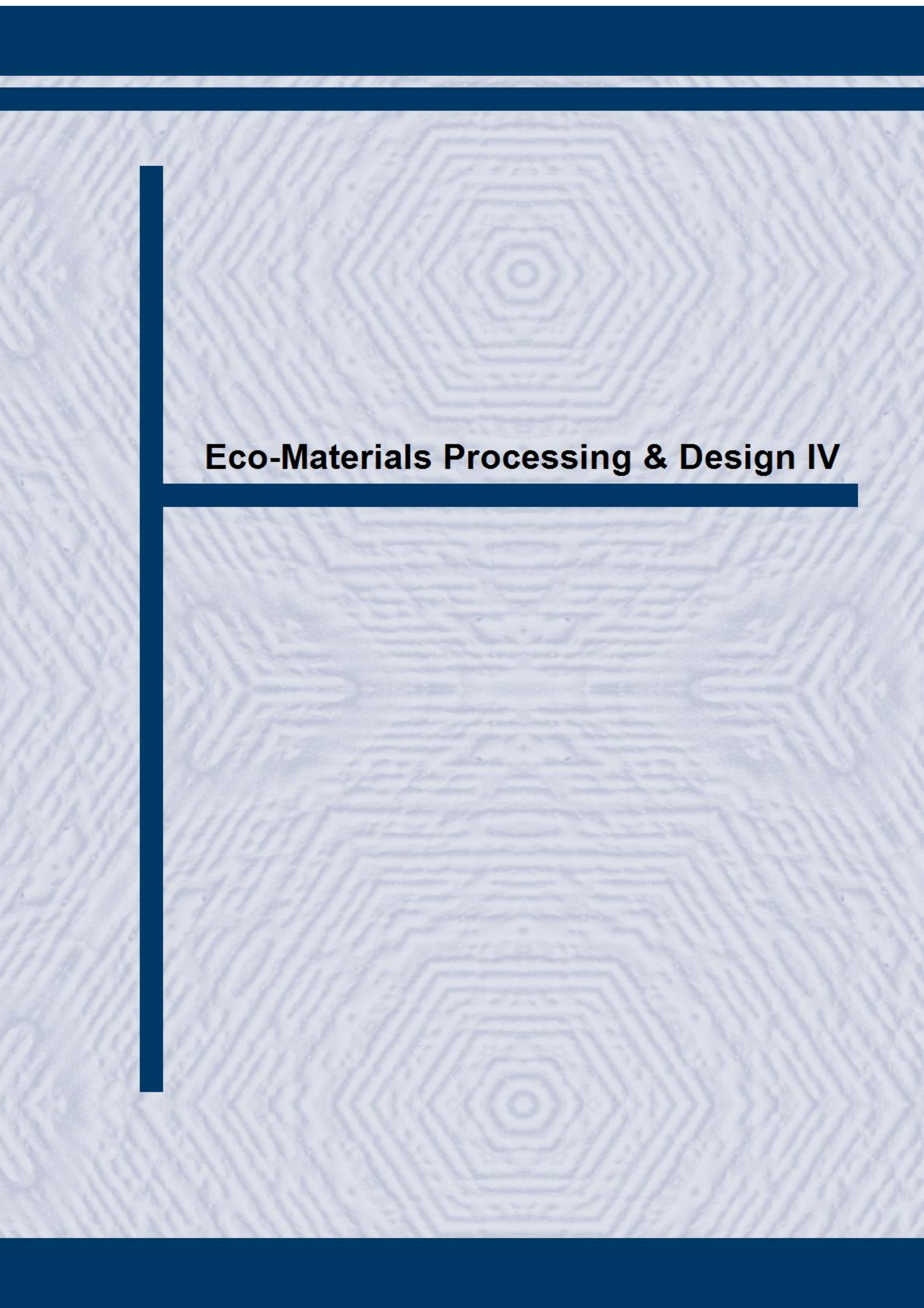


The background features a complex, repeating pattern of concentric hexagons and zig-zag lines in a light blue-grey color. A dark blue L-shaped graphic element is positioned on the left side, with a vertical bar extending from the top and a horizontal bar extending to the right, framing the title text.

Eco-Materials Processing & Design IV

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Edited by
Hyung Sun Kim
Sang-Yeup Park
Soo Wahn Lee

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Table of Contents

Lead-Free Layered Perovskite Film Capacitor for Ferroelectric Random Access Memory U. Chon, J.S. Shim and H.M. Jang	1
Effects of Fourth Alloying Additives on Interfacial Microstructure of Sn-Ag-Cu Lead-Free Soldered Joints K.S. Kim, K. Suganuma, T. Shimozaki and C.G. Lee	7
Effect of Viscosity of Liquid Resin on Resin Self-Alignment Capability J.M. Kim, Y.E. Shin and K. Fujimoto	12
Application of Lead-Free Glass to Barrier Rib Materials in Plasma Display Panel H.S. Kim and B.H. Jung	18
Joining and Processing in Engineering Ceramics to Metallic Materials, in Biomorphic SiC Ceramics, and in Bioactive and Bioinert Ceramics J. Ernesto Indacochea	23
Biocompatibility of Plasma-Sprayed Biomedical Coatings C.X. Ding, X.Y. Liu and X.B. Zheng	30
TiO₂-Coated Plastic Optical Fibers for Purification H.D. Shin and H.K. Joo	34
Porosity Variation on the Compressive Deformation of Pre-Sintered Al-Si-Fe Based Alloy G. Shim, M.S. Kim, W.Y. Kim and H. Yamagata	40
Mechanical Characteristics of Mg and its Composites Recycled from Mg Chips S.Y. Chang, J.C. Kim, S.K. Ryu, S.T. Oh and K.M. Kang	46
Viscosity and Surface Tension of Al and Effects of Additional Element B.Y. Hur, S.H. Park and A. Hiroshi	51
Tin-Cobalt Alloy Plating in a Pyrophosphate Bath S.K. Cho, H.S. Han, C.K. Lee, C.I. Ahn and J.I. Park	57
Porosity-Grading Porous Materials by Centrifugal Sintering Y. Kinemuchi, S. Sato, K. Watari and S. Uchimura	62
Improvement of Strength in Porous Ceramics by Control of Additives K.S. Lee, I.S. Han, D.W. Seo and S.K. Woo	68
Microstructure and Mechanical Behavior of Porous/Dense Alumina Multilayer Composites S.Y. Park, Y. Lee and H. Awaji	74
Microstructure and Wear Properties of Al₂O₃/TiO₂ Nanocomposites S.W. Lee, C. Morillo, S. Visbal and J. Lira-Olivares	79
Preparation of Fine Alumina Dispersed Ytterbia-Stabilized Cubic Zirconia Based Composites M. Wada, T. Sekino, Y.H. Choa, B.S. Kim, T. Kusunose and K. Niihara	85
Fracture and Tribological Behaviors of Al₂O₃ / 5 vol.% SiC Nanocomposites S.H. Kim, S.W. Lee, Y.H. Kim, T. Sekino and K. Niihara	90
Effect of Chemical Composition on the Grain Orientation of Alumina in Oxide Laminate Composites S.Y. Park, K. Pi and J.H. Song	95
Effect of Silicate Addition on the Microstructure Texturing of Alumina Laminate Composites S.Y. Park and J.H. Song	100
Synthesis of Calcium Sulfoaluminate Clinker Using Alunite H.S. Kim, J.W. Ahn, J. Hyun and D. Cho	106
Effect of WC Particle Size on Grain Growth Inhibition in the WC-xVC-Co System S.W. Jung, S.H. Kim, S.Y. Park and S.J.L. Kang	115
Mechanical and Thermal Properties of Hot-Pressed Si₃N₄ with Added AlN R.J. Sung, S.W. Lee, T. Nakayama, T. Kusunose, T. Sekino and K. Niihara	119
Effect of Compaction Pressure on the Microstructure Evolution of Anode Substrate for SOFC Application S.W. Kim, J.H. Lee, H. Song, J.S. Kim and H.W. Lee	125
Properties of Hot-Pressed AlN/BN Nanocomposites T. Kusunose, T. Sekino, B.S. Kim, Y.H. Choa, T. Nomoto, Y. Yamamoto and K. Niihara	131

