Electronic Supplementary Information

Entropy-Driven Segregation in Epoxy-Amine Systems at a Copper Interface

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1. Orientational order parameter

To discuss the interfacial structure, a unit vector was defined for each molecule, and an orientational order parameter S was calculated by the following equation;

$$S = \left\langle \frac{3}{2}(n \cdot a_z)^2 - \frac{1}{2} \right\rangle \quad (1)$$

where **n** is a unit vector defined in a molecule, $\mathbf{a}_z$ is a unit vector normal to the solid surface, and the bracket denotes an average over both molecules and time. Fig. S1 shows the profiles of S for epoxy and amine in all combinations employed. Characters of L and S after a hyphen denote larger and smaller, respectively. The position was defined on the basis of the geometric center of a unit vector. Order parameters of both epoxy and amine were close to −0.5 near the solid interface, indicating that both molecules were oriented with their major axes parallel to the copper surface. In the internal region of the gap, the order parameters for epoxy and amine were almost 0, indicating that they were random in terms of the orientation.

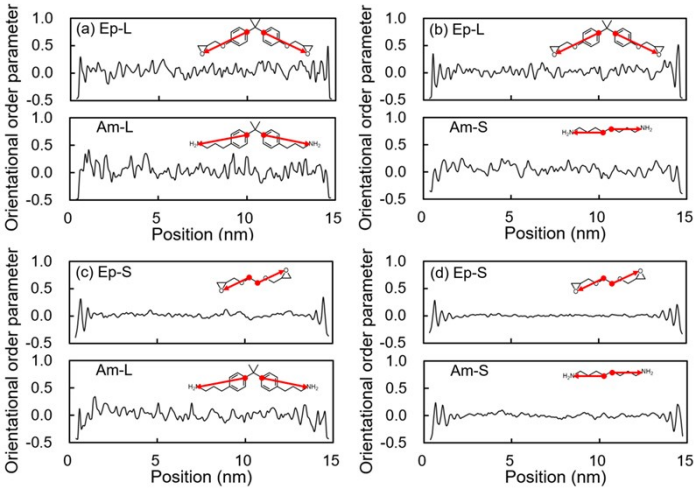

Fig. S1 Profiles of an orientational order parameter for epoxy and amine molecules in (a) Ep-L/Am-L, (b) Ep-L/Am-S, (c) Ep-S/Am-L, and (d) Ep-S/Am-S systems. A red arrow denotes a unit vector for each molecule.

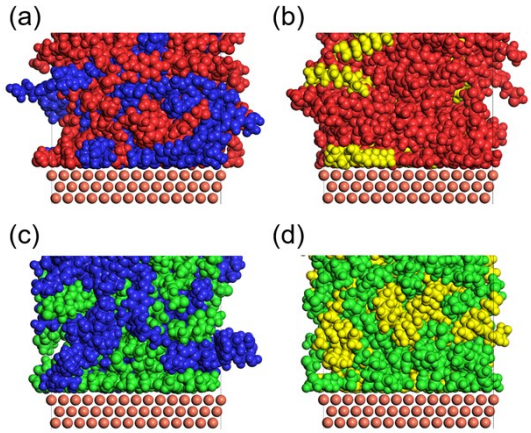

Fig. S2 Snapshots of molecules in the interfacial region for (a) Ep-L/Am-L, (b) Ep-L/Am-S, (c) Ep-S/Am-L, and (d) Ep-S/Am-S systems. Ep-L, Ep-S, Am-L, and Am-S are colored red, green, blue, and yellow, respectively.

Fig. S2 shows the representative snapshots in the interfacial region for the systems. Both epoxy and amine molecules were strongly oriented parallel to the wall near the interface.

Fig. S3 shows the *S* profiles for linear epoxy or amine in the combinations of linear- and round-shaped molecules. In all cases, the order parameters of linear molecules were close to − 0.5 near the solid interface, indicating that they were oriented with their major axes parallel to the copper surface. On the other hand, the values in the internal region were almost 0. That is, they were randomly oriented.

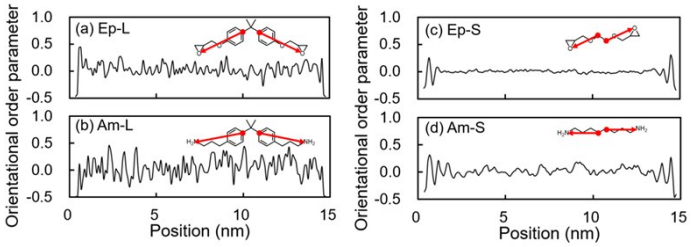

Fig. S3 Profiles of an orientational order parameter for linear-shaped molecules in (a) Ep-L/Am-L(r), (b) Ep-L(r)/Am-L, (c) Ep-S/Am-S(r), and (d) Ep-S(r)/Am-S systems.

Fig. S4 shows the representative snapshots in the interfacial region for the systems. Linear-shaped molecules were oriented parallel to the wall near the interface. On the other hand, round-shaped ones were not tightly packed at the interface due to the geometric shape.

