

Low Temperature and Non-Vacuum Surface Modification for Robust Hybrid Bonding

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Abstract

A solid-state hybrid bonding between inorganic and organic materials is feasible below glass transition temperature (T_g) without vacuum atmosphere. The surface chemical binding condition was modified using the vacuum ultraviolet (VUV) irradiation in nitrogen atmosphere where the vapor of bridging component like water and lower alcohol was included. In the case of alcohol, the radical species of H, OH, and CH were expected to help eliminating the contaminant, activating the surfaces, and creating hydroxyl-carrying acyclic alkyl chains. These bridges caused dehydration condensation upon heating at the temperature around T_g . Simultaneously, waterproof characteristic was expected via thermodynamically equilibrium hydrolysis of carboxylates. The spectroscopic analyses indicated that the growth of bridge layer was tunable with parameter of $s\text{-kg}/\text{m}^3$. At the bond interfaces, sufficient interdiffusion was observed, resulting in high mechanical bond strength. Such a bonding technology will be effective in integrating a lightweight and “smart” structural materials.

1. Introduction

Recently the internet on things (IoT) becomes critical especially in the lightweight vehicles where the organic and inorganic structural materials are combined. For such lightweight structural materials, large number of electronic devices need to be attached to ensure human safety, so the devices tend to be packaged into rigid modules to cope with mechanical assembly although most of the materials are common both to the electronic substrates and structural materials. As shown in Fig. 1, if the hybrid integration is realized with single process regardless of the combination of materials, a seamless signal transmission will be realized easily. Consequently, a solid-state hybrid bonding technology is indispensable to this. We firstly needed to reduce the process temperature to the glass transition temperature (T_g) of organic materials. Secondary the vacuum atmosphere had to be eliminated to fit the method with conventional industrial fabrication. Hence it was necessary to create an ultrathin bridge layer by modifying the chemical structure of the surfaces including the adsorbate in ambient atmosphere. For this, a surface modification method, utilizing vacuum ultraviolet (VUV) in humidified nitrogen atmosphere, was proposed [1]. The radical species of H and OH were effective to activate the surfaces and create hydrate bridge layers with thickness of a few nm in this

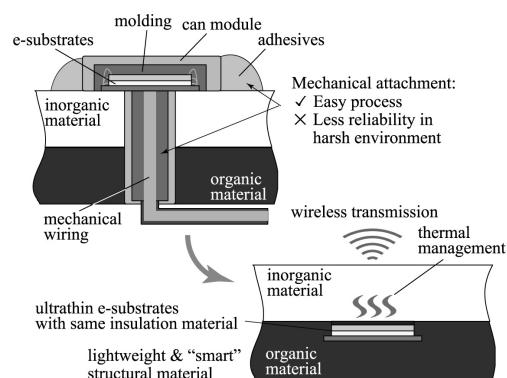


Fig. 1 The concept of lightweight and “smart” structural material.

process. Upon heating at 100 - 150 °C after the touchdown, the dehydration condensation in the hydrate bridges created tight adhesion. Seeing that a large variety of hybrid combinations has been achieved using this method, the remaining issue is the reliability. Especially for the organic materials, it was highly important to provide waterproof characteristic to prevent the interfacial hydrolysis delamination.

Since the water adsorption is unavoidable in actual atmosphere, we have chosen to modify the chemical structure of the bridge layers to keep the hydrolysis reaction thermodynamically equilibrium. The hydroxyl-carrying alkyl chains, which are attached onto the inorganic material surface through multiple coordinate-bonded carboxylates, can be one of the effective structures to obtain good bondability and waterproof characteristic at the same time. Therefore, we propose a novel surface modification method utilizing lower alcohol as the bridge component. In this study, the evolution of chemical binding status is analyzed on the surfaces of metals and polymers to prove the formation of carboxylate bridge layers. After that the bonding experiments are carried out and the bond quality is evaluated.

2. Bridge Layer Formation

The outline of the surface modification process and the targeted bridge structure (on the inorganic side) are illustrated in Fig. 2 (a) and (b) [2], respectively. As the typical examples, Al and polyimide were mainly utilized in this study. In the modification process, the ethanol vapor was included in nitrogen atmosphere at tuned amount of exposure ($s\text{-kg}/\text{m}^3$). Then the VUV irradiation was carried out at the power of $5\text{mW}/\text{cm}^2$ on the sample surface

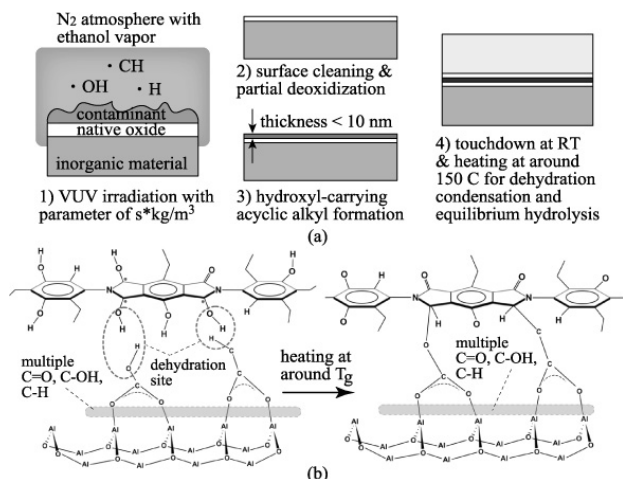


Fig. 2 The outline of: (a) E-VUV process, and (b) intended bridge layer.

