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Letter

Effect of temperature on dielectric properties of Si_3N_4/SiO_2 composite and silica ceramic

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ABSTRACT

In this article, the dielectric properties of Si_3N_4 nanowires reinforced silica ceramic composites compared with pure silica ceramics were investigated by using impedance analyzer, at the frequencies from 10^3 to $10^{7.5}$ Hz and the measuring temperature ranging from 20 to 800 °C. Then the effects of the measuring and sintering temperature on the dielectric behavior of the samples were discussed. It was found that there existed different dielectric behaviors between the pure and composite specimens. Among the measuring temperature studied, the composite displayed better dielectric property as compared with the pure ceramic. The superiority exhibited distinctly at high temperature, which could be explained by the theory of dielectric polarization. For the effect of sintering temperature on the dielectric property, the results showed that the dielectric constants increase with the increase of sintering temperature, which can be mostly associated with the variety of sample density. However, the dielectric losses of both ceramics show a little dependence of the sintering temperature.

1. Introduction

The dielectric property of materials is considerable important for wave transparent application such as radome. Several ceramic materials, due to possessing excellent wave transparent properties, have become the most ideal materials for wave transparence [1–5]. Among them, fused silica has generally been used as such a material for radome due to its low dielectric constant and loss tangent, and high chemical stability. However, the low strength, poor rain erosion resistance, and relatively low temperature toleration cannot meet the requirements for more and more high speed vehicles. By introducing some fine-scale fibers can improve the mechanical strength of fused silica but on the other hand, the dielectric property is impaired. Therefore, it is important to keep dielectric and mechanical properties balanced to meet the practical application. Silica matrix-nitride composites may overcome the drawbacks above and retain the good mechanical and dielectric properties. Since silicon nitride possess a moderate dielectric constant (α-Si_3N_4 is 5.6 and β-Si_3N_4 is 7.9 compared with 3.3 of fused silica at room temperature) and many superior properties including thermal shock resistance, corrosion resistance, creep resistance, high strength and stiffness retention, which make it suitable for various promising applications [6–8]. In our previous work, Si_3N_4 nanowires with an average diameter of about 60–80 nm have been proved to be a good reinforcement phase for the improvement of mechanical property of silica ceramic. And the composite is also expected to combine desired dielectric properties of the components.

In recent years, motivated by the fast development of aerospace technology as well as the improvement of spacecraft flight Mach number, the fore part of the antenna needs to raise its capabilities of temperature tolerance and thermal shock resistance [9–12]. This will also set a higher request to the dielectric performance of wave transparent materials. The most basic request to the dielectric performance is the dielectric constant and loss change small with the environmental temperature and frequency as far as possible. However, many studies of the dielectric properties of wave transparent materials have been only carried out under the temperature within 500 °C so far. The situation with respect to the higher temperature dielectric properties of ceramic matrix composites is, on the other hand, lack of systematic research. So it is necessary to accumulate the experimental data on dielectric properties related to the temperature in the actual.

In the present paper, the dielectric properties of silica ceramic and Si_3N_4 nanowires (NWs)/SiO_2 ceramic composites were investigated as a function of temperature. The aim was to better understand the dielectric behaviors of the composites as a function of measuring and sintering temperature at the frequency range of 10^3 to $10^{7.5}$ Hz. Specifically we addressed the following issues: (i) the comparison of dielectric properties between silica ceramic

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and Si_3N_4 NWs/SiO_2 ceramic composites over a broad frequency range; (ii) the thermal sensitivity of the dielectric response over the measuring temperature in the range of 20 to 800 °C; (iii) effect of sintering temperature on dielectric properties of the above two kinds of materials.

2. Experimental

Required amounts of high-purity Si_3N_4 nanowires were synthesized by the CVD method, using Si and SiO_2 powders in the atmosphere of N_2. A conventional solid-state (ceramic) mixture procedure was employed to prepare the presently investigated specimens. Consequently, SiO_2 ceramic composites enhanced with Si_3N_4 nanowires were obtained with the Si_3N_4 nanowires concentration of 1% (mass fraction). After 6-h ball-milling in absolute alcohol, the mixtures were dried at 120 °C for 2 h in air. Then the ensuing powders were dryly pressed into disk shape pellets approximately 15 mm in diameter and about 2.5 mm in thickness at a pressure of 15 MPa using poly(vinyl alcohol) as the binder. The pellets were finally sintered at the temperature of 1300, 1400 and 1500 °C for 10 h in air. Electrodes were made by painting silver paste on the polished opposite sides of the disk-shaped samples. The phase formation was examined using powder X-ray diffraction (XRD, X'Pert MPD) with Cu-Kα radiation (λ = 0.15418 nm) at room temperature. The densities were calculated using Archimedes measurements. The morphology was studied by Scanning electron microscopy (SEM) (Hitachi S-3500).

