NOTE

Segregation of an amine component in a model epoxy resin at a copper interface

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Introduction

An epoxy resin, which is based on network formation *via* curing reactions of epoxy and amine compounds, is an important class of thermoset resins. Such a resin is used in a wide range of applications such as coating agents [1], adhesives [2], encapsulants [3] and so forth [4] due to good processability, corrosion resistance, electronic insulation and mechanical properties. In most situations, it is used in contact with a solid, meaning that the contact interface is buried in the material. The "buried" interface often plays an essential role in the material performance [5]. One such example can be seen for flip-chip microelectronic packaging, in which the epoxy resin is used as an electronically insulating underfill adhesive. In this case, the interface between the epoxy resin and a metal layer, usually copper, is considered as a significant factor for long-term durability [6]. Thus, a great deal of effort has been devoted to gaining a better understanding of the structure and physical properties of the epoxy resin at the interface contacted with metals [7, 8].

Recently, it has been pointed out that the physical properties of epoxy resins at the solid interface are much different from those in the internal bulk region [7]. For example, a hardening layer exists in close proximity to the metal interface. Postulating that the stiffness of the epoxy resin depends on the stoichiometric balance of epoxy and amine components, the abovementioned result implies that the chemical composition in the resin should be heterogeneous along the direction normal to the interface. Additionally, the initial reaction kinetics for the epoxy and amine components are slower near the solid substrate than in the bulk region [9]. This may lead to a difference in network structure and, thereby, a difference in mechanical properties at the interface [10].

Fourier transform infrared (FTIR) and X-ray photoelectron spectroscopy (XPS) are well-established techniques for characterizing the chemical composition in the epoxy resin. However, these techniques may not be simply applicable to the buried interface. Thus, in general, the interface is supposed to be peeled off from the material and then characterized [11]. If in situ characterization is necessary, the most suitable technique should be sum-frequency generation (SFG) vibrational spectroscopy [12–15]. SFG based on a nonlinear optical effect enables us to gain direct access to the structural information for substances at the surface and/or interface, where the centrosymmetry is broken, at the molecular level [12, 15]. However, it is experimentally difficult to examine the depth profile for the chemical composition along the direction normal to the interface using SFG.

The objective of this study is to examine the chemical composition of the epoxy resin in close proximity to the copper interface in a nondestructive way. We believe that both the structural information as well as the experimental protocol will contribute to the development of polymer materials including adhesives and polymer devices. A bilayer sample of epoxy resin and copper was first prepared on a solid substrate, and the top copper layer was then etched just before the interface using argon-ion (Ar⁺) beams. Next, angular-dependent X-ray photoelectron spectroscopic (ADXPS) measurement, in which an X-ray was guided into the epoxy resin through the ultrathin copper layer, revealed that the amine component was preferentially segregated at the copper interface, with the segregation

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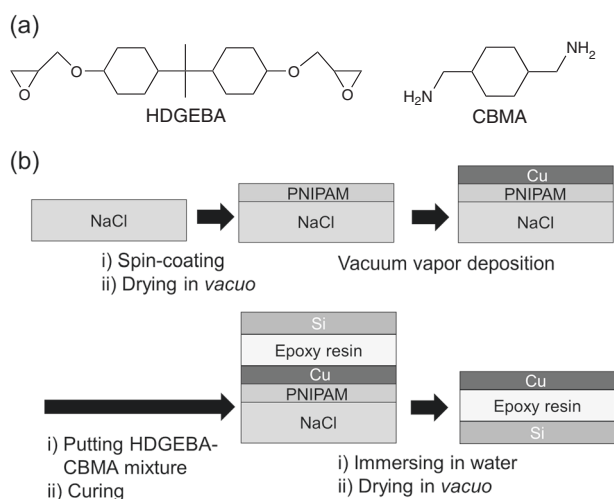
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(a)

HDGEBA

CBMA

(b)

i) Spin-coating
ii) Drying in *vacuo*

Vacuum vapor deposition

i) Putting HDGEBA-
CBMA mixture
ii) Curing

i) Immersing in water
ii) Drying in *vacuo*

Fig. 1 a Chemical structures of HDGEBA and CBMA. **b** Schematic illustration showing a pathway to prepare a (copper/epoxy resin) bilayer supported on a silicon wafer

extending over several nanometers. Finally, SFG was also applied to the interface to strengthen the above observation.