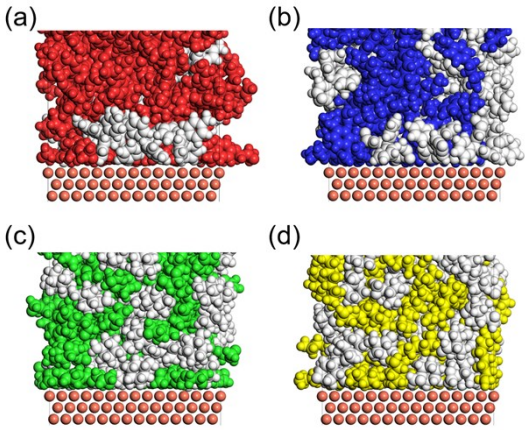

Fig. S4 Snapshots of molecules in the interfacial region for (a) Ep-L/Am-L(r), (b) Ep-L(r)/Am-L, (c) Ep-S/Am-S(r), and (d) Ep-S(r)/Am-S. Ep-L, Ep-S, Am-L, and Am-S are colored red, green, blue, and yellow, respectively. Round-shaped molecules are colored white.

2. A quaternary mixture system

Fig. S5 shows the density profile for a quaternary mixture of Ep-L/Ep-S/Am-L/Am-S as a function of the position from the copper interface with a sampling interval of 0.05 nm. The density increased near the interface as similar to the binary mixtures.

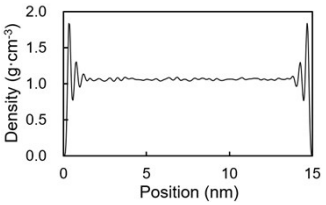

Fig. S5 Density profile of epoxy-amine mixtures along the direction perpendicular to the copper interface for the all mixture system. The position 0 and 15 nm correspond to the bottom and top interfaces, respectively.

Fig. S6 shows the relative number density of epoxy (Ep-L and Ep-S) and amine (Am-L and Am-S) molecules. It seems that the stoichiometric ratio is maintained even near the interface.

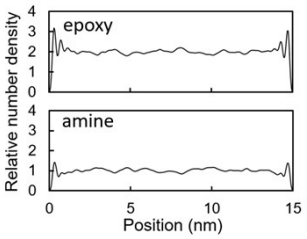

Fig. S6 Relative number densities of epoxy and amine molecules for the all mixture system. Initial relative number densities were 2 for epoxy and 1 for amine.

3. Binary mixture systems after the curing reaction

Fig. S7 shows the density profiles of the binary systems after the curing reaction. The density increase and oscillation were observed as similar to the initial structure before the curing reaction.

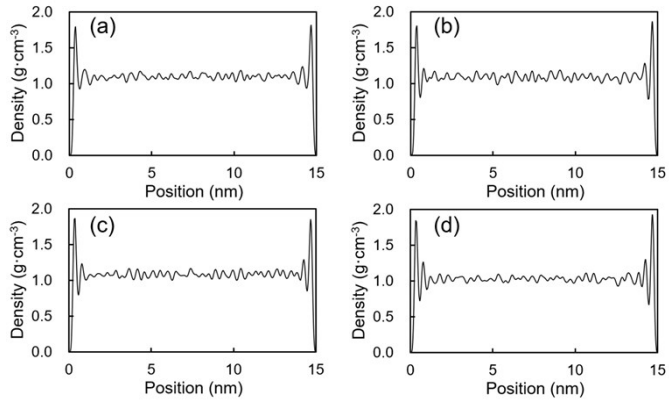

Fig. S7 Density profile of epoxy-amine mixtures along the direction perpendicular to the copper interface after the curing reaction; (a) Ep-L/Am-L, (b) Ep-L/Am-S, (c) Ep-S/Am-L, and (d) Ep-S/Am-S. The position 0 and 15 nm correspond to the bottom and top interfaces, respectively.

Fig. S8 shows the relative number density of epoxy and amine molecules for the binary systems after the curing reaction. The similar profiles to the initial structure remained even after the curing reaction.

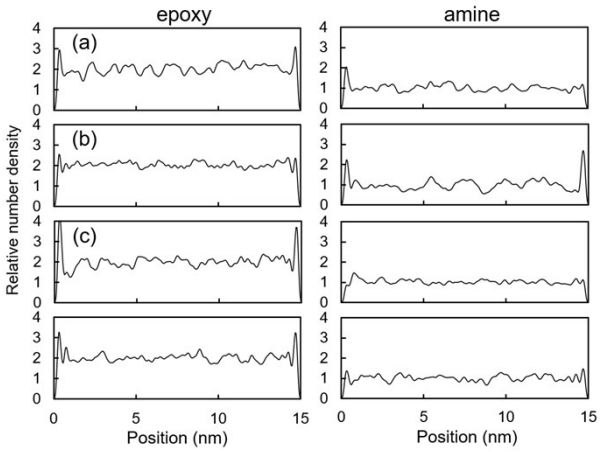

Fig. S8 Relative number densities of epoxy and amine molecules after the curing reaction; (a) Ep-L/Am-L, (b) Ep-L/Am-S, (c) Ep-S/Am-L, and (d) Ep-S/Am-S. Initial relative number densities were 2 for epoxy and 1 for amine.