Measurement Method of Carbon Char Content from Industry Sludge H.S. Kim and J.M. Kim	137
Hydrogen Treatment of Ti Scrap B.Y. Hur, D.K. Ahn, S.Y. Kim, Y.S. Um and A. Hiroshi	143
Effect of Viscosity on the Separation of Copper from Al_2O_3-CaO-SiO₂-10wt%MgO Slag System J.W. Han, E. Kwon, S. Han, J. Chi, B.S. Kim and J.C. Lee	149
Improvement of Silver Recovery Efficiency by High-Speed Rotation A. Da Camara, J. Lira-Olivares, S.W. Lee, H.D. Park and Y.S. Park	156
Synthesis of Ordinary Portland Cement Clinker Using Waste POSCO Sludge J.W. Ahn, H.S. Kim, J.S. Cho, S.M. Joo, G.C. Han, K.S. Han, J.P. Kim and H.C. Cho	163
Characterization of Waste Vinyl from a Farm Village and its Application to Cement Kiln Process W.T. Kwon, Y. Kim and S.R. Kim	170
Characterization of Glass Abrasive Sludge and its Reutilization as a Cement Admixture W.T. Kwon, Y. Kim, S.R. Kim and T.Y. Lim	176
Production and Properties of Glass-Ceramic from Incinerator Fly Ash H.S. Kim, J.M. Kim, T. Oshikawa and K. Ikeda	180
Silica Honeycomb-Crystal Structure Prepared by Fabrication of Silica-Coated Particles Y. Hotta	186
Effect of Gas Bubbling and Impeller Agitation on Degassing Kinetics during Magnesium Alloy (AZ91D) Melt Recycling – Water Model Approach J.W. Han, D.J. Kim, B.D. You, J.Y. Byun and J. Shim	192
Flow Modeling in Negative-Pressure Infiltration Casting Process of Aluminum Open-Cell Fabrication B.Y. Hur and X. Zhu	200
Discharged Photoelectrocatalytic System for the Enhancement of Photocatalytic Performance H.S. Kim, E.A. Lee, C.H. Han, J.W. Ha, Y.G. Shul and G. Yoo	205
Adsorption of Heavy Metal Ions onto the Surface of Metal-Incorporated Hydrous Ferric Oxide Particles K. Sato, T. Kusuyama and K. Tnimura	210
Effect of Phosphorus or Boron Addition on Water-Resistance of Water-Glass Adhesives H.M. Lim, B.Y. Kim and S.H. Lee	215
Fabrication and Sagging Behavior of Three-Layer Al-Si/Al-Mn-Zn/Al-Si Clad Sheets for Automotive Heat Exchanger S.H. Lee, M.S. Kim, D. Jung, J.W. Han and B.D. You	221
Improvement in Mechanical Properties of Magnesium Alloy (AZ31) Sheet Fabricated by Casting and Subsequent Plastic Working J.W. Song, C.W. Kim, J.W. Han, M.S. Kim and S.K. Hwang	227
Fabrication of Various Nano Noble Metal Composite Materials by Ecological Sono-Process Y. Hayashi, T. Sekino and K. Niihara	233
Evaporation Behavior of Magnesium under Reduced Pressure S.W. Kim, D.H. Kim, B.D. You, J.W. Han and M.S. Kim	238
Influence of Final Crystal with Synthesis of Basic Calcium Carbonate by Carbonation Process J.W. Ahn, S.M. Joo, H.S. Kim, D.H. Kim, J.P. Kim and H. Kim	244
Fabrication of Metastable Oxide Ceramics with Oxygen Vacancy M. Nagashima, T. Nakayama, S. Yamanaka, M. Fujikane, T. Sawada, Y. Hayashi, T. Sekino, T. Kusunose and K. Niihara	254
Sintering Behavior and Electrical Properties of $(\text{Bi}_{1/2} \text{Na}_{1/2})_{0.99}\text{Ca}_{0.01}\text{TiO}_3$ Ceramics by Two-Stage Calcination Method J.H. Cho, Y.H. Lee, B.J. Chu and B.I. Kim	259
Effect of Different Annealing Condition on Bake Hardenability for Environmental Automotive Panel B.Y. Hur, S.H. Cho and A. Hiroshi	265
Preparation of TiO_2 Fiber and Its Photocatalytic Properties H.J. Kim, K.H. Nam and Y.G. Shul	271

