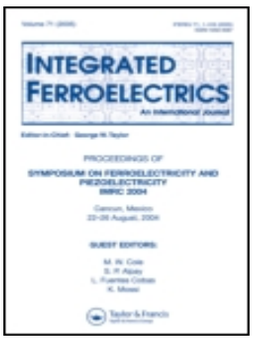

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Diffusion of Silver During Sintering in High Permittivity COG Dielectrics

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To achieve cost reduction in multi-layer ceramic capacitors and actuators, which use a silver-palladium alloy as internal electrode, the trend is to use alloys with the highest silver content possible. This requires ceramic materials which must be sintered at a relative low temperature. Goal is to avoid much diffusion of silver into the ceramics.

Analysis of the composition of the electrode in multilayer components is a good tool to investigate the diffusion of silver during sintering. Analysis of various multi-layer components with different silver-palladium alloys shows that the diffusion of silver during sintering is dependent on the difference between the sintering temperature of the multilayer component and the melting point of the silver-palladium alloy used. Diffusion of silver into the ceramics during sintering is negligible when this difference is at least 100 °C.

Keywords $BaTiO_3$; Sintering; Silver Electrode; Diffusion.

Introduction

In the last two decades the development on multilayer ceramic capacitors (MLCC) is focused on miniaturization and cost reduction. MLCCs are commonly used in electronics like personal computers, mobile phones and other devices. The market of these components is still growing due to global increase of the general usage of electronics. Besides miniaturization of electronic devices and components new technologies use more complex electronic circuits in which an increasing amount of passive components, like MLCCs, are needed. In mobile phones, wireless LAN, notebooks, multilayer capacitors with excellent properties in Radio Frequency (RF) applications are needed. These type of MLCCs are fabricated with materials having low relative permittivity ε_r, temperature stable electrical properties and high quality factor Q [1].

Temperature stable dielectrics, Class 1 dielectrics according Electronic Industries Alliance (EIA) specification, are used in RF applications, in which stable capacitance towards temperature and aging is needed. The most stable type of dielectrics is encoded COG by EIA and is often called NPO ('negative positive zero') in industry. The temperature coefficient

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of relative permittivity of COG dielectrics must be approximately zero and may not exceed ±30 ppm/°C in a temperature range of −55°C to 125°C. Dielectrics which consists of high ε_r and high Q can be made with a wide variety of dielectrics like (Zr,Sn)TiO_4, Ba(Zn,Ta)O_3, Ti-rich BaO-TiO_2, Ba-Ln-Ti-O, BaO-PbO-Nd_2O_3-TiO_2 [2–3]. For COG MLCCs with palladium or palladium rich Ag/Pd electrodes Ba-Nd-Ti-O (BNT) dielectrics are often used [4].

In this study a commercial dielectric based on non-ferroelectric BaO-Nd_2O_3-Gd_2O_3-TiO_2 (AD850DZ, Ferro) was used, which will be called hereafter K85. The sinter temperature of this dielectric is about 1200°C depending on the sintering conditions. To lower the sinter temperature sintering aids were added to this dielectric compound, keeping COG properties and the highest possible ε_r.

In past MLCCs were usually made with palladium or palladium rich electrodes. In order to reduce costs implementation of silver or silver rich electrodes were the drive for new dielectric material development. However silver can diffuse as ions or transport as vapor into the ceramics during co-firing of multilayer ceramic components [5]. The influence of silver on the performance of ceramics was studied and published [5–13]. However, no literature is available about electrode continuity and electrode composition after sintering for silver and silver rich electrodes in multilayer components.

During the development of MLCCs containing silver rich 95Ag/5Pd (wt%/wt%) electrodes it has been observed that a large variation of capacitance and ESR values were measured. Furthermore, it was observed that the electrode layers showed a discontinuity near the outside of the MLCC. For MLCCs the electrode continuity is important for the electrical properties in general, but more specific the equivalent series of resistance (ESR) of the components. The problem was due to the fact that silver diffuse into the ceramics or evaporated in air during co-sintering. That causes the electrode to become discontinuous.

