Connection of various materials via a junction technology is one of the most important basic techniques for making products. Recently, Kunio Mori and coworkers have proposed a new molecular junction technique which connects via chemical bonds using a molecular joining agent in place of the conventional adhesion junction technique using adhesives based on the principle of wettability. The molecular junction technique which operates by using molecular joining agents has very high reliability because its principle is based on the formation of chemical interfacial bonds, forming a joint between different materials with a molecule at the interfaces.

The molecular joining agents are chemical compounds having two type of functional groups which do not react with each other, for example including a combination of a thiol group and an ethoxysilyl group.

In the molecular junction technique between metals and epoxide adhesives using 6-(3-triethoxysilylpropylamino)-1,3,5-triazine-2,4-dithiol-monosodium salt (TES) as the molecular joining agent, it is important to understand which of the thiol groups and/or ethoxysilyl groups react with the metal surfaces. In this paper, the reaction of TES with metal surfaces is investigated to understand the relations between the amount of TES and reaction temperature, between the types and the amount of functional groups for S2p and Si2p peaks in XPS surface analysis, and between the type of functional groups and the reaction temperature.
3. Results and Discussion

As shown in Fig. 1, TES has two different functional groups, a thiol group and an ethoxysilyl group, which can react with metal oxides on various metal surfaces\(^7\). One of the two thiol groups in TES has a dissociation constant (pKa1) of about 5.5\(^8\) and a reactivity similar to organic acids. This value indicates that it should readily react with various metal oxides. On the other hand, the ethoxysilyl group reacts with inorganic OH groups\(^9\) which are contained in the metal oxides of metal surfaces to form methaloxane bonds\(^10,11\). The TES molecules are adsorbed on the metal surfaces after they are immersed in TES alcohol solution and contact with TES molecules. When the adsorbed TES molecules are heated at various temperatures, it is important to know which of the two functional groups reacts with metal surfaces in order to plan the design of the molecular junction. So, the reaction of adsorbed TES with metal surfaces was investigated below.

Figs. 2 and 3 show the effect of treatment temperature on the Si\(_{2p}\) and S\(_{2p}\) peak concentrations of metal surfaces linked with TES by treating with 0.1 wt% TES alcohol solution for 10 min at 20 °C. Here, the Si\(_{2p}\) and S\(_{2p}\) peak concentrations are detected as an elemental ratio concentration which is present up to 7 nm depth from the top surface since X-ray photo electron is irradiated at a 45° angle to the treated metal plates. Si\(_{2p}\) and S\(_{2p}\) peak concentrations on the TES linked to the metal surfaces after heating indicate the amount of reaction of TES with metal surfaces. TES films on the metal surfaces have a film thickness less than 7 nm and are considered to consist of one to three layers, since in the TES treatment of four types of metals, metal atoms were always detected by XPS measurement. In the TES treatment of metal surfaces such Al, Ti and Sn, Si\(_{2p}\) and S\(_{2p}\) peak concentrations increased with an increase in treatment temperature in the range 40 - 200 °C but for Fe plates the concentration first increased with treatment temperature, reached a maximum, and then decreased. The initial increase for Al and Ti follows a parabolic tendency and the reaction is predicted to be a general condensation type where reaction rate increases with temperature. A secondary increase for Sn plates appears near 100 °C. This is considered to be due to an additional reaction differing from the case of Al and Ti. In addition, for Fe plates, the decomposition of TES linked on Fe surfaces is considered to occur because Si\(_{2p}\) and S\(_{2p}\) peak concentrations decrease rapidly. As stated above, the reaction of TES with metal surfaces is influenced by the functional groups of TES and the type of metal.

Table 1 shows the results of resolution of functional groups for S\(_{2p}\) peak. Two peaks assigned to thiocarbonyl groups (C=S groups) and sulfonic groups (SO\(_X\) groups) on TES-linked Al and Ti surfaces were resolved. The C=S groups are

![Fig. 1](image1.png)

**Fig. 1** Structure of 6-(3-triethoxysilylpropylamino)-1,3,5-triazine-2,4-dithiol-monosodium salt (TES).

![Fig. 2](image2.png)

**Fig. 2** Effect of heating temperature on the S\(_{2p}\) concentration of metal surfaces heated after treatment with 0.1 wt% alcohol solution of TES for 10 min at 20 °C.

