For further large-scale integrated packaging, a finer technique to produce copper through-silicon vias (Cu-TSVs), as one of the key techniques of three-dimensional stacking of integrated circuits, is strongly required.\textsuperscript{1−3} The TSV requires bottom-up deposition of Cu to prevent void structures in the filled via, in which well-designed use of additives is important.\textsuperscript{4−9} Because the TSV has a high aspect ratio and large scale (several hundred micrometers), control of the concentration distribution of additives should be the key to improving the filling precision.\textsuperscript{10,11} Hence, it is necessary to analyze the synergetic acts of additives by STM and suggested that an accelerator with the thiol sulfonate group attracts and transfers Cu ions to chloride ions (Cl\textsuperscript{−}) on the Cu surface by Cl\textsuperscript{−} adsorbs on Cu, because it has a larger diffusion coefficient; SPS removes the pre-adsorbed Cl\textsuperscript{−} to dominate the adsorption site of the surface a few minutes later. Pre-adsorbed SPS is sufficiently stable, and is not removed by a highly negative potential (for example, −200 mV vs. Ag/AgCl).

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Finally, the model via was attached on the Cu nanodot array substrate. Notice that at this time, the via structure lies horizontally and the wall is transparent so that the irradiating laser can penetrate it (Figure 2).

**Analysis of additive behaviors.**—In order to analyze the diffusion-adsorption process of additives in the via, they were injected into the model via structure as follows.

First, the via was filled with ultrapure water. Considering its surface tension, the water was injected after a certain pretreatment: ethanol adsorption process of additives in the via, they were injected into the via entrance. It should be noted that since this volume is sufficiently larger than that of the via (40 μm × 30 μm × 400 μm, which corresponds to 4.8 × 10⁻⁶ μl), the change in additive concentration is negligible, and the concentration in the via is saturated to almost the same value as that of the dropped solution. Then, an excitation laser irradiated the Cu nanodot sidewall. The wavelength of the excitation laser was 633 nm.

In the case of measurement with applied potential, 7.0 ml of 0.18 mol/L sulfuric acid as an electrolyte and 1 ml of the same measurement solution with additives as described previously were dropped onto the entrance of the water-filled via. The Cu nanodot pattern substrate with PDMS via structure worked as the working electrode. The counter electrode was a Pt plate and the reference electrode was Ag/AgCl.

All the Raman spectra shown in results were obtained by optical measurement unit assembled in a 3D laser Raman microspectroscopy system, Nanofinder 30 (Tokyo Instruments, Inc.). Here, since all the absolute values of Raman intensity depend on conditions of the optical unit, such as property of the ND filter used, the amplifying mechanism, the slit width for spectrometer, or diameter of the pinhole, so that all the units of intensity are given arbitrary. For meaningful comparison, intensity values in the time-dependent behavior was standardized by the saturated value of the fitting curve.

**Results and Discussion**

**Diffusion behavior of each additive.**—In order to observe the diffusion behavior for each species, time-dependent SERS spectra of the diffusion-adsorption process of each species were measured, by dropping the solution containing only one species, Cl⁻ or SPS, at the entrance of the via. The horizontal depth of the laser focusing spot was 390 μm (bottom part of the via). Figure 3a shows the spectrum for Cl⁻ solution, and Figure 3b is for SPS solution, taken immediately after dropping the solution.

Figure 3a shows a peak near 300 cm⁻¹ after 300 s, which can be assigned to the stretching vibration between Cu and Cl, suggesting it takes ~300 s for Cl⁻ to fully cover the surface of the via bottom. Figure 3b shows a peak near 1030 cm⁻¹ after 360 s, which can be assigned to the stretching vibration of the sulfonate group in SPS, suggesting it takes ~360 s for SPS to fully adsorb on the bottom.

Figure 4 shows the time-dependent changes of the Cl⁻ and SPS peaks. Notice that an approximate curve, processed by curve fitting of the sigmoid function, is also shown in this figure. The result that the fitting with the sigmoid-shaped curve is successful indicates that the adsorption step is described by Prout-Tompkins model, in which the adsorption rate (dθ/dt) is proportional to both coverage (θ) and adsorption site density (1-θ), that is, dθ/dt = kθ(1-θ). Here, k is the rate constant of the adsorption. The approximate curves clearly show the position in which the peak intensity starts to increase. The peak intensity of the sulfonate group in SPS starts to increase just after 300 s, whereas the peak of the stretching vibration of Cu-Cl rises after 200 s. This suggests that the diffusion of SPS to the bottom of the via is much slower than that of Cl⁻ because of the molecular weight difference.

