J Mater Sci (2009) 44:2814–2819
DOI 10.1007/s10853-009-3371-5

Stress-dependent piezoresistivity of tunneling-percolation systems

Yansong Wang · Ligong Zhang · Yi Fan ·
Dapeng Jiang · Linan An

Received: 9 September 2008 / Accepted: 23 February 2009 / Published online: 13 March 2009

Abstract We studied the stress-dependent piezoresistive behavior of tunneling-percolation systems. Starting from percolation-like power law of resistivity, a model relating piezoresistive stress coefficient to the applied stress has been developed by considering the stress-induced changes in the critical exponent and that in the concentration of conducting phases. It is found that the coefficient exhibits reverse and logarithmic dependence on the applied stress in the different stress ranges. We show that the experimental data, obtained from carbon-reinforced polymer composites and polymer-derived ceramics, follow the theoretical prediction of the model very well, indicating that the stress effects described by the model indeed exist in tunneling-percolation systems.

Introduction

Conducting particle-reinforced insulating matrix composites (CPICs) are an important class of multifunctional materials with widespread applications. Notable materials that belong to this family include carbon-black-polymer systems [1–6], metal-inorganic and -organic insulator composites [7–11], and oxide-based thick film resistors (TFRs) [12–16]. Transport behavior of these materials can be described by so-called tunneling-percolation models, in which tunneling coexists with percolation behaviors. Thereby, the electrical resistivity of CPICs follows a percolation-like power law [17, 18]:

$$\rho = \rho_0 (x - x_c)^{-t} \tag{1}$$

where ρ_0 is a constant, x the concentration of the conducting phase, x_c the critical concentration of the conducting phase below which the composite has the resistivity of the matrix phase, and t the critical exponent. According to the standard percolation theory, the critical exponent t is material independent and has a universal value $t_0 \approx 2$ for three-dimensional systems [19–21]. However, it has been found that for tunneling-percolation systems t becomes material dependent and can be significantly different from t_0 [22]. Such nonuniversality has been attributed to specific distributions of both conducting and insulating phases [23].

One unique feature of CPICs is that they exhibit a high piezoresistive effect, i.e., the sensitivity of their resistivity upon applied stress. The significant piezoresistivity can be qualitatively understood in terms of the tunneling-percolation mechanism, in which the tunneling conductance is proportional to $\exp(2d/\xi)$ [24], where d is the interparticle spacing between the conductive particles and ξ is the tunneling factor which depends only on the potential barrier which is the property of the matrix material. Consequently, stress-induced changes in the interparticle spacing can significantly change the resistivity of the material, leading to a high piezoresistive coefficient.

The piezoresistivity of CPICs has been extensively studied since it is very important for the applications of the

Y. Wang · Y. Fan · D. Jiang
Laboratory of Excited State Process, Changchun Institute of Optics, Fine Mechanics and Physics, Chinese Academy of Sciences, Changchun, Jilin 130032, China

Y. Wang
Graduate School of Chinese Academy of Sciences, Beijing 100049, China

L. Zhang · L. An (✉)
Advanced Materials Processing and Analysis Center, University of Central Florida, Orlando, FL 32816, USA
e-mail: lan@mail.ucf.edu

materials in various sensors [25]. However, fundamental understanding of the piezoresistivity of CPICs is rather difficult, because it strongly depends on the detailed microstructures and elastic properties of the materials. Carmona et al. [2] suggested that the piezoresistivity reversely depends on the concentration of conducting phase at the conductivity threshold by simple considering the stress-induced concentration changes. It has also been demonstrated that the nonuniversality of t can yield a logarithmic concentration dependence of piezoresistive response in the systems with conducting phase closer to the critical points [26]. For the systems with their insulating phases having Young's modulus lower than conducting phases, the piezoresistive factors are enhanced due to the local deformation within the insulating phases being higher than the overall deformation [27].