Plasma Model in Aluminum Nano-Films H. Du, S.W. Lee, C. Sun and L.S. Wen	277
Effect on Compression Properties of Al Alloy Foam Materials by Added Si B.Y. Hur, S.Y. Kim and K. Song	282
Effect of TiO₂ Powder Size on the Reactivity of Photocatalyst E.A. Lee, S.W. Lee, C.H. Choi, H.S. Kim and B. Hockey	288
Mechanical Properties of Ti₃SiC₂ Synthesized by Reaction Sintering S.S. Hwang, S.W. Park and C.M. Kim	297
Organism Resolution Ability of Titania Photocatalyst in Water E. Watanabe, M. Fukaya and H. Taoda	302
Synthesis and Photocatalytic Properties of Nano TiO₂ Coated on Fly Ash D.Y. Shin, K.N. Kim and S.M. Han	308
Nano-Scaled Microstructure and Tensile Behavior of Spray-Formed and Subsequently Worked Al-8Fe-2Mo-2V-1Zr Alloys J.S. Park, W.Y. Kim, M.S. Kim, B.D. You, J.W. Han and K. Shibue	314
Precipitation Behavior and Mechanical Properties of a Supersaturated Co-Based Superalloy G. Hong, M.S. Kim, W.Y. Kim, A. Chiba and S.K. Hwang	320
Polypyrrole-Based Methanol Sensors Prepared by Chemical and Vapor State Polymerization H. Jun, L. Jiang, K.M. Lee, Y. Hoh, J.O. Lim and J.S. Huh	326
Sensing Mechanism of Conducting Polymer Sensor for Volatile Organic Compounds J.S. Huh, H.R. Hwang, K.M. Lee, H.G. Byun and J.O. Lim	331
Apatite-Coated Titanium Dioxide Photocatalyst T. Nonami, H. Hase and K. Funakoshi	337
Volatile Organic Gas Recognition Using Conducting Polymer Sensor Array K.M. Lee, J.B. Yu, H. Jun, J.O. Lim, D. Lee, H.G. Byun and J.S. Huh	344
Fabrication and Sensing Behavior of NASICON Thick Film SO₂ Gas Sensor by Screen-Printing Method S.T. Lee, J.C. Bae, H. Jun, D. Lee and J.S. Huh	352
Fabrication and Microstructure of Pt/SiO₂ Composite Membranes by a Reverse Micelle and Sol-Gel D.S. Bae, E.J. Kim, S.W. Kim, C.S. Kim and K.S. Han	358
Gas Sensing Properties of Nanocrystalline ITO Thick Films with Different Particle Sizes W. Baek, D.W. Shin, S.T. Lee, J.O. Lim and J.S. Huh	362

Lead-Free Layered Perovskite Film Capacitor for Ferroelectric Random Access Memory

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Keywords: Lead-Free, Samarium, Layered Perovskite Film, FRAM, Ferroelectric Capacitor

Abstract. Lead-free $\text{Bi}_{3.15}\text{Sm}_{0.85}\text{Ti}_3\text{O}_{12}$ (BSmT) thin films were grown on Pt/TiO₂/SiO₂/Si(100) substrates using the method of metal-organic sol decomposition. The BSmT film capacitor with a top Pt electrode showed significantly improved values of the remanent polarization ($2P_r$) and the nonvolatile charge as compared to those of the $\text{Bi}_{4-x}\text{La}_x\text{Ti}_3\text{O}_{12}$ (BLT; $x=0.75$) film capacitor, recently known as the most promising candidate for nonvolatile memories. $2P_r$ value of the BSmT capacitor was $52 \mu\text{C}/\text{cm}^2$ at an applied voltage of 12 V while the net nonvolatile switching charge was as high as $20 \mu\text{C}/\text{cm}^2$ and remained essentially constant up to 4.5×10^{10} read/write switching cycles at a frequency of 1 MHz. In addition to these, the capacitor demonstrated excellent charge-retention characteristics with its sensing margin of $17 \mu\text{C}/\text{cm}^2$ and a strong resistance against the imprinting failure.

Introduction

There have been extensive research efforts to enhance the reliability of perovskite-based ferroelectric thin films for use in nonvolatile ferroelectric random access memory (NvFRAM) devices. Among these ferroelectrics, lead zirconate titanate (PZT) is known to be the most important candidate for NvFRAM applications. However, it shows a serious degradation of ferroelectric properties after being subjected to $\sim 10^7$ read/write switching cycles. Although the fatigue problem of PZT-based capacitors can be solved by using metal oxide electrodes, these electrodes are difficult to be prepared and increase leakage current [1,2]. Also, the PZT-based oxides can cause an environmental problems related to lead-containing oxide. Some lead-free perovskites such as strontium bismuth tantalate ($\text{SrBi}_2\text{Ta}_2\text{O}_9$, SBT) and lanthanum-modified bismuth titanate ($\text{Bi}_{3.25}\text{La}_{0.75}\text{Ti}_3\text{O}_{12}$, BLT) showed superior fatigue resistances as compared to Pt/PZT/Pt capacitors [3-5].

As one of the lead-free ferroelectrics, the BLT film is of particular interest. This is not only because it can be crystallized at low processing temperatures possibly below 650°C , which is compatible with Si-based IC technology, but also because it shows larger spontaneous polarizations than those of SBT-based films. However, the BLT film prepared by the PLD method was characterized by a mixed orientation of grains [5,6]. The mixed orientation tends to increase bit-to-bit variability in a capacitor for high-density ferroelectric memory devices [6]. More recently, highly c-axis oriented BLT films having fatigue-free characteristics were grown on Pt/Ti/SiO₂/Si(100) substrates using metal-organic sol decomposition [7]. The highly c-axis oriented capacitor showed a well-saturated polarization-electric field (P-E) switching curve with its remanent polarization ($2P_r$) of $27 \mu\text{C}/\text{cm}^2$ at an applied voltage of 10 V [7]. Notwithstanding the fatigue-free characteristics, the $2P_r$ value (or more relevantly, the nonvolatile switching charge) of the highly oriented BLT film needs to be substantially improved to ensure the reliability of devices (i.e., sufficient sensing margin) and to apply the capacitor to high-density NvFRAM.

According to the proposition made by Park and co-workers [5], the fatigue-free behavior of BLT can be attributed to the enhanced stability of oxygen in the Ti-O octahedron layer, which is caused by

the substitution of lanthanum for bismuth located at near the Ti-O octahedron layer. Accepting this proposition, one does expect that the substitution of a stable trivalent cation will enhance the fatigue resistance provided that it stabilizes the oxygen in the octahedron layer and its ionic size is similar to that of bismuth having a high-volatility. In addition to this expectation, one could further control the component of the spontaneous polarization parallel to the c-direction by suitably aligning the texture of a given film. We indeed found that the direction and the magnitude of $2P_r$ of highly c-axis oriented bismuth titanate-based films were very susceptible to the substitution of lanthanides for bismuth [8-10] : $2P_r$ parallel to the c-axis increased from 4~5 $\mu\text{C}/\text{cm}^2$ for $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ to 26~28 $\mu\text{C}/\text{cm}^2$ for $\text{Bi}_{3.25}\text{La}_{0.75}\text{Ti}_3\text{O}_{12}$. Thus, one would expect to obtain bismuth titanate-based thin films having both fatigue-resistance characteristics and large remanent polarizations by suitably substituting stable trivalent ions for volatile bismuth ions that tend to destabilize the oxygen ions located at the Ti-O octahedron layer.

In selecting appropriate trivalent cationic species for this purpose, one has to consider various physicochemical factors. Among these, the following three factors seem to be most appropriate : (i) the stability of perovskite phase, (ii) the ionic radius, and (iii) the Curie-Weiss temperature. Among rare-earth lanthanides, samarium (Sm) seems to satisfy all of the three criteria. Its ionic radius of 1.00Å in the Ahrens' scale is compatible with that of Bi (0.93 Å) [11]. The Curie-Weiss temperature of $\text{Bi}_{3.15}\text{Sm}_{0.85}\text{Ti}_3\text{O}_{12}$ is estimated to be 470°C, which is high enough to be used in ferroelectric memory devices that require a stability of polarization switching against thermal agitation [11]. In view of these, the main purpose of the present study is to develop highly c-axis oriented Sm-modified bismuth titanate (BSmT) films having fatigue-free characteristics as well as improved remanent polarizations along the unique c-direction.

