Supporting Information for

Heterointerfacial adhesion failure mechanism of ultrahigh filler loading containing epoxy composite films for chip substrates

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Figure and Table:

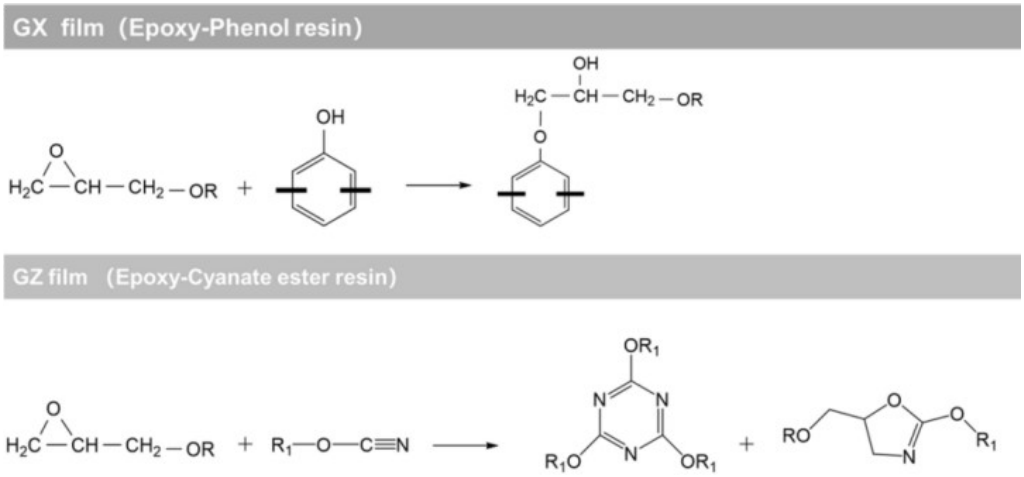


Fig.S 1 Curing mechanism of epoxy-phenolic/silica and epoxy-cyanate ester/silica composites

Fig.S 2 EDS of Pd element on the surface of ABF

Fig.S3 shows the microstructure SEM images of the GX film at different desmear processes. Fig.S3a shows the SEM image of ABF surface after swelling at 70 ℃ for 10 min, and we can observe that there are many swellings in comparing to initial state. This result is mainly attributed to that a large number of solvent molecular enter the interior of the film surface and undergo swelling. Subsequently, after swelling the sample is immersed in potassium permanganate solution to clear epoxy resin on the surface of film by oxidation. Fig.S3b shows that the surface of ABF is not smooth, and epoxy resin from the film surface was oxidized and cleared after oxidation. As a result, the surface roughness of films is increased and at the same time some spherical silica particles is exposed on the surface of the sample. Immediately after, the oxidized surface is cleared by many times, and then it continued the activation process to adsorb palladium ions on the surface and enhance the ability of copper plating. Fig.S3c shows SEM image of film surface after activation. It was found that some soft epoxy resin and spherical silica particles on the surface of ABF were removed and while hard epoxy resins and SiO2 particles are exposed on the film surface. Meanwhile, EDS result also indicates that there is very low loading content in palladium ions because it plays a role in catalyst (See Fig.S2). After activation, the ABF surface will deposit copper layer by electroplating and electroless plating processes to obtain copper layer. Fig.S3d shows SEM image of ABF surface after peeling. It was clearly observed that the following three results: one is that there is an obvious increase in roughness compared with that of other three states; other is that most of the silica particles is embedded inside the epoxy resin; three is that there exist some gaps between epoxy resin and silica particles.