Experimental procedure

Figure 1a shows the chemical structures of hydrogenated bisphenol-A diglycidyl ether (HDGEBA) and 1,4-cyclohexanebis(methylamine) (CBMA) purchased from New Japan Chemical Co., Ltd. and Tokyo Chemical Industry Co., Ltd., respectively. Poly(N-isopropylacrylamide) with a number-average molecular weight of 106k (PNIPAM) was purchased from Sigma-Aldrich Co. LCC. and used as a sacrificial layer as shown later. Dehydrated tetrahydrofuran (THF) was purchased from Wako Pure Chemical Industries, Ltd. All reagents were used as received. Water was obtained after distillation with an Autostill WA33 (Yamato Scientific Co., Ltd.) and successive deionization with a Milli-Q Lab (Merck KGaA). A copper wire (99.999% in purity) purchased from The Nilaco Co. was used for the vacuum deposition. A half-cylinder quartz prism and quartz window were purchased from DAICO MFG Co., Ltd. A sodium chloride (NaCl) window and a silicon (Si) substrate were purchased from Pier Optics Co., Ltd. and SUMCO Co., respectively.

Panel b of Fig. 1 shows a schematic illustration for the preparation of a (copper/epoxy resin) bilayer film supported on a Si substrate for the ADXPS measurements. First, a film of PNIPAM was prepared from a 2 wt%-THF solution on a NaCl plate by a spin-coating method. The film was dried at 433 K for 24 h in a vacuum oven. Second, copper was deposited onto the PNIPAM film surface with a vacuum deposition system, VPC-410 (ULVAC KIKO, Inc.) under a base pressure of 4×10^{-4} Pa. The thickness and root-mean