Figure 4 also shows a difference between the two species in the time required to reach surface adsorption equilibrium (shown by green and black horizontal double-headed arrows), suggesting that Cl⁻ adsorbs faster on the Cu surface than SPS. The related work performed by Broekmann et al supports this result.²⁶

These data clearly show the difference between Cl⁻ and SPS in terms of its diffusion behavior: diffusion and adsorption of Cl⁻ are fast because of its small molecular weight and lone pair electrons to coordinate to surface atoms, whereas those of SPS are slow. In particular, the slow adsorption of SPS should be due to its S-S bond. The S-S bond is difficult to break to form the S-metal bond that is required for the stable adsorption of SPS.

**Interaction between two additives in mixed solution.**—Figure 5a shows the time-dependent SERS spectrum, which illustrates the diffusion-adsorption process and interaction mechanism in the
Cl\(^-\) and SPS mixture. The spectrum was taken immediately after dropping the solution containing both Cl\(^-\) and SPS at the via entrance. The laser spot position was the same as previously described. As described in the previous discussion, the peak of 300 cm\(^{-1}\) is Cu-Cl vibration and the peak of 1030 cm\(^{-1}\) is the stretching vibration of the sulfonate group in SPS. Figure 5b shows the time-dependent change of the 300 cm\(^{-1}\) peak intensity, and Figure 5c shows that of the 1030 cm\(^{-1}\) peak. Figure 5d shows these two figures simultaneously for purposes of comparison.

These figures clearly show the adsorption state transitions of these two species; the peak of 300 cm\(^{-1}\) (Cu-Cl vibration) is first detected at the bottom of the via, suggesting fast diffusion and adsorption of Cl\(^-\), whereas it becomes weak as the 1030 cm\(^{-1}\) peak increases. These data suggest the displacement adsorption between Cl\(^-\) and SPS, which was also reported in the research by Broekmann et al.\(^{26}\) They described the reaction cycle of SPS on a Cl-covered Cu surface during Cu growth. Here, SPS shows physisorption on the Cl layer, where Cl\(^-\) is pre-adsorbed on the Cu substrate, followed by the substitution of SPS for Cl.

Comparison of the time-dependent peak changes of 1030 cm\(^{-1}\) (SPS) between the cases with and without Cl\(^-\) clearly show the influence of Cl\(^-\). Figure 6 shows the plots of SPS solution from Figures 4 and 5c for purposes of comparison.

Figure 6 indicates that it took longer for SPS in the mixed solution to reach the surface adsorption equilibrium. This is because SPS in the mixed solution must remove pre-adsorbed Cl\(^-\) on the surface, which takes time to reach saturation. All these data suggest that the pre-adsorbed Cl\(^-\) is substituted to SPS at the bottom of the via, even though the Cl\(^-\) reaches the bottom faster because of its larger diffusivity. In this context, the driving factor of the substitution is questionable, but we consider this to be the chemical interaction between Cu and S moiety that comes from cleavage of the disulfide bond involved in SPS. S moiety can strongly coordinate to the metal surface to form a chemical bond, whose stability overcomes the destabilization caused by dissociation of the Cu-Cl bond and disulfide bond. Many studies have claimed this, by suggesting that the disulfide of SPS is dissociated to produce 3-mercapto-1-propanesulfonate (MPS). Broekmann et al.\(^{26}\) suggested that MPS can form a strong chemical bond with the Cu surface by thiol in their reaction cycle.\(^{26}\) Their density functional theory calculation also supported the idea that the strong Cu-S bond can be the driving factor for SPS to perform substitution of Cl. In fact, their reaction cycle further involves the removal of MPS by another SPS adsorption, which causes the accumulation of free MPS. This leads to the reformation of disulfide bonds between them to recover SPS, which concludes the cycle. Because our case does not employ Cu deposition, the initial stage of this cycle is shown in this study. Once Cl\(^-\) shows desorption, through the substitution of SPS, little interaction between these two is expected, because electric repulsion between negatively charged Cl\(^-\) and –SO\(_3\)\(^-\) moiety of SPS should be quite strong. This implies that the working mechanism of Cl\(^-\) is not so much complicated, which mainly contributes to the delay of SPS adsorption.

