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A Novel Metallizing Method on Resin Surface Through Silver Spray Using Triazine Compound

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Abstract

Silver layers were fabricated by a spray electroless deposition approach on acrylonitrile-butadiene-styrene (ABS) substrate functionalized by a triazinedithiol compound of 6-(3-triethoxysilylpropyl)amino-1,3,5-triazine-2,4-dithiol monosodium (TES). TES, which acts as an interfacial molecular layer between ABS and silver layer, contains silylpropyl groups which can react with OH groups on resin surfaces treated by plasma. At the same time, thiol groups can react with silver layer. ABS surfaces treated by different processes were characterized with scanning electron microscopy (SEM), atomic force microscopy (AFM), X-ray photoelectron spectroscopy (XPS), and X-ray diffraction (XRD). The SEM and AFM results showed that continuous, uniform layers of silver were obtained. The effect of plasma treatment time on ABS surface chemical structures was investigated. Additionally, the standard peeling test results showed that the silver layer had the adhesion strength of 23.2 N/mm when plasma treated for 10 min on ABS. From the results of XPS, the reaction of TES on the ABS was confirmed. XRD indicated that the silver layer on ABS surface was not oxidized and mainly existed in the metallic state. This method is fast, simple, nontoxic, palladium and chromium free, which could provide a novel consideration in resin plating industry.

Key-words: Triazinedithiol, Silver spray electroless deposition, Molecular adhesive, Echingless

1. Introduction

Silver layers have stimulated a wide range of interest for their superior electrical and thermal conductivity¹⁾, catalytic²⁾, antibacterial³⁾, magnetic⁴⁾ and optical properties^{5,6)}. Different silver deposition processes such as electroless plating⁷⁾, electroplating⁸⁾, vacuum deposition⁹⁾, and sputtering deposition¹⁰⁾ have been conducted on various substrates. Electroless metallization is still one of the most effective processes and is applicable to complex-shaped materials or nonconductors, and is also less energy-consuming than other methods. Successful electroless silver deposition on various substrates, such as carbon fibre, silicate glass and cenospheres has been reported in several studies¹¹⁻¹⁴⁾. Yet, uniform and controllable metallic plating on the substrates surface by electroless metallization still needs further improvement. From this point of view, it is demonstrated that the improved spray electroless deposition can be applied to achieve the continuous silver layer on the substrate surface, and realizes the direct deposition of silver onto the substrate. The process is usually carried out by simultaneously spraying the silver salt solution and reduction solution straightly onto the substrate surface in the metallization step. During which the silver layer can be dispersed uniformly and the thickness of the silver layer can be controlled feasibly by changing the

spray times¹⁵⁻¹⁷⁾.

Acrylonitrile-butadiene-styrene (ABS) polymers are among the most widely used polymers in industry as vehicles and electrical devices for their excellent toughness, dimensional stability, chemical resistance, ease of processing, and low cost¹⁸⁻²⁰⁾, and was employed as substrate in this study. Considering that the adhesion strength between the metal layer and the ABS substrate is the major concern in practical application, a chromic/sulfuric acid etching is usually applied to increase the surface roughness to obtain favorable adhesion strength^{21,22)}. However, the Cr⁶⁺ is hazardous to environment, and the noble metal Pd that is usually introduced as activation catalyst is costly, which has limited the scope of applications. Also the adhesion quality is still not satisfactory due to the absence of chemical conjunction, and the type and the abundance of chemical functionalities on substrate surface play a major role in the adhesion²³⁾. The motivation of our research is based upon the critical need for an environmentally compatible and effective surface modification approach to apply for the adhesion enhancement. Since triazinedithiol compounds have received considerable attention for their functional groups of thermally stable triazine ring and highly reactive thiol groups, which are known to exhibit good chemical conjunction feature with metals such as Cu, Ni, Ag, Au²⁴⁻²⁶⁾, they are expected to

provide a favorable interfacial adhesion enhancement layer as alternatives to the chromic etching.