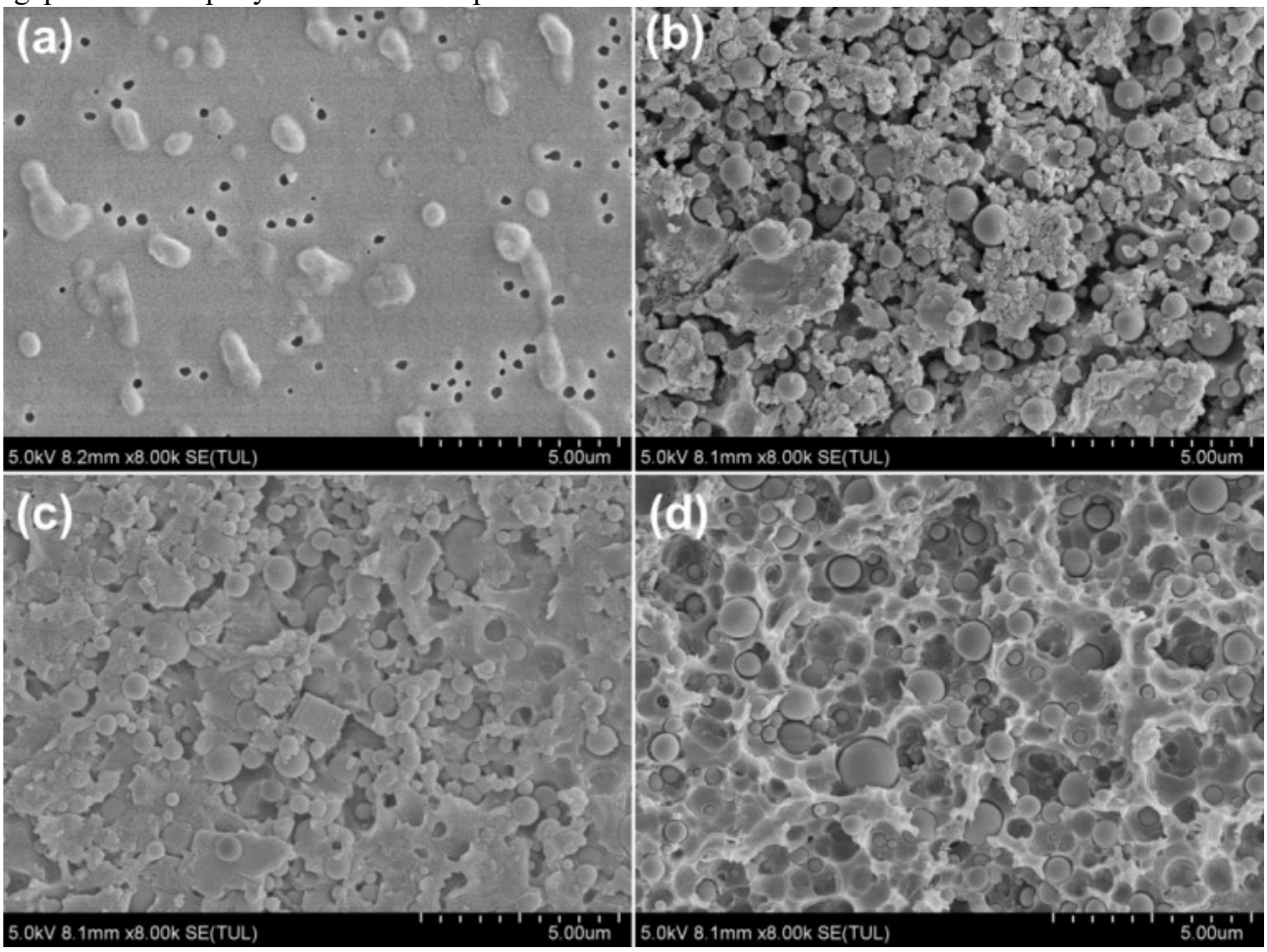


Fig.S 3 SEM images of the GX film at different desmear process: (a) swelling; (b) desmear; (c) activation; (d) after peeling

Fig.**S4** shows the microstructure SEM images of the GZ film at different desmear processes. In comparing to GX film, the GZ film has a higher loading content of silica particles and has a huge difference in chemical structure, which resulting in an obvious different in desmear effect. Fig.**S4**a shows the SEM image

of the film surface after swelling at 70 ℃ for 10 min, and we can see that there are many swellings in comparing to initial state. This result is mainly attributed to that a large number of solvent molecular enter the interior of the surface ABF and undergo swelling. At the same time, we can also found that compared with GX film, the size of swelling of the GZ film is obvious smaller after swelling, and meanwhile silica particles are easier to observe on the surface of films, which indicates that the GZ film may has a high difficulty in swelling and desmear process. Subsequently, after swelling the sample is immersed in potassium permanganate solution to clear epoxy resin on the surface of films by oxidation, Fig.**S4**b shows that the smooth of ABF surface is lightly decreased, and a small portion of epoxy resins from the film surface was oxidized and cleared after oxidation. As a result, the roughness of films is increased, and at the same time some spherical silica particles are obviously exposed on the surface of ABF, but its effect of oxidation is also significantly lower than the former. Immediately after, the oxidized surface is cleared by many times, and then it continued the activation process to adsorb palladium ions on the film surface and enhance the ability of copper plating. Fig.**S4**c shows SEM image of film surfaces after activation. It was found that some soft epoxy resin and spherical silica particles on the surface of films were removed and while hard epoxy resins and are exposed on the film surface. Meanwhile, we can also found that there are some areas that are flat, and some areas are dent, this conclusion confirms the analytical view point of the two adhesive removal processes mentioned above. After activation, the film surface will deposit copper layer by electroplating and electroless plating processes to obtain copper layer. Fig.**S4**d shows SEM image of the film surface after peeling. It was clearly observed that the following three results: one is that there is an obvious increase in roughness compared with that of other three states; other is that most of the silica particles is embedded inside the epoxy resin; three is that there exist some gaps between epoxy resin and silica particles.

