Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

Plasma Treatment Effect on Polymer Buried interfacial Structure and Property

Nathan W. Ulrich[1†], John Andre[2†], Jaimal Williamson[3], Kang-Wook Lee[4], Zhan Chen[1*]

[1]Department of Chemistry, University of Michigan, 930 North University Avenue, Ann Arbor, Michigan 48109, United States

[2]Department of Chemistry, Humboldt State University, 1 Harpst Street, Arcata, California 95521, United States

[3]Texas Instruments Incorporated, Mail Stop 3621, Dallas, Texas 75243, United States

[4]IBM Thomas J. Watson Research Center, Yorktown Heights, NY 10598 USA

[†]These authors contributed equally.

*Correspondence to: Zhan Chen (zhanc@umich.edu), Tel: 734-615-4189

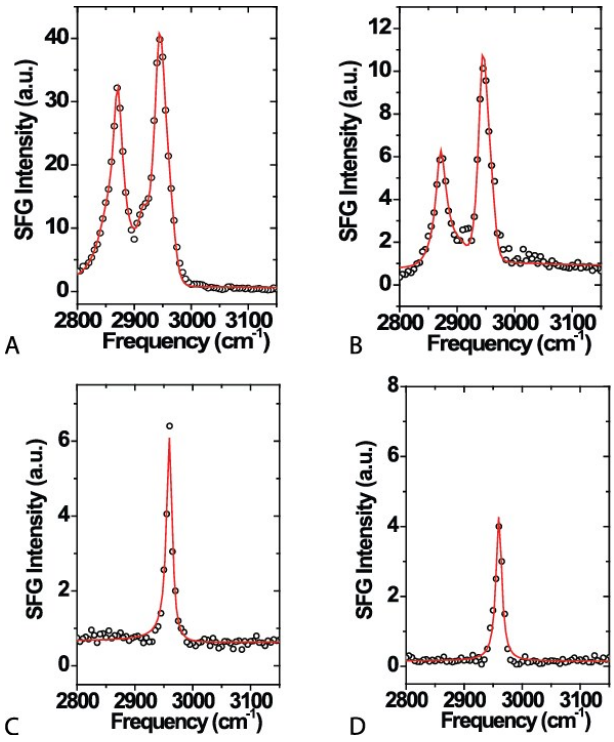

Figure s1: SFG spectra of the dPS/epoxy buried interface, in the ssp (top) and sps (bottom) polarization combination before (left) and after (right) 100s He plasma treatment on dPS. The circles are the experimental data and the red curves are the fitted results. ssp before plasma (A), ssp after plasma (B), sps before plasma (C), sps after plasma (D).

Table s1: Fitting parameters from the dPS/epoxy buried interface before and after 100s plasma treatment on dPS

Pristine surface

			ssp			sps		
Frequency	2855	2870	2915	2944	2965	2960		
Amplitude	26.0	54.0	-60.0	85.8	-60.0	13.9		
Width	15.0	10.9	12.9	10.5	13.1	6.0	$\chi_{yyz,sym}/\chi_{yzy,asym}$	5.7
Amplitude/Width	1.7	4.9	4.6	8.2	4.6	2.3		
Assignment	CH_2 sym	CH_3 sym	CH_2 asym	FR	CH_3 Asym	CH_3 Asym	$\chi_{yyz,asym}/\chi_{yzy,asym}$	2.0

100 s He plasma

			ssp			sps		
Frequency	2855	2870	2915	2944	2965	2962		
Amplitude	4.3	23.7	-20.0	37.7	-15.0	12.2		
Width	15.0	10.9	12.9	10.5	13.1	6.0	$\chi_{yyz,sym}/\chi_{yzy,asym}$	2.8
Amplitude/Width	0.3	2.2	1.5	3.6	1.1	2.0		
Assignment	CH_2 sym	CH_3 sym	CH_2 asym	FR	CH_3 Asym	CH_3 Asym	$\chi_{yyz,asym}/\chi_{yzy,asym}$	0.6

