Presented in the ECWC 10 Conference at IPC Printed
Circuits Expo®, SMEMA Council APEX® and
Designers Summit 05

Polymer-Ceramic Nanocomposites Based on New Concepts for Embedded Capacitor

Akio Takahashi, Takao Miwa1, Toshiyuki Oono and Shinji Yamada
Hitachi, Ltd.
Hitachi-shi, Ibaraki, Japan

Masa-aki Kakimoto, Taka-aki Tsurumi, Jianjun Hao, Li Li and Ryohei Kikuchi
Tokyo Institute of Technology
Meguro-ku, Tokyo, Japan

Abstract

Polymer-ceramic nanocomposites based on new concepts were developed for embedded capacitor applications. The dielectric constant was above 80 at 1 MHz and the specific capacitance was successfully achieved 8 nF/cm^2. By use of this nanocomposites, multilayer printed wiring boards with embedded passive components were fabricated for prototypes. The following technologies would be reported in this conference.

Firstly, based on the investigation of barium titanate ($BaTiO_3$) crystallites, various particles with the sizes from 17 nm to 100 nm were prepared by the 2-step thermal decomposition method from barium titanyl oxalate ($BaTiO(C_2O_4)_2\ 4H_2O$). It was clarified that $BaTiO_3$ particles with a size of around 70 nm exhibited a maximum dielectric constant of over 15,000. Secondary, the $BaTiO_3$ surface modification based on a new concept was applied to improve the affinity between $BaTiO_3$ particles and polymer matrix. Thirdly, the blend polymer of an aromatic polyamide (PA) and an aromatic bismaleimide (BMI) was employed as the matrix from a view-point of both the processabilty during fabricating the substrates with embedded passive components and the thermal stability during assembling LSI chips. Finally, these technologies were combined and optimized for embedded capacitor materials.

Introduction

High density LSI packaging technologies have been developed for high performance and high functionality of communication electronics products such as cellular phones and wireless personal digital assistants (PDAs). The packaging technologies have evolved from peripheral types such as QFP (Quad Flat Package) to area array types such as BGA (Ball Grid Array). Chip Scale Package (CSP), stacked package and flip chip have been intensively investigated for the size reduction of LSI package. As the ultimate approach, system in a package (SiP) has attracted a great deal of attention. SiP is assembled several types of chips such as logic, memory, analog, and passives in a package which works as one system. In a typical electronic system, discrete passives outnumber the active ICs by several times and occupy more than 70% real estate of the substrate. Discrete passives have already become the major barrier of the miniaturization of an electronic system. Especially, the ratio of capacitors to total passive components can be more than 60%.[1] In order to realize SiP, embedded passive technologies play an important role, as shown in Figure 1. Embedded passives are components placed between the interconnecting substrates of a printed wiring board. Moreover, integration of passives in a package has the following benefits: better electrical performance, higher reliability, lower cost, and improved design options. Under the above mentioned circumstances, organic substrates with embedded devices are predicted to grow rapidly from 2005 to 2010 in the world market.[2]