In this paper the development of MLCCs, based on new dielectrics and silver rich Ag/Pd electrodes, are described with respect to electrode quality. A new dielectric composition was developed, based on commercial powder AD850DZ of Ferro. This commercial powder AD850DZ is called K85 in this paper. A sintering aid was used to decrease the sintering temperature of K85. MLCCs with this new dielectric formulation were made using 95Ag/5Pd and 90Ag/10Pd powders and are called respectively K72 and K75. These K72 and K75 0805–100pF MLCCs consisted of 10 electrodes. After co-firing the MLCCs at 950°C for 2 hours the electrodes were analyzed with SEM-EDS to detect the Ag loss. This analysis revealed that silver diffusion can be avoided if the melting point of the Ag/Pd alloy exceeds the sinter temperature of the dielectric at least with 100°C. This knowledge can be used to select the best suitable Ag/Pd alloy for co-sintering with a certain new dielectric composition.

In order to observe the ESR 0603–10pF MLCCs were prepared containing 5 electrodes. Material combinations of K85 with pure palladium, K80 with 80Ag/20Pd alloy and K75 with 90Ag/10Pd alloy were tested. It was observed that electrodes with high silver content the ESR properties improved.

Experimental

The powders for K80 were made starting from K85 (AD850DZ, Ferro) and sintering aid 1, which is prepared from ZnO (Sigma Aldrich 99.0%), SiO_2 (Degussa, aerosil R975), TiO_2 (Riedel de Haën, 99.0%) and CuO (Pan-Continental Chemical Co, 99%). The dielectric powders for K72 and K75 were made starting from K85 (AD850DZ, Ferro) and sintering

aid 2, which is prepared from ZnO (Sigma Aldrich 99.0%), SiO_2 (Degussa, aerosil R975), H_3BO_3 (Sigma Aldrich, 99.99%) and CuO (Pan-Continental Chemical Co, 99%) and Bi_2O_3 (Merck, 99%). The powders were weighed according non-disclosed formulations into a PE flask PE flask with 2 mm YTZ beads. The powders were mixed for 16 hrs with isopropyl alcohol as medium. The powders were dried, grounded and uniaxial pressed (Fontijne SRA100) into discs of 8 mm diameter $\times$ 7.55 mm height. The discs were pressed cold isostatically (EPSI *Engineered Pressure Systems International* B.V.) at 4000 bar for 3 minutes. The discs were measured using a NETZCH Dil 402 C dilatometer. The samples were sintered at a 5°C/ min heating rate in static air. Then kept for 30 minutes at 1200°C (K80 and K72) or at 1250°C (K85) before the samples were cooled down by 10°C/min.

Ag Content Characterization of Electrodes

Green MLCC chips were produced on regular production equipment at Yageo in Roermond, The Netherlands. The 0805 MLCCs consisted of 10 electrode layers in a brick with an overall size of 2.0 $\times$ 1.25 $\times$ 0.6 mm^3. The dielectric thickness after sintering was 10 μm; the electrode thickness was 2.5 μm. The MLCCs of K80, dielectrics made from K85 and sintering aid 1, were made with 80Ag/20Pd paste. The MLCCs of K80 were sintered in air at 1080°C for 2 hours. The MLCCs of K72 and K75, dielectrics made from K85 and sintering aid 2, were respectively made of 95Ag/5Pd and 90Ag/10Pd paste. Both samples were sintered at 950°C for 2 hours in an air atmosphere.

The silver and palladium content of the electrodes were determined using a SEM (Philips XL20) equipped with an EDS system (EDAX).

ESR Measurements

MLCCs of K85/100 Palladium, K80–80Ag/Pd20 and K72–90Ag/10Pd were prepared by making 0603 green chips in 1.6 $\times$ 0.8 $\times$ 0.8 mm^3 with 5 electrodes. The MLCCs had a capacitance of 10 pF measured at 1 MHz /1V after sintering. End contacts were applied onto the brick with glass containing silver paste. The ESR was measured with an Agilent LCR meter 4287a and fixture 16196A. The measuring frequency range was 30 MHz upto 3 GHz with 32 measuring points.

