

# Origin of insoluble residual in ZEP520 e-beam resist development

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ZEP520 (1:1-chloromethacrylate and methylstyrene, Nippon Zeon) is one of the most popular positive electron beam resists due to its sub-20-nm resolution, moderately high sensitivity and a dry etching resistance comparable to many novolac photoresists. However, high-resolution lift-off process with single ZEP520 resist layer doesn't exhibit good reliability. Our previous experiments revealed that its poor lift-off reliability is caused by a very thin resist residual layer which can not be dissolved in regular ZEP520 developers, preventing a good adhesion from the substrate. While the existence of this insoluble residual has been visually confirmed, its origin has not been identified. Here we report our latest investigation on the mechanism of this residual layer.

We analyze the ZEP520 residual using FTIR, photo-emission spectroscopy (XPS) and X-ray absorption near edge structure spectroscopy (NEXAFS) technologies. The samples are exposed at 1.2 times and twice the clear dose and developed in xylene and rinsed in isopropanol. Both XPS and NEXAFS spectra show that the chlorine signals are ignorable. NEXAFS spectra shows a strong O-C bonds peak at oxygen K-absorption edge near 533.8 eV, which is confirmed by a strong signal of C-O bonds (285.5 eV) on XPS spectra. However, on XPS spectra, the signal for C-C bonds (284 eV) is relatively weaker compared to the signal for C-O bonds and the O-C=O peak (288.3 eV) is barely visible. The signal of C=O bonds on NEXAFS is also not identifiable. In addition FTIR spectral show weak signals from main chain. Overall, spectroscopic data indicate that, after exposure and development, long chains of ZEP520 polymer has been broken or removed. No evidence shows there is cross-linked polymer (positive-negative tone inversion). However, a significant strong signal of C-O bonds implies oxygen-bridge might form on the interface of resist and native silicon-oxide. Short segments of molecule could be chemically bonded to these oxygen atoms, a strong bond that regular developer could not break (dissolve).

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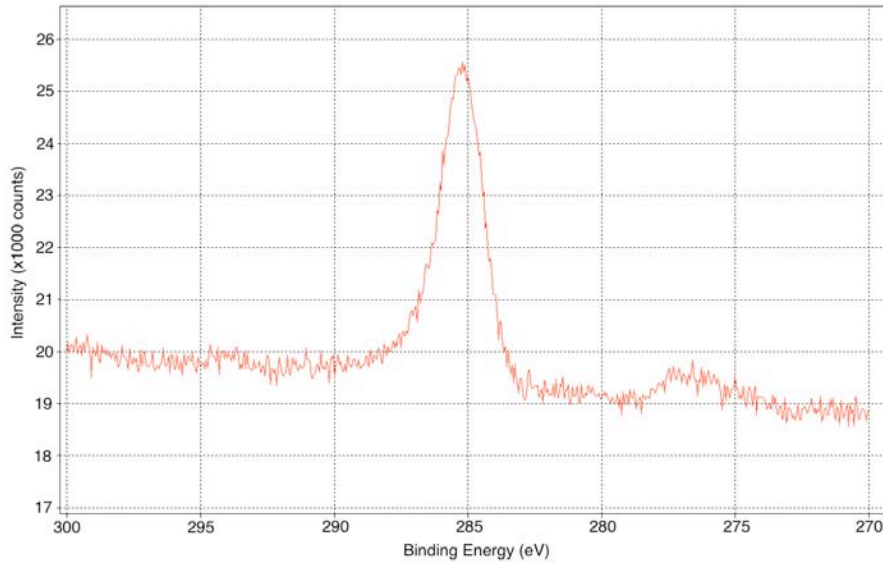


Figure 1: X-ray photon emission spectrum of ZEP520 residual: carbon peaks.

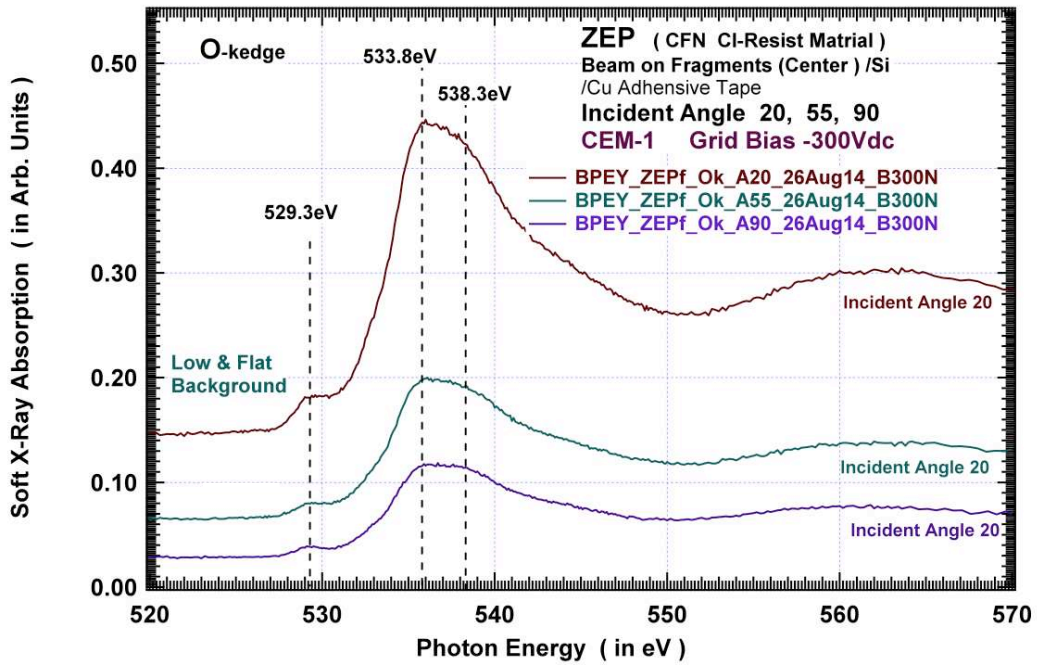


Figure 2: X-ray absorption near edge structure spectrum of a ZEP520 residual at oxygen K-edge.