In this work, the triazinedithiol compound 6-(3-triethoxysilylpropyl)amino-1,3,5-triazine-2,4-dithiol monosodium (TES) was initially introduced onto the plasma pretreated acrylonitrile-butadiene-styrene (ABS) surface, with further sensitization, silver layer was finally fabricated on the ABS surface using spray electroless deposition, which was carried out by simultaneously spraying the silver salt solution and reducing solution onto the ABS surface. Silver nitrate and ammonia aqueous solution was applied as silver salt solution and glyoxal was used as reduction agent. The ABS substrate surface according to the electroless deposition procedure was characterized by scanning electron microscopy (SEM), atomic force microscopy (AFM), X-ray photoelectron spectroscopy (XPS), and X-ray diffraction (XRD). Adhesion test was carried out to study the effect of the plasma exposure time on the cohesive force between the silver layer and the ABS substrates. The formation mechanism of silver layer was also investigated with XPS.

2. Experimental

2.1 Spray electroless silver deposition

The outline of the spray electroless silver deposition procedure was mainly divided into two steps, and is schematically illustrated in Fig. 1.

Surface Modification. Prior to the modification, the ABS substrates (60 mm × 30 mm × 1 mm, Naruse Ltd. Japan) were degreased by sonication in ethanol twice for 10 min. The well-cleaned ABS surface was then exposed to argon plasma (Diener electronic Femto apparatus, Diener electronic. Plasma-Surface-Technology, Germany) with HF-Generators of 50 Hz, input power of 30 W, bias voltage of 230 V and exposure time of 5, 10, 15, 20 and 30 min. The distance between the ABS surface and the plasma was 30 mm.

Different exposure times (5, 10, 15, 20 and 30 min) were selected in order to evaluate the effect of the plasma exposure time on the cohesive force between the deposited silver layer and ABS surface. Subsequently, the plasma treated ABS surface was modified with 6-(3-triethoxysilylpropyl) amino-1,3,5-triazine-2,4-dithiol monosodium (TES) by simply immersing the surface in the 0.1 wt% TES aqueous solution for 20 min to allow the covalent grafting. TES was synthesized by reaction between 6-(3-triethoxysilylpropyl) amino-1,3,5-triazine-2,4-dichloride and NaSH, according to the method described in the previous paper^{27,28}.

Metallization. The TES modified ABS surface was then immersed in the 10% sensitizer (S-10X, C. Uyemura & Co., Ltd. Japan) aqueous solution for 3 min at 40°C as sensitization of the surface for the silver metallization. In a typical electroless silver deposition process, the silver salt solution was prepared by addition of 2.5% ammonia aqueous solution dropwise into 1.5 wt% silver nitrate (99.8% AgNO₃, Nacalai Tesque, Inc., Japan) aqueous solution just until the brown precipitate disappeared and the solution became transparent. The reducing aqueous solution was obtained by mixing 1% 2,2',2''-nitrilotriethanol (98% N(CH₂CH₂OH)₃, Wako Pure Chemical Industries, Ltd., Japan) and 3.8% glyoxal (40% (CHO)₂, Wako Pure Chemical Industries, Ltd., Japan) together. Finally, silver layer was fabricated by simultaneously spraying the silver salt solution and reducing solution onto the functionalized ABS surface.

2.2 Characterization

The morphologies of the as prepared ABS samples were observed by scanning electron microscopy (SEM, 3D Real Surface View Microscope VE-8800, Keyence. co., Japan) with an accelerating voltage of 2.0 kV.

The surface topography and arithmetic mean roughness (Ra) were evaluated by atomic force microscopy (AFM, Scanning Probe Microscope SPM-9700, Shimadzu Co.,

Fig. 1 Schematic illustration of the silver spray electroless deposition on ABS substrate.

Japan) under dynamic mode using a NCHR-10 silicon pointprobe (Force constant: 42 N/m). The scan range and scan rate were set at 1 μm and 1.0 Hz, respectively.

The chemical state of bonding and composition changes of the ABS substrates surface according to the spray electroless silver deposition procedure were analyzed by X-ray photoelectron spectroscopy (XPS, PHI 5000 VersaProbe, Ulvac-Phi. Inc., Japan) X-ray photoelectron spectrometer equipped with monochromated Al K α radiation (1486.6 eV) at 25.4 W source energy. The measurement was carried out at 45° takeoff angle under analysis chamber pressure of $\sim 2 \times 10^{-7}$ Pa. Charge compensation was achieved by charge neutralizer. All XPS data were referenced with respect to the C1s binding energy of 284.8 eV. Both analyses and curve fitting were performed on MultiPak VERSION 8 (Ulvac-Phi. Inc., Japan).