Close examination on experimental data revealed that the resistivities of CPICs generally exhibited a non-linear relationship with the applied stress. This implies that the piezoresistive stress coefficient, defined as $\mathrm{d}\ln\rho/\mathrm{d}\sigma$ (where σ is the applied stress), is not a constant value, but depends on the applied stress level. This is more profound in carbon-black-polymer systems, where the rate of the change in resistivity decreases significantly with increasing the applied stress [1–4, 28–30]. This phenomenon is worth detailed investigations since it becomes important when comes to sensor design and fundamental understanding of transport mechanisms.

In this paper, we show that for the materials where the Young's modulus of the insulating matrix phase is much less than that of conducting phase, the piezoresistive stress coefficient depends on the applied stress reversely at lower stresses and logarithmically at higher stresses at the percolation threshold. We obtain these results by an analytic solution of the piezoresistive stress coefficient based on the power law described by Eq. 1. We demonstrate that the prediction of the model agrees well with experimental results.

Model

The piezoresistivity of a material can be described by its piezoresistive factor, K (also known as gauge factor) or piezoresistive stress coefficient, Π, defined as

$$K = \frac{\mathrm{d}\rho/\rho}{\mathrm{d}\varepsilon} = \frac{\mathrm{d}\ln(\rho)}{\mathrm{d}\varepsilon} \tag{2a}$$

$$\Pi = \frac{\mathrm{d}\rho/\rho}{\mathrm{d}\sigma} = \frac{\mathrm{d}\ln(\rho)}{\mathrm{d}\sigma} \tag{2b}$$

where ε is the strain and σ is the applied stress. The two parameters are related to each other by $K = E \cdot \Pi$, where E is the Young's modulus of the material.

By inserting Eq. 1 into Eq. 2b, the piezoresistive stress coefficient of a tunneling-percolation system can be expressed as

$$\Pi = \frac{\partial \ln \rho_0}{\partial \sigma} - \ln(x - x_c)\frac{\partial t}{\partial \sigma} - \frac{t}{x - x_c}\frac{\partial x}{\partial \sigma} \tag{3}$$

The first term on the right-hand side of Eq. 3 is a constant for a given system [22], referred as to Π_0 here. Its contribution to the overall piezoresistivity is typically very small for a tunneling-percolation system [26]. The second and third terms are resulted from stress dependent t and concentration, respectively.

Previous study showed that the t has the following relationship with the microstructure of the material [22],

$$t = 0.88 + 2\lambda/\xi \tag{4}$$

where λ is the average interparticle spacing of neighboring conducting phase, which can be related to the stress as $\lambda = \lambda_0(1 + \alpha\sigma/E)$, where λ_0 is the average interparticle spacing without the applied stress and α is a factor to correct the difference between the local strain within the insulating phase and the overall strain of the composite. Consequently, the piezoresistive stress coefficient of a tunneling-percolation system can then be expressed as

$$\Pi = \Pi_0 - \frac{2\alpha\lambda_0}{\xi E}\ln(x - x_0) - \frac{t}{(x - x_c)}\frac{\partial x}{\partial \sigma} \tag{5}$$

Equation 5 relates the piezoresistive stress factor of a tunneling-percolation system to the concentration of conducting phase.

Now, we relate the change in the concentration of conducting phase (x) to the applied stress. Assuming the composite is an isotropic material, the change in volume of the composite under uniaxial stress is

$$\frac{\mathrm{d}V}{V} = \frac{\mathrm{d}\sigma}{E}(1 - 2v) \tag{6a}$$

where V is the volume at stress σ and v is the Poisson's ratio of the composite. Similarly, the change in the volume under hydrostatic stress is

$$\frac{\mathrm{d}V}{V} = 3\frac{\mathrm{d}\sigma}{E}(1 - 2v) \tag{6b}$$

For a composite with Young's modulus of the conducting phase being different from that of the matrix, the stress-induced volume changes in the matrix phase is different from that in the conducting phase, leading to changes in the volume fraction of the conducting phase. Detailed solution of the problem needs a complicated stress partitioning analysis. Here, we consider the case where the Young's modulus of the insulating matrix phase is much lower than that of the conducting phase so that the change in the conducting phase can be neglected. In these cases, the volume fraction of the conducting phase can be related to the applied stress as