Results and Discussion

The BSmT films were fabricated on Pt/TiO₂/SiO₂/Si(100) substrates using the method of metal-organic sol decomposition (MOSD). The precursor sol for the coating was prepared by dissolving appropriate amounts of bismuth acetate $[\text{Bi}(\text{CH}_3\text{COO})_3]$, samarium acetate hydrate $[\text{Sm}(\text{CH}_3\text{COO})_3 \cdot 2\text{H}_2\text{O}]$, and titanium isopropoxide $\{\text{Ti}[(\text{CH}_3)_2\text{CHO}]_4\}$ in acetic acid solution at room temperature in a glove box being flushed with nitrogen gas. The dried amorphous films were crystallized by thermal annealing in oxygen ambient at various temperatures ranging between 400 and 680°C for 1 h.

As-annealed films were specular, crack-free, dense, and adhered well on the substrates used. Microstructural examination using a field-emission scanning electron microscope (FE-SEM) showed only fine-sized, uniform grains in the films. The chemical composition of the BSmT film was determined using energy dispersive x-ray and electron microprobe techniques. The stoichiometry of the BSmT film annealed at 680°C was Bi:Sm:Ti = 3.15:0.85:3. In order to fabricate capacitors, top Pt electrodes were deposited using a rf magnetron sputter. A typical area of the top electrode was 10⁻⁴ cm². The ferroelectric and dielectric measurements were performed on the BSmT capacitors using a RT6000S ferroelectric tester and a HP4194A impedance analyzer equipped with a micrometer probe station.

Figure 1 shows the XRD θ -2 θ scan results of the BSmT films annealed at various indicated temperatures for 1 h. All the XRD patterns of the BSmT films could be identified and indexed using the XRD data of the perovskite $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ (BT) phase compiled in the JCPDS card. This indicates that the BSmT maintains a pseudo-tetragonal-layered structure similar to the perovskite BT even under extensive modifications by samarium. The most prominent feature of the XRD patterns in Fig. 1 is

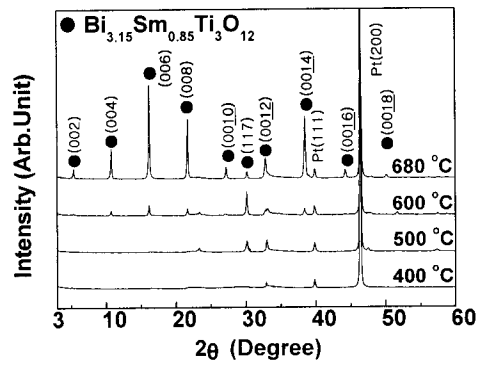


Fig. 1 Out-of-plane and in-plane orientation of BSmT films grown on Pt/TiO₂/SiO₂/Si(100) substrates : XRD θ - 2θ scan results of the BSmT films annealed at various indicated temperatures ranging between 400 and 680°C for 1 h.

that the BSmT film annealed at 680°C shows a highly c-axis oriented preferential growth with a minor fraction of (117) orientation. The degree of the (00 l)-type preferential growth, as estimated using Lotgering's orientation factor [12], is 96 % for the film annealed at 680°C. Four XRD patterns, separated one from another by 90°, should appear in the result of ϕ scan provided that the tetragonal BSmT film with c-axis orientation has a homogeneous in-plane orientation.

Figure 2 represents hysteresis loops of the capacitor measured with various applied voltages ranging between 3 V and 12 V. The film was annealed at 680°C for 1 h and its thickness, as estimated using cross-sectional FE-SEM, was 280 nm. The values of $2P_r$ and E_c increase steeply as the voltage increases from 3 V to 10 V. However, the values of those do not change much over the voltage of 10 V. This means that the capacitor is saturated at the voltage over 10 V. The $2P_r$ value of the capacitor is 52 $\mu\text{C}/\text{cm}^2$ at an applied voltage of 12 V. This value is significantly higher than $2P_r$ of 27 $\mu\text{C}/\text{cm}^2$ for the highly c-axis oriented Bi_{3.25}La_{0.75}Ti₃O₁₂ capacitor, recently reported as a fatigue-free ferroelectric capacitor [7]. The coercive field (E_c) of the BSmT capacitor is in the vicinity of 100 kV/cm at an applied voltage of 10 V, which is within the allowed limit for practical applications to NvFRAM devices. More importantly, these values, i.e., $2P_r$ and E_c , were constant throughout the whole area of the film (with an electrode area of 10^{-4} cm^2), which presumably resulted from the homogeneity of the grain orientation in the present MOSD-derived film. These features of the ferroelectric properties can possibly remove the problems associated with the bit-to-bit variability in a film capacitor for high-density NvFRAM applications.

The relative dielectric permittivity [$\epsilon'(\omega)$] and the dissipation factor [$\epsilon''(\omega)/\epsilon'(\omega) = \tan\delta$] of the capacitor were measured at 25°C as a function of frequency. As shown in Fig. 3, the relative permittivity and the dissipation factor are 387 and 0.054 at a frequency of 1 MHz, respectively. These values are comparable to those of PZT, SBT, and BLT capacitors [3,5,15]. Although the dielectric permittivity decreases steadily with increasing frequency, there is no sudden change in its value up to 1 MHz. The dielectric loss ($\tan\delta$) improves slightly but shows little change with increasing frequency up to 1 MHz. All these indicate that the observed P-E hysteresis behavior of the BSmT capacitor is originated from the ferroelectric polarization switching of bound charges, not from the response of freely moving charges.

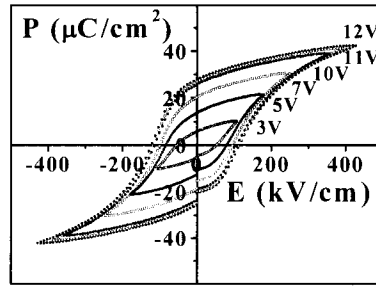


Fig. 2 Hysteresis loops of the capacitor measured with various applied voltages ranging between 3 V and 12 V. The corresponding film was thermally annealed at 680°C for 1 h. The size of the top Pt electrode was 10^{-4} cm^2 .

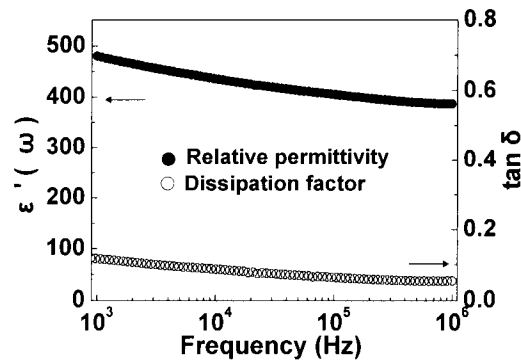


Fig. 3 The relative dielectric permittivity and the dissipation factor of the Pt/BSmT/Pt capacitor as a function of frequency. The corresponding film was thermally annealed at 680°C for 1 h.