The crystalline structure of the silver layer was measured by X-ray diffraction (XRD, Bruker D8 Advanced, Bruker Corporation, Germany) using Cu K α radiation operated at 40 kV and 40 mA. The scan speed was 0.1 s/step, and the diffraction patterns were recorded in the 2 θ range of 2°-90°.

Adhesion strength was quantitatively investigated by a standard peel test (Force Measurement IMADA ZTA-50N, IMADA Co., Ltd., Japan) at a constant rate of 50 mm min⁻¹. The thickness of the electroless deposited silver film was increased in order to perform the quantitative adhesion strength tests. Copper was electroplated on the silver film using an acidic copper electroplating bath at a current density of 20 mA/cm² under room temperature for 60 min. The 90° peel test was then performed to quantify the adhesion strength of the electroless silver film. The test involved vertically peeling a 1 cm wide silver-copper strip from the

substrate surface. The pull force was measured as a function of displacement. The average pull force was divided by the width of the copper strip to give the peel strength in N/mm. The morphology of the peeled surface was also observed by SEM with an accelerating voltage of 2.0 kV.

3. Results and Discussion

3.1 Surface observation of the ABS substrate

The morphologies of the ABS surface according to the spray electroless silver deposition procedure (modification, sensitization, and deposition) were first observed by SEM (**Fig. 2**). As seen in Fig. 2 (a), the surface of the bare ABS substrate is almost smooth. After the argon plasma exposure for 10 min, it is seen that the smooth surface of ABS becomes rougher, obvious small pits can be observed, and are even distributed on the surface (Fig. 2 (b)). With the TES modification on the plasma treated ABS surface, the pits appearance becomes less obvious, only the large rough pit and pots texture can be seen (Fig. 2 (c)), it was assumed that the plasma treated ABS surface was covered by TES compound to a certain extent. By further sensitization, the ABS surface shows no significant change, only the pits on the surface become less (Fig. 2 (d)). As for the silver decorated ABS surface, the brown color distributes uniformly on the ABS surface, and the silver film can be clearly seen in the form of small grains (Fig. 2 (e)), indicating that the obtained silver layer was uniform, continuous, and compact²⁹⁻³¹).

AFM 3D images were also observed to evaluate the change of the texture topography and roughness of the ABS surface according to the spray electroless silver deposition procedure (**Fig. 3**). All topographic images are shown with the same vertical scale (correlated with height of the topographic

Fig. 2 Top-view SEM images of the ABS surface, (a) bare ABS surface, (b) plasma treated ABS surface, (c) TES modified ABS surface, (d) sensitized ABS surface, (e) silver decorated ABS surface.

Fig. 3 AFM images of the ABS surface, (a) bare ABS surface, (b) plasma treated ABS surface, (c) TES modified ABS surface, (d) sensitized ABS surface, (e) silver decorated ABS surface.

features). The bare ABS surface presents a smooth topography, and the arithmetic average roughness (Ra) is 5.9 nm (Fig. 3 (a)). After the argon plasma exposure for 10 min, the texture of the bare ABS disappears, meanwhile, pits of large clusters evenly distribute on the surface, and the Ra decreases to 3.6 nm, indicating that the a homogeneous ABS surface formed by plasma pretreatment (Fig. 3 (b)). With the TES modification on the plasma treated ABS surface, the Ra decreases to 3.0 nm, and the surface becomes more homogeneous with a few of the pits still observed, it was interpreted that the poly-TES layer was formed and the clusters of pits were covered to a certain extent (Fig. 3 (c)). By further sensitization, no significant change is observed with the surface Ra of 3.1 nm, except the pits can hardly be seen (Fig. 3 (d)). The surface topography changes notably after silver decoration on the ABS surface, the deposited film appears granular, as has been observed, and the surface Ra increases to 7.2 nm, which could be attributed to the minor difference in size of the silver layer, and it is noteworthy that the silver grains were uniformly distributed on the ABS surface (Fig. 3 (e))³⁰⁾. The above results are in accordance with the SEM results.

