

Vacuum Ultraviolet (VUV) / Vapor-Assisted Bonding for Organic / Inorganic Hybrid Integration

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Abstract

The feasibility of vacuum ultraviolet (VUV) / vapor-assisted bonding method was demonstrated for the low temperature hybrid integration of Cu, Ti, quartz, polydimethylsiloxane (PDMS), and graphite (multi-layered graphene) at the temperatures lower than 150 °C and atmospheric pressure. The bridging molecular layers, which were based on metal hydrates and hydrophilic functional groups such as silanol and carboxyl, were prepared by introducing water vapor onto the surfaces modified with VUV irradiation (wavelength of 172 nm) in nitrogen atmosphere. The VUV irradiation was effective not only to eliminate the initial contaminant layers and create hydrophilic surfaces, but also to less defects formation on the graphite surfaces. At the temperature of 150 °C, the starting materials were successfully bonded through those thin amorphous bridging layers, where the dehydration condensation created tight adhesion.

1. Introduction

Hybrid bonding among conventional interconnection materials and flex/transparent organic substrates are considered promising in the development of high-density 3D packaging of MEMS (Micro Electro Mechanical Systems), optical, and power devices. In order to provide sufficient bondability to diverse materials with good compensation for thermal expansion mismatch, the bonding process has to be carried out at low temperatures, for example, lower than 150 °C. Additionally, the bonding sequence should be compatible to different materials and free from high vacuum condition for the sake of reduced process complexity. However, it is definitely difficult to prevent the adsorption of molecules onto the surfaces in the ambient condition, therefore those adsorbate layers have to exert sufficient bridging function. Given Cu, Ti, quartz, polydimethylsiloxane (PDMS), and ultrathin graphite (namely multi-layered graphene) as typical materials for preparing conventional interconnection, transparent substrate, and transparent conductive layers, one of the simplest chemical species to create a bridging layer is H₂O. In our previous work^[1], Cu, SiO₂, and polyimide surfaces were tightly bonded via the bridging layers created on atomically clean surfaces. Those bridging layers were composed of metal hydrate, silanol groups, and carboxy (or acyl) groups, respectively, and were created by introducing water molecules onto atomically clean surfaces. Upon heating at 150 °C after surface touchdown, dehydration condensation and low temperature diffusion inside the bridging layer strengthened

the bond interface. However, in this process, the surface modification had to be done in high vacuum condition due to the use of Ar fast atom beam. Meanwhile, the modified diffusion Cu bonding^[2], which was carried out in oxygen condition at 150 °C, proved that it was not necessary to create a perfect atomically clean surface to obtain good bondability. We needed to develop novel surface modification method in which the initial surface contaminant was perfectly eliminated and the chemical binding condition was tuned to allow the successive water adsorption.

Herein, we proposed the use of vacuum ultraviolet (VUV) irradiation in inert condition such as nitrogen gas at atmospheric pressure. X-ray photoelectron (XPS) and Raman spectroscopy analyses were carried out mainly to PDMS and graphite surfaces, respectively, to prove the effect of initial surface modification and bridge formation. After that, the bond quality was examined by using transmission electron microscopy (TEM).

2. Experiments

The starting materials were prepared in thin films on thermally oxidized Si chips. Cu and Ti films were fabricated by using chemical mechanical polishing (CMP) to reduce the mean surface roughness to less than 2 nm, where an undesired influence of surface roughness can be ignored. PDMS films were spin-coated with thickness of around 30 μm and 10-nm-thick graphite films were prepared on the chips with Ni catalyst. Fig. 1(a) and 1(b) show schematic representations of the experimental apparatus and sequences, respectively. This apparatus is composed of several chambers for VUV irradiation, XPS, and flip-chip bonding. In the VUV chamber, the source has the wavelength of 172 nm and the atomized water can be introduced with N₂ gas at controlled volume humidity. The overall experimental procedure was as follows: 1) VUV irradiation to the initial surfaces in nitrogen gas

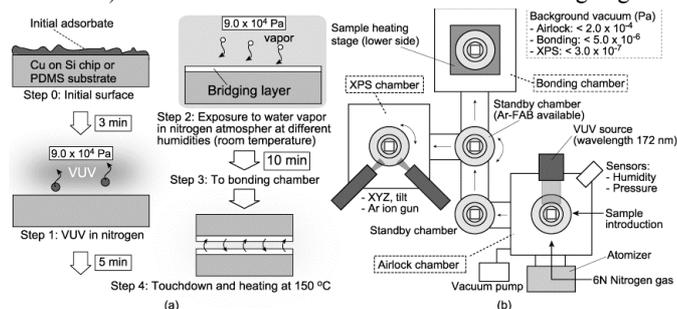


Fig. 1. (a) Schematic of bonding/surface analysis apparatus, and (b) outline of the VUV/vapor-assisted surface modification bonding method.

at atmospheric pressure; 2) introduction of atomized water for 300 s; 3) sample transfer; 4) touchdown and heating at 150 °C for 600 s. The XPS analysis was conducted before and after step 2, and the durations of steps 2 and 4 were determined from the restriction of machine configuration.