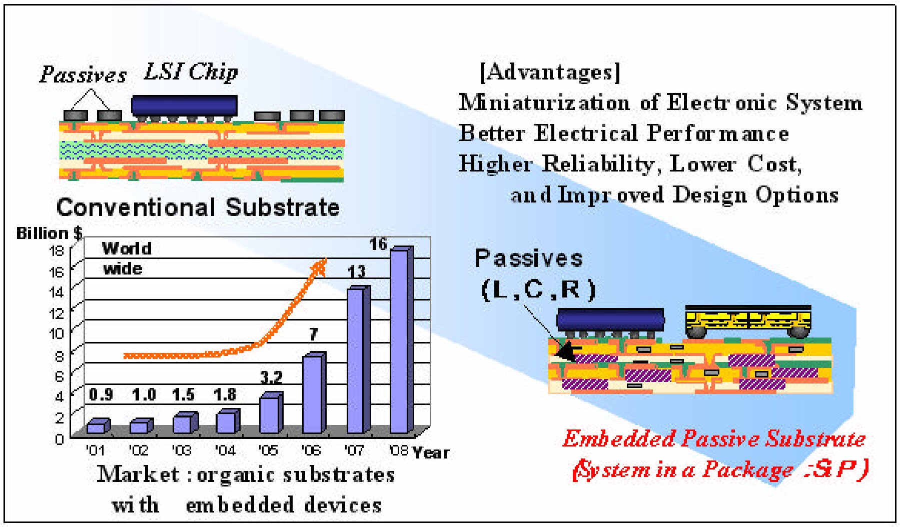

Figure 1 – Technology Trend and Market for Organic Substrates

Polymer-ceramic composites have been studied and are candidate materials for embedded capacitors in organic substrates because they combine the low processing temperature of polymers and the high dielectric constant of ceramics. Using bimodal mixture of barium titanium oxide ($BaTiO_3$) powders, dielectric constant around 100 was reported. 7 µm thick capacitor film showed 10 nF/cm^2 with less than ±5% tolerances.[3] According to the report by Tummala et al, by modifying the processing of a bimodal distribution, a dielectric constant of 135 has been obtained with ceramic-epoxy composites. Specific capacitance of 35 nF/cm^2 was achieved with 3.5 µm films. However, they conclude that the ideal composite is about 35% filled because beyond that loading, metallization becomes difficult to achieve. With this loading, dielectric constant values can be expected to be between 25-35.[4] Accordingly, the highest composite dielectric constants reported for commercialized products to date do not exceed 36 and films thinner than a few microns are very difficult to produce with good tolerance, so the maximum capacitance densities are around about 5 nF/cm^2.[5]

In order to solve above problem, polymer-ceramic composites, which have both the processability to fabricate the embedded substrates and the thermal stability to assemble LSI chips, have been developed based on a new concept. Nanometer sized Barium titanate fine particles

The preparation of nanometer sized Barium titanate ($BaTiO_3$) fine particles and their powder dielectric properties were reported in detail.[6] In this section, the outline is introduced. $BaTiO_3$ crystallites with various particle sizes from 17 to 100 nm were prepared by the 2-step thermal decomposition method of barium titanyl oxalate ($BaTiO(C_2O_4)_2\ 4H_2O$). This method is composed of the following two steps, as shown in Figure 2.

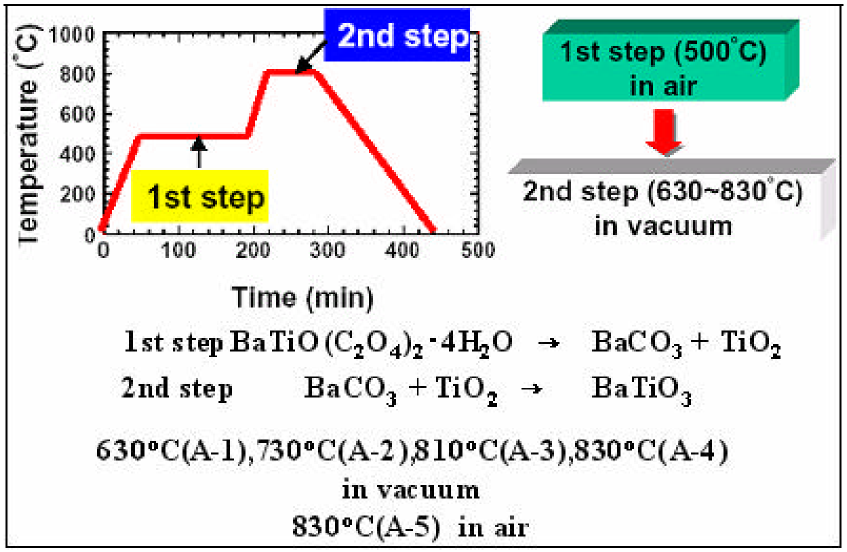

Figure 2 – Preparation of $BaTiO_3$ Ultra-Fine Particles

The first step is the thermal treatment of $BaTiO(C_2O_4)_2$ $4H_2O$ at around 500°C for 1 hr under O_2 flow for the removal of carbon species. The second step is the formation of fine $BaTiO_3$ crystallites by the thermal treatment at various temperatures above 600 °C in the vacuum. Depending on the second step temperature, the particle size can be controlled from 17 nm to 100 nm.[7]