To carry out the high temperature dielectric conductivity measurements, the samples were mounted into a tubular furnace, which was held at a constant temperature for at least 15 min prior to each measurement. Pt wires were attached to the coated pellet using a spring load contact. The measurement was operated by heating the sample from room temperature with a heating rate of 10 °C/min, and the measurements were made during both the heating and the cooling cycles. Variable-temperature (20–800 °C) measurements of the dielectric properties of these pressed pellets were made between 10^3 and $10^{7.5}$ Hz using Agilent 4294A impedance analyzer at a bias voltage of 500 mV. The analyzer was calibrated to the short and open standards using its internal automatic calibration routine. The values of the capacitance (C) and the dielectric loss (D) of the samples were recorded by a computer. Using the following equation, the relative dielectric constant (ε) can be calculated:

$$\varepsilon = \frac{Cd}{\varepsilon_0 A}$$

where ε_o, d, A, and C are the dielectric constant in vacuum, the thickness, the area, and the measured C value of sample, respectively.

3. Results and discussion

3.1. X-ray and morphology characterization

To facilitate the description of the following part, the composition and the density of the as-prepared samples are given in Table 1. Fig. 1 shows the XRD patterns. All the reflections in samples 1, 3 and 5 can be readily indexed to the pure phase of SiO_2 (JCPDS Card No. 89-3434, a = 4.958 Å and c = 6.907 Å). Most of the reflection peaks in samples 2, 4 and 6 are in good agreement with SiO_2 and the positions of the diffraction peaks have no obvious changes, except the additional peak marked by asterisk. The marked peak is due to the Si_3N_4 phase (JCPDS Card No. 72-1253, a = 7.753 Å and c = 5.618 Å),

Table 1
Number lists of the as-prepared samples and their relative densities as a function of sintering temperature.

Number	Sample	Sintering temperature	Density (%)
1	SiO_2 ceramic	1300 °C	94.6
2	Si_3N_4 NWs/SiO_2 composite	1300 °C	85.1
3	SiO_2 ceramic	1400 °C	97.1
4	Si_3N_4 NWs/SiO_2 composite	1400 °C	87.3
5	SiO_2 ceramic	1500 °C	98.6
6	Si_3N_4 NWs/SiO_2 composite	1500 °C	89.2

suggesting that the chemical compositions of the composite are SiO_2 and Si_3N_4. Due to the small quantity and poor crystallization of Si_3N_4 nanowires, the intensity of Si_3N_4 reflection peak is much lower than that of SiO_2.

SEM images of the above as-prepared samples are shown in Supplementary Fig. 1. From the images, it is clear that the surfaces of pure SiO_2 (sample 1, 3, 5) are relatively smooth and compact, while the surfaces of composite (sample 2, 4, 6) are loose owing to the evident pores. According to the sintering theory, the microstructure and the density of sintered body are influenced by the sintering temperature. At high temperature volume diffusion is the main diffusion mechanism, while at low temperature surface diffusion is dominated. Only volume diffusion results in the density of sintered body, so it is favorable for mass transfer by increasing the temperature.

3.2. Effect of measuring temperature on the dielectric properties of the samples

Dielectric constant (ε) is a material dependent permittivity, reflecting the polarization capacity of the material. All materials have a dielectric constant larger than 1. The dielectric constant of any given material varies with both frequency and temperature, and this is pretty important when applied on high temperature designs. In view of the practical applications at high temperature, the dielectric constant was measured at five different temperatures in the frequency scope of 10^3 to $10^{7.5}$ Hz.