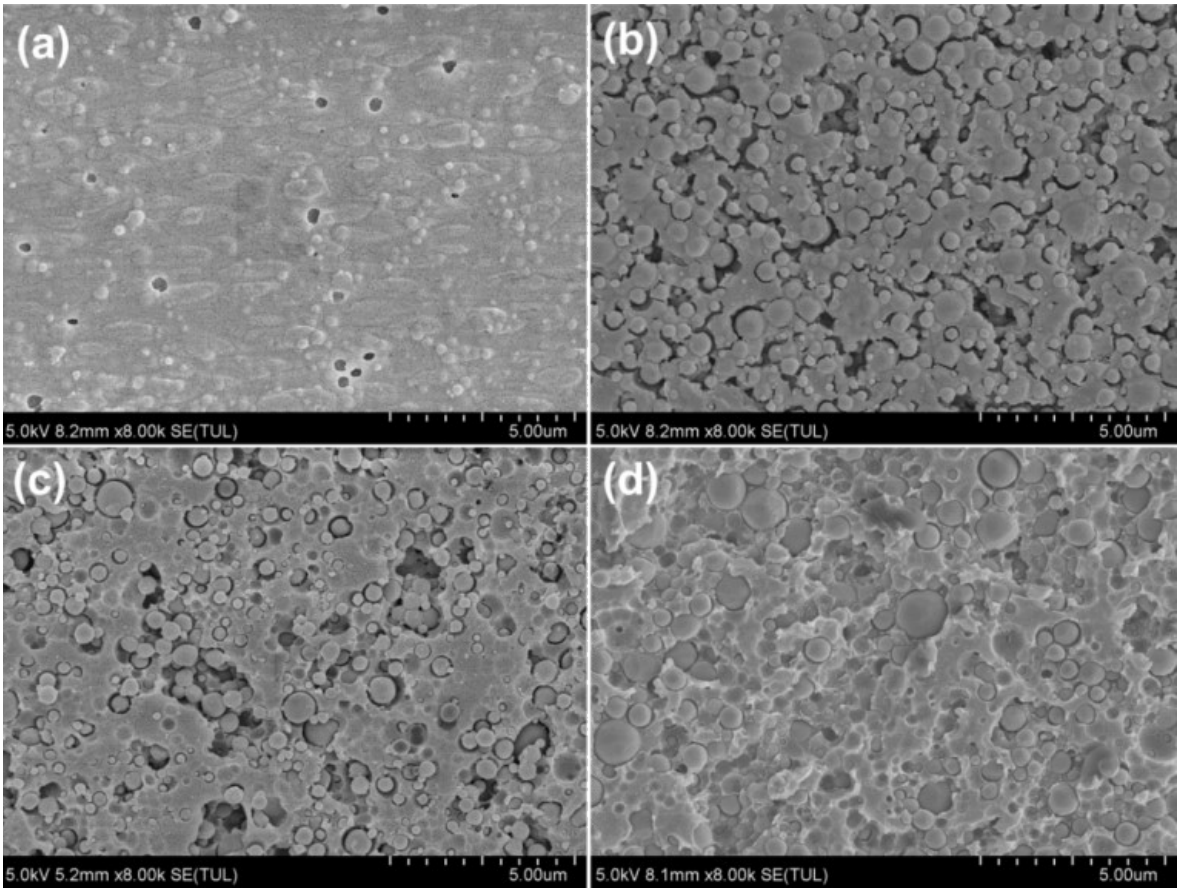
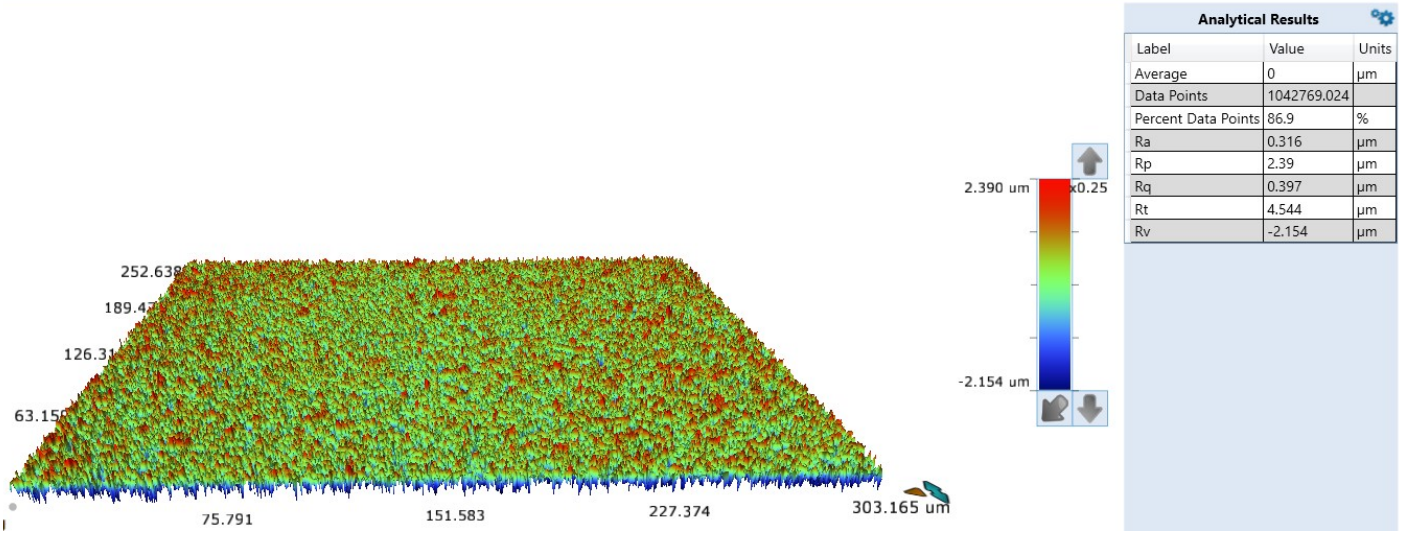
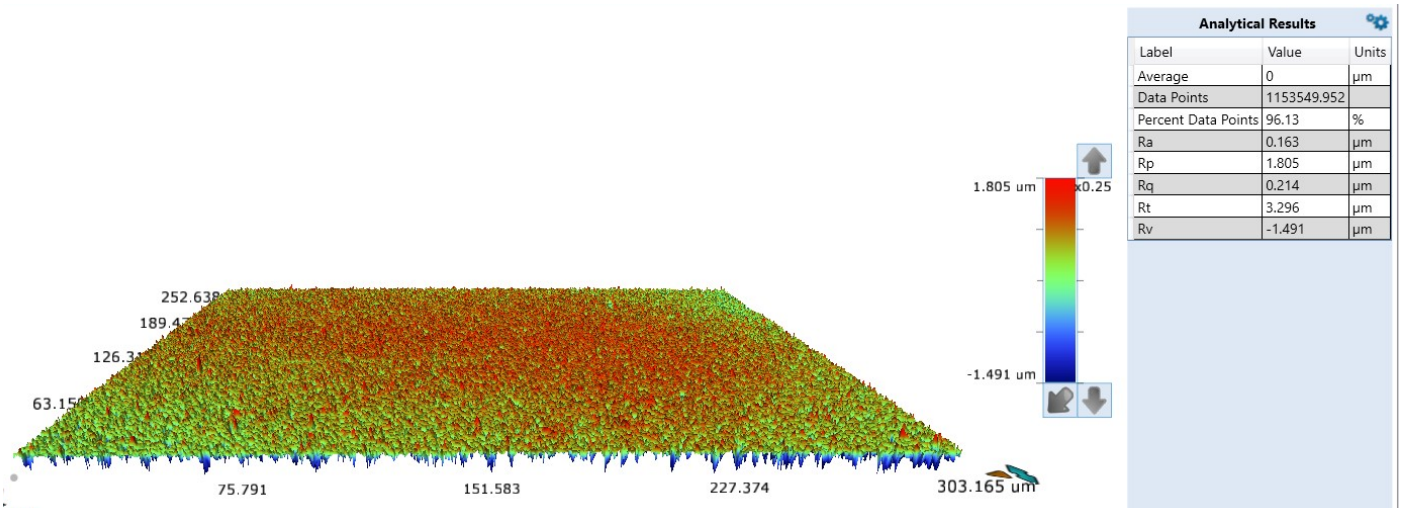