$$x = x_0 \exp(-\frac{\sigma}{E}(1-2v)) = x_0(1-\frac{\sigma}{E}(1-2v)) \tag{7a}$$

$$x = x_0 \exp(-\frac{3\sigma}{E}(1-2v)) = x_0(1-\frac{3\sigma}{E}(1-2v)) \tag{7b}$$

where x_0 is the volume fraction of the conducting phase without the applied stress. Equations 7a and 7b are for uniaxial and hydrostatic stress, respectively. It can be seen that under compressive stress (σ has a negative value), the volume fraction of the conducting phase increases with increasing the applied stress.

By inserting Eqs. 7a and 7b into Eq. 5, we obtain

$$\Pi = \Pi_0 - \frac{2\alpha\lambda_0}{\xi E}\ln((x_0 - x_c) - x_0\frac{\sigma}{E}(1-2v)) + \frac{t^{\frac{x_0(1-2v)}{E}}}{(x_0 - x_c) - \frac{\sigma x_0}{E}(1-2v)} \tag{8a}$$

$$\Pi = \Pi_0 - \frac{2\alpha\lambda_0}{\xi E}\ln((x_0 - x_c) - x_0\frac{3\sigma}{E}(1-2v)) + \frac{t^{\frac{3x_0(1-2v)}{E}}}{(x_0 - x_c) - 3\frac{\sigma x_0}{E}(1-2v)} \tag{8b}$$

Equations 8a and 8b are for uniaxial and hydrostatic stress states, respectively. When $x_0 \rightarrow x_c$, or stress-induced changes are larger than $x_0 - x_c$, the above equations can be simplified as

$$\Pi = \Pi_0 - \frac{2\alpha\lambda_0}{\xi E}\ln(-x_0\frac{\sigma}{E}(1-2v)) - \frac{t}{\sigma} \tag{9a}$$

$$\Pi = \Pi_0 - \frac{2\alpha\lambda_0}{\xi E}\ln(-x_0\frac{3\sigma}{E}(1-2v)) - \frac{t}{\sigma} \tag{9b}$$

Since $t = 0.88 + 2\lambda/\xi$ and $\lambda = \lambda_0(1 + \alpha\sigma/E)$, we have

$$\Pi = \Pi_0 - \frac{2\alpha\lambda_0}{\xi E}\ln[-x_0\frac{\sigma}{E}(1-2v)] - \frac{0.88 + 2\lambda_0/\xi}{\sigma} - \frac{2\lambda_0\alpha}{E\xi} \tag{10a}$$

$$\Pi = \Pi_0 - \frac{2\alpha\lambda_0}{\xi E}\ln(-x_0\frac{3\sigma}{E}(1-2v)) - \frac{0.88 + 2\lambda_0/\xi}{\sigma} - \frac{2\lambda_0\alpha}{E\xi} \tag{10b}$$

The last term in Eqs. 10a and 10b are very small and can be neglected,

$$\Pi = \Pi_0 - \frac{2\alpha\lambda_0}{\xi E}\ln[-x_0\frac{\sigma}{E}(1-2v)] - \frac{t_0}{\sigma} \tag{11a}$$

$$\Pi = \Pi_0 - \frac{2\alpha\lambda_0}{\xi E}\ln(-x_0\frac{3\sigma}{E}(1-2v)) - \frac{t_0}{\sigma} \tag{11b}$$

The equations predict that at lower stress level the piezoresistive stress coefficient of a tunneling-percolation system reversely depends on the applied stress, while at higher stress level it logarithmically depends on the applied stress.