square roughness of the copper layer so prepared was ca. 30 and 1.1 ± 0.2 nm, respectively. Third, a mixture of HDGEBA and CBMA with a molar ratio of 2:1 was placed onto the copper layer and then covered with the Si substrate. The mixture was cured at 296 K under a nitrogen atmosphere. After 24 h, a layer of epoxy resin with a thickness of ca. 35 μm was formed. Finally, the (copper/epoxy resin) bilayer film on the Si substrate was obtained by dissolving NaCl and PNIPAM into pure water followed by drying at 296 K for 24 h in the vacuum oven.
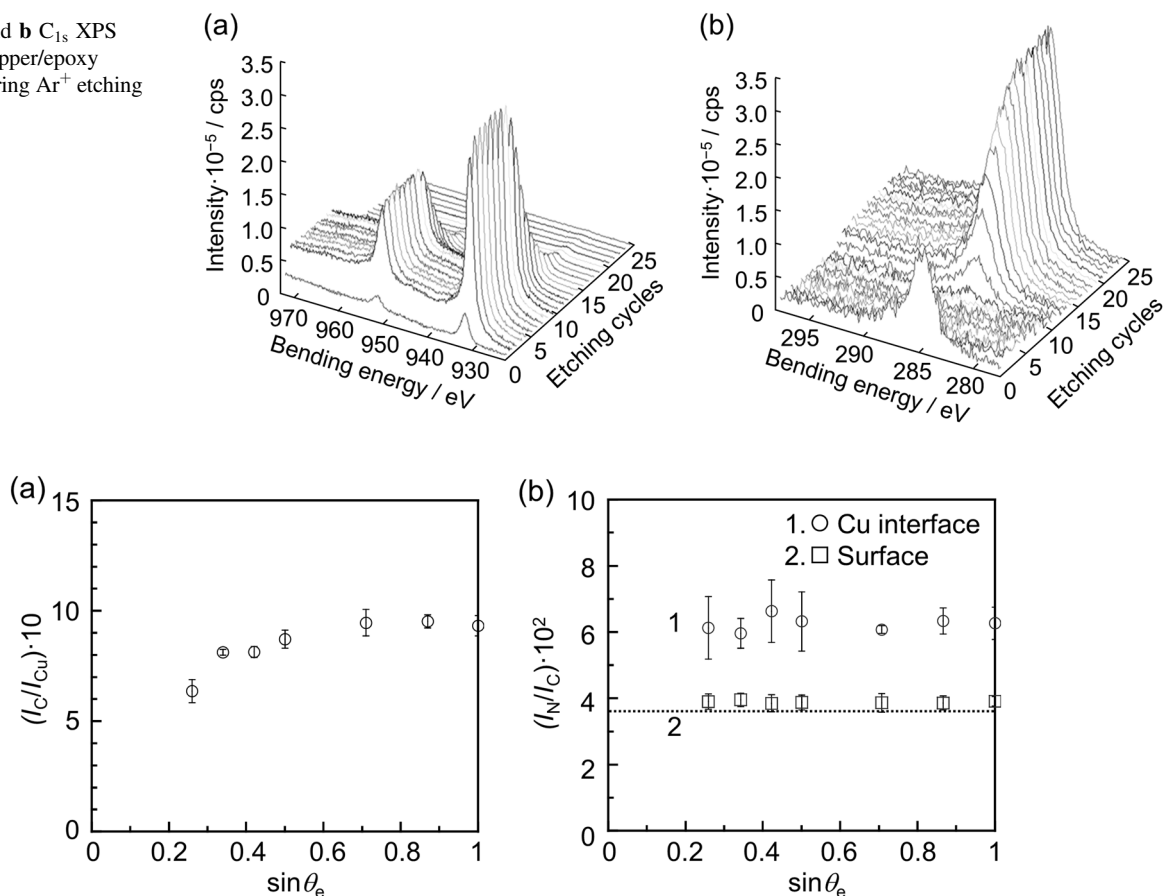
The (copper/epoxy resin) bilayer film was subjected to ADXPS. Prior to the measurements, the copper layer was etched just before the interface with Ar$^+$ beams (PHI5000 VersaProbe II, ULVAC-PHI, Inc.). The etching area and rate were 2×2 mm^2 and 2.8 nm min^{-1}, respectively. During the etching cycles, the change in XPS spectra was monitored at an emission angle (θ_e) of 45°. The chemical composition of the epoxy resin in close proximity to the copper interface was examined by ADXPS (PHI5000 VersaProbe II, ULVAC-PHI, Inc.) with a monochromatized Al Kα source operated at 15 kV and 25 W. The C_{1s} peak was calibrated to a binding energy of 284.8 eV for neutral carbons, to correct for charging energy shifts. The XPS spectra were collected at various θ_e values ranging from 15° to 90°. The analytical depth (d) for the XPS for the outermost surface is defined by $3\lambda \cdot \sin \theta_e$, where λ is the inelastic mean-free path of the photoelectrons in the resin. The λ values for C_{1s}, N_{1s}, and Cu_{2p} photoelectrons were taken as 3.2, 2.9, and 2.1 nm, respectively [16].

For the measurement, the mixture of HDGEBA and CBMA with a molar ratio of 2:1 was placed on a half-cylinder quartz prism, onto which a copper layer was deposited before being covered with a copper-coated quartz substrate in a face-to-face geometry. Thus, the epoxy resin had only the copper interface. The mixture was cured at 296 K for 24 h under a nitrogen atmosphere. As references, individual HDGEBA and CBMA specimens were also prepared following the same procedure. The SFG spectra were collected with 532 nm visible and tunable IR beams from an EKSPLA system [15] traveling through the prism and overlapping at the (copper/epoxy resin) interface. The intensity of the SFG signals was normalized to those of the original IR and visible beams. The measurements were carried out at room temperature using polarization combinations of *ppp* (SFG output, visible input, and infrared input).

