Adhesive-free joining and application for flexible devices - a review

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Abstract. Interface has been recognized for a long time as a part of materials such as surface and grain boundary in bulk in spite of the fact that interface gives decisive influences on the performance and durability of devices in practical use. Interface is also well known to have four principal performances and roles such as mechanical, electrical, magnetic and optical properties. Here, I will at first review the interface behavior with special emphasis on materials science and then introduce typical examples of case study. Mechanical behavior of interface can be attributed to joining of different materials in particularly at low temperature and intrinsic defects introduced in the process of joining caused by difference in thermal expansion. Defects thus introduced is known to result in work hardening of interface. Recently, an epoch-making method of joining to utilize water gas adsorption layer as an adhesive agent. This gas adsorption joining (GAJ) was demonstrated in cycloolefin polymer (COP) film and borosilicate glass system. Both surfaces were first modified by atmospheric pressure plasma, followed by close lamination to reaction distance and heated at about 100°C to result in the formation of a strong covalent bond for joining. Durability thus formed system was found to remain unchanged even after weathering test in 60°C, 95%RH for 2000 hrs. Joining mechanism can be explained in terms of an increase in density of functional molecules at the interface, followed by dehydration. Thickness of joining layer was confirmed by X-ray photoelectron spectroscopy and STEM and EELS to be 1~2 nm. Sealing performance of GAJ was examined by measuring Water Vapor Transmission Rate (WVTR) by MOCON system using joined PET films on which high barrier layer was coated. The WVTR of line sealing with 1 mm width and 1-2 nm thick was found to be better than 5 x 10^-4 g/m^2/day. Practical applications of thus developed GAJ for joining and sealing are now in progress for flexible film devices such as OLED display, solar cells, and healthcare devices. Finally, roles of interface in materials science in future will be critically discussed.

1. Introduction

Great advantage of nanotechnologies brought us highly comfort, convenient, energy-saving and environment-friendly social life, which we are enjoying today [1-3]. In the course, materials science always played a leading role in research and development of device and system. Outstanding examples in materials science will be carbon-nanotube [4], fullerene [5], graphene [6] and mesoporous silica [7], [8]. Basic concept of nanotechnology will be the process innovation of downsizing, which can be expressed simply to manufacture products in light, thin, short and small scale, emphasizing compactness and flexibility. In manufacturing process, law materials of natural resources will become fabricated materials as a result of modification such as refining, distillation and purification. Materials thus modified will be transferred to the most important process of manufacturing including surface treatment and joining for modularization and systemization. Especially, joining with surface treatment is well-known to give a significant impact on the performance and durability of the devices and final products. Nowadays, a huge amount of research and development and accumulation of know-how were devoted to establish the final method of joining with chemical adhesives for all of the joining system by joining system. Newly emerging important nanomaterials [4-8] must be incorporated in the today’s device and
system by joining using chemical adhesives. In fact, there exist a lot of difficulties in joining of nanomaterials and conventional materials due to the lack of know-how accumulation. Recently, the ultimate bonding method of adhesive-free gas adsorption joining was explored by the present authors [9]. Joining process was well-known to be affected significantly by the conditions of interface such as cleanliness, roughness, mechanical properties such as internal friction and plastic deformability, and chemical properties [10-11]. Particularly, joining by chemical reaction at the interface is attracting much attention from the viewpoint of low temperature joining of different materials for all-solid-state battery and fuel cell. However, interface conditions give a large influence not only on joining but also on a wide range of materials science. Interface has long been considered as a part of bulk materials but as of today, interface became recognized as one of the materials with special properties such as composition and structure. In this review manuscript, we will at first introduce new concept of interface and the classification and then demonstrate GAJ and the application by way of examples.

2. New concept of interface: Function and role
Interface has long been recognized to be very important because of the fatal influence on the performance and durability of device and system made of functional materials [12-15]. Composition and structure of interface are usually different from those of bulk caused by surface treatments in manufacturing process such as physical and chemical and mechanical modifications and annealing. In fact, impurities in the bulk are well known to migrate toward surface and interface by annealing, resulting in the formation of non-stoichiometric interface with large number of defects. Another essential problem of interface is lack of non-destructive method of analytical characterization. Actually, interface is usually buried in deep region from surface and is normally very thin. For example, it is really difficult to evaluate the composition and structure of buried interface layer by analytical method using X-ray beams due to lack of detection sensitivity. Also, in the case of Auger electron spectroscopy and X-ray photoelectron spectroscopy (XPS), Ar ions are usually used for in depth etching from the surface to buried interface in deep region, which will be destructive to alter the original interface properties. On the other hand, interface can be classified into four genres of mechanical, electrical, magnetic and optical properties summarized in Table 1.

