

Graduate School of Advanced Science and Engineering
Waseda University

博士論文概要

Doctoral Thesis Synopsis

論文題目

Thesis Theme

Surface modification and bonding of
advanced polymer materials through
vacuum ultraviolet (VUV) -induced
technology

真空紫外線を用いた先端機能性高分子材料の
表面改質と接合

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This doctoral thesis elaborates on novel surface modification technologies for advanced polymer materials and metals for the sake of low temperature direct hybrid bonding among these materials.

For the recent biomedical micro electromechanical system (bio-MEMS), flexible materials such as polymers and resins play an important role. In particular, poly-oxymethylene (POM) and poly-ether ether ketone (PEEK) are considered most suitable polymers to bio-inert substrate materials because of their excellent dielectricity, robust chemical properties, and low production cost. In order to reduce the weight, volume, and chemical toxicity of bio-MEMS packaging, the substrates had to be integrated via the metal wiring layers without using thick adhesive and solders. For this, a direct bonding technology between polymers and metals was required. Precisely, three kinds interfaces, where the internal bond mechanisms were totally different, had to be created simultaneously with sufficient electronic and mechanical reliability: a polymeric interface, a metallic interface, and a polymer-metal interface. However, the surfaces of POM and PEEK were hard to be bonded due to their low surface free energy. Especially, very few previous studies had succeeded in creating strong chemical bonds, such as covalent and/or coordinate bonds, between polymers and metals at the process temperature below glass transition temperature (T_g).

In order to provide sufficient bondability both to polymers and metals at the same time without using high temperature and thick adhesive, we needed to create an ultrathin compatible bridge layer. To create such bridge layers on material surfaces, an appropriate surface modification method, which must be carried out at low temperature and atmospheric pressure, was inevitable to avoid possible heat damage and outgas problems to polymers. Therefore, we have chosen to use vacuum ultraviolet (VUV) for initial surface treatment. Although VUV was found highly effective in eliminating surface contamination and in activating the surface both of POM and PEEK, we needed to take different bridge formation processes due to diverse operating temperature of those materials. POM had an operating temperature of 110 ~ 120 °C, consequently the bridge layer had to be formed at temperature lower than this. Therefore, our choice for POM was not the dehydration condensation reaction but the reaction between amine and epoxy functional groups, which allowed a temperature of 100 °C to create chemical bonds between the surfaces. To achieve this reaction, the self-assembled monolayer (SAM) was introduced. In case of PEEK and other metal materials, which are tolerant of the process temperature higher than 250 °C, a key challenge was a partial deoxidization of stable oxides at atmospheric pressure, in order to increase the possible active/reaction sites on the surfaces. Hence a vapor-assisted VUV technology was proposed. By introducing water vapor to the VUV chamber at highly tuned humidity (i.e. the number of water molecules), the hydrogen radicals could partly deoxidize the surface of the metal oxide, and the hydroxyl radicals could create a hydrate bridge layer on those cation sites. As for the PEEK surface, the hydroxyl radicals contributed in creating hydrophilic functional groups.

In order to realize these hybrid bonding technologies based on SAM and vapor-assisted VUV methods, the following issues were studied in this thesis: a) The evolution of surface chemical structures via the surface modification, b) optimization of process parameters, c) bonding experiments and interfacial observations of nanostructures.

The doctoral thesis is consisted of six chapters: the detail of each chapter is shown as follows:

Chapter 1: Introduction. The necessity of low temperature direct hybrid bonding technologies for POM, PEEK, and wiring metals, is elaborated on, then the fundamental technical requirements and process schematics are presented, which has been briefly mentioned in the previous paragraph.

