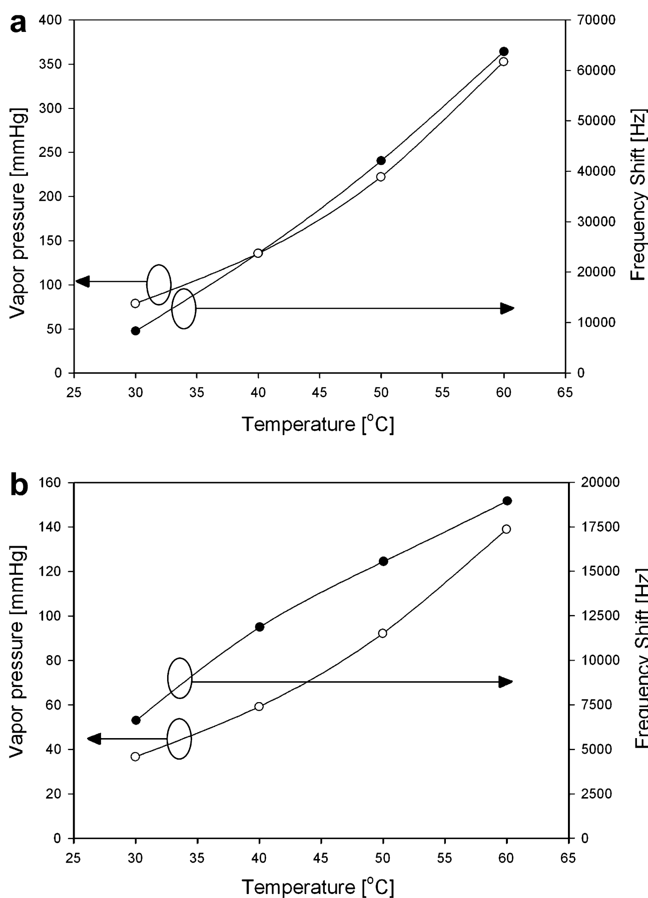

Fig. 4. The shift frequency for the fabricated PZT sensor under the vapour pressure of toluene.

4. Conclusions

The combination of the sol–gel technique and the hydrothermal process in the novel microwave system is successfully used to prepare the polycrystalline PZT thin films from 30 ml 2 M KOH/0.2 M $Pb(NO_3)_2$ solution under 160 °C. The hydrothermal treatment in microwave system can shorten the reaction time for the PZT film. The PZT sensor has the ability to detect toluene vapour.

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References

[1] Y. Okahata, Y. Matsunobu, K. Ijiro, M. Mukae, A. Murakami, K. Makinolb, J. Am. Chem. Soc. 114 (1992) 8299.
[2] M. Minunni, M. Mascini, R.M. Carter, M.B. Jacobs, G.J. Lubrano, G.G. Guilbault, Anal. Chim. Acta 325 (1996) 169.
[3] K. Nagashima, H. Funakubo, Jpn. J. Appl. Phys. Part 1 39 (2000) 212.
[4] R.E. Alonso, A.L. García, A. Ayala, P. de la Presa, J. Phys.-Conden. Mater. 10 (1998) 2139.
[5] C.M. Foster, G.R. Bai, R. Csencsits, J. Vetrone, R. Jammy, L.A. Wills, E. Carr, J. Amano, J. Appl. Phys. 81 (1997) 2349.
[6] H.H. Park, W.S. Kim, J.K. Yang, H.H. Park, R.H. Hill, Microelectron. Eng. 71 (2004) 215.
[7] B.S. Kwak, E.P. Boyd, A. Erbil, Appl. Phys. Lett. 53 (1988) 1702.
[8] I. Kanno, S. Fujii, T. Kamada, R. Takayama, Appl. Phys. Lett. 70 (1997) 1378.
[9] I. Taguchi, A. Pignolet, L. Wang, M. Proctor, F. Lavy, P.E. Shmid, J. Appl. Phys. 73 (1993) 394.
[10] T. Hase, T. Sakuma, Y. Miyasaka, K. Hirata, N. Hosokawa, Jpn. J. Appl. Phys. Part 1 32 (1993) 4061.
[11] S.B. Krupanidhi, N. Maffei, M. Sayer, K. El-Assal, J. Appl. Phys. 54 (1983) 6601.
[12] K. Sreenivas, M. Sayer, P. Grarett, Thin Solid Films 172 (1989) 251.
[13] R. Gupta, M.P. Srivastava, V.R. Balakrishnan, R. Kodama, M.C. Peterson, J. Phys. D 37 (2004) 1091.
[14] Y.C. Zhou, Z.Y. Yang, X.J. Zheng, Surface & Coatings Technol. 162 (2003) 202.
[15] S.T. Zhang, W.S. Tan, G.L. Yuan, X.J. Zhang, H.W. Cheng, Y.F. Chen, Z.G. Liu, N.B. Ming, Microelectron. Eng. 66 (2003) 701.
[16] J.M. Liu, L.C. Yu, G.L. Yuan, Y. Yang, H.L.W. Chan, Z.G. Liu, Microelectron. Eng. 66 (2003) 798.
[17] Y.J. Yu, H.L.W. Chan, F.P. Wang, L.C. Zhao, Microelectron. Eng. 66 (2003) 726.
[18] V. Snitka, A. Ulcinas, K. Nemciauskas, V. Lendraitis, Microelectron. Eng. 83 (2006) 1456.
[19] J.S. Hwang, W.S. Kim, H.H. Park, T.S. Kim, Microelectron. Eng. 70 (2003) 73.
[20] C.-J. Ko, C.-Y. Lee, F.-H. Ko, H.-L. Chen, T.-C. Chu, Microelectron. Eng. 73–74 (2004) 570.
[21] F.-H. Ko, C.-Y. Lee, C.-J. Ko, T.-C. Chu, Carbon 43 (2005) 727.
[22] Y.-C. Chang, F.-H. Ko, C.-J. Ko, T.-C. Chu, Anal. Chim. Acta 526 (2004) 121.
[23] F.-H. Ko, H.-L. Chen, J. Anal. At. Spectrom. 16 (2001) 1337.