Results and Discussion

The MLCC samples were based on commercial BaO-Nd_2O_3-Gd_2O_3-TiO_2 dielectrics, AD850DZ, of Ferro. In this paper the commercial dielectric is called K85 and it sinters dense at temperature of around 1180°C depending on sinter conditions. This material can be co-sintered with pure palladium or high content palladium like 20Ag/80Pd. For MLCCs with 80Ag20Pd electrodes a dielectric composition was already developed using a sinter aid, see table 1. With the addition of sinter aid 1, which is based on a ZnO-SiO_2-CuO-TiO_2 compound, to K85 the sinter temperature was decreased. The samples made of this new formulation and 80Ag/20Pd electrodes are called K80. The sinter temperature for these K80 MLCCs is 1080°C when sintered in air for 2 hours. To use high silver content Ag/Pd alloys like 95Ag/5Pd another sinter aid was developed to obtain a dielectric formulation, which could sinter below the melting temperature of pure silver. This material is called K72 and based upon K85 and sinter aid 2, which was made of a mixture of the following oxides; B_2O_3, ZnO, SiO_2, Bi_2O_3 and CuO. The dilatometer results, see Fig. 1, show that K72 sinter dense at lower temperature than K80. In this study these dielectrics were first used in

Table 1
Sample overview of dielectrics, electrode composition and sintertemperature

Material code	Dielectrics	Electrode Ag/Pd (wt/wt)	Sintertemperature (°C)
K85	AD850DZ	Pd	1180
K80	AD850DZ+ sinteraid 1	80Ag/20Pd	1080
K75	AD850DZ+ sinteraid 2	90Ag/10Pd	950
K72	AD850DZ+ sinteraid 2	95Ag/5Pd	950

combination with 95Ag/5Pd electrodes and the samples are called K72. The samples made of the same new dielectrics in combination with 90Ag/10Pd are called K75. Both samples were sintered dense at 950°C for 2 hours in air.

After sintering of the MLCC samples it was observed that the electrodes were discontinuous near the surface of the brick, see Fig. 2. However the electrodes in the middle of the brick are continuous. This discontinuity of the silver palladium electrodes is due to evaporation or diffusion of silver during sintering. The elemental compositions of the electrodes were analyzed in detail by SEM/EDS using a spot size of 5 at 20 kV. Because the silver and the palladium energy absorption bandwidth are overlapping each other partly a series of standards were made; 95Ag/5Pd, 90Ag/10Pd, 80Ag/20Pd and 70Ag/30Pd. Powder alloys were used to sinter 10 mm x 5 mm discs at 450–500°C in air. These discs were used to calibrate for the EDS analysis. At several points the electrodes were analyzed, beginning near the outside of the brick at 10 μm to about 560 μm inside the brick, see Fig. 3.

The Ag/Pd ratios of the electrodes of the 3 MLCC samples were determined and the results are summarized in Table 2. From the results we can observe that for K80–80Ag/20Pd