3. Influence of VUV irradiation on water adsorption^[3,4]

Fig. 2 (a) and 2 (b) shows the change in XPS spectra of PDMS surfaces before/after the VUV irradiation and vapor exposure with parameter of volume humidity, respectively. 2 (a) indicates that the spectrum of Si 2p contains Si-C and Si-O bonds, and Si-O bond becomes dominant concomitantly with increasing VUV irradiation time. This suggests that the VUV irradiation dissociated methyl group and resulted in the formation of SiO₂-like outmost surface, which is considered effective to water adsorption. Since this reaction was saturated within 300 s, the VUV irradiation time was decided at 300 s. In 2(b), the water adsorption behavior was compared with that of bulk SiO₂ sample. The binding energy of PDMS after the water exposure is almost same as SiO₂ sample, which indicates the main structure of the outmost surface is close to SiO₂. Moreover, the secondary peak appears at the lower binding energy than main peak, concomitantly with increasing humidity; this suggests the presence of silanol groups. Because this change stopped at the humidity of around 13.8 g/m³, this condition was used in the successive bonding experiment.

Similarly, the VUV irradiation and water exposure was found effective to create the bridging layer on graphite surfaces. Fig. 3 shows the change in Raman spectra of graphite surface (D, G, 2D bands) throughout the surface modification process. It is readily understood that the VUV irradiation provoked the reduction of D intensity and the increment of G and 2D bands, which suggests the elimination of surface contaminant and the less formation of internal defects. After the water exposure, small intensity of D band is maintained while a little decrease of G and 2D intensity. Therefore, the less-defect graphite surface is inferred to be maintained even after the water adsorption.

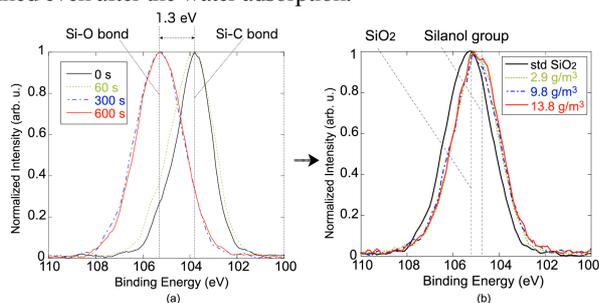


Fig. 2. The change in XPS spectra of PDMS surfaces; (a) before/after the VUV irradiation, and (b) after water exposure.

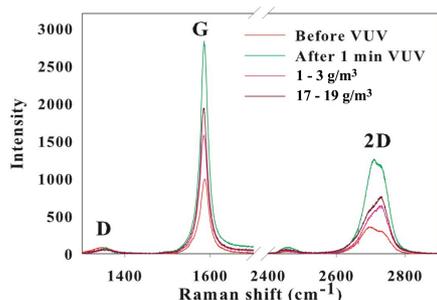


Fig. 3. The change in Raman spectra of graphite surfaces throughout the surface modification process.

4. Bond qualities

Fig. 4 (a) – (f) show the TEM (and scanning microscope for Ti) images of bond interfaces of various combinations of starting materials. Results show that the surfaces adhere each other tightly and there is no readily visible void at the interfaces. All of bonded pairs showed a sharing strength higher than 12 kgf at which no breakage occurred at the interface. Furthermore, the VUV/vapor-assisted method turned out effective to keep good transmittance of light at PDMS-PDMS interface (data not shown). The transmittance of visible light (wavelength: 380 - 960 nm) was tested using a pair of bonded PDMS substrates with thickness of 1 mm (0.5 mm x 2). Compared with the bulk PDMS plate, the decrease of transmittance at the interface was less than 5 % throughout all region of wavelength.

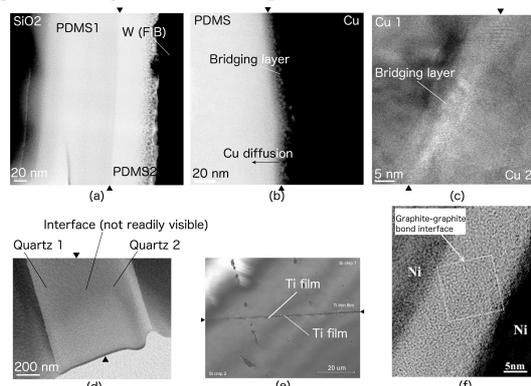


Fig. 4. TEM (and SEM) images of bond interfaces; (a) PDMS-PDMS, (b) PDMS-Cu, (c) Cu-Cu, (d) quartz-quartz, (e) Ti-Ti, and (f) graphite-graphite.

3. Conclusions

In this study, hybrid bonding among Cu, Ti, quartz, PDMS, and graphite were realized by using a VUV/vapor-assisted surface modification method at 150 °C. In this, the initial surface treatment was carried out by using VUV irradiation (wavelength 172 nm) in nitrogen atmosphere, which was followed by the vapor exposure with tunable volume humidity. XPS and Raman spectroscopy analyses were conducted mainly on the surfaces of PDMS and graphite, respectively, and the results showed that the VUV irradiation contributed in creating effective chemical sites to successive water adsorption. On the PDMS surfaces, the chemical binding condition turned into silanol-rich SiO₂ due to the dissociation of methyl groups. Similarly, less defect introduction was observed on the graphite surfaces even after the surface cleaning and water adsorption. Upon touchdown and heating at 150 °C, TEM analyses result proved that the surfaces of all testing materials were adhered to each other tightly through these bridging layers without any visible voids. Moreover, good transmittance of light was ensured at PDMS-PDMS interface.

Acknowledgements

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