Fig. 2 shows the relationship between the frequency and dielectric constant of silica ceramics and Si_3N_4 NWs/SiO_2 composite, under different temperature sintered at 1300 °C. For each sample, the dielectric constant increases with the increasing measuring temperature. Because when the measuring temperature increases, the facilitation of the orientation of electric dipoles promotes the orientational polarization, which leading to the increase of ε. The curves also show that the variations of ε with frequency are different, depending on the measuring temperature. At measuring temperature of 20, 200 and 400 °C, the dielectric constant of both

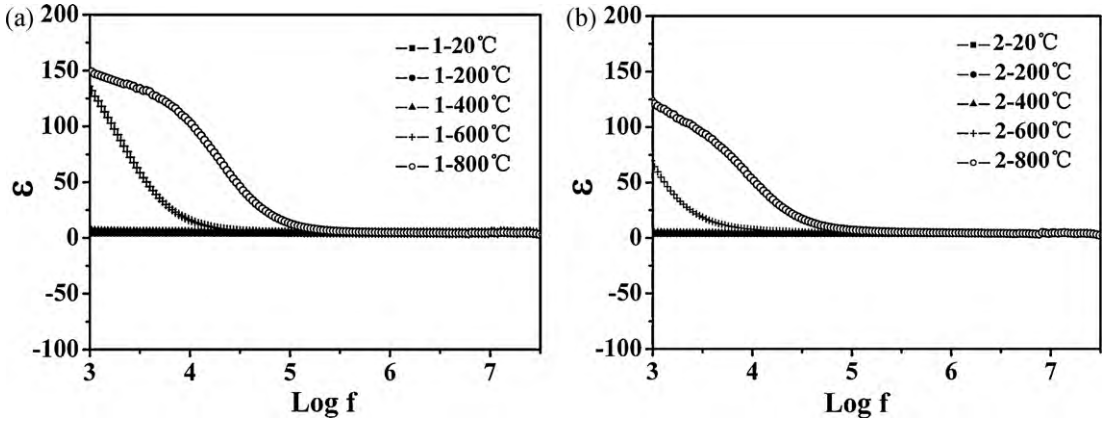

Fig. 1. XRD patterns of the as-prepared samples.

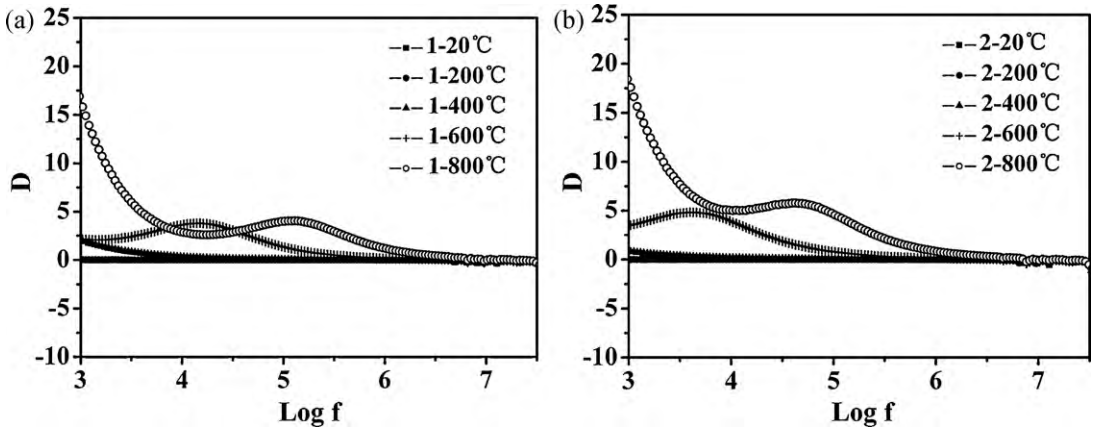

Fig. 2. The relationship between the frequency and dielectric constant of silica ceramics (a) and Si_3N_4 NWs/SiO_2 composite (b) under different temperature sintered at 1300 °C.