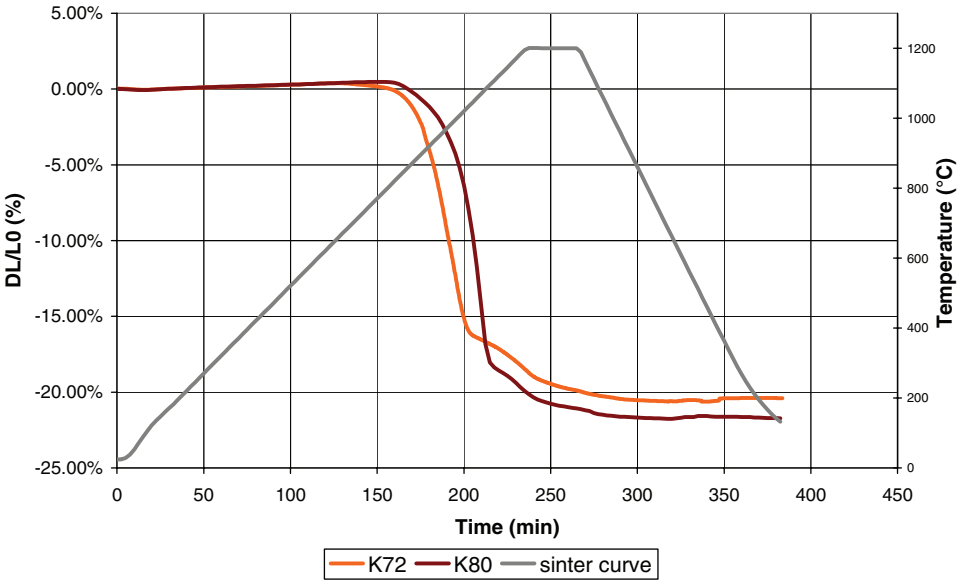

Figure 1. The TMA curve of K80 and K72 dielectrics. (See Color Plate XI)

Figure 2. Discontinuous electrodes near surface of MLCC brick.

and K72–95Ag/5Pd the values of the measured Ag/Pd ratio at 10 μm from outside brick were much different compared to the initial electrode composition. Of K80 MLCCs an electrode ratio of 50Ag/50Pd was determined at 10 μm from outside the brick, which means that most of silver was diffused or evaporated during co-firing. Also for K72–95Ag/5Pd a large difference of Ag/Pd compared to initial value was found. For K75–90Ag/10Pd system however this difference between initial and final Ag/Pd ratio is less. The results of the measuring point at a distance of 500–520 μm of the brick indicate that the sintered alloy is almost equal to the initial alloys used to prepare the samples.

To take a closer investigation and to normalize these results a new calculation was performed. At each measuring data point the remaining silver content was quantified

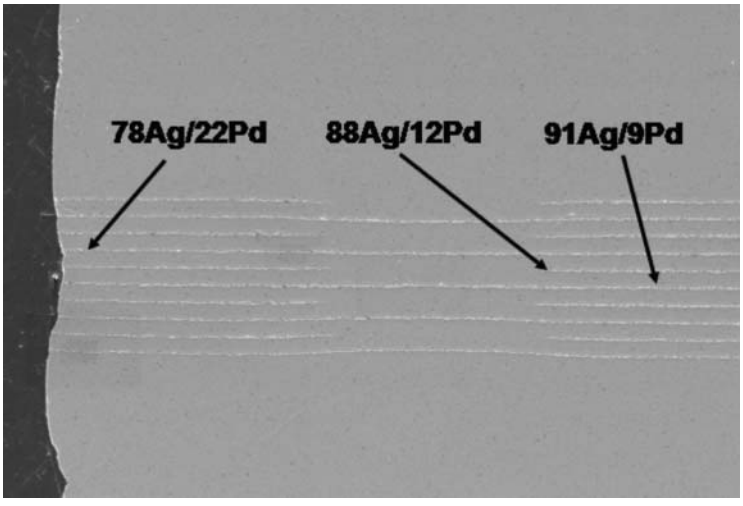

Figure 3. Quantitative analysis by SEM/EDS of K72–95Ag/5Pd electrodes.

Table 2
Quantitative analysis of elements in Ag/Pd electrodes by SEM-EDS

K72 95Ag-5Pd		K80 80Ag-20Pd		K72 90Ag-10Pd	
Distance in brick from end-termination (μm)	Ag-Pd content (wt/wt)	Distance in brick from end-termination (μm)	Ag-Pd content (wt/wt)	Distance in brick from end-termination (μm)	Ag-Pd content (wt/wt)
10	78-22	10	50-50	10	85-15
400	88-12	520	73-27	520	89-11
500	91-9	560	70-30	560	87-13

amongst the initial silver palladium content of the electrode material. So the silver content before and after sintering is then given as a percentage yield. The results are shown in Fig. 4. The results show that for K80 and K72 at 10 μm from the edge of the chip only 20% of the initial silver content remained. For K75 around 60% of the initial silver remains in the electrode. More inside the brick at 500 to 560 μm K80 and K72 the electrodes had 60 to 70% of the initial silver remained. However the measurement on the K75 sample showed that at 520 μm all silver remained.