3.2 Chemical characterization of the ABS surface

XPS were analyzed to investigate the state of chemical bonding and composition changes of ABS substrates surface according to the spray electroless silver deposition procedure (Fig. 4). Initially, XPS survey scans were performed to

Fig. 4 (a) and (b) XPS survey spectra of the ABS surface according to the electroless silver deposition procedure, (c) partial amplification graph.

characterize the overall atomic composition of the as prepared ABS surfaces, the results are summarized in **Table 1**. All spectra were normalized to the highest peak intensity (Fig. 4 (a) and 4 (b)). The bare ABS survey scan displays the characteristic peaks of C1s at 284.8 eV, N1s at 399.6 eV and O1s at 532.5 eV. With the TES modification, the spectra showed signals around 102.3 and 162.9 eV corresponding to the Si2p and S2p regions, which are attributed to TES

Table 1 The atomic percentage of elements on the ABS substrate surface according to the silver electroless deposition procedure for the plasma pretreatment of 10 min.

Sample	Atomic percentage / at. %							
	C	N	O	Si	S	Cl	Sn	Ag
Bare ABS	93.4	4.6	2.0	—	—	—	—	—
Plasma treated ABS	79.8	5.3	14.9	—	—	—	—	—
TES modified ABS	81.1	3.6	14.8	0.3	0.1	—	—	—
Sensitized ABS	66.1	3.5	22.7	0.3	0.2	0.7	6.5	—
Silver decorated ABS	30.7	0.0	13.6	17.0	5.1	2.1	0.0	31.5

Table 2 The C1s components on the ABS substrate surface according to the silver electroless deposition procedure for the plasma pretreatment of 10 min.

Sample	C-C/C-H / %	C-NH / %	CN/C-OH / %	C=O / %
	284.8±0.1 eV	285.7 eV	286.6±0.3 eV	288.6±0.1 eV
Bare ABS	90.3	—	9.7	—
Plasma treated ABS	69.2	—	25.9	4.9
TES modified ABS	78.7	6.5	11.9	2.9
Sensitized ABS	78.0	8.2	10.8	3.0
Silver decorated ABS	81.0	—	11.9	7.1

compound, indicating the presence of TES layer on the ABS surface (Fig. 4 (c)). As for the sensitized ABS surface, the characteristic peaks of Sn3d were detected. Finally, as shown in the survey scan of the silver decorated ABS surface, Ag3d peak was detected as the main peak, which indicated the formation of the silver film.

To study more precisely the chemical modifications induced by the TES compound and the silver electroless deposition, the representative high-resolution C1s spectra were investigated by curve fitting (Fig. 5 (a)). The hydrocarbon (C-C/C-H) component was used as reference for charge shifting and centered at a binding energy of 284.8 eV. The fitting data are summarized in Table 2. The C1s peak of the bare ABS were fitted into two components at 284.8 and 286.4 eV, corresponding to aliphatic carbon bonds or carbon-hydrogen bonds (C-C or C-H) and nitrile group (CN) $\pi \rightarrow \pi^*$ groups, respectively. And the carbon-hydrogen bonds were dominant in the existing forms of C atoms. In the spectrum of plasma treated ABS surface for 10 min, the peak at 286.4 eV shifted to 286.3 eV, and new carbon species of carbonyl groups (C=O) were found at a binding energy of 288.5 eV. Additionally, from the data summarized in Table 2, it is seen that the proportion of the components at 286.3 eV appreciably increased to 25.9%, which was mainly attributed to the new carbon species of alcoholic/ether groups (C-OH or C-O-C). It was suggested that hydrophilic groups of -C-OH, >C=O have been introduced onto the ABS surface with plasma treatment. As for the TES modified ABS sample, the peak binding energy of C-C/C-H, CN and C=O shifted to 284.7, 286.8 and 288.6 eV, respectively. In addition to these four components, the spectrum reveals a new carbon species with a binding energy of 285.7 eV, which can be assigned to carbon-bonded nitrogen (C-NH), indicating that the ABS

Fig. 5 (a) Deconvoluted C1s spectra of the ABS surface according to the electroless silver deposition procedure, (b) high-resolution S2p spectra, (c) Sn3d spectra, (d) Ag3d spectra.

surface was covered by TES compound. Additionally, the proportion of the carbon-hydrogen components increased as compared to the plasma treated sample, which was also attributed to the TES chemical structure. With the further treatment of sensitization, the C1s peak presented the same components as that of the TES modified ABS, the proportion of the components also showed no obvious change. For the silver decorated ABS surface, the peak corresponding to the C-NH completely disappeared, suggesting that the TES layer was covered by silver layer. And the C1s peak were fitted to three components as previously described, C-C/C-H, C-OH and C=O groups at 284.8, 286.6 and 288.7 eV, respectively³².