| Properties | Function | Role |
|------------|----------|------|
| Mechanical | Joining and adhesion strengthening induced by defects. Cutting and processing | Control of chemical and mechanical reaction for adding new functions |
| Electrical | Ohmic contact. Rectifying contact Barrier height control for electron and hole injection | Design for electric and electronic contact of devices |
| Magnetic | Magnetic exchange interaction | Giant magnetoresistance effect |
| Optical | Transmission, absorption, reflection. Birefringence for retardation | Phase retardation plate by obliquely deposited thin films |

Mechanical property includes functions of joining, adhesion and strengthening induced by defects, and cutting and processing and modification, and their roles for adding new functions of chemical and mechanical reactions. Among the functions, special attention was focused on joining process with special emphasis of interface chemical reaction. In electrical properties, major function will be electric contact controlling ohmic or rectifying current flow through contact interface and electron and hole injections through at the interface. Main magnetic function will be the so-called exchange interaction between both sides of interface in contact. Typical example of exchange interaction at the interface is Giant magnet-resistance (GMR) effect discovered in 1988 [16] and in 1987 [17]. There exist many functions in optical properties of interface such as transmission, absorption and reflection [18-19]. In addition, growth of retardation film by oblique deposition revealed optical birefringent effect [18] at the interface called Motohiro-Taga interface [20]. Typical example of interface function will be presented in the following sections.
3. Gas adsorption induced adhesive-free joining and application [9]

Looking back the practical joining process as of today, plasma treatment of both surfaces was primarily used to control surface wettability, and then chemical adhesives of 5-10 μm in thickness such as an acrylic resin or a silane coupling agent [21] were coated in solution for adhesion, resulting in strong adhesion by chemical reaction. Challenge for a direct joining of poly (methyl methacrylate) for polymer microchips has been made after plasma treatment without coating chemical adhesives. This type of joining, however, is fundamentally considered to be hydrogen bond at the interface, resulting in insufficient durability. In 2014, Taga and Fukumura [9] developed an epoch-making method of gas adsorption induced adhesive-free joining with enough durability in practical use, where design and control of interface played an important role in interface chemical reaction.

3.1 Overview of GAJ

Process flow chart of GAJ was shown in Figure 1. As mentioned above, joining is so sensitive to the surface conditions such as cleanliness and therefore the surfaces before joining must be at first cleaned ultrasonically using isopropanol to remove organic contamination such as floating oil particles and fingerprint consisting of oleic acid. The surfaces thus cleaned were modified by surface treatments such as plasma exposure, ultraviolet light irradiation and beads blasting.

![Figure 1. Flow chart of gas adsorption joining process](image)

Typical example of changes surface chemical conditions by air pressure plasma of borosilicate glass and cycloolefin polymer (COP) film, and water contact angle measured using distilled water droplet of 3 μL according to standard method [22] was depicted in Fig.2. As shown by X-ray photoelectron spectroscopy (XPS) analysis using Mg Kα X-ray source, the spectrum at binding energy of 286 eV~287 eV assigned to surface functional groups of ether or alcohol (C-O, C-OH, C-O-O) and carbonyl (C=O) increased by plasma treatment and the water contact angle drastically decreased, indicating the changes of surface wettability from hydrophobic to hydrophilic. Borosilicate glass sheet of 0.7 mm thick and COP film with 100 μm in thickness were directly joined at low temperature by GAJ. A necessary condition for joining of COP and glass is at first to make the contact surfaces clean. After plasma treatment to control surface functional groups on both surfaces, joining was carried out by a roll laminator in surface contact pressure of 0.7 MPa at room temperature, followed by annealing at 100°C for 10 min in an oven. Adhesion strength was evaluated by 180 degree peel test based on ASTM D-903 and durability was examined under the weathering conditions of 60°C and 95% RH.

