

Compositional Analysis on Epoxy-resin/inorganic Interfaces using Scanning Transmission Electron Microcopy

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Epoxy resins are widely used in adhesives and fiber-reinforced plastics owing to their excellent adhesive and workable properties. Because the adhesive strength between the epoxy resin and inorganic materials directly affects the fracture strength of composite materials, understanding the adhesion mechanisms and controlling the adhesive strength have been anticipated. Recently, it has been indicated that the compositional ratio between the main components of epoxy resin (epoxides and amines) varies at adhesive interfaces from those inside the epoxy resin region, resulting in different crosslinked structures at the adhesive interfaces [1-3]. However, detailed measurements have never been performed because measuring the compositional-ratio distribution at such “buried” interfaces at molecular scales is challenging. This study prepared the adhesive interfaces of an epoxy resin and two types of silicon substrates with different surface chemical states. These epoxy resin-silicon interfaces were analyzed using scanning transmission electron microscopy (STEM) and electron energy-loss spectroscopy (EELS) to elucidate the compositional distribution at the adhesive interfaces.

Diglycidyl ether of bisphenol A (DGEBA) (Mitsubishi Chemical Co., Ltd., Japan) and *para*-diaminodicyclohexylmethane (PACM) (Tokyo Chemical Industry Co., Ltd., Japan) were used as the epoxy-resin prepolymer and curing agent (Fig. 1). They were mixed so that the stoichiometric ratio of the epoxy groups to the active hydrogens of the amino groups becomes 1:1. (111) substrates of a high-purity silicon single crystal (>99.999%, Crystal Base Co., Ltd., Japan) were purchased. The organic residue on the surface was removed with piranha solution. Subsequently, hydrogen (H)-terminated surfaces were prepared with 1.5 wt% hydrofluoric acid for 30 min. Some of the H-terminated surfaces were processed by water vapor plasma to be terminated with hydroxyl (OH) groups. The water contact angles of the H- and OH-terminated surfaces were 79° and 0°, respectively. The mixture of DGEBA and PACM was pasted on these silicon substrates and then cured at 100 °C for 90 min. The thin cross-sectional samples of the epoxy resin-silicon interfaces were fabricated by a focused ion beam system NB5000 (Hitachi High-Tech Co., Japan). The cross-sectional samples of the adhesive interfaces were analyzed by annular dark-field STEM (ADF-STEM) and STEM-EELS using a transmission electron microscope JEM-ARM200F (JEOL Ltd., Japan).

The chemical structures of DGEBA and PACM are shown in Fig. 1. Because DGEBA contains aromatic rings in the molecular structure, the peak corresponding to the electron transition from the 1s to antibonding π orbital (π^* peak) appears at ~285 eV in the C-K absorption edge in EEL spectrum. On the other hand, PACM does not show the π^* peak in the C-K edge because it does not have π bonds in the

molecular structure.

Fig. 2(a) shows an atomic-resolution ADF-STEM image of the adhesive interface between the epoxy resin and OH-terminated silicon. The epoxy resin appeared to be darker than the silicon single crystal. An oxidized silicon layer with a thickness of 2~3 nm was found at the adhesive interface. Fig. 2(b) shows the C-K edge spectra, originating from the epoxy resin, measured at 0.5 nm intervals from the adhesive interface. The spectrum numbers 1 to 9 demonstrate the acquired positions in (a). The intensities of the C-K edge spectra were normalized so that the maximum intensities become equal. We note that C-K edge spectra were detectable inside the oxidized layer, although their absolute intensities become much smaller than those in the epoxy resin region. Furthermore, their fine structures revealed that the π^* peak became smaller inside the oxidized layer, suggesting that the compositional ratio of PACM to DGEBA became more significant in the vicinity of the adhesive interface than inside the epoxy resin region.

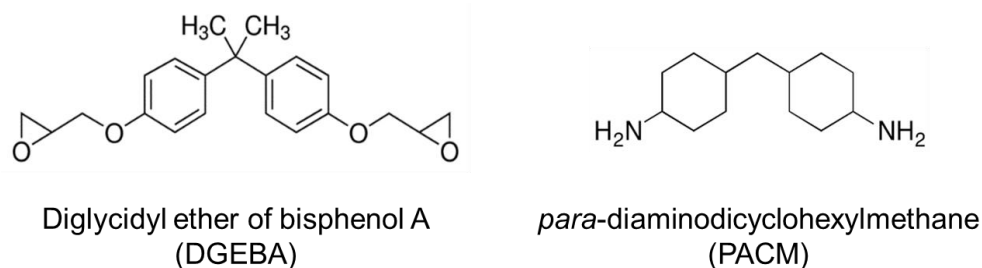


Figure 1. Molecular structures of DGEBA and PACM.

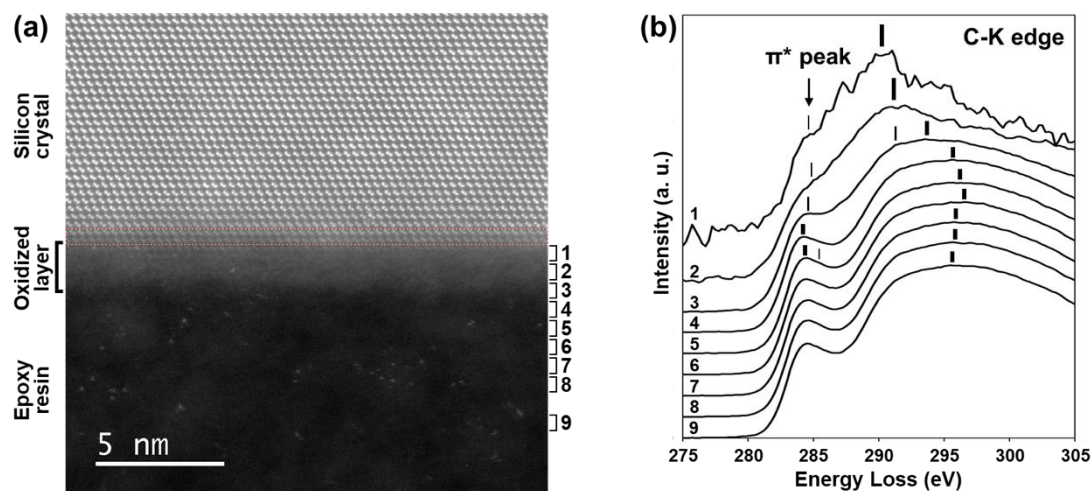


Figure 2. (a) ADF-STEM image and (b) C-K edge spectra of the epoxy resin-silicon interface.

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