To further clarify the interfacial characteristics of the modified samples and to study the bond formation between silver and the TES modified ABS surface, high-resolution XPS analysis of S2p regions was also carried out (Fig. 5 (b)). The representative S2p spectrum of the TES modified ABS surface was comprised of two components with binding energy at 162.9 and 164.1 eV, which were assigned to carbon-bonded thiol groups, showing the characteristic of sulfur in thiol group (-SH). It was concluded that the TES modified ABS substrate contains thiols on the surface. With silver decorated on the TES modified ABS surface, the S2p binding energies shifted to 161.5 and 162.7 eV, which was typical of sulfur in Ag-S groups resulting from the chemical conjunction between Ag and thiol groups of TES molecules, also, the peak intensity clearly increased, demonstrating the strong interaction between silver layer and -SH groups. The high-resolution Sn3d spectrum of the further sensitized ABS surface was also given (Fig. 5 (c)). The spectrum exhibits two peaks for the Sn3d5/2 and Sn3d3/2 with binding energies at 487.1 and 495.5 eV, respectively. It was suggested that the sensitizer was in the Sn²⁺ chemical state rather than Sn⁴⁺ for the in situ reduction of Ag⁺ by Sn²⁺³³. Fig. 5 (d) shows the high-resolution Ag3d spectrum of the silver decorated ABS surface. The spectrum exhibits two distinct primary peaks for the 3d5/2 and Ag3d3/2 binding energies. The two high intensity primary peaks with binding energy at 368.3 and 374.3 eV are associated with elemental Ag. The spin energy separation was identified as 6.0 eV, which further confirmed the presence of the silver in the metallic state (Ag⁰). The other two subpeaks located at 369.4 and 375.4 eV were attributed to the Ag-S bonds, suggesting that the thiol group bond with silver on the ABS surface. It was also indicated that the Ag⁰ peak was predominant over Ag-S peak. Thus, silver mainly existed in the metallic state. All of the above results confirmed that based on the hydrophilic groups of C-OH and C=O groups generated by plasma treatment, TES was grafted onto the ABS substrate with thiol groups on the surface, which could chemically conjunct with silver layer

Table 3 The effect of exposure time on C1s components of the plasma treated ABS substrate surface.

Plasma treatment time / min	C-C/C-H / % 284.8±0.1 eV	CN/C-OH / % 286.3±0.1 eV	C=O / % 288.6±0.1 eV
5	72.6	21.6	5.7
10	69.2	25.9	4.9
15	71.7	22.2	6.1
20	72.7	21.6	5.7
30	70.7	21.8	7.5

Fig. 6 Typical XRD patterns of the bare ABS surface and silver decorated ABS surface.

through Ag-S bond, and is also proposed as the interfacial adhesion enhancement layer^{34,35}.

Additionally, in order to study the effect of plasma pretreatment time on the final adhesion strength between the deposited electroless silver layer and the ABS substrate, the high-resolution C1s spectra of the ABS surface pretreated under different plasma exposure time were investigated and the curve fitting data are summarized in **Table 3**. As was described above, the C1s peak of the plasma ABS were fitted to three components of C-C/C-H, CN/C-OH (mainly C-OH) and C=O groups. The hydrophilic surface with hydroxyls was supposed to chemically conjunct with TES compound. It was indicated that with 10 min plasma treatment, the amount of the generated C-OH groups on the surface reached a maximum.

XRD patterns of the bare ABS surface and the silver decorated ABS surface are shown in **Fig. 6**. It can be seen that a broad peak at around 20° originates from the bare ABS surface. As for the silver decorated ABS surface, the peak around 20° decreases in strength, meanwhile, the characteristic peaks for crystalline metallic silver appear at 2θ=38.1, 44.2, 64.4, 77.3 and 81.4°, corresponding to (111), (200), (220), (311) and (222) planes, respectively^{36,37}. Ag₂O peaks were not observed in the diffraction patterns, indicating that the silver layer on ABS surface was not oxidized and mainly existed in the metallic state, which was also consistent with the XPS results.