Figure 3 showed the results of joining force by water gas adsorption followed by annealing in oven for reaction. Actually, GAJ became possible only after plasma treatment in air atmospheric conditions.
As shown in the figure, joining force after low temperature below 80°C was rather low but steeply increased with temperature to reach high value of over 20 N/25 mm after annealing at 100°C. In addition, joining force can be controllable between 0 to 20 N/25 mm depending on annealing temperature. GAJ interface layer is evaluated to be 1-2 nm in thickness by taking inelastic scattering mean free path of photoelectrons into consideration [9]. Durability of this joined couple has been confirmed to remain unchanged under the conditions of the weathering condition of 60°C, 95% RH and Xe lamp irradiation by 60 W/mm² for more than 2000 hrs. Reaction mechanism of water GAJ is not yet fully elucidated by data as of today. The reaction mechanism of water GAJ can be explained as follows: Water molecules may adsorb on as received glass and COP in air atmospheric conditions before plasma treatment and no joining is possible at this stage between these glass and COP surfaces. Joining becomes possible after plasma treatment and XPS analyses of both surfaces to be joined revealed an increase in peak at 532 eV of binding energy assigned to OH in O 1s spectrum, resulting in possible joining by lamination followed by dehydration to form H-H hydrogen and Si-O-C covalent bonds with strength between 0-20 N/25mm. On the other hand, plasma treatment may also bring alteration of order of orientation and crystallinity of COP surface [23].

3.2 SFG investigation of COP surface and interface to glass [23]

Infrared visible SFG spectroscopy has recently been demonstrated to be a highly sensitive surface-specific tool for the examination of polymer surfaces and buried interfaces, as it can probe the orientation and alignment of the surface molecules of thick polymer films. Thus, we investigate here the characterization of the COP surfaces modified by plasma using sum frequency generation (SFG) vibrational spectroscopy [24] to determine how surface pre-treatment improves adhesion between the COP films and borosilicate glass surfaces. The COP/glass buried interfaces and the influence of thermal annealing are also probed directly by SFG measurements. The variation in adhesive force between the borosilicate glass and the COP film with the number of argon/oxygen (i.e., Ar-5% O₂) atmospheric pressure plasma scans is shown in Figure 4.

Although an adhesive force of <1 N/10 mm was observed in the absence of plasma treatment, this force increased to 18 N/10 mm following the initial plasma scan. Further treatment with the plasma gas resulted in a gradual degrease in the adhesive force to a relatively stable value of 14 N/10 mm. In order to minimize the denaturation of the surface by the leaving time after plasma irradiation, plasma irradiation was performed immediately before SFG measurement (~ 1 minute before). It takes about 30 min for measuring the spectrum. Figure 5 shows the SFG spectra of the COP polymer surfaces both before and after argon/oxygen (i.e., Ar-5% O₂) plasma exposure using the SSP polarization combination, which relates to polarizations of the SFG, visible, and infrared light, respectively.

Figure 2. Changes in Cls and Ols spectra, and water contact angle with plasma treatment time

Figure 3. Changes in joining force by GAJ with annealing temperature

Figure 4. Changes in joining force by GAJ with annealing temperature
In the SFG spectra of the pristine COP surface, symmetric and antisymmetric stretching vibrations corresponding to the CH$_2$ unit of the COP were observed at 2837 and 2907 cm$^{-1}$, respectively. Upon exposure of the COP surfaces to the argon/oxygen plasma, an increase in SFG peak intensities was observed. This qualitative increase in the intensities of the antisymmetric/symmetric CH$_2$ stretching signals upon argon/oxygen plasma treatment therefore indicates that the orientation of the CH$_2$ group becomes slightly tilted following plasma exposure. Although the observed changes in the SFG intensities are partly caused by changes in the molecular orientation of the surface functional groups following plasma treatment. It should be noted that orientation angle and its distribution will not be quantified, but such a change in the SFG peak intensities can be explained by variation in the orientational order of the functional groups of the surface molecules. As COP is classified as an amorphous polymer, the molecular orientation at the untreated surface should have a relatively broad orientational distribution. Indeed, we note that the formation of oxalic acid on COP surfaces has been previously observed following similar plasma and vaporization treatments, which may influence the COP surface structure, including the degree of the orientational order. More specifically, the increase in SFG signal intensities can be interpreted as an enhancement in the orientational order at the surface COP molecules. Finally, we investigated the COP/glass interfaces in the OH stretching region. Here, it could be expected that if the surface functional groups and surface-adsorbed water molecules reacted to form Si-O-C covalent bonds between the COP and the glass surfaces. However, this hydrogen-bonded OH stretching vibration did not fully disappear in SFG signals by annealing. The improvement in adhesion strength by chemical reaction at the interface is not simply due to the chemical bonding taking place at the glass surface, but an increase in the density of the CH$_2$ groups and an enhancement in the surface molecular orientational order may modify the hardness of the COP at the interface, thereby increasing the adhesion strength.