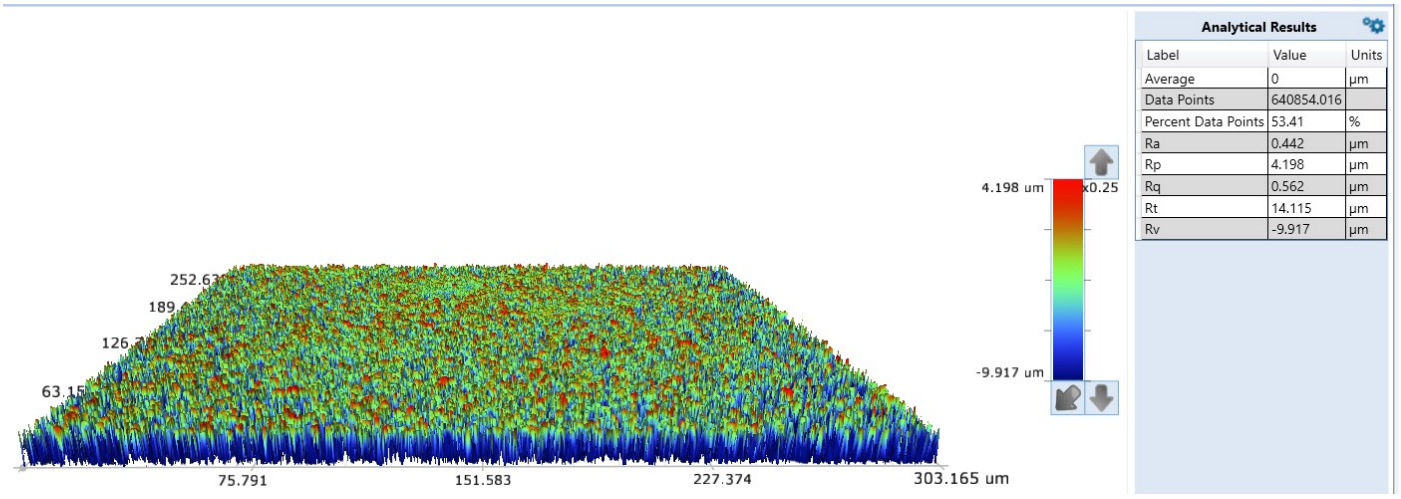
Fig.S 4 SEM images of the GZ film surface with different desmear processes: (a) swelling; (b) desmear; (c) activation; (d) after peeling.



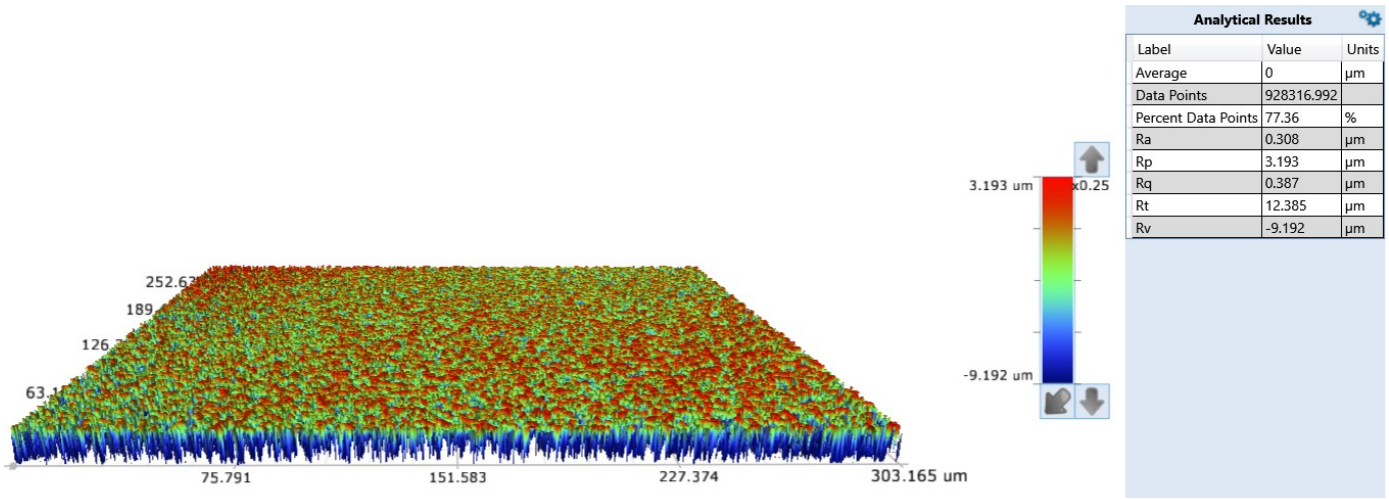
(a) GX film after desmear



(b) GZ film after desmear



(c) GX film after peeling.