The fatigue-free characteristics of the BSmT capacitor are summarized in Fig. 4. The capacitor shows little change both in the switching polarization (P_{sw}) and in the non-switching polarization (P_{ns}) up to 4.5×10^{10} read/write cycles. The values of the nonvolatile charge [i.e., $(+P_{sw}) - (+P_{ns})$ or $(-P_{sw}) - (-P_{ns})$] are approximately $20 \mu\text{C}/\text{cm}^2$, and these values remain essentially constant throughout the switching cycles. The P-E curves of Fig. 4(a) were obtained at an applied voltage of 5 V before and after the electrical fatigue test using a fatigue voltage of 3 V. The values of $2P_r$ and E_c before the fatigue test were $27 \mu\text{C}/\text{cm}^2$ and 79 kV/cm, respectively, at an applied voltage of 5 V. After being subjected to 4.5×10^{10} cycles, these were still retained at $25 \mu\text{C}/\text{cm}^2$ and 76 kV/cm. Besides, the P-E curves do not show any noticeable asymmetric behavior resulting in imprint failures, even after being subjected to 4.5×10^{10} switching cycles.

The charge-retention characteristics of the BSmT capacitor are summarized in Fig. 5 by plotting the switching polarization ($\pm P_{sw}$) and the non-switching polarization ($\pm P_{ns}$) as a function of relaxation time. The sensing margin, as defined by $P_{nv} = (\pm P_{sw}) - (\pm P_{ns})$, of the capacitor was $17 \mu\text{C}/\text{cm}^2$ and remained essentially constant up to 10^4 sec after applying a writing pulse, demonstrating an excellent charge-retaining ability of the BSmT capacitor. Compared with the reported sensing margin of a highly c-axis oriented SBT capacitor ($6 \mu\text{C}/\text{cm}^2$) and that of a $\text{SrBi}_2(\text{Ta}, \text{Nb})_2\text{O}_9$ capacitor ($11 \mu\text{C}/\text{cm}^2$), this is a substantial improvement [14,15]. In addition to this, $|-P_{sw}|$ was essentially the same as $+P_{sw}$

throughout the relaxation (retaining) time, and the same trend was also observed for $|-P_{ns}|$ and $+P_{ns}$. This indicates that the BSmT capacitor has a strong resistance against the imprinting failure.

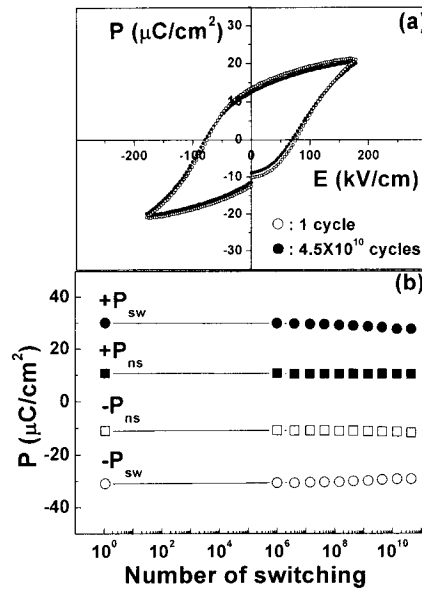


Fig. 4 Electrical fatigue characteristics of the Pt/BSmT/Pt capacitor before and after being subjected to 4.5×10^{10} read/write cycles at a frequency of 1 MHz : (a) P-E hysteresis loops measured at an applied voltage of 5 V before and after the switching cycle, and (b) the fatigue test results determined using a fatigue voltage of 3 V, and a measuring voltage of 5 V at a frequency of 1 MHz.

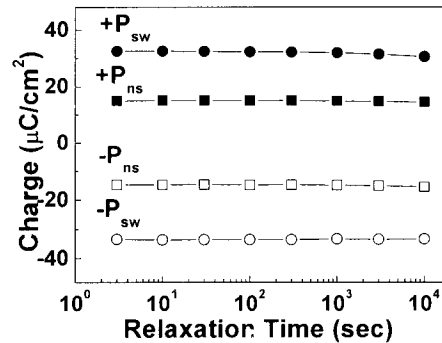


Fig. 5 Charge-retention characteristics of the Pt/BSmT/Pt capacitor at 85°C plotted as a function of time after the application of a writing pulse.

Summary

In conclusion, the fatigue-free $\text{Bi}_{3.15}\text{Sm}_{0.85}\text{Ti}_3\text{O}_{12}$ (BSmT) thin films characterized by a preferential c-axis orientation were successfully grown on Pt/TiO₂/SiO₂/Si(100) substrates for the first time. The BSmT capacitor fabricated using a top Pt electrode showed well-saturated P-E curves with the remanent polarization ($2P_r$) of $52 \mu\text{C}/\text{cm}^2$ at an applied voltage of 12 V. More importantly, the capacitor did not show any significant fatigue up to 4.5×10^{10} switching cycles at a frequency of 1 MHz. In addition to these, the capacitor demonstrated excellent charge-retention characteristics with a resistance against the imprinting failure.

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Effects of Fourth Alloying Additives on Interfacial Microstructure of Sn-Ag-Cu Lead-Free Soldered Joints

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Abstract. The effects of the fourth elements, i.e., Ni and Co, on microstructural features of Sn-3wt%Ag-0.5wt%Cu lead-free solder and Cu joints were investigated. The interfacial phases of Sn-3Ag-0.5Cu/Cu joints are typical Cu₆Sn₅ scallops. Sn-3Ag-0.5Cu (-0.1wt%X; X = Ni and Co)/Cu joints form very fine Sn-Cu-Ni and Sn-Cu-Co scallops at interface. The growth kinetics of total ternary compound layers was examined. The apparent activation energies of Sn-Cu-Ni and Sn-Cu-Co layers were 64 and 112 kJ/mol, respectively.

Introduction

Among various lead-free alloys that have been proposed and have been examined intensively in the past decade, Sn-Ag-Cu ternary alloy takes a major part as a standard lead-free solder in industries. There are, however, other requirements from the formation of solidification cracks, cavities or the lift-off phenomenon [1]. Such solidification defects are formed by localized time difference in solidification and by large undercooling. Further alloying of fourth elements to Sn-Ag-Cu can improve microstructure, for instances, by being nucleation sites for solidification resulting in uniform solidification without defects. In a previous study [2], we reported the effects of small addition of fourth elements such as Fe, Ni, Co, Mn and Ti on microstructural properties, undercooling, and tensile properties in Sn-3wt%Ag-0.5wt%Cu ternary alloy. The effective elements for improving solderability are Ni and Co. Thus, Ni and Co were selected as forth alloying additives. The purpose of the present work was to characterize the interfacial reactions between the Sn-3Ag-0.5Cu (-0.1wt%X; X = Ni and Co) and Cu substrate during the reflow process, and to investigate the reaction layer growth kinetics during thermal aging.