Results and discussion

The chemical composition of the resin near the buried copper interface was examined by ADXPS, in which an X-ray was guided into the underneath resin through the upper copper layer. Since the copper layer was much thicker than

Fig. 2 a Cu_{2p} and **b** C_{1s} XPS spectra for a (copper/epoxy resin) bilayer during Ar^+ etching cycles


Fig. 3 Sin θ_e dependence of the XPS peak intensity ratio of **a** C_{1s} to Cu_{2p} (I_C/I_{Cu}) and **b** N_{1s} to C_{1s} (I_N/I_C) for the (copper/epoxy resin) bilayer and the epoxy resin layer on a Si wafer

the travel distance for C_{1s} photoelectrons, it was first etched as stated in the Experimental procedure's section. During etching, the time course change in the XPS spectra was monitored at a θ_e of 45°. Figure 2 shows the (a) Cu_{2p} and (b) C_{1s} core level spectra as a function of etching cycle. In the beginning, two peaks arising from the 3/2 and 1/2 spin orbit components of Cu_{2p} were observed. At the same time, the C_{1s} peak was also observed, implying that a residual layer of PNIPAM, which could not dissolve into water even at room temperature, existed on the copper surface [17]. After a while, the Cu_{2p} peaks intensified due to the removal of the PNIPAM layer. As the etching proceeded, these peaks started to decrease. Concurrently, the C_{1s} peak became more remarkable. These spectral changes clearly correspond to a thinning of the copper layer. The etching was truncated at a time when the Cu_{2p} peak intensity reached 6% of the maximum. Based on the etching rate and total time, the thickness of the remaining copper layer on the epoxy resin was estimated to be 1.7 nm.

To address the chemical composition in the epoxy resin in the interfacial region with copper, ADXPS measurements were made. Panel a of Fig. 3 shows the sin θ_e dependence

for the peak intensity ratio of C_{1s} to Cu_{2p} (I_C/I_{Cu}). A small sin θ_e value corresponds to a shallower analytical depth from the outermost region. The I_C/I_{Cu} value decreased with decreasing sin θ_e. This observation makes it clear that more copper exits in the outermost region of the sample. Taking into account the bilayer structure composed of copper and epoxy resin, this trend is quite reasonable. Figure 3b shows the peak intensity ratio of N_{1s} to C_{1s} (I_N/I_C) as a function of sin θ_e. Since nitrogen atoms exist only in CBMA, the I_N/I_C ratio reflects the relative concentration of CBMA in the epoxy resin. Here, the experimental data obtained for the epoxy resin on the Si substrate were also shown as a reference representing the epoxy surface. For the epoxy surface, the I_N/I_C value seems to be independent of sin θ_e and identical to the value of 3.6×10^{-2} calculated on the basis of the bulk composition of HDGEBA and CBMA. This result makes it clear that the chemical composition in the analytical depth region determined by XPS is almost the same as that in the bulk.

On the other hand, the I_N/I_C value near the copper interface was greater than the bulk value. The averaged I_N/I_C value over sin θ_e was 6.2×10^{-2}. This number
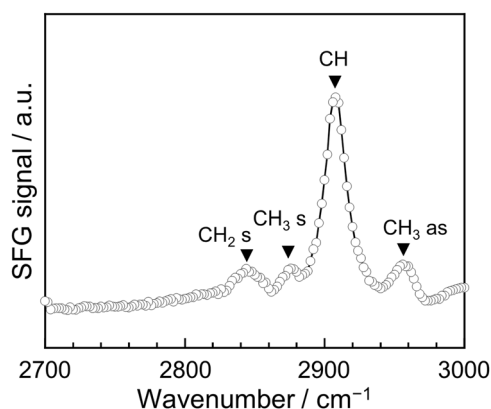
Fig. 4 SFG spectrum in the C–H stretching region for the (copper/epoxy resin) interfaces using a *ppp* polarization combination

corresponds to an HDGEBA/CBMA molar ratio of 1:1, meaning that the CBMA concentration in the interfacial region was two-fold higher than that in the bulk. In addition, this number remained unchanged over the entire $\sin \theta_e$ range. Taking into account $d = 3\lambda \cdot \sin \theta_e$, the x-axis of Fig. 3 can be converted to a depth range of 2.5–9.5 nm from the outermost surface. Thus, it is most likely that CBMA molecules were preferentially segregated to the copper interface, with the interfacial segregation of CBMA extending over at least ~9.5 nm. This result is consistent with the previously reported result that the interfacial depth region with a higher stiffness in an epoxy film extends over several hundreds of nanometers [7].