Chapter 2: Bonding method for POM. The surfaces cleaning/activation process for POM, which utilizes the VUV in the presence of oxygen gas (VUV/O₃) treatment followed by SAM coating, is described. Firstly, the evolution of chemical structure before and after VUV/O₃ treatment is shown. The C-O bonds in POM main chain was found dissociated, thus active dangling bonds were created. Upon the exposure to ambient atmosphere, once water molecule approached on these active sites, the dangling bonds could react and form hydroxyl groups on POM surface. After the activation, 3-aminopropyl triethoxysilane (APTES) and 3-glycidyloxypropyl trimethoxysilane (GOPTS), in which the functional groups were amine and epoxy, were coated on the surface to let the hydroxyl groups on POM surface react with methyl groups in APTES and GOPTS. The x-ray photoelectron spectroscopy (XPS) results showed that the Si spectra owing to the SAM adhesion were successfully observed. As for the physical bonding factor, scanning electron microscope (SEM) observation results showed that the micro pore formation occurred on POM surface due to the dissociation of C-O bonds resulting in C condensation. The ratio between pore area and total surface area started to increase suddenly from the VUV irradiation time for 60 s. The reason for this tendency was considered that during the first 60 s, VUV light energy was mainly consumed by organic contamination removal to activate the surface, and few C condensation was considered to occur. The C condensation was also proven from the XPS valence band observation, where obvious peak shifting to Fermi level was found at the irradiation times longer than 60 s. Therefore, we decided the optimum surface modification condition was 60 s for POM. After that, the bonding of POM surfaces was carried out at 100 °C, and the bond strength of 372 kPa was obtained at maximum. Assuming that the crack propagation in this sample was mode I and all the fracture energy was consumed to create a pair of new surfaces, this strength value could be converted to a strain release energy of 51.3 mN/m. Since the theoretical value of POM was 38.0 mN/m, it was considered that sufficient chemical bindings were created on POM surfaces.

Chapter 3: The direct bonding between POM and poly-methyl methacrylate (PMMA). A similar bonding mechanism was applied to the hybrid bonding between PMMA, for PMMA was also popular bio-MEMS substrate materials, and is considered effective to solve the pore formation problem of POM. The PMMA test vehicle was prepared in powder, which was mixed with liquid monomer (mixture of methyl methacrylate (MMA) and 4-methacryloxyethyl trimellitic anhydride (4-META)) and catalyst (partly oxidized tri-n-butyl boron) to accelerate the polymerization into PMMA after the mixing process. Through the same surface modification process mentioned above, the POM-PMMA hybrid bonding was achieved with a maximum bond strength of 8.54 MPa at 300 s irradiation. The reason for this improvement was considered as interface reinforcement effect due to PMMA gluing into POM surface dissociation pores because a calculated strain release energy was 34.4 mJ/m² while the ideal values of POM and PMMA were 38.0 and 36.0 mJ/m².

Chapter 4: A novel bonding method to PEEK and metals using vapor-assisted VUV technology. In the vapor-assisted VUV method, in particular on metal surfaces, three reactions occurred in sequence: (1) Organic

contaminations were removed by VUV irradiation; (2) the stable metal oxide on metal surface was partly deoxidized by hydrogen radicals, and cation sites are created; (3) the hydroxyl radicals reacted on those cation sites to create a hydrate bridge layer. Firstly, the modification effect was confirmed by XPS using different humidity conditions. The results showed that the carboxyl binding peak occurred on PEEK surface after vapor-assisted VUV, which was attributing to the water molecules. In order to quantify the reversible occurring on the surface, a calculation model was established as follows. With increasing vapor humidity, there were three stages in the modification: (1) When vapor concentration was low, the modification was dominated by VUV dissociating. (2) when vapor concentration further increased, singlet oxygen O(¹D) became dominating the modification. The O(¹D) was generated by dissociating hydroxyl radicals. Since O(¹D) concentration increased with vapor inlet, the modification effect increased with vapor inlet. (3) when the vapor inlet was excessive and VUV light energy was totally consumed by water molecules, with vapor further increasing, the excessive vapor consumed energy that generated O(¹D). Therefore, the bridge layer formation on cation sites has a maximum condition (humidity value). According to the experiment data, an optimized vapor inlet condition was confirmed at 88.0 mmol/m³.