(d) GZ film after peeling.

Fig.S 5 The surface roughness of two ABF surfaces: (a) GX and (b) GZ films after desmear; (c) GX and (d) GZ after peeling.

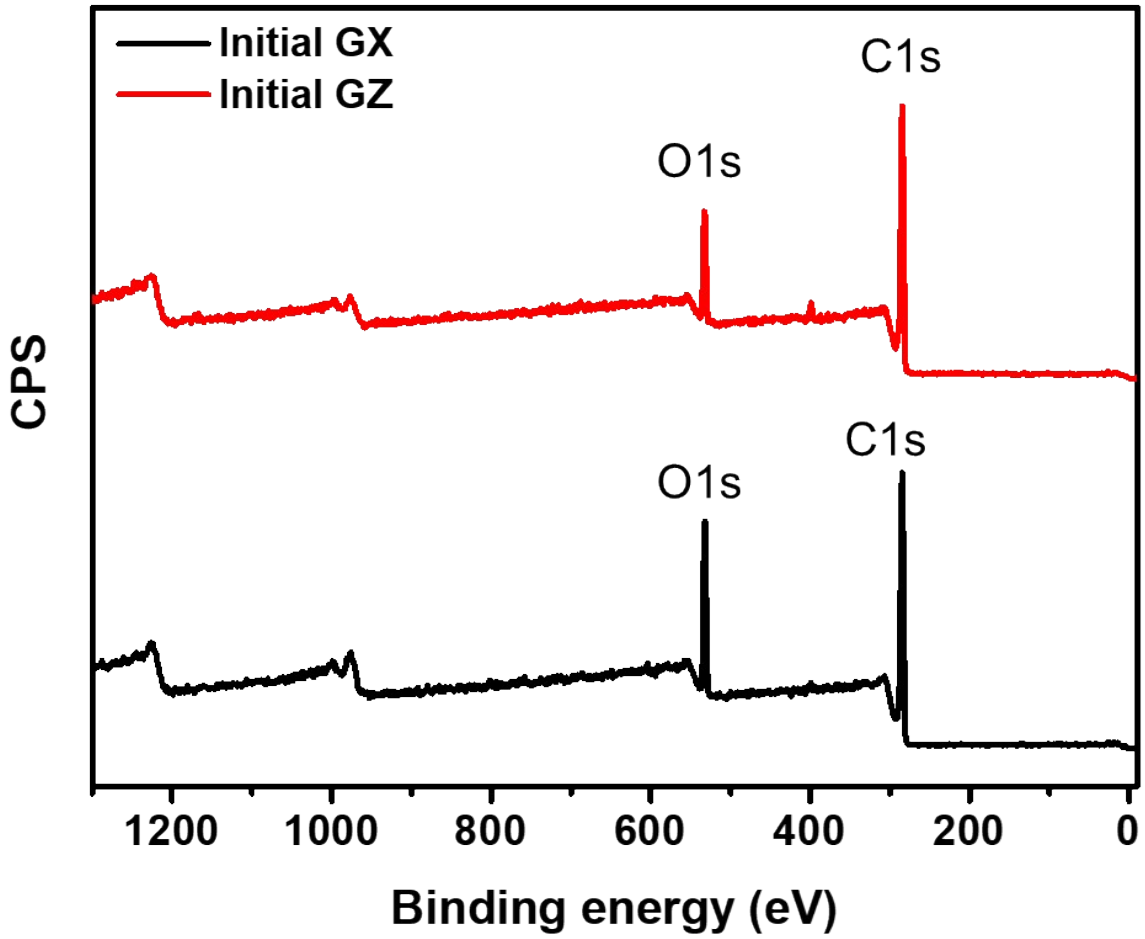


Fig.S 6 XPS survey spectrum of surfaces of initial GX and GZ films

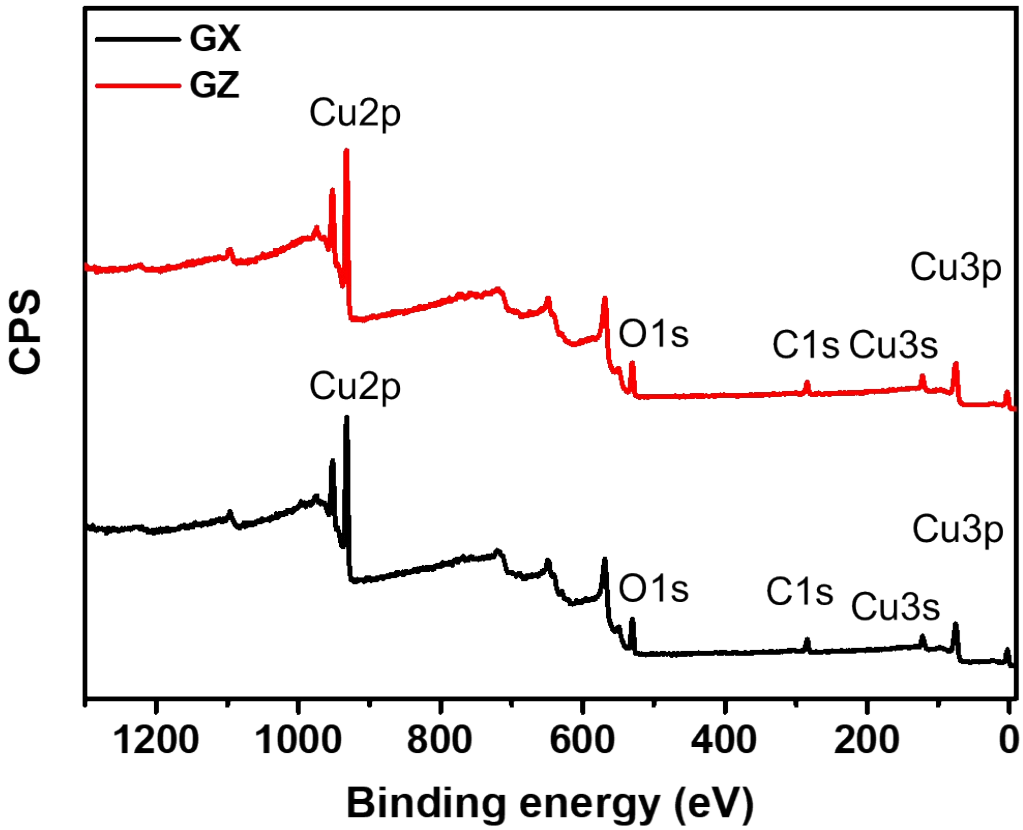