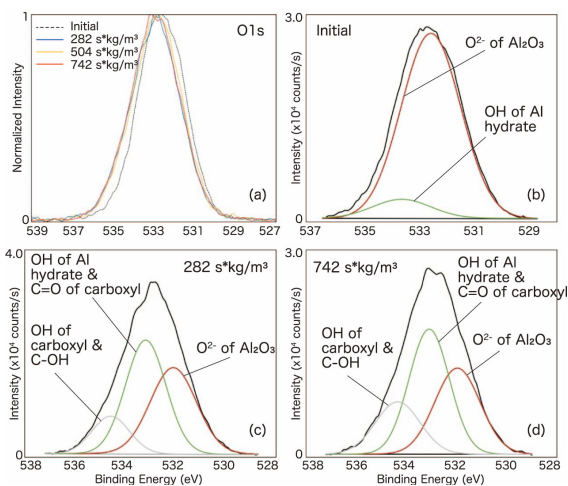


Fig. 3 XPS spectra of O1s on Al at different amounts of exposure. (a) Normalized spectra of all conditions, (b) before E-VUV, (c) at low exposure, and (d) at high exposure.

(hereafter E-VUV). In this step the radical species of H, OH, and CH are generated, then they activate the surfaces and create the hydroxyl-carrying alkyl layer. The bridge layer results in tight adhesion via the dehydration of hydroxyls upon low temperature heating. Simultaneously, the hydrolysis reaction comes to thermodynamically equilibrium when the monomer of bridge chain consisted of multiple carboxylates.

Fig. 3 shows the evolution of chemical binding status of Al surface, which were observed using X-ray photoelectron spectroscopy (XPS) after the E-VUV at different amount of exposure. The O1s synthetic spectra presented in 3(a) were normalized with the maximum peak intensity to highlight the difference in peak positions, 3(b)-(d) indicate the peak fitting results to identify the corresponding chemical groups. Results showed that the E-VUV process successfully eliminated the surface contaminant, deoxidized native oxide partially, and created effective bridge components like $C=O$ and $C-OH$ groups on the Al surface with rising amount of exposure. From the Fourier transform infrared spectroscopy (FT-IR) analyses, these $C=O$ and $C-OH$ components in E-VUV were identified to be attributable to $COOH$ groups, which implies the formation of metal carboxylate bridge layer. The growth of bridge layer was in proportion to the amount of exposure until the generation of hydroxyl-carrying acyclic alkyl chain was saturated.

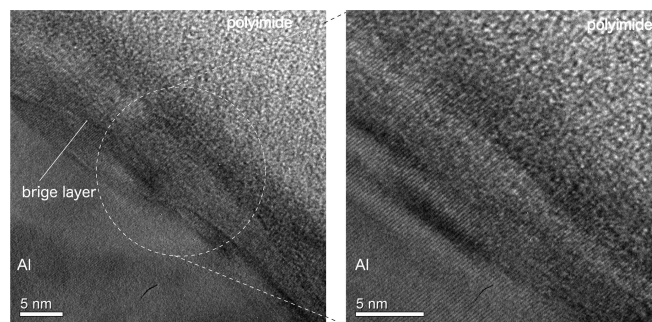


Fig. 4 TEM images of the interface between Al – polyimide bonded with E-VUV method.

3. Bonding Experiments

Fig. 4 presents the transmission electron microscopy (TEM) images of the bond interface between Al and polyimide. After creating the bridge layers to the point of saturation on both surfaces, the samples were brought into contact with the nominal pressure of 0.04 MPa at room temperature, then heated at $150^\circ C$ for 300 s. The contact pressure was necessary only to obtain sufficient parallel between the samples. Results showed that the interface contained no readily visible void, tightly adhered via the amorphous bridge layer. The lattice structure inside Al extended to the polyimide side penetrating the bridge layer and a grain boundary-like obvious linear interface gradually disappeared with time, even at room temperature. The electron energy loss spectroscopy (EELS) detected the ions of both starting materials across the bridge layer and the interface region became stable through a gradient layer with thickness of less than a several tens of nm. In the tensile testing, the samples failed at the strength larger than that of bulk polyimide block, showing the cohesive fracture mode. The bond strength and interfacial structure did not change significantly even after being kept in ambient air for 6 months.

4. Conclusions

In this study, the E-VUV surface modification method was proposed to realize a robust hybrid bonding between inorganic and organic materials without vacuum, at the temperatures lower than T_g . In this process the lower alcohol like ethanol was introduced into nitrogen atmosphere to provoke the generation of radical species of H, OH, and CH via the VUV irradiation, which helped activate the surfaces and create hydroxyl-carrying alkyl bridging chains. Those bridging chains were expected to provide the waterproof characteristic to the interface through thermodynamically equilibrium hydrolysis reaction of the carboxylates, as well as a strong ionic bond. Given Al and polyimide as the starting materials, the XPS and FT-IR analyses showed that the intended bridge structure was created with parameter of the amount of exposure. The TEM and EELS results indicated that the hybrid bonding among those materials was successfully obtained with considerably high robustness.

Acknowledgements

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References

- [1] A. Shigetou, J. Mizuno, and S. Shoji, *Proc. 65th ECTC* (2015) 1498.
- [2] A. Shigetou and Hong-Wei Yang, Japanese Patent Application No. 2018-096240.