These results show that the selection of a high silver content electrode for a certain dielectric is important to achieve good electrode continuity. K80 was sintered at 1080°C and K72 was sintered at 950°C. If we plot these temperatures in the binary phase diagram of Ag/Pd [14], Fig. 5, we can determine that K80 is sintered 60°C below the melting point of 80Ag/20Pd. K72 dielectric sinters 60°C below the melting point of 95Ag/5Pd. However K72 and K75 dielectrics are sintered well below the melting point of 90Ag/10Pd.

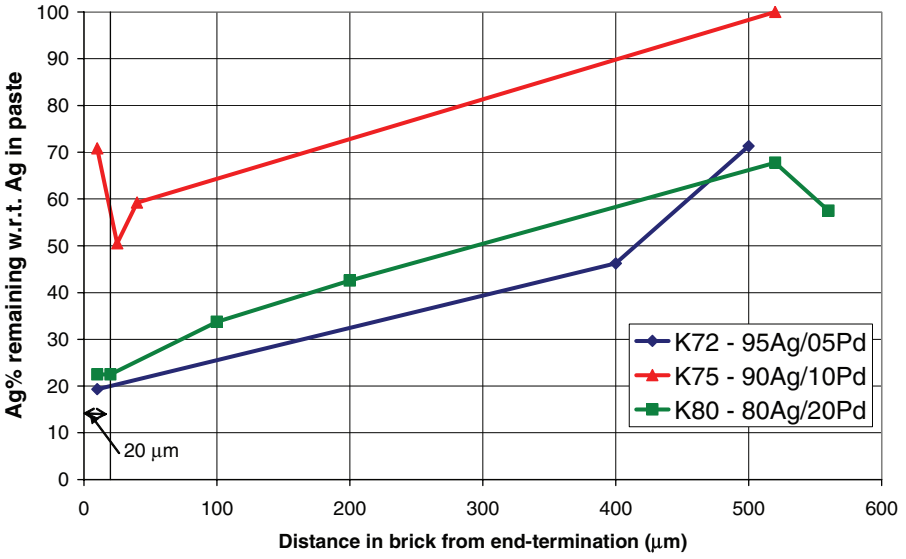

Figure 4. Ag% remaining in electrodes after sintering. (See Color Plate XII)

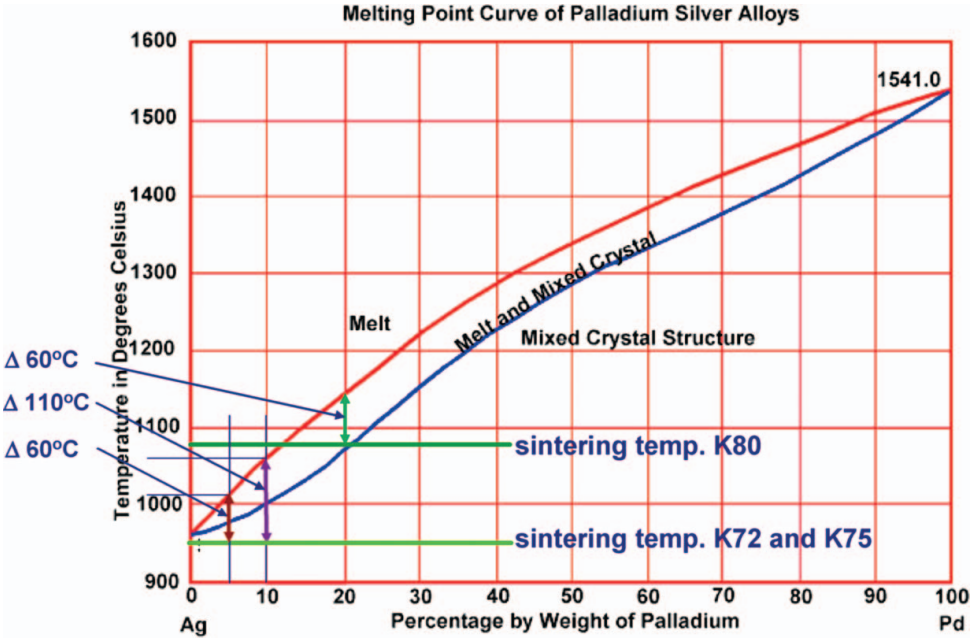

Figure 5. Binary phase diagram of Ag-Pd and sintering temperature of K72, K75 and K80 [14]. (See Color Plate XIII)