Case studies

Carbon-reinforced insulating polymer matrix composites

Carbon-reinforced insulating polymer matrix composites are typical tunneling-percolation systems, which have been extensively studied due to their applications in a variety of sensors and others. The system is particularly suitable for testing our models since the carbon phase has much higher Young's modulus than the polymeric matrixes. Here we select two sets of data to compare with our models: one measured under hydrostatic stresses and the other measured under uniaxial stresses.

Celzard et al. studied stress-dependent resistivities of single crystal graphite flakes (referred as to flat micronic graphite (FMG), with mean diameter of 10 μm and thickness of 0.1 μm) reinforced epoxy and polyurethane composites under hydrostatic stresses [3]. The respective critical percolation concentrations are 1.3 vol.% and 1.7 vol.% for the epoxy and polyurethane composites [31]. Here, piezoresistive stress coefficients are calculated using the stress-dependent resistivity data in Ref. [3] for two composites: one of them is epoxy-based composites containing 1.36 vol.% FMG (Fig. 7c in Ref. [3]); and the other one is polyurethane-based composite containing 2 vol.% FMG (Fig. 8d in Ref. [3]). Figure 1 plots the calculated Π as a function of the applied stress. It is seen that for the both composites the data in a low stress range follow the $\log \Pi - \log \sigma$ plot, while the data in the high stress range follows $\Pi - \log \sigma$ plot.

For the uniaxial stress situation, the experimental results from three silicone rubber composites are used here: two of them contain 1.35 and 1.8 vol.% carbon fibers of 9 μm in diameter and 1 mm in length [2], and the third one is reinforced with 35.5 vol.% carbon micro-balls of 8 μm in diameter [4]. The carbon-fiber-reinforced composites have the critical concentration of 1.1 vol.% [2], while the critical concentration of the carbon micro-ball-reinforced composite was not reported, but should be much less than 35.5 vol.%.[1] Figure 2 plots the calculated piezoresistive stress coefficients. For the two carbon-fiber-reinforced composites the Π exhibit the $\log \Pi - \log \sigma$ plot in the whole stress range, while for the carbon micro-ball-reinforced composite, the

---

[1] For random distributed spherical reinforcements, the up bound of the percolation critical concentration should be ~15 vol.%.

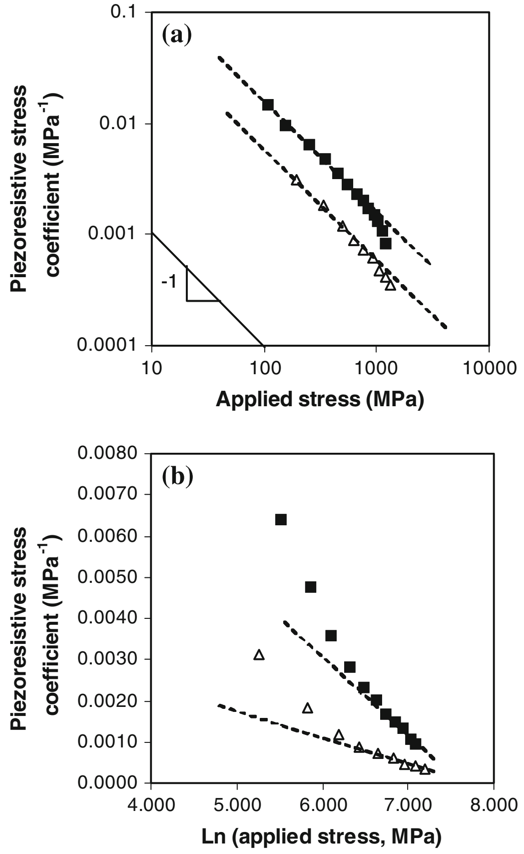

Fig. 1 Plots of piezoresistive stress coefficient as a function of applied hydrostatic stress in **a** log-log scale and **b** linear-log scale. *Solid symbols* epoxy based composites. *Open symbol* polyurethane based composite

