Control of the Surface Modification of Epoxy Resin by VUV-Redox Method using Vacuum Ultraviolet Light

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Abstract
This study evaluates the adhesion strength between epoxy and copper, employing vacuum ultraviolet (VUV) light treatment on epoxy resin as a pre-treatment for medium vacuum sputtering. To augment the concentration of hydroxyl groups on the resin surface, we modified the VUV light irradiation atmosphere using reducing and redox gases. We assessed the changes in contact angle and adhesion strength. The VUV-Redox method was found to generate COH groups on the epoxy resin surface, thereby enhancing the adhesion at the interface between epoxy resin and copper.

Key words
VUV-Reduction method, VUV-Redox method, Direct sputtering, Vacuum ultraviolet light, X-ray photoelectron spectroscopy analysis.

I. Introduction
The surface modification of epoxy resin in semi-additive processes is critical for the miniaturization of semiconductor packages. With the aim to minimize transmission loss of high-frequency signals, enhanced surface smoothness and stronger adhesion between the epoxy resin and copper wiring are required. Surface modification using vacuum ultraviolet light has been investigated, yet controlling and evaluating the surface condition remains challenging [1].

At ICEP2023, the surface of epoxy resin irradiated with vacuum ultraviolet light was evaluated, establishing a correlation between the hydroxyl group concentration and adhesion strength. Although adhesion improved, it remained suboptimal [2]. Li et al. demonstrated the reduction of copper oxide through VUV light irradiation in a hydrogen atmosphere at room temperature [3]. We reported that it is possible to activate copper surfaces by the VUV-Redox method, which irradiates VUV light in an atmosphere using hydrogen and water vapor [4,5].

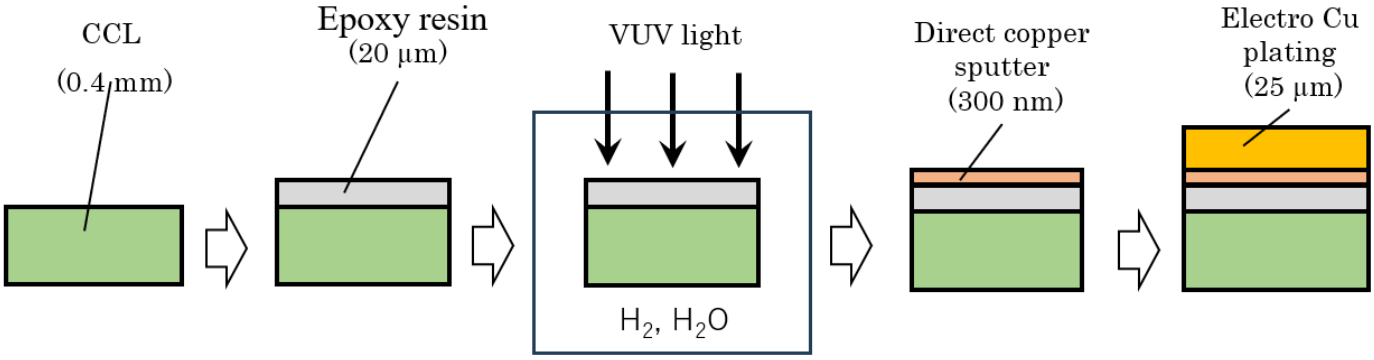

Fig. 1 Sample preparation procedure and the analysis point.

II. Method

A. Sample fabrication.

We fabricated samples (74 × 50 mm) by vacuum laminating dielectric resin (ABF-GX-T31, Ajinomoto Fine Techno Co., Ltd.) onto copper-clad laminates (MCL-679, Hitachi Chemical Co., Ltd.) using a semi-additive process. The samples were prebaked and then irradiated with VUV light (Fig. 1,2) in the atmosphere. Immediately following VUV irradiation, the samples were placed in medium vacuum sputtering devices (VMS-B1, Shibaura Machine Co., Ltd.). Plasma treatment occurred in these devices, followed by copper sputtering to a target thickness of 300 nm. Subsequently, copper was electroplated to a thickness of 25 microns and annealed at 200°C for 1 h (PR-2K, Espec Corp.).

B. Analysis method

The VUV dose was determined to be 0-3300 mJ/cm² based on preliminary evaluations of the contact angle of deionized water. Adhesion strength was measured using a peel tester (EZ-LX, Shimadzu Corporation). A portion of each sample was reserved for XPS analysis (Quantera II, ULVAC-PHI Inc.) following VUV light irradiation and prebaking. C1s spectra comparisons were conducted using XPS analysis after VUV light irradiation.

