

Revealing interfacial chemistry between metal and polymer by hard X-ray photoelectron spectroscopy

The interfacial chemistry between metals and polymers has been one of the most important topics in materials science and engineering because of its broad applications based on metal/polymer junctions. Polyimide (PI) has been widely used in various applications including automobiles and semiconductors because of its excellent heat resistance and mechanical strength. Fabrication process for metal/PI junctions can be classified into two main categories. Process A involves the formation of a metal layer on a PI substrate. Process B involves the use of a PI precursor, polyamide acid (PAA), and its subsequent imidization onto the metal substrate. To investigate the chemistry of materials, X-ray photoelectron spectroscopy (XPS) is the most effective method. The nondestructive use of XPS with a conventional X-ray source (e.g., Al- $K\alpha$) requires the fabrication of samples with an interface with a depth of several nanometers from the sample surface because of the analysis depth of XPS. One approach involves the formation of several atomic layers of metal on PI by vapor deposition (VD); the interface can be analyzed by conventional XPS together with other analytical techniques [1]. This approach simulates Process A. On the other hand, the study of interfaces formed by Process B is extremely limited [2]. This is due to the lack of fabrication techniques to simulate Process B and produce samples suitable for surface analyses, including XPS. We proposed a new fabrication technique for a metal/PI bilayer structure [3]. This technique is considered for Process B. Figure 1 shows a schematic illustration of the technique: 1. A SiO₂ layer is deposited on a GaAs wafer by plasma-enhanced chemical vapor deposition (PECVD). 2. A metal layer is deposited on the SiO₂ layer by resistance heating vacuum deposition (RHVD). 3. A PAA coating solution is applied to the metal layer by the doctor-blade method and then imidized by heat treatment to obtain a PI film. A PI/metal/SiO₂/

GaAs layer structure can thus be obtained. 4. The sample is turned upside down. 5. The GaAs wafer is peeled from the SiO₂ film (the GaAs/SiO₂ interface can be very easily exfoliated). 6. The SiO₂ layer is selectively removed by reactive ion etching (RIE), thus obtaining the metal and PI bilayer. We emphasize that the metal layer thickness in Step 2 can be accurately tuned in 1 nm increments by controlling the deposition conditions. We fabricated a Cu (of 30 nm thickness) and PI bilayer sample by this technique. A sample was also fabricated by a conventional VD: a PI film was prepared on a similar GaAs substrate, followed by RHVD of a Cu layer (30 nm) directly on the PI film. These samples are denoted as A-30 (conventional technique) and B-30 (proposed technique).

To investigate elemental distributions and chemical states around the Cu/PI interface, time-of-flight secondary ion mass spectrometry was performed for PI without Cu, A-30, and B-30. Figure 2 presents intensity depth profiles of secondary ions for the three samples. Cu₃ is derived from the 30-nm-thick Cu layer, and C₆ and C₃N originate from the PI layer. Here, we can observe differences in the C₆ and C₃N profiles between A-30 and B-30. The counts of C₆ and C₃N secondary ions detected in the depth range of 0–50 nm from the top of the Cu layer were calculated as follows. The C₆+C₃N intensity of A-30 (3.2×10^5) was almost equal to that of B-30 (3.3×10^5), the C₆ intensity of B-30 (1.6×10^5) was larger than that of A-30 (1.1×10^5), and the C₃N intensity of A-30 (2.1×10^5) was larger than that of B-30 (1.7×10^5). This is attributed to PI decomposition with the concentration of nitrogen-related chemical species in the A-30 Cu/PI interface region. Indeed, Miyamura suggested that the PI decomposes after heat treatment of a Cu/PI sample fabricated by conventional VD [4]. Here we found that PI decomposes during the deposition of Cu on the PI layer at room temperature, i.e., high-kinetic-energy evaporated Cu atoms can decompose PI.

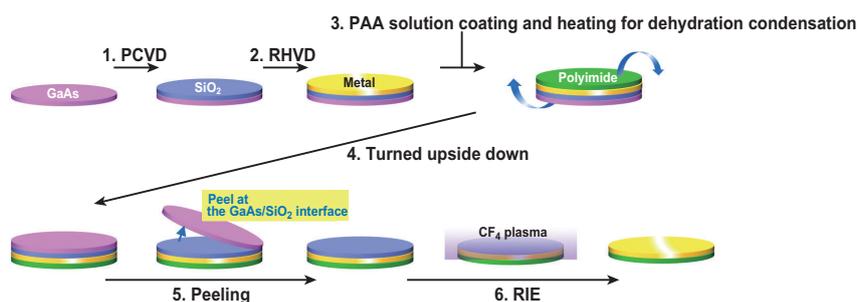


Fig. 1. Schematic of the procedures for the fabrication of a sample modeled on Process B.