Chapter 5: Hybrid bonding between PEEK and Pt utilizing vapor-assisted VUV method. Pt had been chosen as an example of bio-inert wiring metal. Note that the vapor-assisted VUV method is available to other bio-compatible metals such as Ti. The modifications were carried out using two vapor concentrations: 36.0 and 656 mmol/m³ to compare the modification effects on bonding. As comparison, Ar fast atom beam bombardment (Ar-FAB) was conducted because this method usually utilized much higher energy in high vacuum condition. Additionally, a simple VUV irradiation was tried as a reference. From the XPS analyses, we found that ultrathin hydrophilic bridge layers of Pt hydrate and carboxyl groups on PEEK were successfully created. These layers could create hydrogen bonds at the moment of contact, then strengthened via dehydration condensation upon heating at 150 °C. The sample bonded in the vapor condition of 36.0 mmol/m³ had a bond strength of 0.75 MPa, which corresponded to the strain release energy of 197 mN/m according to the calculation model in the previous chapter. Because the theoretical value of PEEK was 42.1 mN/m, we could imply that the modification effect has a peak value relating to the vapor concentration, as discussed in chapter 4. Furthermore, the vapor-assisted VUV modified samples had strengths comparable with conventional methods (FAB modified sample strength: 0.088 MPa; simple VUV modified sample strength: 0.21 MPa) that required high vacuum conditions.

Chapter 6: Concludes and future researches. From all the results presented in former chapters, we can conclude that a low temperature hybrid bonding among bio-inert polymers and metals is highly feasible.

早稲田大学 博士（工学） 学位申請 研究業績書

(List of research achievements for application of doctorate (Dr. of Engineering), Waseda University)

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種 類 別 (By Type)	題名、 発表・発行掲載誌名、 発表・発行年月、 連名者（申請者含む） (theme, journal name, date & year of publication, name of authors inc. yourself)
Academic papers (refereed)	<ol style="list-style-type: none"> 1. ○<u>Weixin Fu</u>, Bo Ma, Hiroyuki Kuwae, Shuichi Shoji, and Jun Mizuno, “Low-temperature polyoxymethylene direct bonding via self-assembled monolayer”, Japanese Journal of Applied Physics, Vol. 57, 02BB01, 2018. 2. ○<u>Weixin Fu</u>, Akitsu Shigetou, Shuichi Shoji, and Jun Mizuno, “Low Temperature Direct Bonding between PEEK (Polyetheretherketone) and Pt via Vapor-Assisted Vacuum Ultraviolet Surface Modification”, Journals of Materials Science and Engineering B, Vol. 7, No. 3-4, p. 49-62, 2017. 3. ○<u>Weixin Fu</u>, Akitsu Shigetou, Shuichi Shoji, and Jun Mizuno, “Low-temperature direct heterogeneous bonding of poly ether ether ketone and platinum”, Materials Science and Engineering C, Vol. 79, p. 860-865, 2017. 4. Takeshi Komino, Hiroyuki Kuwae, Akiko Okada, <u>Weixin Fu</u>, Jun Mizuno, Jean Charles Ribierre, Yuji Oki, and Chihaya Adachi, “In-Plane Anisotropic Molecular Orientation of Pentafluorene and Its Application to Linearly Polarized Electroluminescence”, ACS Applied Materials and Interfaces, Vol. 9(32), p. 27054-27061, 2017. 5. <u>Weixin Fu</u>, Masatsugu Nimura, Takashi Kasahara, Hayata Mimatsu, Akiko Okada, Shuichi Shoji, Shugo Ishizuka, and Jun Mizuno, “A Metal Bump Bonding Method Using Ag Nanoparticles as Intermediate Layer”, Journal of Electronic Materials, Vol. 44, No. 11, p. 4646-4652, 2015.
Lectures (refereed)	<ol style="list-style-type: none"> 1. <u>Weixin Fu</u>, Bo Ma, Hiroyuki Kuwae, Shuichi Shoji, and Jun Mizuno, “A study on low temperature SAM modified POM direct bonding affected by VUV/O₃ irradiation”, 5th IEEE international workshop on low temperature bonding for 3D integration (LTB-3D), p. 211, May, 2017. 2. <u>Weixin Fu</u>, Akitsu Shigetou, Shuichi Shoji, and Jun Mizuno, “Low Temperature Bonding Between Polyether Ether Ketone (PEEK) and Pt Through Vapor-Assisted VUV Surface Modification”, Research and Education Consortium for Innovation of Advanced Integrated Science International Symposium 2017 (CIAiS 2017), February, 2017.