Fig.S 7 XPS survey spectrum of coppers on the surface of GX and GZ films

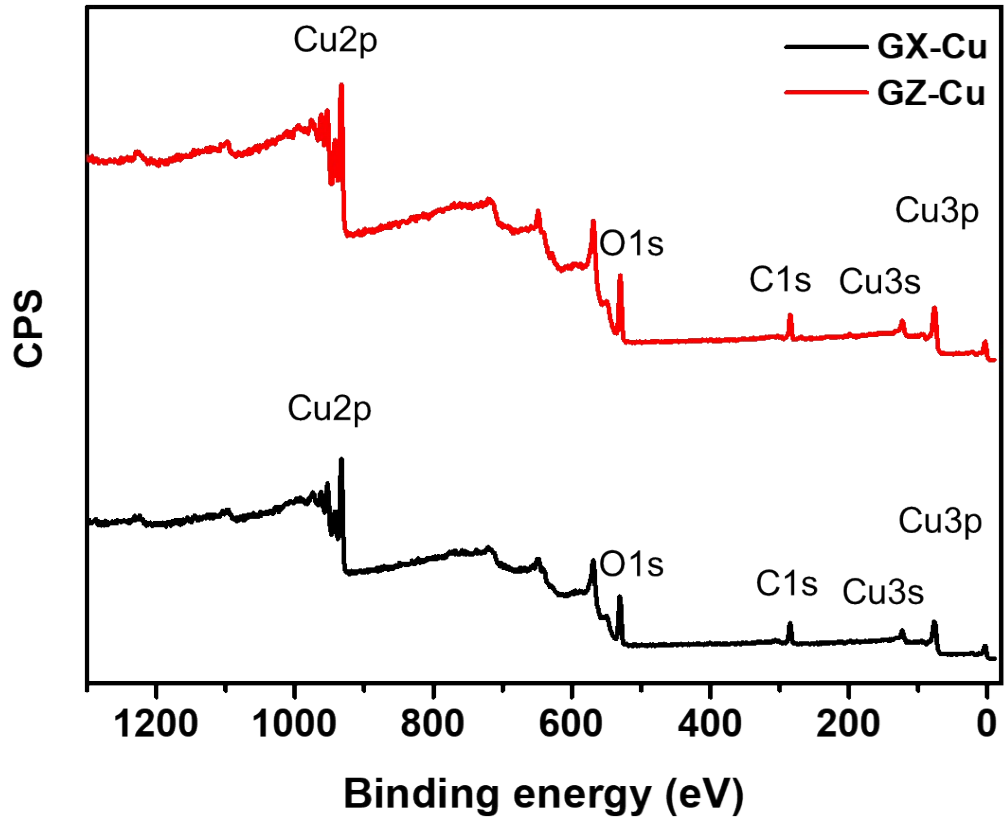


Fig.S 8 XPS survey spectrum of coppers on the surface of GX and GZ films

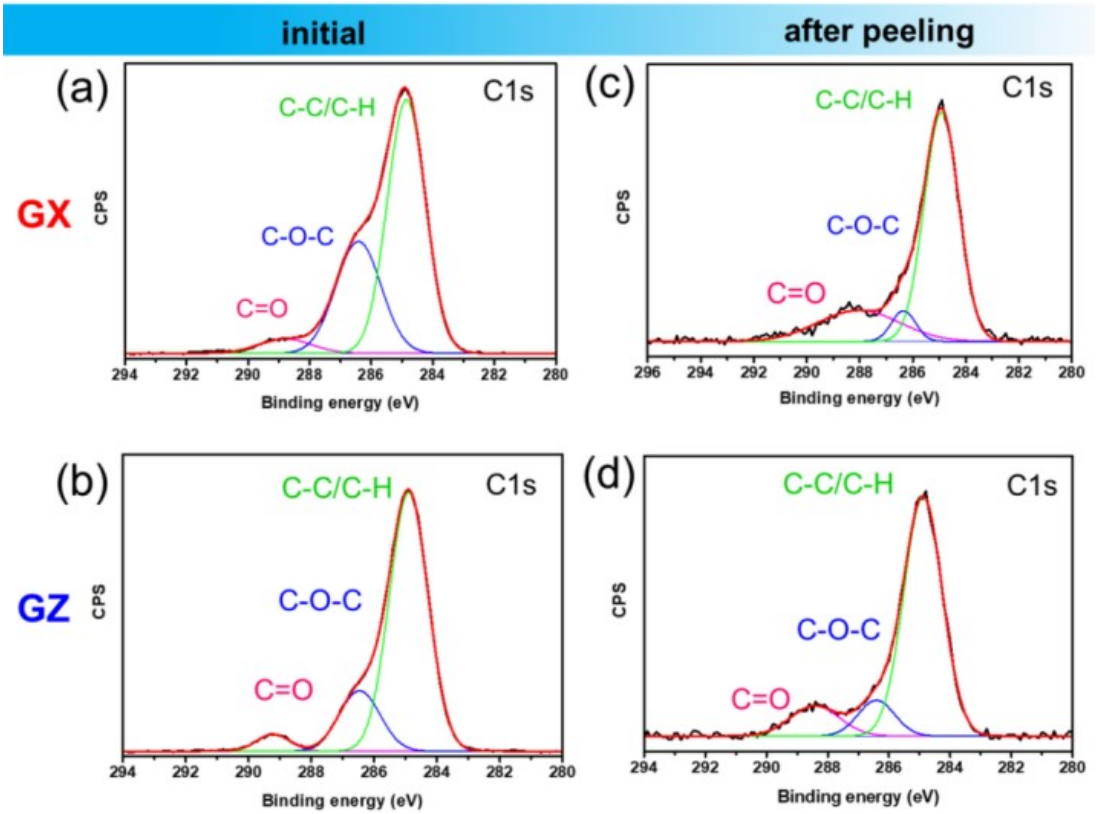


Fig.S 9 C1s XPS spectra of as-prepared (a) GX and (b) GZ films, (c) desmeared GX and (d) GZ films, copper peeled fracture surface on the surface of (e) GX and (f) GZ films.

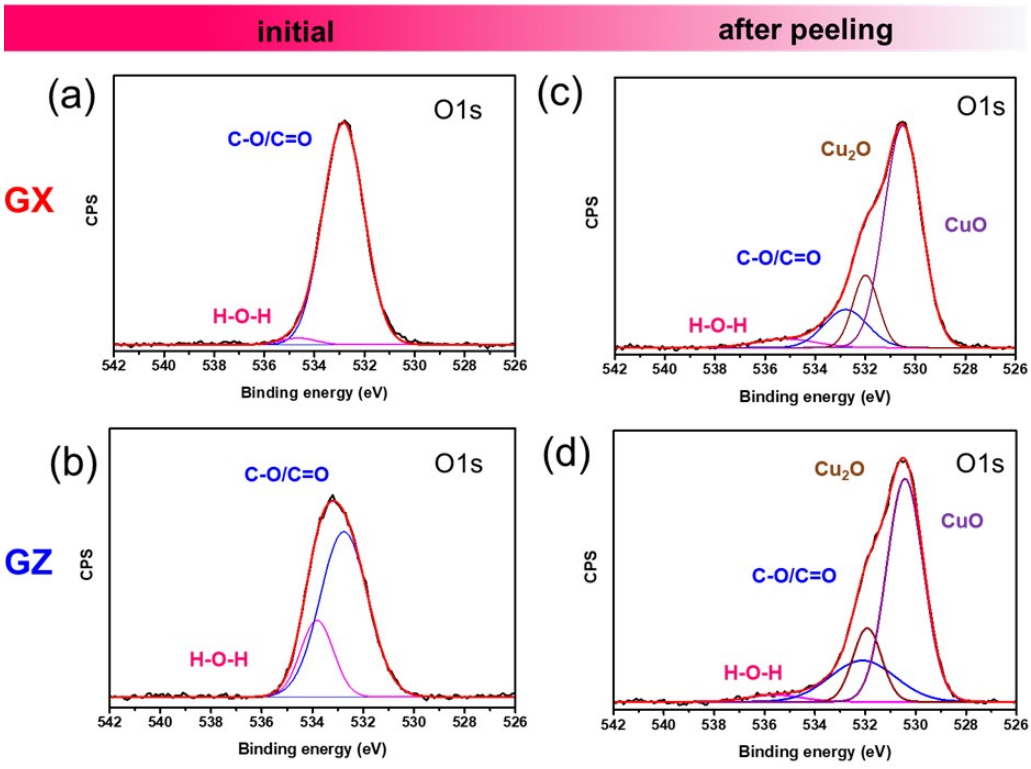


Fig.S 10 O1s XPS spectra of as-prepared (a) GX and (b) GZ films, (c) desmeared GX and (d) GZ films, copper strip peeled fracture surface on the surface of (e) GX and (f) GZ films.