samples kept almost 4 over the investigated frequency range. Moreover, the dielectric constant of composite is slightly lower compared with that of silica ceramic, but the difference is minute. At measuring temperature of 600 and 800 °C, ε dependence of the frequency tends to follow a normal pattern, i.e., on the whole both curves monotonously decrease with the increasing of frequency. In the frequency range of 10^3 to 10^5 Hz, the values of ε reduce rapidly and the decline velocity of silica ceramic is larger than that of composite. But when the frequency exceeds 10^5 Hz, the values of ε vary little. This feature can be explained based the theory of dielectric polarization. At low frequency a variety of polarizations in the two samples can keep up with the changes of external electric field. Polarization is very full, which exhibits a relatively high dielectric constant. Besides, as the relaxation time of ion relaxation polarization is usually 10^{-2} to 10^{-5} s, the influence of frequency on the polarization achieves the greatest when the electric field changes from 10^3 up to 10^5 Hz. That leads to the sharp decline in dielectric constant. However, at high frequency, both samples almost have the same ε value, indicating that the mobility of polar groups in the two samples is too small to contribute to the dielectric constant. The contribution of ion relaxation polarization to the dielectric constant decreases, leading to the dielectric constant decreases with the increase of frequency at first and finally tends to be stable. In addition, on account of the larger dielectric constant of silicon nitride, the dielectric constant of Si_3N_4 NWs/SiO_2 composite should increase theoretically, but actually it decreases

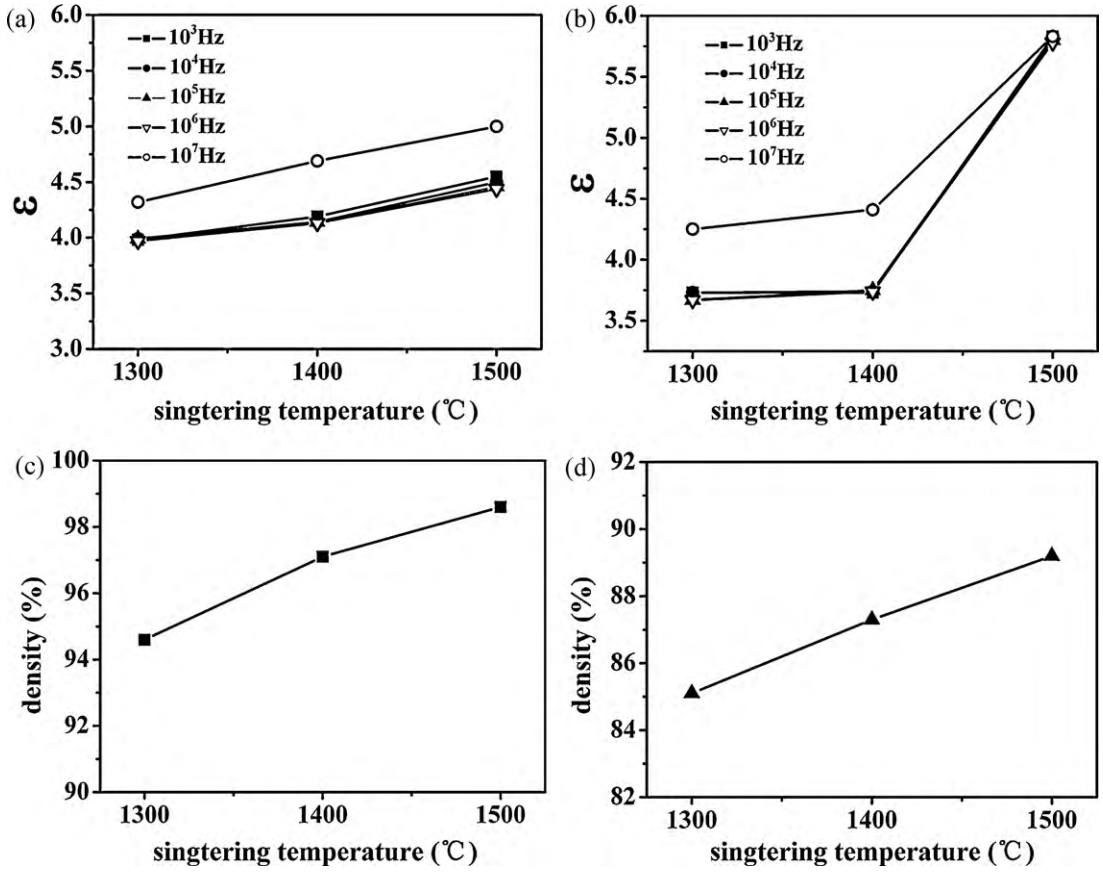

Fig. 3. The relationship between the frequency and dielectric loss of silica ceramics (a) and Si_3N_4 NWs/SiO_2 composite (b) under different temperature sintered at 1300 °C.