A TEM bright field image for the A-1, A-2, A-3, A-4 and A-5 samples prepared through above mentioned method is shown in Figure 3. Their average particle sizes were estimated as 17, 33, 59, 68 and 102 nm, respectively. The dielectric constants of these particles were measured using a $BaTiO_3$ suspension by the modified powder dielectric measurement method composed of two parts. One is the dielectric measurement using the suspension of the $BaTiO_3$ crystallites with an organic solvent, and the other is the simulation using the electrostatic field analysis of the FEM (Finite Element Method). These dielectric measurements indicated that the dielectric constants of $BaTiO_3$ suspensions over 300 nm were almost constant while below 200 nm, those of $BaTiO_3$ suspensions increased with decreasing particle sizes down to 70 nm. Moreover, the dielectric constants of $BaTiO_3$ suspensions decreased with decreasing particle sizes below 70 nm. The dielectric constants of these $BaTiO_3$ particles were estimated by FEM from the measured dielectric constants of $BaTiO_3$ suspensions shown in Figure 3. The dielectric constant of $BaTiO_3$ particles with a size of around 70 nm exhibited a maximum of over 15,000.

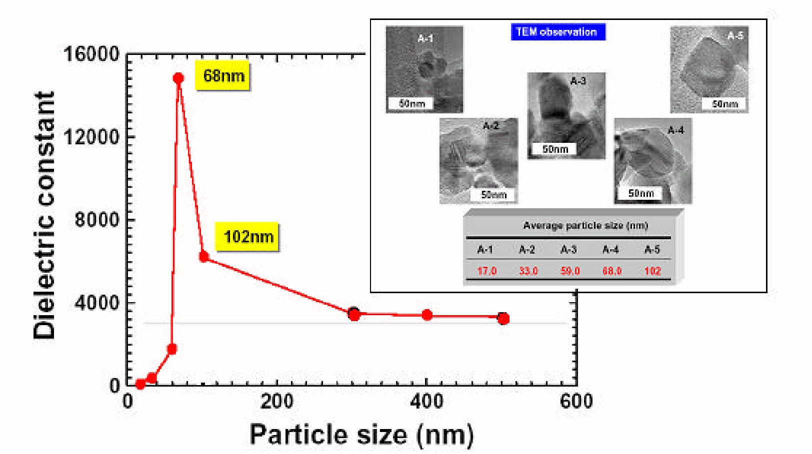

Figure 3 – TEM Images and Dielectric Constants of $BaTiO_3$ Ultra-Fine Particles

Surface modification of $BaTiO_3$

The surface modification of $BaTiO_3$ particles was examined based on a new concept. The sheet-like polymers of copper phthalocyane show quite high dielectric constants compared with the conventional polymers. Although the dielectric constant decreases with increasing frequency, the value keeps around 10 at 100kHz.[8] And, methallophthalocyanine olygomers, copper-phthalocyanines are used as the filler for high dielectric constant organic materials.[9] Based on these information, a $BaTiO_3$ surface modification by metallophthalocyanine structure was examined to increase the dielectric constant of polymer ceramic composites. In addition, The $BaTiO_3$ surface has an outer coating of the chemical groups that have a good compatibility with matrix polymers and a good affinity with electrode metals. This is another objective of the modification of $BaTiO_3$ surface.

Polymer ceramics composite film, which applied the above-mentioned surface modification of $BaTiO_3$, showed a dielectric constant of 80 and a tan δ of 0.02 at 1 MHz.

Matrix Polymer

The blend polymer of an aromatic polyamide (PA) and an aromatic bismaleimide (BMI) was examined as a matrix polymer. PA shows enough thermal stability and mechanical properties as a matrix polymer for ceramic composite materials. However, PA does not melt by heating. The matrix polymer is required to melt and flow for the adhesion with other wiring layers during the multi-layer bonding process under heating and pressure. In order to add the fluidity during the bonding process, BMI was selected. BMI, a relatively low molecular weight compound having a good miscibility with PA, melts around 160 °C and polymerizes from 180 °C to 220 °C by heating to form a highly heat-resistant polymer. However, because of the brittleness after curing, it is difficult to obtain a self-standing film. So, PA/BMI was chosen as the matrix polymer.

The TG/DTA (Thermo Gravimetry / Differential Thermal Analysis) curves and the DSC (Differential Scanning Calorimetry) curves of PA/BMI blend polymers are shown in Figure 4 and Figure 5, respectively.