III. Results and discussion

A. Contact Angle and Adhesion Strengths

Figure 3 illustrates the variation in contact angle resulting from vacuum ultraviolet light irradiation under reducing and redox gases. Initially, the contact angle of 78° gradually increased under reducing gas conditions due to vacuum ultraviolet light irradiation. This increase suggests the reduction of hydrophilic groups on the epoxy resin surface, leading to a hydrocarbon-based structure. Conversely, under redox gas conditions, the contact angle decreased, but more moderately compared to conventional irradiation in an oxidizing atmosphere. The results were intermediate between those obtained under reducing and oxidizing gas conditions.

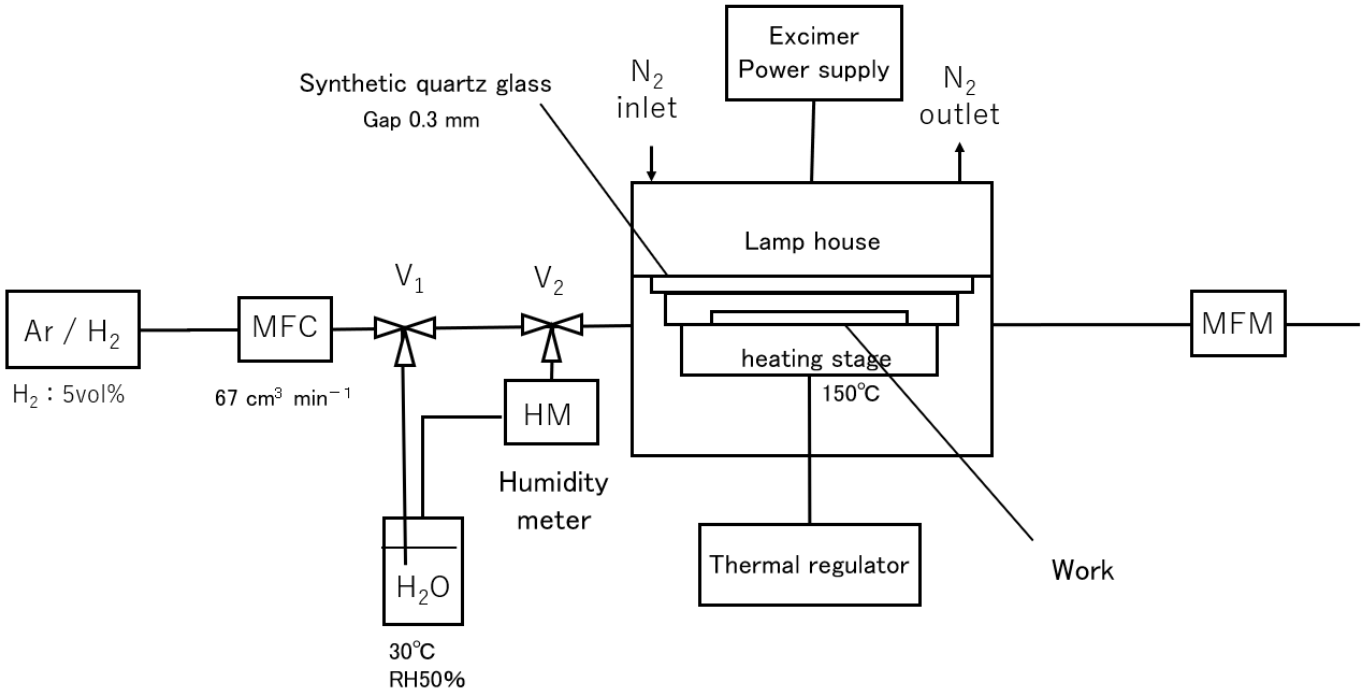

Fig. 2 Block diagram of VUV irradiation equipment for mixed gas.

Figure 4 presents comparative data on the adhesion strength of copper plating on workpieces irradiated with vacuum ultraviolet light at intensities ranging from 0 to 3300 mJ/cm². The adhesion strength was significantly lower under conventional atmospheric conditions; however, it increased approximately twofold under redox gas conditions.