Experimental Procedure

The fourth alloying elements examined were Ni and Co. The amount added was fixed at 0.1 wt% for all alloys. Hereafter, those alloys are simply called SAC-0.1Ni and SAC-0.1Co. Sn-3Ag-0.5Cu alloy ingots were melted at 800 °C for two hours in a vacuum with the fourth alloying elements and quenched with water. The alloys were re-melted at 300 °C for 1 hour in a crucible and cast into steel mould. The cooling rate of the final ingots was about 8 °C/s, equivalent to the practical soldering conditions adopted in industries.

The alloy ingots were cold-rolled and were punched to sheets of 120µm thickness × 3mm diameter. The Cu plate was used as the substrate. Cu is the most widely used base metal for component metallization pads, PWB pads and lead frames. The solder sheets were placed on the substrate and they were reflowed at 260°C in air with the aid of RA type flux. They were cooled at 0.45 °C/s. All joining samples were aged for 100, 500, 750, 1000 hours at 125, 135, 150 and 170°C. For microstructure observation, the specimens were polished with 0.05 µm Al₂O₃ powders and were

etched with 5% HCl-95% C₂H₅OH solution. The microstructure of the alloys was observed primarily by optical microscope (OM) and scanning electron microscope (SEM). The elemental distribution was evaluated by using energy dispersive X-ray analysis (EDX) and by electron probe microanalysis (EPMA).

Result and Discussion

Joining microstructure

Typical interfaces of various Sn-3Ag-0.5Cu (-0.1X; X = Ni and Co) alloy/Cu joints after reflow treatment are shown in Fig. 1. The reaction layer formed between the Sn-3Ag-0.5Cu and Cu is the scallop type Cu₆Sn₅ phase that is about 10 μm in thickness. On the other hand, the reaction layers of the SAC-0.1Ni and SAC-0.1Co joints with Cu are relatively thin and flat (about 2~3 μm), compared to the Sn-3Ag-0.5Cu alloy, as shown in Fig. 1(b, c). Fig. 2 shows the three-dimensional morphology of reaction layer for the Sn-3Ag-0.5Cu, SAC-0.1Ni, and SAC-0.1Co/Cu joints after deep etching. The scallops of SAC-0.1Ni and SAC-0.1Co are very fine comparing with Sn-3Ag-0.5Cu.

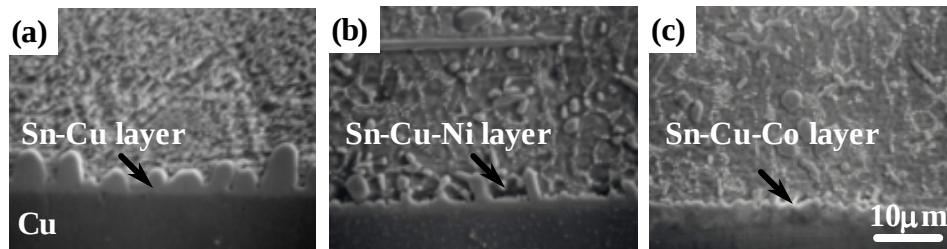


Fig. 1 SEM images of various Sn-3Ag-0.5Cu(-X)/Cu joints: (a) Sn-3Ag-0.5Cu; (b) SAC-0.1Ni; (c) SAC-0.1Co.

From EDX analysis, the composition of the Sn-Cu-Ni compound corresponds to the (Cu, Ni)₆Sn₅ phase. This phase is also observed for the Sn-Ag-Cu/Ni solder joint. Zribi, et al. reported that the (Cu, Ni)₆Sn₅ phase can be formed by substituting Ni for Cu atom in binary compounds with Sn [3]. Thus, adding small amounts of Co and Ni can control the thickness of reaction layer and the Cu flux from the Cu substrate to the solder. These fine ternary reaction layers play an important role in thermal aging.

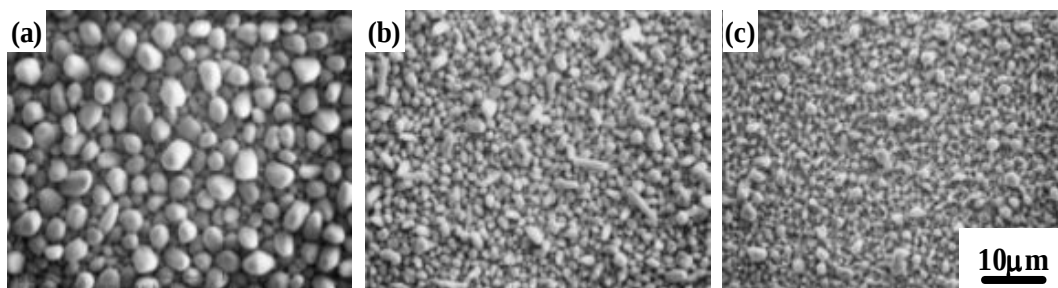


Fig. 2 SEM micrographs showing the top view of various scallops: (a) Sn-3Ag-0.5Cu, (b) SAC-0.1Ni and (c) SAC-0.1Co.

Growth kinetics of ternary compound

To investigate the reaction layer growth kinetics in SAC-0.1Ni and SAC-0.1Co solder joints, the growth of the total reaction layer during thermal aging at 125, 135, 150 and 170 °C up to 1000 h was examined. The reaction layer growth in Sn-Pb solder/Cu joints is generally assumed to occur by

diffusion. The experimental time exponent is near 0.5 [4,5]. The diffusion growth of the reaction layer was represented by the following equation:

$$W = kt^{1/2} \quad (1)$$

where W is the thickness of the reaction layer, k is a growth rate constant, and t is the aging time.

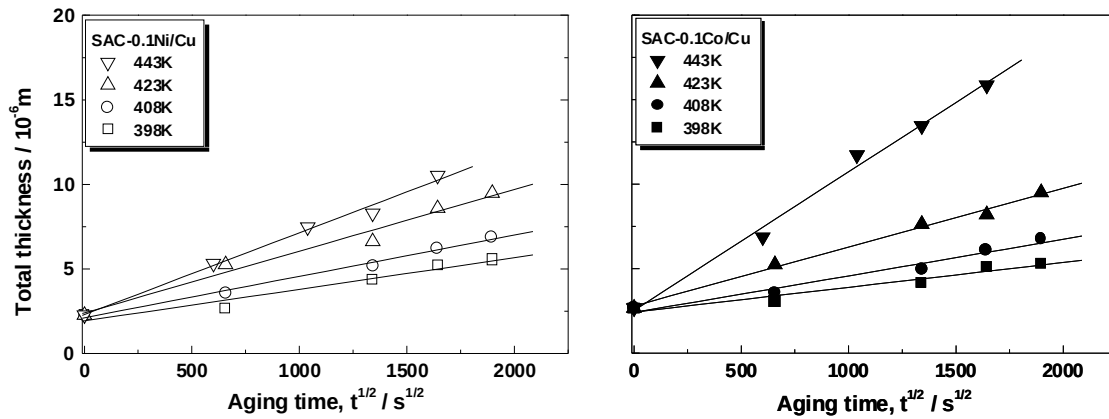


Fig. 3 Total thickness vs. $t^{1/2}$ for the growth of the total reaction layer.