3.3 Adhesion strength between the ABS surface and the silver layer

In order to estimate the adhesion enhancement quantitatively, adhesion strength measurements were performed using a standard peel test. The adhesion strength between the deposited electroless silver film and the ABS substrate was measured, and the effect of the plasma treatment time was evaluated. From five sample measurements, the average adhesion strength values of silver film on ABS were measured to be 9.4, 23.2, 14.1, 13.5, 12.7 N/mm for the silver decorated ABS sample with the plasma pretreatment time of 5, 10, 15, 20, 30 min, respectively (as is shown in Fig. 7). The adhesion strength reached a maximum by 10 min plasma pretreatment, which was up to 23.2 N/mm, and was considered to be the optimal pretreatment condition. As it was suggested by XPS results that the hydrophilic groups of C-OH and C=O groups were first introduced onto the ABS surface by plasma pretreatment, thus, TES could be grafted onto the ABS surface by Si-O bond based on the generated hydroxyl groups. Finally, TES modified ABS contains thiols (-SH) that could chemically conjunct with silver layer, hence resulting a strong adherence of silver film on ABS surface²¹⁾. It was also suggested by XPS results that under 10 min plasma treatment, the amount of the generated hydroxyl groups on the surface reached a maximum. Thus, it was inferred that the amount of TES compounds grafted onto the ABS surface reached a maximum with the maximum amount of thiols. Therefore,

Fig. 7 The effect of plasma treatment time on the adhesion strength between the silver layer and the ABS substrate.

Fig. 8 Top-view SEM images of the peeled surfaces, (a) the peeled ABS surface, (b) the peeled silver layer surface.

the adhesion strength under 10 min plasma pretreatment reached a maximum. Additionally, it was proposed that the prolonging of plasma pretreatment time could possibly result in excessive oxidation, thus, the ABS substrate surface became broken to some extent as the plasma pretreatment times was prolonged, and resulting in weak boundary layer for the further silver layer adherence. Fig. 8 also presents the top views of the peeled surfaces for the ABS side and the silver film side in the case of plasma treatment of 10 min. It could be obviously seen that the ABS surface was completely exfoliated, which also suggested the strong adhesion of silver layer to ABS surface.

4. Summary

In this work, an effective and environmentally silver spray electroless deposition was accomplished on ABS substrate, which was functionalized with a triazinedithiol compound TES via plasma pretreatment for the adhesion enhancement. The SEM and AFM results showed that a continuous, uniform and compact layer of silver layer was achieved. XRD patterns revealed that the silver layer deposited on ABS surface mainly existed in the metallic state. It was also proposed by XPS results that the functionalized ABS contains thiols that can chemically conjunct with silver layer, resulting in a high adhesion strength of silver layer on ABS substrate. The peel test also indicated that the obtained silver layer showed strong adherence. And the cohesive force between ABS and silver layer reached a maximum under plasma pretreatment by 10 min, which was up to 23.2 N/mm. The results of this study are encouraging, the spray electroless deposition approach reported here is expected to be possible with different metallization on various substrates. The triazinedithiol compound TES in this study can evolve as a promising alternative for toxic chromate-based treatment and also an effective interfacial adhesion enhancement layer.

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多官能性トリアジン化合物による樹脂上への無電解スプレー銀めっきに関する研究

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要 旨

プラズマ処理したABS樹脂を用い, その平滑表面に6-(3-トリエトキシシリルプロピルアミノ)-1,3,5-トリアジン-2,4-ジチオールモノナトリウム塩 (TES) を導入し, スプレー方式による無電解銀めっき性について検討した。XPSによりTES被膜の吸着と銀との反応を明らかにした。TES処理表面にはTESに特徴的なSi2pとS2p, 銀めっき処理後ABS表面にはS2pとAg3dが検出されTESのSH基とAgの結合を明らかにした。XRDからスプレー方式無電解銀めっきによって形成したABS樹脂上への銀皮膜がAg⁰の状態であることがわかった。SEMとAFMからTES改質表面において, スプレー方式無電解銀めっきによって銀皮膜は均一な表面を形成することを確認した。めっきは離試験から, プラズマ処理10分の場合, 銀めっき密着強度は最大23.2 N/mmとなった。

キーワード: トリアジンチオール, スプレー方式無電解銀めっき, 分子接合, エッチングレス