![Fig. 3](image3.png)

**Fig. 3** Effect of heating temperature on the Si\(_{2p}\) concentration of metal surfaces heated after treatment with 0.1 wt% alcohol solution of TES for 10 min at 20 °C.
Effect of heating temperature on the S2p concentration of metal surfaces treated with 0.1 wt% alcohol solution of TES for 10 min at 20 °C.

<table>
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<th>Temp. °C</th>
<th>Ti C=S</th>
<th>SOx</th>
<th>Fe C=S</th>
<th>SS</th>
<th>SOx</th>
<th>Al C=S</th>
<th>SOx</th>
<th>Sn-S</th>
<th>C=S</th>
<th>SS</th>
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</table>

References


Note


observed as a thione type on metal surfaces because TES is a tautomer existing as a thione type at a solid state and a thiol type in solution12). The formation of SOX groups is explained as being the result of the oxidation of thiol groups. The concentration of SOX groups decreased with increase in heating temperature for TES-adsorbed Al and Ti plates. In the case of TES-treated Ti surfaces, since the SOX group concentration is nearly constant in the temperature range 40 - 200 °C, the SOX salts of Ti are stable even at high temperature. In addition, since the SOX group concentration is always constant, it is possible that the SOX groups may already be contained in the source material (TES alcohol solution).

On the TES-linked Fe surfaces, three types of functional groups, namely C=S, Sn-S, SS and SOX groups were observed. The C=S and SOX groups are formed by the TES treatment of Sn plates and then Sn-S and SS groups are newly generated by the reactions of C=S groups with Sn plates and with oxygen in air. The former increased with an increase in treatment temperature and the latter decreased with an increase in treatment temperature. The decrease of SS group concentration with temperature is because SS groups are oxidized to SOX groups in air and decompose at high temperature.

On the TES linked Sn surfaces, four types of functional groups, namely C=S, Sn-S, SS and SOX groups were detected. The SS and SOX groups increased and the C=S groups decreased with the increase of temperature in the range 40 - 200 °C. As shown in Fig. 2, S2p peak concentration on the Fe surfaces decreases as the temperature increases as a result of the thermal decomposition of SOX groups.

The above changes of S2p and Si2p peak concentrations, functional group concentrations and types relate to ionization tendency series as described below; the ionization tendency increases in the order of Sn < Fe < Al < Ti. Ti and Al surfaces with a high ionization tendency are linked to TES by the reaction of ethoxysilyl groups of TES with inorganic OH groups on the metal oxide surfaces of metal plates. However, C=S groups react with metal oxides but do not produce mercaptide groups (Ti-S or Al-S). Fe surfaces with a moderate ionization tendency are also linked to TES by the reaction of ethoxysilyl groups of TES with inorganic OH groups on the metal oxide surfaces of metal plates. At the same time the C=S groups are oxidized to SS groups and finally SOX group. The SOX groups are released from the triazine ring of TES at a high temperature. Sn surfaces with a low ionization tendency are linked to TES after the reaction of ethoxysilyl groups of TES with inorganic OH groups on the metal oxide surfaces of metal plates. In addition, the C=S groups react with Sn oxides on Sn surfaces to form Sn-S groups. At the same time the C=S groups are oxidized to SS groups and subsequently SOX groups. The SOX groups are released from the triazine ring at low temperature.
6-(3-トリエトキシシルプロピルアミノ)-1,3,5-トリアジン-2,4-ジチオールモノナトリウム塩と金属表面の反応

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要　旨

Ti, Al, FeおよびSn等の金属と6-(3-トリエトキシシルプロピルアミノ)-1,3,5-トリアジン-2,4-ジチオールモノナトリウム塩（TES）のエトキシシル基およびチオール基の反応が研究された。金属の種類と加熱温度はイオン化傾向と関係して、エトキシシル基とチオール基の反応の種類に影響した。エトキシシル基はイオン化傾向の大きいレベル、中間レベルおよび小レベルの3タイプすべてと反応した。チオール基はスズ酸化フィルムと反応してSn-S結合法生成した。FeとSnは空気中でチオール基の酸化してSS結合法生成した。

キーワード：金属, 6-(3-トリエトキシシルプロピルアミノ)-1,3,5-トリアジン-2,4-ジチオールモノナトリウム塩, XPS表面分析, イオン化傾向列