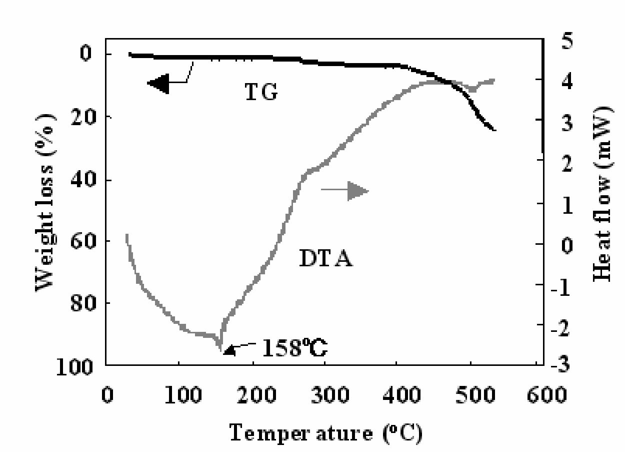

Figure 4 – TG/DTA Curves of Blend Polymer

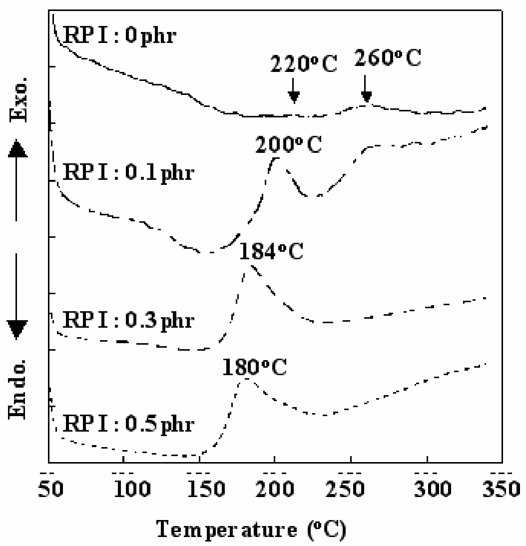

Figure 5 – DSC Curves of Blend Polymers

An endothermic peak due to the fusion was confirmed at 158 °C by DTA curve of PA/BMI blend polymer. The weight loss by the TG curve starts above 400 °C, which is enough in heat resistance as required for a LSI packaging substrate. On the other hand, by the DSC curves in Figure 5, an exothermic peak due to the polymerization reaction is observed at 220 °C and 260 °C. This exothermic peak shifted from 220 °C to 180–200°C by the addition of a radical polymerization initiator (RPI) for double bonds in BMI. The RPI amounts of 0.1, 0.3, and 0.5 wt% were examined.

0.1 wt% was the amount selected from the process window. The PA/BMI blend polymer with 0.1 wt% of RPI is melted and flowed around 160 °C and cures by heating from 180 °C to 200 °C for 2 hours. As the tensile properties indicated in Table 1, the film prepared from PA/BMI blend polymer exhibited better mechanical properties than PA film.

Table 1 – Tensile Properties of Matrix Polymers

Application	Unit	PA/BMI	PA
Tensile Strength	MPa	91.4	51.5
Elastic Modulus	GPa	1.23	0.84
Elongation	%	7.5	6.1

Optimization of Paste Preparation

A bimodal system using the mixture of 500 nm size and 100 nm size $BaTiO_3$ particle (mixing ratio is 3:1), with a 70 vol% of surface modified $BaTiO_3$ content in polymer-ceramic composites was selected by the preliminary examinations. To the DMAc solution containing a dispersant, $BaTiO_3$ particles were added. The slurry was treated in a ball-mixer for 8 hours to 72 hours. As the dispersant, the amount of 0.1 wt% to 5.0 wt% of $BaTiO_3$ powder was examined. After the ball milling treatment the sedimentation rates were evaluated. The slowest sedimentation rates were found in dispersant amounts of 2.0 wt% that required 72 hours of ball milling and in 5 wt% which required 48 hours of ball milling.

Furthermore, a PA/BMI/RPI dissolved in DMAc and $BaTiO_3$ solution was mixed for 10 minutes by a hybrid mixer. A relationship between the dispersant amounts and the paste viscosities, and the relationships between the share rate and the share stress at each dispersant amount are shown in Figure 6 and 7, respectively. While keeping ball milling time as 72 hours, with increasing of the dispersant amounts, the viscosity decreased and reached to the lowest viscosity at 2.0 wt%, i.e. 7 Pa.s. From Figure 7, both pastes at 2 wt% and 5 wt% showed almost same behavior, indicating the best miscibility. From the above mentioned results about the sedimentation rate and the paste viscosity, the dispersant amount: 2.0 wt% and the ball milling time: 72 hours were decided as the optimum condition for the paste preparation.