The total thickness of the reaction layer in SAC-0.1Ni and SAC-0.1Co joints as a function of $t^{1/2}$ is shown in Fig. 3. The growth rates, k 's, at various temperatures were determined by least square fitting from linear lines. The growth behaviors of Sn-Cu-Ni and Sn-Cu-Co layers indicate similar tendency from 125 to 150 °C. At 170 °C, however, k of Sn-Cu-Co layer is larger than that of Sn-Cu-Ni layer. Figure 4 shows the element mapping of interface in SAC-0.1Ni/Cu and SAC-0.1Co/Cu joints after aging at 170 °C for 500 hours. After long-term and high temperature aging, Ni and Co are still present in reaction layer, respectively, but the distribution features are quite different. The Ni compounds are mainly distributed at interface between Cu_3Sn and Cu_6Sn_5 continuously, as the aspect of short-term aging. However, the Co compounds are dispersed as particle for all the area of reaction layer. This dispersion observed only 170 °C aging. Thus, Co compounds do not affect the reaction layer growth at 170 °C aging.

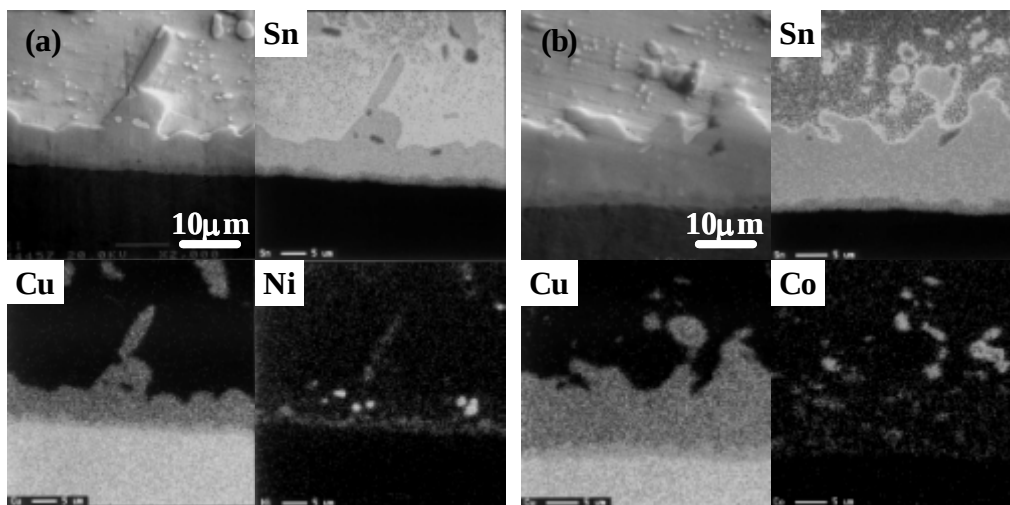


Fig. 4 EPMA X-ray images of (a) SAC-0.1Ni/Cu and (b) SAC-0.1Co/Cu joint at 170 °C for 500 h.

The Arrhenius plots of k^2 for various solder joints are shown in Fig. 5. The apparent activation energy was determined from a linear regression fit shows in Fig. 5. The linear lines in Fig. 5 can be expressed by the following equations

$$k^2 = 1.09 \times 10^{-3} \exp (-112 \text{ kJ} \cdot \text{mol}^{-1} / RT),$$

for SAC-0.1Co/Cu joint,

$$k^2 = 8.58 \times 10^{-10} \exp (-64 \text{ kJ} \cdot \text{mol}^{-1} / RT),$$

for SAC-0.1Ni/Cu joint, respectively, where k^2 is the square of growth rate constant, R is the universal gas constant and T is the temperature. Lee, et al. reported that the apparent activation energy of total Sn-Cu reaction layer growth in Sn-3.8Ag-0.75Cu/Cu joint was 64 kJ/mol and of total Sn-Cu-Ni reaction layer growth in Sn-3.8Ag-0.75Cu/Ni-P joint was 70 kJ/mol [6]. The activation energy value of Sn-Cu-Co layer growth in SAC-0.1Co/Cu joint is larger than that of Sn-Cu-Ni layer growth in SAC-0.1Ni/Cu joint and Sn-Ag-Cu ternary solder joints, as shown in Fig. 5.

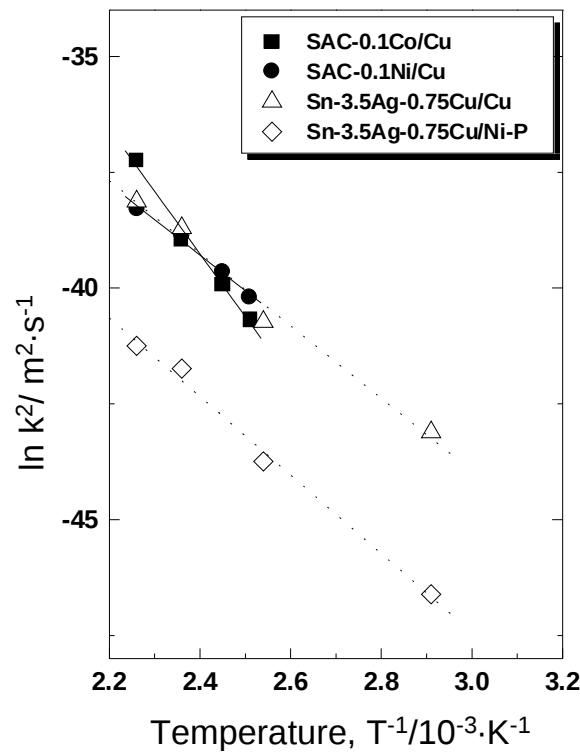


Fig. 5 Apparent activation energy analysis of the SAC-0.1Ni/Cu and SAC-0.1Co/Cu system.

