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Preparation of Contaminant-free Copper Sulfide Surfaces for Adsorption Study of 2-methyl-2-butene

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1 Introduction

Adhesion between rubber and brass is one of subjects for research and development of automotive tires, because brass-plated steel cords are embedded in the tires to give a mechanical strength while maintaining flexibility. It has long been recognized that strong rubber-brass adhesion originates from the formation of a copper-sulfide layer at the rubber/brass interface. X-ray photoelectron spectroscopy and X-ray diffraction measurements have revealed the Cu-to-S ratio of 1.8 - 2 [1]. Our recent photoelectron spectroscopy study [2] have further shown that the copper-sulfide layer has a hierarchical structure; although CuS is a dominant species throughout the adhesion layer, Cu_xS ($x \simeq 2$) is formed with a relatively high density at the rubber side of the interface. The results of these studies imply that Cu_xS rather than CuS must be responsible for strong adhesion.

Two interaction mechanism between rubber and copper sulfide is proposed; one is the mechanical or physical interaction, which is realized by rubber penetration into dendrically structured copper sulfide to form tight interlocking, and the other is the chemical interaction by the formation of covalent bonds. With importance of the latter interaction in mind, the present study aims to shed the light on chemical bonding between rubber and copper sulfide at an atomic level so that a simple question why rubber-Cu_xS ($x \simeq 2$) bonding is stronger than rubber-CuS bonding will be answered.

2 **Experimental**

Our strategy to examine the chemical interaction at the rubber/copper sulfide interface is as follows. (1) 2-methyl-2-butene is used as a model molecule of rubber, since the molecule has a same structure as a part of rubber (*cis*-polyisoprene) as shown in Fig. 1. (2) CuS and Cu_2S pellets prepared by compressing high purity (99.99 %) powder of CuS and Cu_2S are used as substrates. (3) After cleaning the substrate surfaces using surface science techniques, the surfaces are exposed to vapor of 2-methyl-2-butene. (4) Chemical state analysis of Cu, S and C is carried out by photoelectron spectroscopy and X-ray absorption spectroscopy measurements.

3 **Results and Discussion**

Obtaining clean substrate surfaces is important so that we first examined whether the surfaces of the pellets can be chemically cleaned by annealing and Ar^+ sputtering while maintaining the chemical structure and composition of copper sulfides. Carbon is the main contaminant on the Cu_2S surface followed by oxygen as recognized in the Auger electron spectrum in Fig. 2. Ar^+ sputtering (2 and 3 keV, 60 min) and annealing (330°C, 60 min) completely remove the O atoms, whereas a small amount of C exits even after the extensive treatments. The Cu/S ratio is unchanged throughout the treatments, indicating no preferential sputtering, accumulation or desorption occurs. Valence band and S 2p core-level photoemission spectra (Fig. 2) have lineshapes characteristic of Cu_2S. Therefore, although there remains a small amount of C (less than 10% of the Cu atomic density), the contaminant-free Cu_2S can be obtained without changing the stoichiometry and atomic structure of Cu_2S.

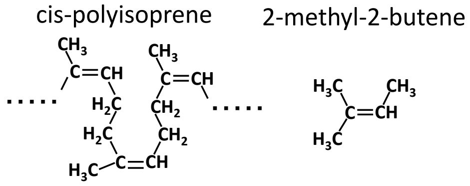

Fig. 1 Chemical formulas of *cis*-polyisoprene and 2-methyl-2-butene.

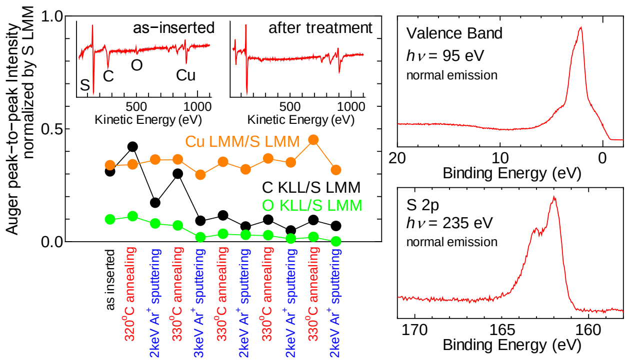

Fig. 2 (Left) Variation of the Auger peak-to-peak intensities normalized by the S LMM intensity, and Auger electron spectra before and after the cleaning treatments. (Right) Photoelectron spectra in the valence band and S 2p core-level regions of Cu_2S after the cleaning procedure.

Acknowledgement

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References

[1] B. Crowther (Ed.), "Handbook of Rubber Bonding" Para Technology Ltd., UK (2001).
[2] K. Ozawa *et al.*, *Appl. Surf. Sci.* **264**, 297 (2013); **268**, 117 (2013).

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