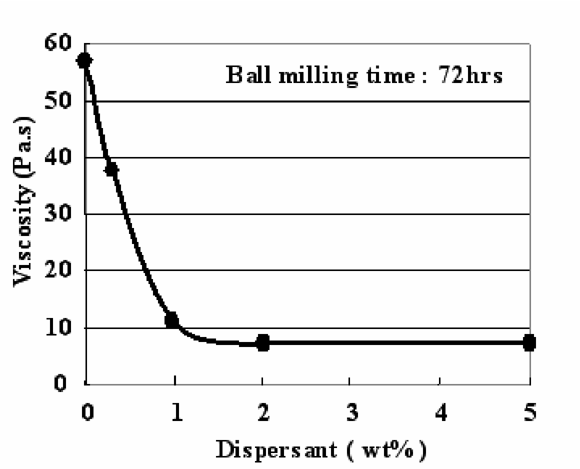

Figure 6 – Viscosity Changes to the Amount of Dispersant

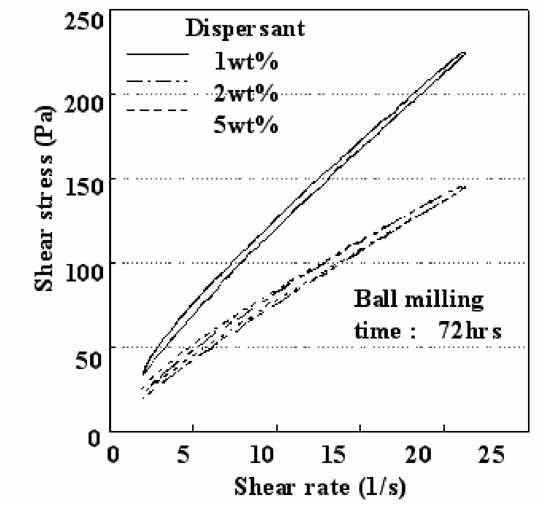

Figure 7 – Relationship between Shear Rate and Shear Stress

General Properties of Polymer Ceramic Composites

The composite film on copper foil was laminated on the substrate with copper electrodes on the surface. The lamination was performed to heat at 200 °C for 2 hours under vacuum condition. The dependences of dielectric constant and tan δ on the frequency are shown in Figure 8.

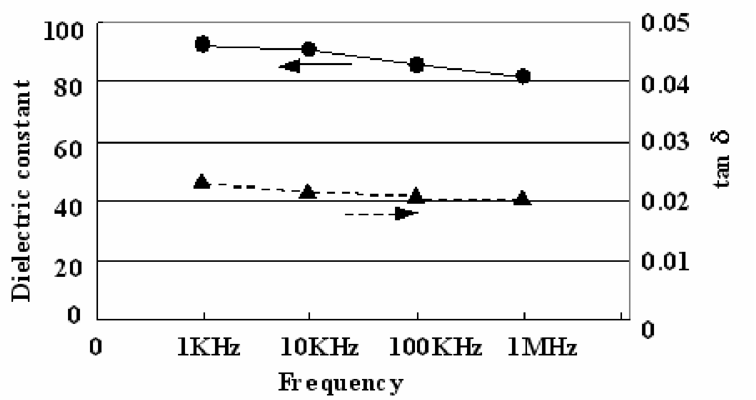

Figure 8 – Dependence of dielectric Constant and tan d on Frequency

The thickness of evaluated film was 9 µm. The dielectric constant, tan δ and specific capacitance were 82, 0.02 and 8.1 nF/cm^2 at 1 MHz, respectively.

Table 2 shows the general properties of composite film laminated on a substrate. This film has a break down voltage above 200 V and a leakage current below 10^{-10} A/cm^2 at 10 V. Its peel strength is 0.7 kN/m, indicating of the high adhesion. This composite film passed 800 hours migration test under the condition of 85RH/85°C/35V.

From these results, a newly developed polymer ceramic nano-composite was demonstrated to show not only high capacitance but also well balanced properties required for printed wiring boards. By applying this material, prototype multiplayer wiring substrates with embedded passive components were fabricated to confirm the feasibility of the production process.

A photograph of the multilayer wiring substrate with six wiring layers is shown in Figure 9. Photographs of the surface and the cross section of this substrate are shown in Figure 10. The nanocomposite layer for the capacitor in the cross section and the spiral pattern for the inductor through the surface are confirmed.