Fig. S9 shows the molecular ratio for the binary systems after the curing reaction, obtained from Fig. S8. The molar ratio of amine to epoxy was 0.5 on average in the internal region, meaning that there stoichiometrically existed the both. In panel (c), The molar ratio of epoxy to amine was inserted, which is the opposite to the main panel, and in this case the stoichiometric value is supposed to be 2.0 on average. These profiles are similar to the initial ones before the curing reaction.

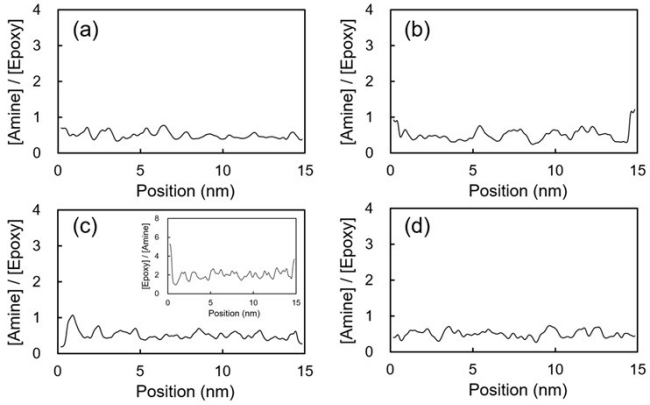

Fig. S9 Molar ratios of amine to epoxy after the curing reaction; (a) Ep-L/Am-L, (b) Ep-L/Am-S, (c) Ep-S/Am-L, and (d) Ep-S/Am-S mixtures with a bulk ratio of 0.5. In panel (c), the inverse molar ratio of epoxy to amine was inserted, in which a bulk ratio is 2.0 on average.

Fig. S10 shows the relative concentration of primary, secondary, and tertiary amines for the binary systems after the curing reaction. The unreacted primary amine was localized in close proximity to the interface for all systems.

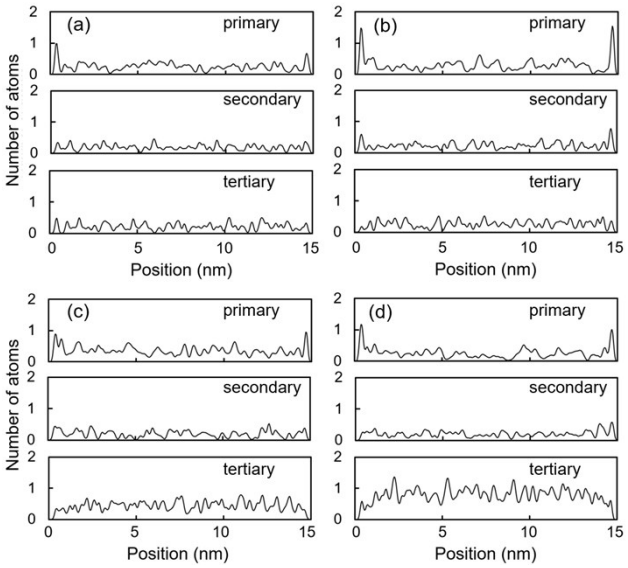

Fig. S10 Distribution of primary, secondary, and tertiary amine after the curing reaction; (a) Ep-L/Am-L, (b) Ep-L/Am-S, (c) Ep-S/Am-L, and (d) Ep-S/Am-S.

Fig. S11 shows the reaction conversion profiles. As a general trend, the conversion was lower in the interfacial region than in the internal one. This was more striking in panel (d).

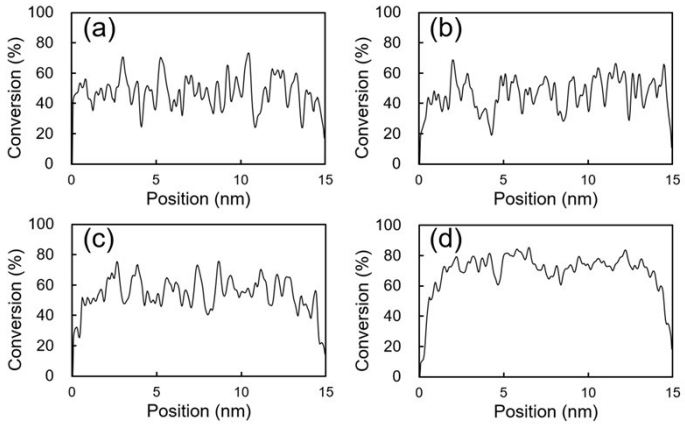

Fig. S11 The depth-dependent reaction conversion for (a) Ep-L/Am-L, (b) Ep-L/Am-S, (c) Ep-S/Am-L, and (d) Ep-S/Am-S systems.