We could therefore conclude that the increased molecular orientational order and the density of the COP surfaces can be considered a key factor in achieving the strong adhesive force to glass [23].

3.3 Direct observation of gas adsorption joined interface [25]

There exists primary interest to observe directly how joined COP and glass without using chemical adhesives. Scanning Transmission Electron Microscope (STEM) equipped with Electron Energy Loss Spectroscope (EELS) was applied for direct observation of SiO$_x$/COP interface, where Si wafer on which SiO$_x$ film of 2 μm thick was used in GAJ process.

Gas adsorption joined specimen of COP/ SiO$_x}$/Si was manipulated for STEM observation by using the Ar ion-milling system. Annular Dark Field (ADF) images of both interfaces of COP/SiO$_x$ and SiO$_x}$/Si was shown in Figure 6 Interfaces at COP/SiO$_x$ and SiO$_x}$/COP can be clearly seen together with mixed amorphous region between SiO$_x$, and COP. As a result, it can be concluded that uniform and tight joining with 1–2 nm thick can be possible by adhesive-free GAJ at low temperature.
3.4 Application for gas adsorption sealing (GAS) [25]

Recently, electronics and photonics devices on organic film substrate have become popular from the viewpoints of compactness and flexibility, where typical examples can be seen in mobile phone, tablet and displays. In addition, these devices are usually made of organic materials, which are well known to deteriorate easily due to water molecules. In the case of inorganic substrate, however, device sealing was usually carried out by melting of substrate edges by local heating up to higher temperature. Though chemical adhesive is now widely used in manufacturing process for sealing of organic film substrate. In this section, we showed the sealing performance of gas adsorption joined high barrier films for water vapor permeation by monitoring the change in the visible light opaque Mg film to transparent MgO due to oxidation. Figure 7 shows the sample structure and gas adsorption sealing (GAS) processes. Barrier layer formed on 120 μm thick PET film for Water Vapor Transmission Rate (WVTR) measurement. The PET film with barrier layer comprising 3 layers of inorganic/organic/inorganic films, where inorganic films were made of silicon compound was provided by courtesy of Konica-Minolta Corporation [26]. More detailed information of composition and preparation method of the barrier film was not known because of confidential business information. The WVTR value of thus provided barrier layer on PET film was evaluated by Aquatran of MOCON Corporation and confirmed to be less than 5x10^{-5} g/m²/day. As shown in fig.6, Mg film of 10 nm thick was sputter deposited in an area of 20 mm x 20 mm. Metallic mask of thin stainless steel foil for line sealing was set on the Mg film, where line width and length was 1 mm and 120 mm, respectively. Both surfaces were exposed to Ar-O₂ air pressure plasma for 30 seconds and then laminated at the pressure of 1 MPa followed by annealing in oven at 80°C, 90°C and 100°C for 5 min for interface chemical reaction. Sample number and sealing conditions were summarized in Table 2. Evaluation of sealing performance was carried out by exposing samples to the conditions of 60°C, 90%RH for 500 hrs. During the course of exposure process, changes in Mg film conditions was checked visually. It was found that metallic Mg films of sample Nos.1 and 2 became transparent gradually from the surrounding of periphery of Mg film with exposure time.

| Sample preparation | Confirmed limit of Water Vapor Transmission Rate (WVTR) measurement by MOCON : 5X10⁻⁵ g/m²/day |
|-------------------|--------------------------------------------------------------------------------------------------|
| Sample preparation | 3 layer structure of barrier film of inorganic/organic/inorganic with WVTR of 5X10⁻⁴ g/m²/day |
| No. 1 After heating at 80 °C 1 hr |  |
| No. 2 After heating at 90 °C 1 hr |  |
| No. 3 After heating at 100 °C 1 hr |  |
| Sealing line structure | Line width : 1 mm Length: 12 cm |
| Evaluation of WVTR | Visual confirmation of optical transmittance of vacuum deposited metallic Mg film with 100 nm thick |
Figure 7. Schematic representation of samples for evaluation of gas adsorption sealing

Figure 8. Optical microscope image of sample No. 2 evaluation of GA sealing

Figure 9. Optical microscope image of sample for evaluation of GA sealing No. 3 for evaluation of GA sealing