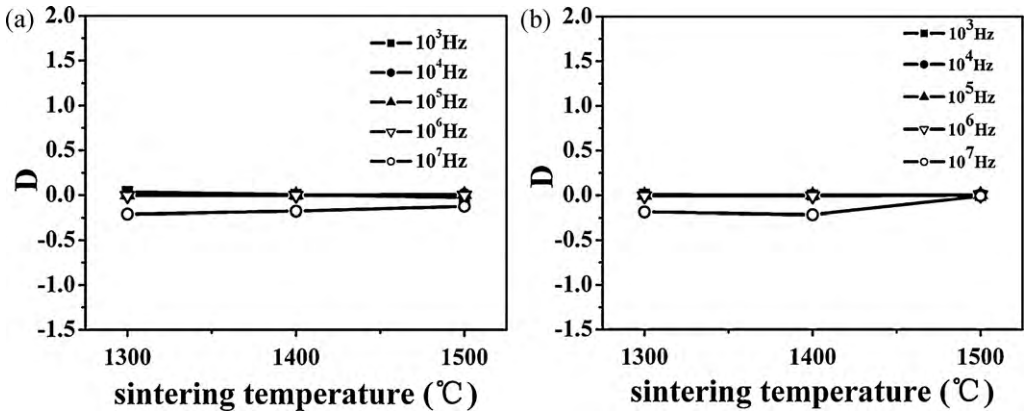

Fig. 4. Effect of sintering temperature on the dielectric constants and densities of silica ceramic (a and c) and Si_3N_4 nanowires/SiO_2 composite (b and d).

because of the impact of density on the dielectric constant. In general, the dielectric constant increases with the increasing of density. The dielectric properties and material density are closely linked. Walton gives the relationship of dielectric constant and porosity [13].

$$\log \varepsilon_p = (1-p)\log \varepsilon_0$$

where p is the porosity and $1-p$ can be regarded as the relative density; ε_p and ε_0 are the dielectric constants of the porous and fully dense materials, respectively. From the experimental results, it basically conforms to this relationship, that is, the greater the density of the sample results in a greater dielectric constant.

Any dielectric medium in the electric field always converts more or less part of electromagnetic energy into heat, which will lead to heat in the medium. Then, the energy consumption due to heat per unit time is called dielectric loss ($\tan\delta$ or D) [14]. A comparison of the dielectric loss between silica ceramic and Si_3N_4 NWs/SiO_2 composite at 5 temperature points is shown in Fig. 3, which are sintered at 1300 °C over a wide range of frequency. The result shows that at the temperature of 20, 200 and 400 °C, the dielectric losses of two samples vary little in the entire frequency range and the values of D are basically the same. At the temperature of 600 and 800 °C, peaks are observed in plots of D versus the logarithm of frequency. The positions of the peaks shift to higher frequencies with the increasing of temperature, whereas the peak heights do not significantly change. This suggests a temperature dependent relaxation. Silica ceramic and Si_3N_4 NWs/SiO_2 composite are both non-homogeneous systems consisted of grain, grain boundary, pore and impurity. The electrical conductivity of the main crystalline phase and grain boundary are different. When the electric field operates, the movement of the carriers from one phase to another phase will be hampered at the interface. This leads to an accumulation of the free electric charge at the contact interface and space charge polarization. Therefore, in addition to the performance of the ion relaxation polarization, silica ceramic and Si_3N_4 NWs/SiO_2 composite also display space charge polarization. According to Debye polarization relaxation equation [15], the dielectric loss can be expressed as:

$$tg\delta = \frac{\varepsilon''}{\varepsilon} = \frac{(\varepsilon_s - \varepsilon_\infty)\omega\tau}{\varepsilon_s + \varepsilon_\infty \omega^2\tau^2}$$