This difference is 110°C and it is much larger than the other two systems. Due to this larger difference between the sintering temperature of the K75 MLCCs and the melting point of 90Ag/10Pd less silver will diffuse into the ceramics or evaporate during co-firing. Because less silver is lost, a qualitatively good and continuous electrode layer remained in the sintered MLCCs. Beside the improvement of the electrical properties, which are not discussed in this paper, also the ESR of the MLCCs were improved when better quality electrodes were used.

The ESR is derived from various parameters such as the dissipation in dielectrics, electrode resistivity and termination resistivity. And it is also dependant on the construction of the MLCC such as size, number of electrodes, electrode thickness and so fort. The ESR was measured directly with the LCR analyzer and the results are plotted in Fig. 6. The 0603 MLCCs used for these measurements had 5 metal electrodes. The capacitances of these MLCCs were 10 pF measured at 1 MHz/1V. The dielectric thicknesses of the samples were 10 μm and the electrode thicknesses were 2.5 μm after sintering. The resonance frequencies of the 3 samples are around 125.8 MHz.

For K85 with pure palladium electrodes the ERS is larger than the other two samples. We would expect that the ESR of K85-Pd would be same as K80–80Ag-20Pd due to same bulk specific resistivity of palladium and 80Ag/20Pd alloy, both 11 $\mu\Omega$.cm [15]. However the ESR of the K80–80Ag/20Pd MLCC samples were considerably lower than K85-Pd. Thus not only the resistivity contributed to a lower ESR for K80, but also other parameters like the insulation resistance of the ceramics. At the resonance frequency the ESR of K75–90Ag/10Pd MLCC samples were lower than K80 as we would expect from the specific resistivity values of Ag-Pd alloys. MLCCs made with K72 dielectrics and 90Ag/10Pd electrodes show an improvement regarding the ESR compared to K80 MLCCs.

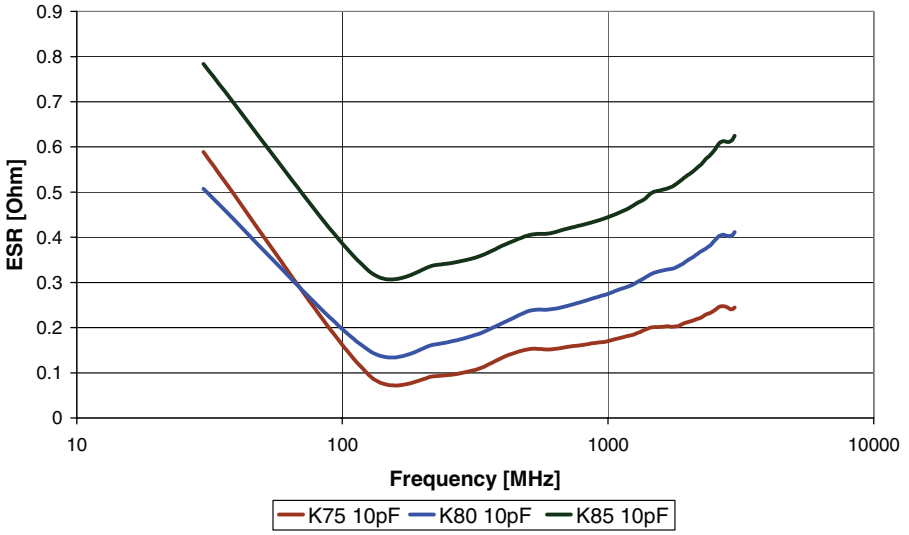

Figure 6. ESR as function of frequency for K85, K80 and K75 0603–10pF MLCCs. (See Color Plate XIV)

Conclusions

This study shows that besides the development of the dielectrics towards COG properties also the choice of proper Ag/Pd alloy must be chosen in such way that silver diffusion of evaporation is avoided. Therefore an Ag/Pd alloy must be chosen, which melts at least 100°C above the sinter temperature of the dielectrics.

