Adhesion of Electroless NiB Film on Modified Polyimide with Aminosilane

Tetsuya Osaka<sup>1, 2, \*</sup>, Shumpei Matsui<sup>1</sup>, Kazuya Tadokoro<sup>1</sup>, Takuma Hachisu<sup>2</sup>, Atsushi Sugiyama<sup>2</sup>, Itsuaki Matsuda<sup>1</sup> and Tokihiko Yokoshima<sup>1</sup>

<sup>1.</sup> Faculty of Science and Engineering, Waseda University, 3-4-1 Okubo, Shinjuku-ku, Tokyo, 169-8555, JAPAN

 <sup>2</sup> Institute for Nanoscience and Nanotechnology, Waseda University,
513, Waseda-tsurumaki-cho, Shinjuku-ku, Tokyo, 162-0041, JAPAN

## \*osakatets@waseda.jp

Polyimide (PI) film is widely used in several applications especially in the electronics industry, e.g., as the base material for flexible printed wiring assembly, because of its excellent mechanical and thermal stability and low dielectric constant. Our group proposed an all-wet process to fabricate the diffusion barrier layer and Cu wiring by using an organosilane layer as an adhesive/catalyst layer [1]. Additionally, wet processes offer relatively simple procedures and tools, and usually are cost effective.

In previous study, an immobilized aminosilane film on polyimide works as an adhesion layer and a catalyst supporting layer for electroless deposition (ELD). Increasing the adhesion of ELD film on ultra-smooth polyimide is a particular need for realizing a high-density printed circuit board [2]. We have reported that an induction time of ELD was changed by the number of amino groups in aminosilane, and a shorter induction time was found in the aminosilane having two or three amino groups as compared with that having single. In the present work, we used various types of aminosilane and examined the effect of the number of amino groups or the functional group in aminosilane on the adhesion of ELD NiB film.

A spin-coating PI film was used as a substrate. After UV treatment ( $\lambda$ =172 nm) in air was performed to activate the PI surface, four aminosilames: (3-amino-(E-1), propyl)-triethoxysilane (3-aminopropyl)-trimethoxysilane (M-1), 3-(2-amino-ethyl-3-aminopropyl) trimethoxysilane (M-2), 3-[2-(2-aminoethylamino)ethylamino]-propyl-trimethoxysilane (M-3), each was formed on the PI film by immersion in a toluene solution containing 1 wt% aminosilane at 60°C for 10 min. Subsequently, palladium was immobilized on the modified substrate by immersion into a PdCl<sub>2</sub> solution. After rinse, NiB layer was formed by electroless deposition with the plating bath containing of NiSO<sub>4</sub>·6H<sub>2</sub>O, citric acid, and tetramethyl-ammonium hydroxide (DMAB). The chemical bonding states of the samples were evaluated by X-ray Photoelectron Spectroscopy (XPS). A plan-view and cross-sectional Transmission Electron Microscope (TEM) investigations were carried out at an acceleration voltage of 200 kV. The ELD film thickness was measured with X-ray Fluorescence (XRF).

Figure 1 shows XPS spectra Si 2p for each sample after the modification of aminosilane. The peak area of M-1 shows the largest, i.e., the aminosilane was modified densely. As for the result of the NiB adhesion, M-3 and M-2 showed the good compared with M-1, and M-1 and E-1 were comparable.

Figure 2 shows the ratio of the chemical states of Pd before and after the immersion of DMAB solution. The

characters of 'Pd<sup>\*'</sup>, 'Pd<sup>2+'</sup>, 'Pd<sup>0'</sup> indicates metallic complex, ionic, metallic state, respectively. The ratio before DMAB immersion would be independent on the number of amino groups. The DMAB immersion yielded the Pd<sup>0</sup>, and the peak areas of XPS spectra (equivalent to the amount of Pd<sup>0</sup>) were almost same. However, the metallic complex state of M-3 exhibit a higher ratio than that of M-1, as shown in Fig. 2. From these results, the amount of amino group is an important factor, but it was thought that the chemical state of the amino group is more important and affected the amount of the metal complex for the NiB adhesion.

In the meeting, we will introduce more details of our recent achievements including TEM results.



Fig.1 XPS spectra of Si 2p on PI film after aminosilane modification. E-1: (3-Aminopropyl)-triethoxy silane, M-1: (3-Aminopropyl)-trimethoxysilane, M-2: 3-(2-Aminoethyl-3-aminopropyl)-trimethoxysilane, M-3: 3-[2-(2-Aminoethylamino)ethylamino]-propyl-trimethoxysilane.



Fig.2 The ratio of the chemical states of Pd on various aminosilanes.

References

[1] T. Osaka, et al., Electrochim. Acta, 53, 271(2007).

[2] T. Osaka, et al., Electrochemistry, 76, 191 (2008).

## Acknowledgement

This work was partly supported by the Grant-in-Aid for Specially Promoted Research "Establishment of Electrochemical Device Engineering" from the Ministry of Education, Culture, Sports, Science and Technology (MEXT), Japan, by Global COE program "Center for Practical Chemical Wisdom" from MEXT.