where ε_s, ε_∞, ω and τ are static dielectric constant, optical frequency dielectric constant, frequency and relaxation time of polarization, respectively. Moreover, the relaxation time and temperature meet the following relationship $\tau = Ae^{B/T}$, that is, relaxation time decreases with the increasing of temperature. When the relaxation time is shorter, $\omega\tau = 1$ is satisfied, peak comes into being in the plot of frequency-dependent dielectric loss. According to the theory of space charge polarization, space charge polarization relaxation time is positively related with resistivity of material. So, when the temperature increases, the resistivity of material reduces and relaxation time shortens, leading to the positions of dielectric loss peaks shifting to higher frequencies. And according to the index relationship between conductivity and temperature $\gamma = Ae^{-B/T}$, the dielectric loss guided by the leakage current is more obvious at high temperature. That results in the rapidly increases of dielectric loss. As the relaxation time quickly shortened with the increasing of temperature, the dielectric constant also increases.

3.3. *Effect of sintering temperature on the dielectric properties of the samples*

To study the effect of sintering temperature on the dielectric properties of silica ceramic and Si_3N_4 NWs/SiO_2 composite, three samples were prepared by pressureless sintering at 1300, 1400 and 1500 °C, respectively. The densities of the sintered samples were tested by the Archimedes method. Fig. 4 shows that the dielectric constant of silica ceramic varies with sintering temperature at 5 frequency points and the relative density varies as a function of sintering temperature. From the curves it can be seen that both the sintering density and the dielectric constant of the samples increase with the increase of sintering temperature. The dielectric constants of composite increase faster from 1400 to 1500 °C and slower from 1300 to 1400 °C, while which of silica ceramic increase steadily throughout. Thus, it is obvious that the dielectric constants of the samples are dependent on their densities. So

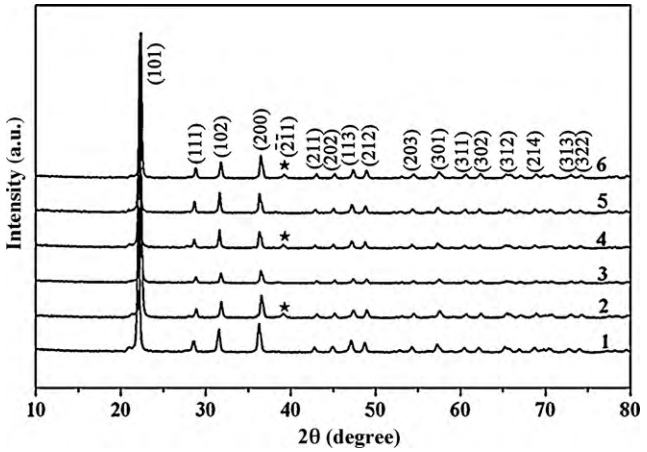

Fig. 5. Effect of sintering temperature on dielectric losses of silica ceramic (a) and Si_3N_4 nanowires/SiO_2 composite (b).

the density is an important factor affecting the dielectric constant during the increase of sintering temperature.

The relationship between the dielectric loss and the sintering temperature was plotted in Fig. 5. The curves show the dielectric loss changes little with the increasing of sintering temperature and roughly constant. These results suggest that the dielectric loss of silica ceramic and Si_3N_4 NWs/SiO_2 composite is affected little by the sintering temperature. However, at the frequency of 10^7 Hz, negative dielectric losses are observed which might be the result of the following reasons: (1) the precision of instruments (As the value of dielectric loss is very small, slight fluctuations in measuring might result in large errors.); (2) contact resistance; (3) complex residues impedance.

4. Conclusions

In summary, the comparative experimental results of dielectric behaviors in the silica ceramic and Si_3N_4 NWs/SiO_2 ceramic composite were reported using impedance analyzer covering temperature range from 20 to 800 °C and frequency range 10^3 to $10^{7.5}$ Hz. Some differences between the two kinds of materials were found. The temperature dependence of the dielectric property was discussed. The results showed that the introduction of the second phase silicon nitride nanowires did not deteriorate the dielectric properties. While to some extent, the composite ceramic display better dielectric properties compared to silica ceramic, especially at high measuring temperature. In addition, the results showed that the dielectric constants of silica ceramic and Si_3N_4 NWs/SiO_2 composite were obviously influenced by the sintering temperature, which was most probably ascribed to the variety of the density. While the dielectric losses showed a little dependence of the sintering temperature.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jallcom.2010.04.240.

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