MLCCs made with low temperature sintering dielectrics and 90Ag/10Pd electrodes show lower ESR values than MLCC made with 80Ag/20Pd electrodes. The use of silver rich electrodes helps to decrease the ESR of MLCCs.

References

1. H. Ohsato, Research and development of microwave dielectric ceramics for wireless communications. *J. Ceramic Soc. Japan* **113**(1323), 703–711 (2005).
2. R. J. Cava, Dielectric materials for applications in microwave communications. *J. Mater. Chem.* **11**, 54–62 (2001).
3. S. J. Fiedziuszko, I. C. Hunter, T. Itoh, Y. Kobayashi, T. Nishikawa, S. N. Stitzer, and K. Wakino, Dielectric materials, devices and circuits. *IEEE Trans. Microw. Theory Tech.* **50**, 706–720 (2002).
4. X. Xu, BME COG MLCCs: The High Capacitance Class-I solution. *CARTS Europe* 1–7 (2007).
5. S. J. Shih and W. H. Tuan, Solubility of silver and palladium in BaTiO3. *J. Am. Ceram. Soc.* **87**, 401–407 (2004).
6. R. Z. Zuo, L. T. Li, Z. L. Gui, C. X. Ji, and X. B. Hu, Vapor diffusion of silver in cofired silver/palladium ferroelectric ceramic multilayer. *Materials Science and Engineering B-Solid State Materials for Advanced Technology* **83**, 152–157 (2001).
7. W. H. Tuan, Y. W. Cheng, and Y. C. Huang, Solubility of silver in non-stoichiometric barium titanate. *J. Electroceram.* **21**, 29–33 (2008).
8. J. H. Jean and C. R. Chang, Interfacial reaction kinetics between silver and ceramic-filled glass substrate. *J. Am. Ceram. Soc.* **87**, 1287–1293 (2004).

9. R. Z. Zuo, L. T. Li, Z. L. Gui, T. F. Hung, and Z. K. Xu, TEM and EDS investigation of heterogeneous interfaces in cofired multilayer ceramic capacitors. *Materials Science and Engineering B-Solid State Materials for Advanced Technology* **95**, 1–5 (2002).
10. D. J. Lewis, D. Gupta, M. R. Notis, and Y. Imanaka, Diffusion of Ag-110nm tracer in polycrystalline and single crystal lead-containing piezoelectric ceramics. *J. Am. Ceram. Soc.* **84**, 1777–1784 (2001).
11. R. Z. Zuo, L. T. Li, and Z. L. Gui, Interfacial development and microstructural imperfection of multilayer ceramic chips with Ag/Pd electrodes. *Ceramics International* **27**, 889–893 (2001).
12. C. Y. Chen and W. H. Tuan, Evaporation of silver during cofiring with barium titanate. *J. Am. Ceram. Soc.* **83**, 1693–1698 (2000).
13. W. H. Lee, C. Y. Su, Y. C. Lee, J. Yang, T. Yang, and P. L. Shih, Effect of inner electrode on reliability of (Zn,Mg)TiO3-based multilayer ceramic capacitor. *Japanese Journal of Applied Physics Part 1-Regular Papers Brief Communications & Review Papers* **45**, 5859–5864 (2006).
14. C. J. Smithells. Metals Reference Book, 3rd edition; London: Butterworths & Co Limited 2, 280 (1962).
15. S. F. Wang, J. P. Dougherty, W. Huebner, and J. G. Pepin, Silver-palladium thick film conductors. *J. Am. Ceram. Soc.* **77**, 3051–3072 (1994).