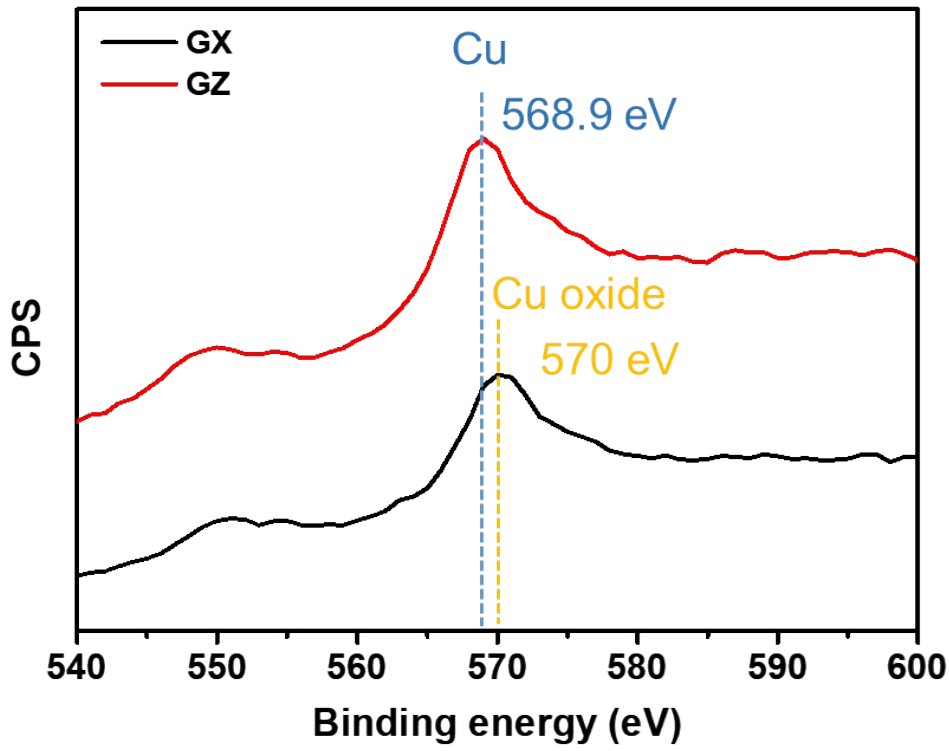


Fig.S 11 Cu LMM Auger peaks of the copper surface from GX and GZ films

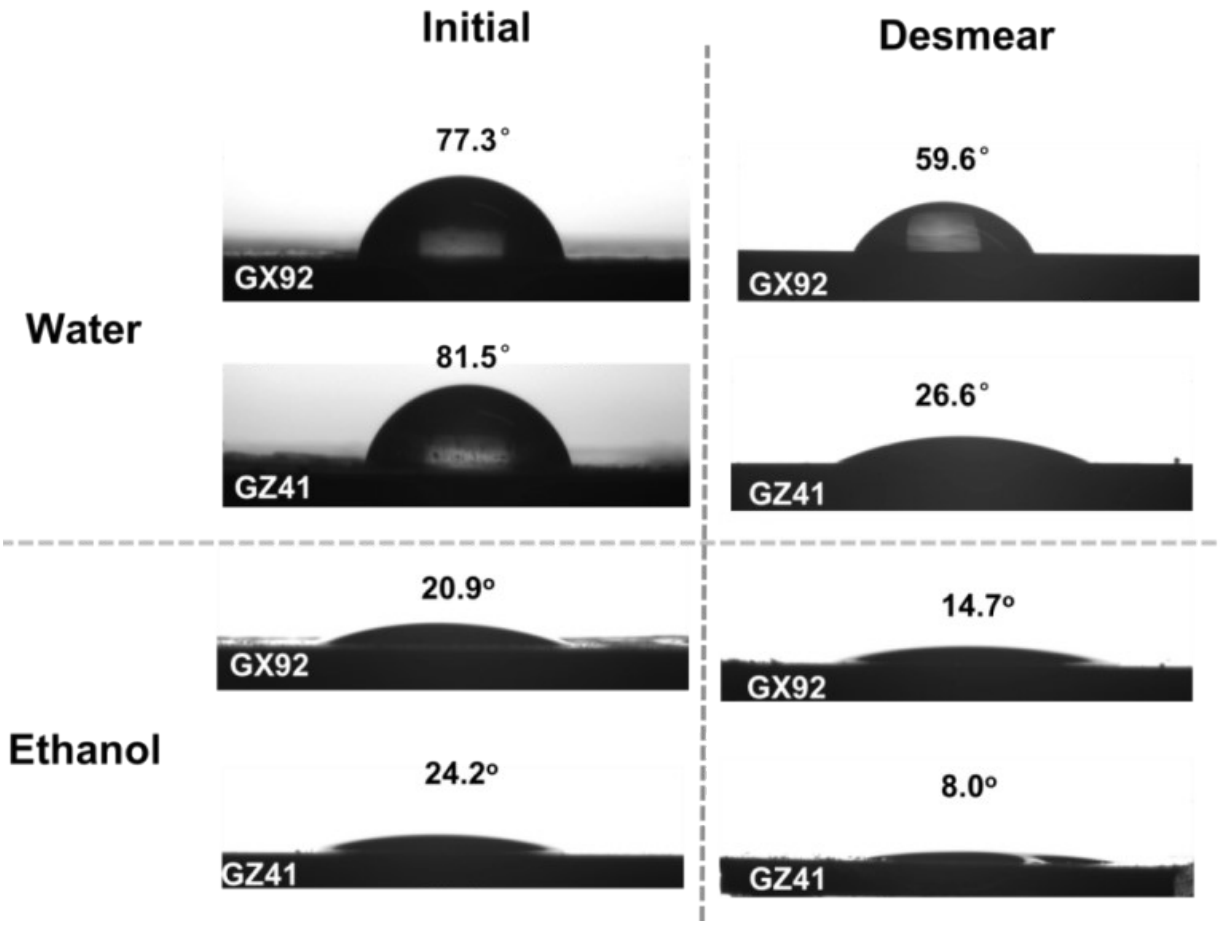


Fig.S 12 Contact angles of samples before and after desmear

Table.S 1 Contact angles of ABF and copper

Sample	Water phase		Ethanol phase	
	initial	desmear	initial	desmear
GX92	77.3°	59.6°	20.9°	14.7°
GZ41	81.5°	26.6°	24.2°	8.0°

Table.S 2 Dispersive and polar component and surface free energy of water and ethanol

Reagent	Dispersive component (mJ/m^2)	Polar component (mJ/m^2)	surface free energy (mJ/m^2)
water	21.8	51.0	72.8
ethanol	17.0	5.4	22.4

Table.S 3 The dispersive and polar components, surface free energy of GX and GZ film and copper and their work of adhesion.

Sample	γ^d (mJ/m^2)	γ^p (mJ/m^2)	γ (mJ/m^2)	W_a (mJ/m^2)
Initial GX	6.7	22.2	29.0	33.3
Desmeared GX	2.3	44.1	46.4	25.4
Initial GZ	7.9	18.7	26.6	34.9
Desmeared GZ	0.0027	88.5	88.5	14.1
Copper	25.1	0.6	25.7	-