Table 2 – General Properties Composite Film

Thickness	-	9µ
Peel strength	A	0.7 kN/m
Dielectric constant	1 MHz	82
Tan δ	1 MHz	0.02

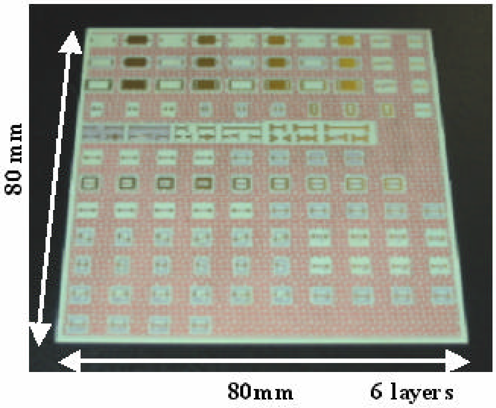

Figure 9 – Multilayer Wiring Substrate with EPC

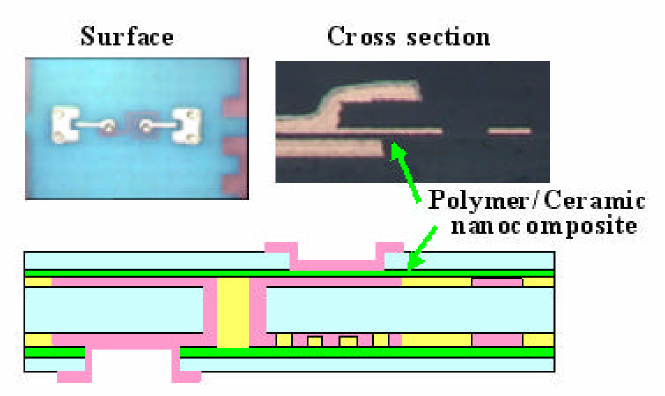

Figure 10 – Surface and Cross-Section

Conclusions

Polymer-ceramic nanocomposites based on a new concept were developed and the dielectric constant was above 80 at 1 MHz that realized a capacitance density of 8.1 nF/cm^2. The break down voltage was above 200V and the leakage current was below 10^{-10} A/cm^2 at 10 V. This novel nanocomposites were demonstrated to show well balanced properties such as peel strength and solder resistance required for printed wiring applications. By use of this nanocomposite, multilayer printed wiring boards were fabricated for prototypes. In this work, we have developed the following technologies: (a) Based on the investigation of barium titanate ($BaTiO_3$) crystallites prepared by the 2-step thermal decomposition method from barium titanyl oxalate ($BaTiO(C_2O_4)_2$ $4H_2O$), 70nm$BaTiO_3$ particles with a maximum dielectric constant over 15,000 was successfully prepared; (b) A newly designed $BaTiO_3$ surface modification was applied to improve the affinity between $BaTiO_3$ particles and polymer matrix; (c) The blend polymer of an aromatic polyamide (PA) and an aromatic bismaleimide (BMI) was selected as the matrix from a view-point of both the processability and the thermal stability during assembling LSI chips. Finally, these technologies were combined and optimized to afford a new concept material for embedded capacitor application.

Acknowledgement

This work is supported by Key Technology Research Promotion Program of New Energy and Industrial Technology Development Organization (NEDO), Japan.

Reference

1. Yang Rao, S.Ogitani, Paul Koul, C.P.Wong, Journal of Applied Polymer Science, 83, 1084-1090 (2002).
2. Fuji Chimera Research Report 118 (2004-1)
3. S-D.Cho, J.Y.Lee, K-W.Paik, 2002 Electronic Components and Technology Conference.
4. R.R.Tummala et al, 2002 ICEP Proceedings, 116-123.
5. R.Ulrich, Circuit World, 30/1, 20-24 (2003).
6. S.Wada, H.Yasuno, T.Hoshina, S-M.Nam, H.Kakemoto and T.Tsurumi, Jpn.J.Appl.Phys. 42, 6118-6195 (2003).
7. S.Wada, M.Narahara, T.Hoshina, H.Kakemoto and T.Tsurumi, J.Mater.Sci. (2003).
8. H.S.Nalwa, L.R.Dalton and P.Vasdevan, Eur.Polym.J. 21 (11), 943-947 (1985).
9. Q.M.Zhang et.al. NATURE, 419, 284-287 (2002).