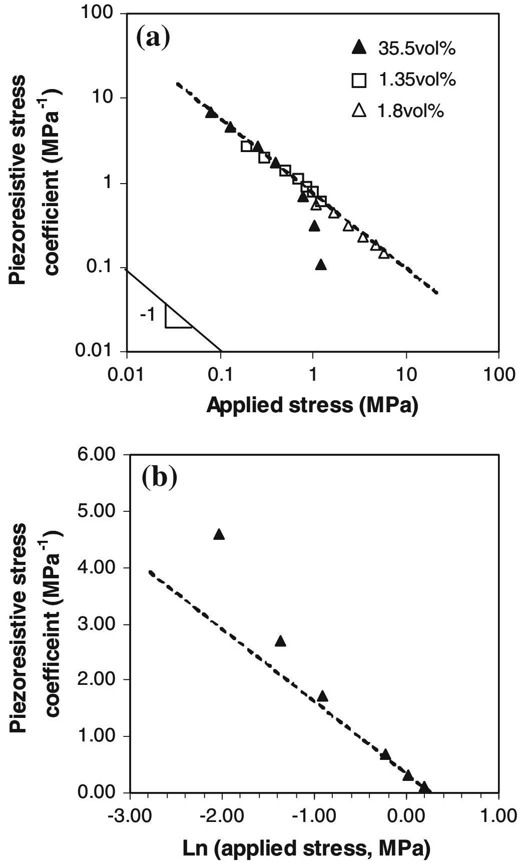

Fig. 2 Plots of piezoresistive stress coefficient as a function of applied uniaxial stress in **a** log-log scale and **b** linear-log scale. *Open symbol* Ref. [2]. *Solid symbols* Ref. [4]

low-stress data fit the log Π − log σ plot, but the high-stress data follow the Π − log σ plot.

Polymer-derived ceramics

Polymer-derived ceramics (PDCs) are a new class of high-temperature multifunctional materials synthesized by thermal decomposition of polymeric precursors [32, 33]. Due to their unique manufacturing capability, PDCs have been considered for fabricating micro-electro-mechanical systems (MEMS) and micro-sensors [34–36].

PDCs exhibit a unique structure, which contains "free" carbon clusters within the amorphous matrix. Previous study demonstrated that with proper control of chemistry the precursor, the "free" carbon can form a tunneling-percolation network, resulting in anomalously high gauge factors [37]. PDCs are also suitable for testing the model of Eqs. 11a and 11b since the carbon phase has much higher Young's modulus than the amorphous matrix phase [37].

The polymer-derived amorphous silicon carbonitride (SiCN) studied here is the same as we reported previously [37], which exhibited tunneling-percolation behavior. The stress-dependent resistivity of the SiCN is measured along longitudinal direction (parallel to the loading direction) under uniaxial compressive stress, using the procedure described in Ref. [37], and summarized in Fig. 3. It is seen that the resistivity of the SiCN decreases steeply with the applied stress, and then slowly with the higher applied tress. The piezoresistive stress coefficient of the SiCN is calculated using the data of Fig. 3 and plotted in Fig. 4. The results reveal that in the low-stress range the Π fit log Π − log σ plot, but the high-stress data follow the Π − log σ plot.

Discussion and conclusion

It is seen from section "Case studies" that the experimental data from various materials fit very well with the prediction of Eqs. 11a and 11b. Note that the material systems examined in section "Case studies" covered a wide range of variations in the size, concentration, and morphology of the conducting phases, and in the elastic properties of the "insulating" matrix phases. The data used

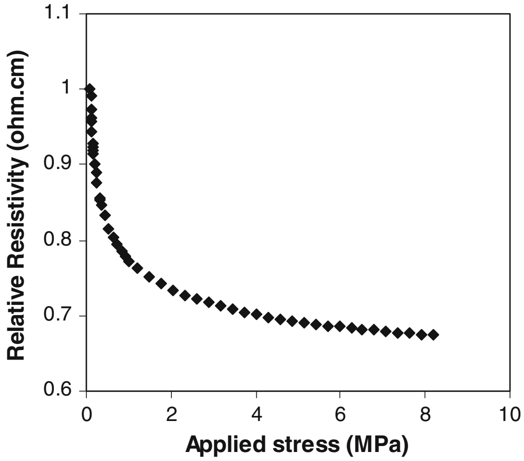

Fig. 3 A plot of the relative resistivity of the SiCN polymer-derived amorphous ceramics versus the applied uniaxial stress. The resistivity is normalized with respect to the unstressed state