Some of the works reported that the degradation of the joining mechanical properties was significantly influenced by growth of reaction layer in lead-free solders with various substrates [4,7-10]. The growth of the reaction layer resulted in degradation of the joining strength. In the present work, the thickness of the Sn-Cu-Ni and Sn-Cu-Co scallops increases from 3 to 7 μm , and the thickness of the Cu_6Sn_5 scallops increases from 10 to 26 μm during thermal aging at 125 $^{\circ}\text{C}$ up to 1000h. Thus, the addition of Ni and Co in Sn-3Ag-0.5Cu alloy affects the suppression of the reaction layer growth and, consequently, joining mechanical properties can be improved

Summary

In the present work, the effects of fourth element additions to Sn-Ag-Cu solder alloy were investigated by microstructure analysis. And, the kinetics of the growth of the reaction layer in SAC-0.1Ni and SAC-0.1Co/Cu joints was determined. The results are summarized as follows:

- The interfacial layers with a Cu substrate consist of Sn-Cu binary compounds for Sn-3Ag-0.5Cu alloy, and of ternary compounds such as Sn-Cu-Ni and Sn-Cu-Co for SAC-0.1Ni and SAC-0.1Co alloys, respectively.
- The Sn-Cu-Ni and Sn-Cu-Co layers grow according to the parabolic law, meaning that the growth mechanism was diffusion reaction process.
- From the time and temperature dependence of Sn-Cu-Ni and Sn-Cu-Co reaction layer thickness, the apparent activation energies are measured to be 64 and 112 kJ/mol, respectively.

Acknowledgements

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Effect of Viscosity of Liquid Resin on Resin Self-Alignment Capability

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Keywords: Lead-Free, Low Process Temperature, Microelectromechanical Systems (MEMS), Micro-Opto-Electro-Mechanical Systems (MOEMS), Optoelectronic Multichip Modules (OE-MCMs), Self-Alignment

Abstract. We developed highly precise self-alignment process using resin materials for next generation microelectromechanical systems (MEMS), micro-opto-electro-mechanical systems (MOEMS) and optoelectronic multichip modules (OE-MCMs) applications. Although liquid resins have a characteristic as low as one tenth of the surface tension of solder in general, self-alignment capability could be achieved by using 3-D pads for positioning boundary. In this research, we propose the novel passive alignment mechanism in order to enhance understanding of alignment motion. Moreover, the influence of viscosity on alignment motion and alignment accuracy is demonstrated by scaled-up experiment. We could achieve highly precise alignment accuracy less than 0.4 μm .

Introduction

In recent years, with the increase in demands for global environmental conservation, green or environment-friendly materials are being actively developed. From these environmental points of view, two different classes of materials have been actively studied for alternatives to Pb containing solders in electronic industries. One is Pb-free solders [1] and the other is electrically conductive adhesives (ECAs) [2]. Especially, along the advances of micro fabrication, the polymeric electronic packaging using resin materials include ECAs has been actively investigated as a key technology for future microelectromechanical systems (MEMS), micro-opto-electro-mechanical systems (MOEMS) [3], and optoelectronic multichip modules (OE-MCMs) [4] applications because of their potential advantages of low process temperature including low thermal stress during the process, fine pitch capability, and compatibility with non-solderable ones, etc.[5,6], besides the environmental issue. In spite of these potential advantages, unfortunately it still has been known that the resin materials do not have self-alignment capability due to their low surface tensions [7,8]. Because of this critical drawback, few researches have been carried out [9].

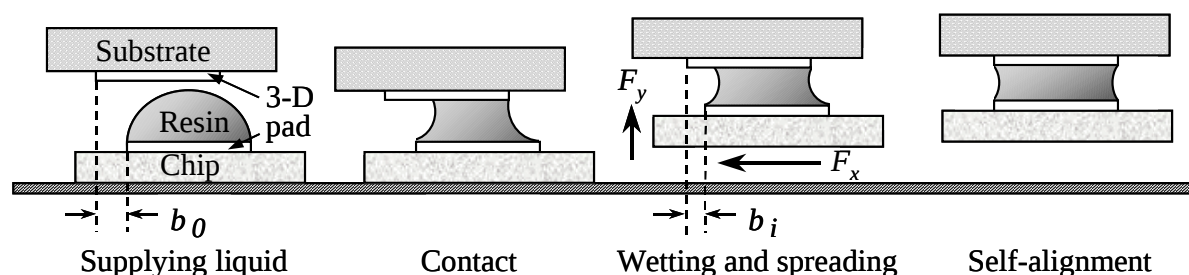


Fig. 1 Resin self-alignment process using liquid surface tension.

In this paper, a novel self-alignment process is presented using liquid resin with low surface tension. Fundamental concept for achieving the self-alignment capability and principle are described. In addition, the effect of the viscosity of liquid resin on the self-alignment capability includes aligning motion and alignment accuracy was demonstrated by the scaled-up experiment.

Novel Resin Self-Alignment Process

In conventional solder self-alignment process [10], the chip is self-aligned by restoring forces produced by the molten solder constrained in the pads without spreading outward beyond the positioning boundary between metallized pad and non wettable dielectric material. However, as the materials with low surface tension such as resin materials have a good wetting and spreading characteristics on the surface of both metal and resin, it has been known that it is impossible to obtain the self-alignment capability with them. In previous work [11-13], we could achieve the self-alignment capability even if it uses resin materials with low surface tension by the making the pad 3-dimensional configuration for positioning boundary. Figure 1 shows the proposed novel self-alignment process. This process appears as follows:

- (a) Supply the liquid resin on 3-D pads of chip part or substrate.
- (b) Bring the pre-aligned substrate into contact with the chip part.
- (c) Pull up the chip part, it start to move toward the predetermined position.
- (d) Self-alignment is completed.

As the chip part is mounted upward, a possibility for liquid resin to spread outward beyond pad edge, and a more stable alignment can be achieved contrast to the earlier processes include the conventional one.

Experimental Procedure

The interconnection material used in this study was phenoxy resin supplied by Matsusita Electric Industrial Co. Material properties of resin materials diluted with BCA (Butyl Carbitol Acetate) were shown in Table 1. The surface tension and viscosity values were determined by pendant drop method and spiral viscometer (PC-1TL: Malcom Co.) respectively. The size of the test vehicle was 16 mm $\times$ 16 mm $\times$ 0.23 mm. Test vehicles have 2 $\times$ 2 area array distributed 3-D bond pads with radius of 3 mm and thickness of 1 mm.

Table 1. Material properties of phenoxy resin as a function of content of BCA.

Material	Thinner [Vol.%]	Viscosity [Pa·s]	Specific gravity	Surface Tension at 25 °C [Pa·s]
Phenoxy resin	0	27.57	1.04	0.0236
	5	16.50	1.03	0.0231
	10	11.94	1.02	0.0240
	20	7.08	1.01	0.0227
	25	4.55	1.01	0.0231

Since the surface state of the pad affects the wetting property of liquid resin on the pad, we performed surface treatment, followed by polishing and degreasing. Moreover, the relative accuracy between the chip part and the substrate was measured because it is impossible to measure absolute alignment accuracy of the chip part. Once the chip part was self-aligned as previously mentioned in Fig. 1, apply specified misalignment level (1 ~ 100 μ m) with movable misalignment fixture. The chip part was released and the relative motion of the chip part and the alignment accuracy were measured