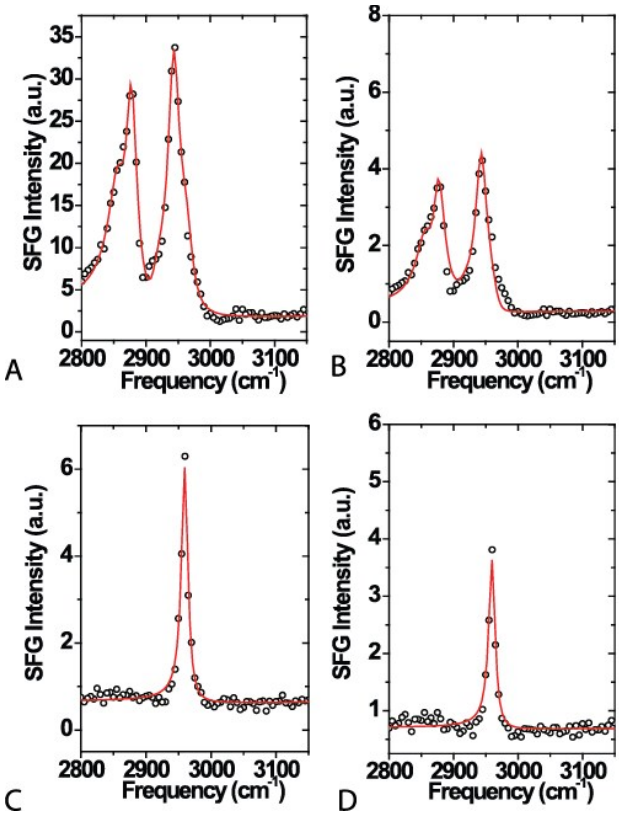

Figure s2 SFG spectra of the PI/epoxy buried interface, in the ssp (top) and sps (bottom) polarization combination before (left) and after (right) 100s He plasma treatment on PI. The circles are the experimental data and the red curves are the fitted results. ssp before plasma (A), ssp after plasma (B), sps before plasma (C), sps after plasma (D).

Table 2: Fitting parameters from the PI/epoxy buried interface before and after 100s plasma treatment on PI

Pristine surface

			SSP			SPS		
Frequency	2859	2878	2915	2944	2965	2960		
Amplitude	34.6	52.1	-50.0	77.6	-60.0	13.9		
Width	15.0	10.9	12.9	10.5	13.1	6.0	$\chi_{yyz,sym}/\chi_{yzy,asym}$	5.2
Amplitude/Width	2.3	4.8	3.9	7.4	4.6	2.3		
Assignment	CH_2 sym	CH_3 sym	CH_2 asym	FR	CH_3 Asym	CH_3 Asym	$\chi_{yyz,asym}/\chi_{yzy,asym}$	2.0

100 s He plasma

			SSP			SPS		
Frequency	2859	2877	2915	2944	2965	2962		
Amplitude	12.1	18.0	-17.0	27.0	-12.0	10.3		
Width	15.0	10.9	12.9	10.5	13.1	6.0	$\chi_{yyz,sym}/\chi_{yzy,asym}$	2.5
Amplitude/Width	0.8	1.6	1.3	2.6	0.9	1.7		
Assignment	CH_2 sym	CH_3 sym	CH_2 asym	FR	CH_3 Asym	CH_3 Asym	$\chi_{yyz,asym}/\chi_{yzy,asym}$	0.5

AFM results

It was reported that the plasma treatment may change the surface roughness.[1] AFM measurements were performed on the PS and PI surfaces before and after 100 s He plasma treatment (Figure s3). It was found that the RMS for PS went from 0.49 nm to 1.34 nm; and the PI went from 0.28 nm to 2.83 nm. This generally agrees with the trend of the polymer film becoming slightly rougher following He plasma. In the literature, one study found that the roughness ranged from 2.3 to 4.1 after He plasma, by varying different parameters, but the bottom line is the PI roughness increases by nanometers following He plasma.[2] Such a small roughness change would not decrease SFG signal because of the diffused reflection instead of the specular reflection. In the SFG experiment, the input and output beams have wavelengths of hundreds or thousands of nanometers. Specular reflection will occur even if the roughness is in the order of tens of nanometers or even larger.

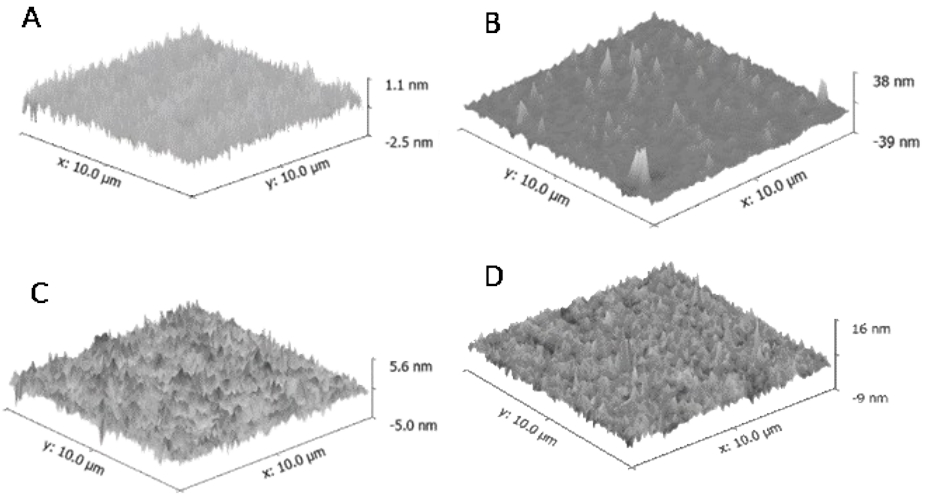

Figure s3: A. PI pristine (Rms=0.28 nm), B. PI after plasma (Rms=03.47) nm, C. PS pristine (Rms=0.49 nm), and D. PS after plasma (Rms=1.34 nm).

References

1. S. H. Kim, S. W. Na, N. E. Lee, Y. W. Nam and Y.-H. Kim, *Surface and Coatings Technology*, 2005, 200, 2072-2079.
2. B. Tae Joon, K. Sung Il, K. Youn Joon, C. Yoon Suk, C. In Sik, S. Yuichi and H. Jeon Geon, *Japanese Journal of Applied Physics*, 2009, 48, 08HL01.