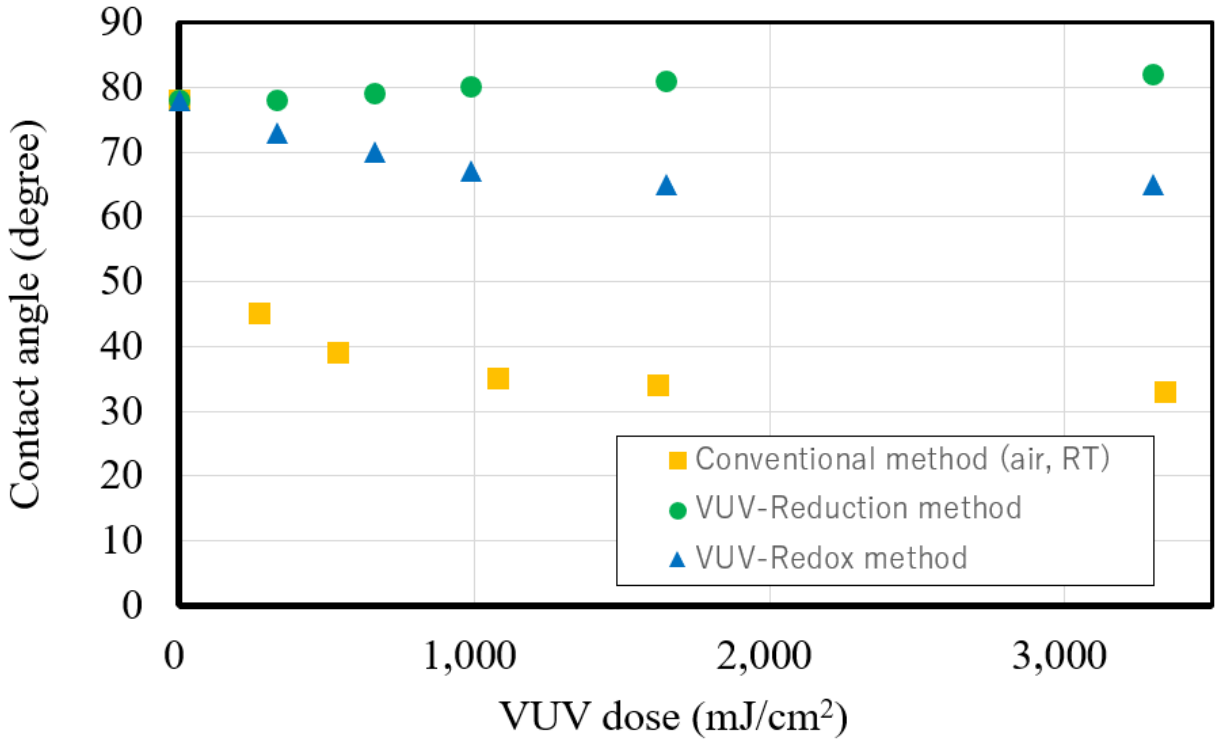

Fig. 3 Contact angle of VUV irradiated epoxy resin in Reduction gas and Redox gas.

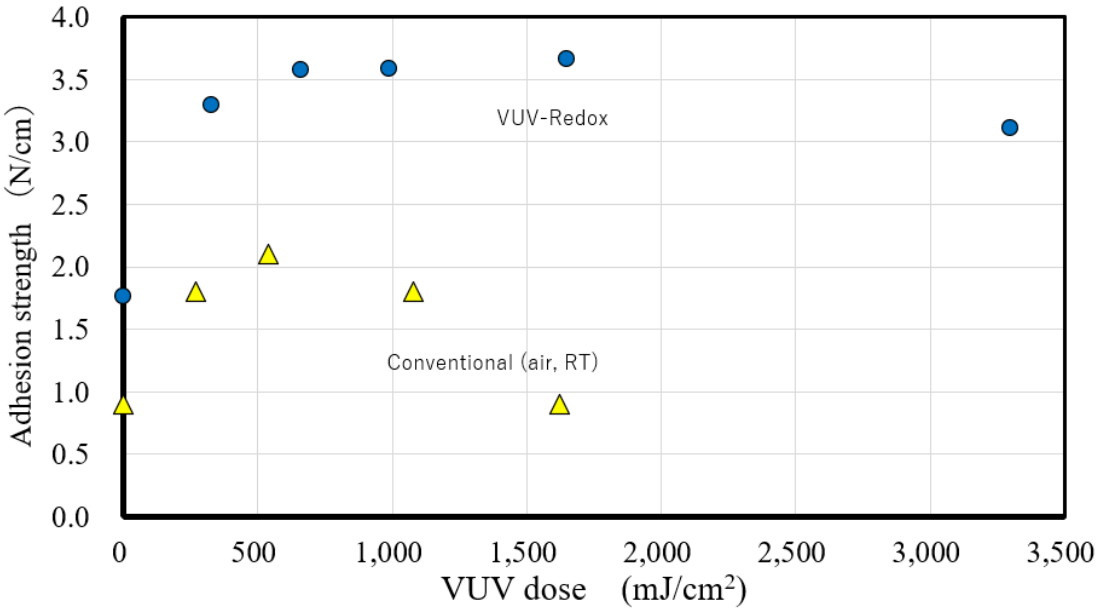

Fig. 4 Adhesion strength of epoxy resin and copper sputtered film irradiated with VUV light in Redox gas and air.