To examine the aggregation states in the epoxy resin, an SFG measurement was made. Figure 4 shows the SFG spectrum for the (copper/epoxy resin) interface with the *ppp* polarization combination. With this polarization combination, functional groups oriented along all directions can be detected [12, 15]. Three small peaks were observed near 2845, 2880, and 2960 cm^{-1}. They can be assigned to the symmetric C-H stretching vibration ($\nu_{s,CH2}$) of methylene groups in cyclohexane rings [13] and the symmetric and antisymmetric C–H stretching vibrations of methyl groups ($\nu_{s,CH3}$ and $\nu_{as,CH3}$), respectively [8]. Taking into account that methyl groups exist only in HDGEBA, the SFG spectrum indicates the existence of HDGEBA components at the (copper/epoxy resin) interface. Here, it should be noted that the $\nu_{s,CH2}$ peak position was not the same as that for HDGEBA but close to that for CBMA. The wavenumbers for the former and latter were 2855 and 2845 cm^{-1}, respectively. Comparing the $\nu_{s,CH2}$ peak position among the three specimens of HDGEBA, CBMA, and epoxy resin, it can be claimed that CBMA components were also present at the (copper/epoxy resin) interface. In addition, a sharp and intense peak appeared at 2910 cm^{-1}, where any peaks were observed for HDGEBA and CBMA. This peak is assignable to the C–H stretching

vibration of methyne groups next to hydroxyl groups, which are generated after the epoxy-amine reaction. Thus, it can be claimed that the epoxy-amine reaction proceeded at the copper interface.

Finally, we discuss a possible formation mechanism for the CBMA-enriched layer at the copper interface. If the layer formation results from preferential interfacial segregation of CBMA due only to the surface energy difference in the two components, the thickness should be on the order of the concentration fluctuation, or molecular size of the components. As aforementioned, however, the interfacial segregation of CBMA extends over approximately 10 nm. Thus, the simple energy difference in the two components can be excluded as the reason for the layer formation. When an attractive interaction exists between a component and the substrate surface, an interfacial segregation layer can also be formed [11, 17]. Previously, it has been reported that copper ions diffused out from the metal copper into the epoxy and amine mixture and reacted with amine to form complexes by coordination [18]. In fact, using dynamic secondary ion mass spectroscopy, it was found that copper species deeply migrated into a polymer phase across the copper interface [19]. Additionally, energy dispersive X-ray spectrometry for a cross-section of the epoxy resin contacted with the copper substrate revealed that copper species in the resin existed within a region of 20–120 nm from the substrate [20]. Thus, at present, it seems most likely that the interfacial enrichment of CBMA observed in this study originates from preferential adsorption onto the copper substrate due to the attractive interaction followed by the complex formation.

Conclusions

We have studied the chemical composition of the epoxy and amine components, HDGEBA and CBMA, of an epoxy resin in close proximity to a copper interface by using ADXPS in conjunction with SFG vibrational spectroscopy. A bilayer sample of epoxy resin and copper was first prepared on a solid substrate before etching the copper layer just before the interface with Ar$^+$ beams. Using ADXPS, in which an incident X-ray was guided from the copper surface, it was found that the CBMA component was preferentially segregated at the copper interface, with the segregation extending over ~10 nm. SFG spectroscopy was used to confirm the above observation. Postulating that copper ions diffused from the metal copper into the internal phase during the curing process and reacted with amine groups to form copper complexes, the interfacial segregation of CBMA can be understood. This knowledge should be useful for understanding and controlling the adhesive properties of epoxy resins.

Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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