For the oxygen-related secondary ions in Fig. 2, Cu_3O , $\text{Cu}_2\text{O}_3\text{H}$, and Cu_4O_4 originating from Cu_2O , Cu hydroxides, and CuO , respectively, could be detected. The amounts of the three fragments at the Cu/PI interface are larger for A-30 than for B-30, which is attributed to the suppression of interfacial oxidation for B-30. These results are consistent with those of scanning transmission electron microscopy [3,5]. For A-30, the Cu/PI interfacial oxidation is mainly induced by O_2 gas that permeates through the PI layer after interface formation. For B-30, the PI film is formed in Step 3 (Fig. 1) on the Cu layer, the surface of which was atmospherically oxidized after Step 2. O_2 gas permeates through the PI layer, which then oxidizes the Cu layer after formation of the interface in B-30; therefore, it is reasonable to consider that the interfacial oxidation of B-30 progresses to an equal or greater extent than that of A-30. However, opposite was observed in experimental observations. Accordingly, we can deduce that the chemical bonding between Cu and PI suppresses the oxidation of the interface.

Hard X-ray photoelectron spectroscopy (HAXPES) measurements of A-30, and B-30 were performed at SPring-8 BL16XU and BL46XU. The XPS spectrum of the PI surface was obtained using commercial Al- $K\alpha$ XPS equipment. Figure 3 shows the N 1s

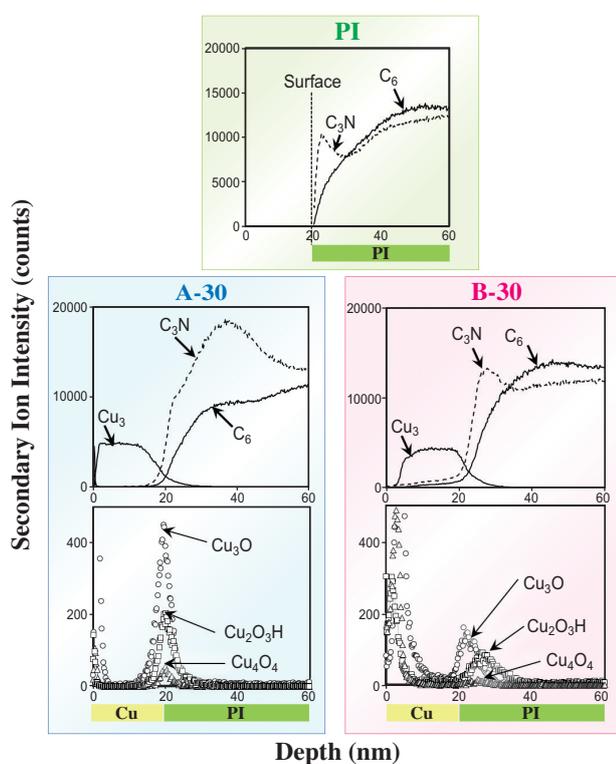


Fig. 2. Time-of-flight secondary ion mass spectrometry depth profiles of the secondary ion intensities for PI, A-30, and B-30. The profiles of secondary ions related to carbon, nitrogen, and copper (upper) and oxygen (lower) are shown separately in the A-30 and B-30 profiles for clarity.

spectra of PI, A-30, and B-30. The spectrum of PI consists of a single component, C-N in PI (400.8 eV), whereas the N 1s spectrum of A-30 consists of two components, one at 400.8 eV and the other at ca. 398.6 eV. For B-30, peaks were confirmed at around 403.5 eV, 400.0 eV, and 398.6 eV. We postulate that the 398.6 eV peak is attributable to the ionic bonding between Cu and N in the open-ring part of PI. The strong interaction between Cu and N probably hinders the subsequent formation of the interfacial oxidation layer by O_2 gas that permeates through the PI layer.

This analysis protocol can also be broadly utilized for the investigation of various interfaces fabricated by metal deposition on a polymer or polymer coating on a metal, which are significant in a wide range of engineering fields.

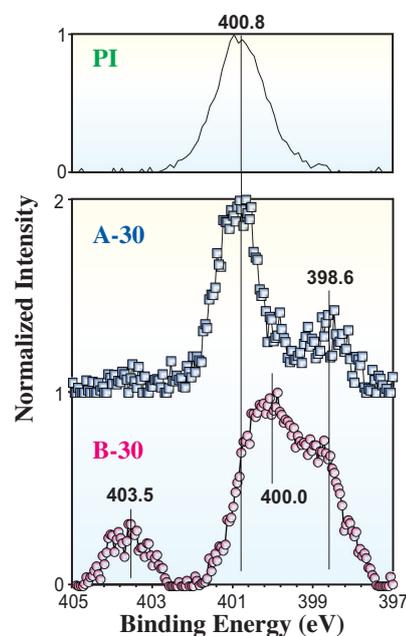


Fig. 3. Normalized Al- $K\alpha$ XPS ($h\nu=1.5$ keV) and HAXPES ($h\nu=8.0$ keV) spectra for N 1s of PI, A-30, and B-30.

Yugo Kubo

Analysis Technology Research Center,
Sumitomo Electric Industries, Ltd.

Email: kubo-yugo@sei.co.jp

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