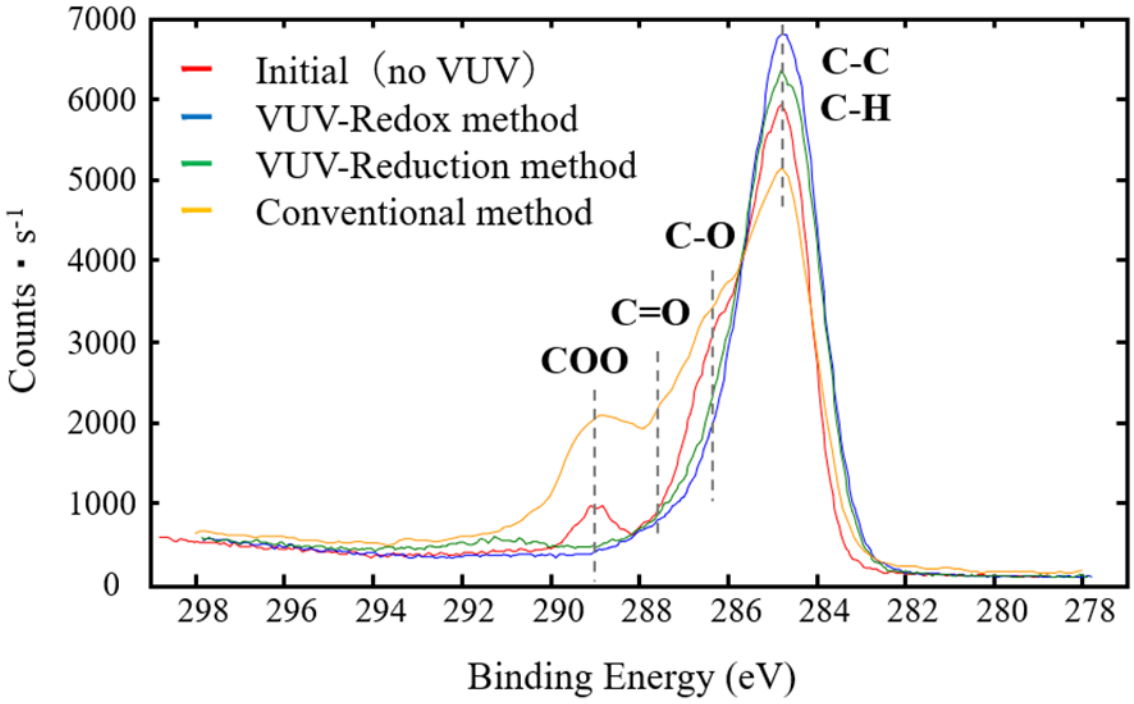

Fig. 5 Comparison of XPS C1s spectra of epoxy resin surfaces by VUV irradiation.

B. XPS Analysis

Figure 5 compares XPS spectra of carbon C1s from epoxy resin irradiated with vacuum ultraviolet light at a consistent intensity of 1.5 J/cm². The spectra reveal a distinction between the 284.6 eV peak, indicating the carbon main chain, and the satellite peak, representing functional groups. This difference suggests a change in the surface state, as inferred from the contact angle data.

In the C1s data from the VUV-Reduction method, a decrease in surface COOH groups and an increase in the carbon main chain component (C-C) were observed, indicating a reduction of the epoxy resin surface. In the C1s data from the VUV-Redox method, there was an increase in COH groups and C=O groups, alongside a decrease in COOH groups. These findings demonstrate that the concentration of surface functional groups can be modulated by VUV light irradiation in different gas environments.

III. Conclusion

This study successfully controlled the surface modification of epoxy resins by irradiating them with vacuum ultraviolet light in the presence of reducing and redox gases. This method enables appropriate processing of vacuum ultraviolet light and has potential applications in other processes, such as hybrid bonding.

References

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