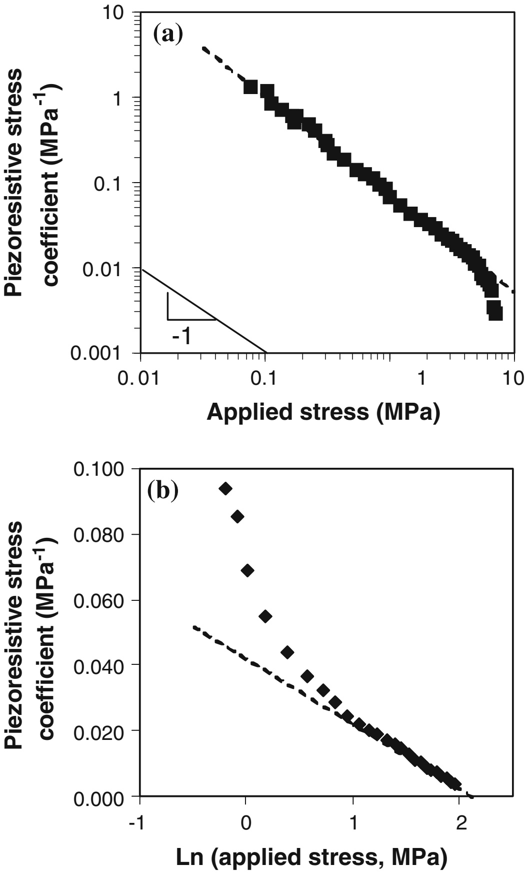

Fig. 4 Piezoresistive stress coefficient of the SiCN as a function of applied stress: **a** the log-log plot and **b** the linear-log plot

are from both hydrostatic and uniaxial loading configurations. This suggests that the effect described in Eqs. 11a and 11b should be widely valid in tunneling-percolation systems.

The transition from reverse dependence of the piezoresistive stress coefficient on the applied stress to logarithmic dependence is rather interesting. It is seen that the reverse dependent relationship always occurred at relatively low stress range, while the logarithmic dependence always occurred at high stress level. Closely examining the experimental results suggests that such transition occurred either at very high stress level when the initial concentration of the conducting phase is close to the critical value (Fig. 1) or at low stress level when the concentration of the conducting phase is much higher than the critical value (Fig. 2). In both cases, the concentrations of the conducting phases at the transition points are much higher than the critical values. Eq. 3 suggests that the reverse dependence resulted from the stress-induced change in conducting phase concentration, while the logarithmic dependence comes from the stress-induced change in the critical exponent, *t*. When conducting-phase concentration approaches the critical value the resistance change significantly with a small change in the concentration, thus the reverse dependence should be dominant. On the other hand, when conducting-phase concentration is much higher than the critical value the resistance change slightly with a change in the concentration, the logarithmic dependence becomes dominant.

In summary, we have shown by means of analytical results that the piezoresistive stress coefficient of a tunneling system exhibits both reversely and logarithmically dependent on the applied stress in different stress ranges. These features seem to be consistent with experimental results from various material systems, such as carbon-polymer systems and polymer-derived ceramics. The good agreements between the experimental results and theoretical prediction suggest that the stress dependence of the piezoresistive stress coefficient in tunneling-percolation systems indeed follow the effect described by Eqs. 11a and 11b.

Acknowledgement This work was supported by National Science Foundation of US (DMR-0706526).