Typical example of sample No. 2 was shown in Figure 8, where opaque Mg film to transparent MgO due to oxidation by the water vapor permeated from the directions shown by arrow via sealing line in the periphery. Water vapor permeation will be caused by insufficient chemical reaction at the interface. Mg film of sample No. 3, however, showed different performance from Nos. 1 and 2. Optical microscope image of No. 3 was shown in Figure 9, periphery of Mg film remains unchanged even after exposure to the conditions of 60°C, 90%RH for 500 hrs. However, many transparent spots over the hale area can be seen as shown in the figure. Observation by higher magnification, transparent spots can be seen more clearly. These results showed that permeation of water vapor was caused from the direction perpendicular to the surface of barrier film shown by arrows, indicating that the WVTR value of molecular sealed line of 1 mm width was smaller than the limit of the WVTR value of 5x10^-5 g/m²/day of barrier layer. This is the first application report of GAJ method for sealing of water permeation at least less than 5x10^-5 g/m²/day. It can be concluded that no permeation of water vapor through GAS line occurred even exposure for 500 hr, which can be explained in terms of higher degree of chemical
reaction to form covalent bonds formed by annealing temperature of 100°C.

4. Summary
In this manuscript, we showed composition and structure of the interface is different from the adjacent both layers due to chemical and physical reaction. In addition, the interface thus formed give a fatal influence on the performance and durability of thin film devices. As a result, we can recognize the interface as a functional material.

Interface is normally metastable state and buried in deep region from the surfaces and therefore, especially difficult to investigate. As a result, interface became a key material and new method of research and development of interface analysis is strongly required.

In conclusion, we will be approaching to the advanced stage of materials science by controlling the interface freely.

References
[1] Taga Y 2001 Thin Solid Films C15 231
[2] Taga Y 2009 Thin Solid Films 517 3167
[3] Asahi R, Morikawa T, Ohwaki T, Aoki K and Taga Y 2001 Science 293 269
[4] Iijima S 1991 Nature 354 56
[5] Kroto H W, Heath R H, Brien S C, Curl R F, and Smally R E 1985 Nature 352 139
[6] Novoselov K S, Geim A K, Morozov S V, and Jiang D 2004 Science 306 666
[7] Wang W Lofgreen J E, Ozin G A 2010 Small 6 2634
[8] Darder E, Aranda P, Ariga K 2010 Adv. Mater. 22 323
[9] Taga Y and Fukumura T 2014 Appl. Surface Science 315 527
[10] Taga Y 2011 IOP Conference Series: Materials Science and Technology 24 012011 https://doi.org/10.1088/1757-899X/24/1/012011
[11] Taga Y 2011 Joined structure manufacturing method and joined structure, PCT W0/2011/010738
[12] Taga Y 1999 Surface and Coating Technology 112 339
[13] Taga Y 1993 Applied Optics 32 5519
[14] Taga Y 1995 J. Vac. Sci. Technol. A 13 990
[15] Taga Y 2001 Proceeding of European Materials Society Strasbourg, France
[16] Baibish M N, Broto J M, Fert A, Nguyen Van Dau F, Petroff F, Etienne P, Greuzet G, Friendrich A and Chazelas J 1988 Phys. Rev. Lett. 61 2472
[17] Binasch G, Grunberg P, Saurebach F, and Zinn W 1989 Phys. Rev. B 39 4828
[18] Taga Y Taga, and Itoh T 1989 Applied Optics 28 2690
[19] Taga Y Targa, and Motohiro T 1990 J. Crystal Growth 99 638
[20] Lalhtakia A and and Messier R 1994 Optical Engineering 33 2529
[21] Arkles B 1977 Chem. Tech. 7 766
[22] Adamson A 1995 Physical chemistry of surface John Wiley & Sons, Academic Press Inc. London
[23] Miyamae T, and Taga Y 2017 J of Adhesion https://doi.org/10.1018/00218464.2017.1391657
[24] Young M, Rioux R M, and Somorjai G. A 2005 J. Catal. 237 https://doi.org/10.1016/j.jcat.2005.10.025
[25] Taga Y 2018 Int. Conf. on Competitive Materials and Technology Processes Book of Abstract ed. L A Gömze Published by Igrex Ltd. (Miskolc, Hungary) ISBN 978-615-00-3114-9
[26] Mori T, Gotou Y, Takemura C, Hirabayashi K 2014 Konica Minolta Technology Report 11 831