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	<p>3. <u>Weixin Fu</u>, Hiroyuki Kuwae, Bo Ma, Shuichi Shoji, and Jun Mizuno, “Low Temperature Direct Bonding of Polyoxymethylene (POM) through Self Assembly Monolayer (SAM)”, International conference on electronics packaging (ICEP), p. 167-170, April, 2017.</p> <p>4. <u>Weixin Fu</u>, Akitsu Shigetou, Shuichi Shoji, and Jun Mizuno, “Low temperature bonding between polyether ether ketone (PEEK) and Pt through vapor assisted VUV surface modification”, IEEE 66th Electronic Components and Technology Conference (ECTC), p. 2541-2546, May, 2016.</p> <p>5. Bo Ma, Hiroyuki Kuwae, Akiko Okada, <u>Weixin Fu</u>, Shuichi Shoji, and Jun Mizuno, “VUV/O₃ assisted single crystal quartz bonding with amorphous SiO₂ intermedicate layer for manufacturing optical low pass filter”, International conference on electronics packaging (ICEP), p. 447-450, April, 2016.</p> <p>6. <u>Weixin Fu</u>, Akitsu Shigetou, Shuichi Shoji, and Jun Mizuno, “Low temperature direct bonding of PEEK and Pt through VUV/FAB surface treatment”, International conference on electronics packaging (ICEP), p. 302-305, April, 2016.</p> <p>7. Bo Ma, Hiroyuki Kuwae, Akiko Okada, <u>Weixin Fu</u>, Shuichi Shoji, and Jun Mizuno, “Low temperature direct bonding of single crystal quartz substrates for high performance optical low pass filter using amorphous SiO₂ intermediate layers”, IEEE International conference on micro electro mechanical systems (MEMS), p. 25-28, 2016.</p> <p>8. <u>Weixin Fu</u>, Akitsu Shigetou, Shuichi Shoji, and Jun Mizuno, “Low Temperature Direct Bonding of Polyether Ether Ketone (PEEK) and Pt”, 10th international microsystems, packaging, assembly and circuits technology conference (IMPACT), p. 217-220, October, 2015. (Best student paper award)</p> <p>9. <u>Weixin Fu</u>, Jun Mizuno, Takashi Kasahara, Akiko Okada, Hiroshi Nishikawa, Akitsu Shigetou, and Shuichi Shoji, “Low temperature bump bonding realized by single-micrometer Ag-nanoparticle bumps”, The 5th International Symposium on Advanced Materials Development and Integration of Novel Structured Metallic and Inorganic Materials (AMDI-5) Conjunction with 6th IBB Frontier Symposium, November, 2014.</p> <p>10. <u>Weixin Fu</u>, Takashi Kasahara, Akiko Okada, Shuichi Shoji, Akitsu Shigetou, and Jun Mizuno, “Low temperature and low pressure bump bonding realized by single-micrometer Ag-nanoparticle bumps”, 4th IEEE international workshop on low temperature bonding for 3D integration (LTB-3D), p. 47, June, 2014.</p>

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	<p>11. Weixin Fu, Takashi Kasahara, Akiko Okada, Jun Mizuno and Shuichi Shoji, “Novel Bump Bonding method using Ag nanoparticle coated Cu bump through squeegee-coating”, The 5th NIMS/MANA-Waseda Univesity International Symposium, March, 2014.</p> <p>12. Weixin Fu, Jun Mizuno, Shuichi Shoji, Takashi Kasahara, Akiko Okada, and Shugo Ishizuka, “Novel Bonding Method Using Cu Bumps Coated With Flexible Ag Nanoparticle Layer Formed By Squeegee-Coating”, IEEE CPMT symposium Japan (ICSJ), p. 1-4, November, 2013. (Young award)</p>