References

1. Lunberg B, Sundqvist B (1986) J Appl Phys 60:1074
2. Carmona F, Canet R, Delhaes P (1987) J Appl Phys 61:2550
3. Celzard A, McRae E, Maêché JF, Furdin G (1998) J Appl Phys 83:1410
4. Husain M, Choa Y, Niihara K (2001) Composites Part A 32:1689
5. Heaney MB (1995) Phys Rev B 52:12477
6. Chen CC, Chou YC (1985) Phys Rev Lett 54:2529
7. Chiteme C, McLachlan DS (2003) Phys Rev B 67:024206
8. Lee S-I, Song Y, Noh TW, Chen X-D, Gaines JR (1986) Phys Rev B 34:6719
9. Abeles B, Pinch HL, Gittleman JI (1975) Phys Rev Lett 35:247
10. Deptuck D, Harrison JP, Zawadzki P (1985) Phys Rev Lett 54:913

11. Maaroufi A, Haboubi K, El Amarti A, Carmona F (2004) J Mater Sci 39:265. doi:10.1023/B:JMSC.0000007752.08385.e0
12. Pike GE (1978) In: Garland JC, Tanner DB (eds) Electrical and optical properties of inhomogeneous media. American Institute of Physics, New York, p 366
13. de Jeu WH, Geuskens RWJ, Pike GE (1981) J Appl Phys 52:4128
14. Kusy A (1997) Physica B 240:226
15. Carcia PF, Ferretti A, Suna A (1982) J Appl Phys 53:5282
16. Dziedzic A (1987) Mater Sci 13:199
17. Stauffer D, Aharony A (1994) Introduction to percolation theory. Taylor & Francis, London
18. Sahimi M (2003) Heterogeneous materials I: linear transport and optical properties. Springer, New York
19. Batrouni GG, Hansen A, Larson B (1996) Phys Rev E 53:2292
20. Normand JM, Hermann HJ (1995) Int J Mod Phys C 6:813
21. Clere JP, Podolskiy VA, Sarychev AK (2000) Eur Phys J B 15:507
22. Vionnet-Menot S, Grimaldi C, Maeder T, Strässler S, Ryser P (2005) Phys Rev B 71:064201
23. Kogut PM, Stralcy J (1979) J Phys C 12:2151
24. Sheng P, Abeles B, Arie Y (1973) Phys Rev Lett 31:44
25. Kovacs G (1998) Micromachined transducer sourcebook. WCB/McGraw-Hill, New York
26. Grimaldi C, Maeder T, Ryser P, Strässler S (2003) Phys Rev B 67:014205
27. Grimaldi C, Ryser P, Strässler S (2001) J Appl Phys 90:322
28. Wang L, Ding T, Wang P (2007) Sens Actuators A 135:587
29. Beruto DT, Capurro M, Marro G (2005) Sens Actuators A 117:301
30. Heaney MB (1996) Appl Phys Lett 69:2602
31. Celzard A, McRae E, Marêchê JF, Furdin G, Dufort M, Sundqvist B (1996) J Phys Chem Solids 57:715
32. Riedel R, Passing G, Schonfelder H, Brook RJ (1992) Nature 35:714
33. Kroke E, Li YL, Konetschny C, Lecomte E, Fasel C, Riedel R (2000) Mater Sci Eng R 26:97
34. Liew L, Zhang W, An L, Shah S, Lou R, Liu Y, Cross T, Anseth K, Bright V, Raj R (2001) Am Ceram Soc Bull 80:25
35. Liu Y, Liew L, Lou R, An L, Bright VM, Dunn ML, Daily JW, Raj R (2002) Sens Actuators A Phys 95(2–3):143
36. Liew L, Liu Y, Luo R, Cross T, An L, Bright VM, Dunn ML, Daily JW, Raj R (2002) Sens Actuators A Phys 95(2–3):120
37. Zhang L, Wang Y, Wei Y, Xu W, Fang D, Zhai L, Lin K, An L (2008) J Am Ceram Soc 91:1346