Potential application.—In order to discuss the influence of applied potential in the actual deposition processes, the time-dependent SERS spectrum of Cl\(^-\)-SPS mixed solution was measured, with cathodic potential applied to the working electrode (Cu nanodot sidewall of the via), as shown in Figure 7. For this measurement, the horizontal depth of the excitation laser was 190 \(\mu\)m, which was not as deep as that described in the previous section. This is to save time for the saturation, which has been shown to take time in the previous section. The inside of the via was filled with sulfuric acid solution, and \(-200\) mV vs. Ag/AgCl was applied from 300 s after dropping the mixed solution.

Figure 8b shows the time-dependent SERS peak changes of 300 cm\(^{-1}\) (Cl\(^-\) or SO\(_4\)\(^{2-}\)), plots of which were collected from the original SERS spectrum shown in Figure 8a. This figure shows the clear up-down tendency of the peak intensities, indicating displacement adsorption of Cl\(^-\) (or SO\(_4\)\(^{2-}\)) and SPS, which was discussed previously. Figure 8c, which shows the peak changes of SPS, also suggests the displacement adsorption; the SPS peak increases just after the
beginning of the Cl\(^{-}\) peak decrease. Overpotential was applied immediately after reaching the adsorption equilibrium of these species. The time-dependent changes of 300 and 1030 cm\(^{-1}\) after 300 s (during the potential application) show the steady state, indicating the adsorption equilibrium state is not significantly influenced by the applied potential. SO\(_4^{2-}\) and Cl\(^{-}\) have negative charge, and electric repulsion exists between the electrode and these species, whereas the adsorbed SPS is considered stable on the potential applied electrode surface because of its stable chemical bond with Cu. As mentioned previously, SPS itself is not considered to strongly adsorb on the Cu surface, but MPS, which is the product of SPS dissociation, adsorbs on the Cu surface strongly because of the coordinate bond between the sulfur atom of the thiol group in the MPS and the Cu atom of the surface. Such a discussion leads to the conclusion that SO\(_4^{2-}\) and Cl\(^{-}\) are kept far from the Cu surface with the negative applied potential because of electrostatic repulsion, whereas adsorbed SPS is not affected by the negative potential because of its thiol-related molecular structure. Notice that the past work by Jin et al. also supported this conclusion.\(^{27}\)

Summary

Diffusion-adsorption behavior of Cl\(^{-}\) and SPS in the TSV was directly observed, by using a micro-model via equipped with a sidewall

Figure 5. (a) Spectra of mixed solution. (b) Peak transition of 300 cm\(^{-1}\) over time. (c) Peak transition of 1030 cm\(^{-1}\) over time. (d) Superposition of (b) and (c).

Figure 6. Peak at 1030 cm\(^{-1}\) of both the SPS-only solution and the mixed solution of SPS and Cl\(^{-}\) over time.

Figure 7. Schematic image of the experimental setup for potential applying experiment with the via structure.
with a Cu nano-patterned structure that enables SERS measurement for the diffusion species. The time-dependent SERS spectrum from the bottom part of the via identified the diffusion behaviors of each additive (Cl\textsuperscript{−} and SPS), into the via; although Cl\textsuperscript{−}, with a larger diffusion coefficient and strong affinity to the Cu surface, first adsorbed on the Cu, it was substituted by SPS after sufficient time for SPS diffusion. Furthermore, the SPS, with strong affinity to the Cu surface, turned out to keep its adsorption state even under negative potential applied on the via, at least more than −200 mV vs Ag/AgCl. The stability of SPS is due to strong Cu-S bond formation, the consumed time for which leads to the delayed appearance of the SPS peak. As described here, our SERS measurement setup has excellent performance to provide a molecular-level insight in a micro via structure directly, and is expected to become a powerful tool for the analysis of the synergetic interactions of the chemical species inside.

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