Photoelectron spectra of backbone polymer of chemically amplified resist studied by ultraviolet photoelectron spectroscopy

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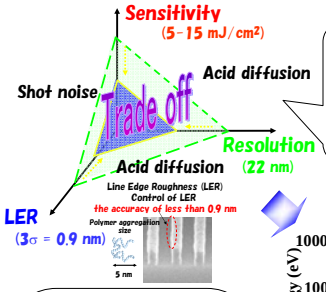
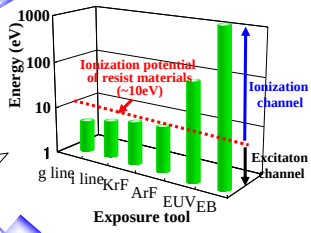
Introduction

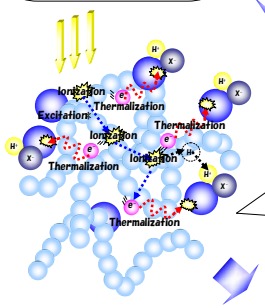
Specification of DRAM ½ pitch = 22 nm



. The trade-off relationship between sensitivity, resolution and line edge roughness (LER) is the most serious problem in EUV lithography. Thus, the resist requirements for the EUV lithography are so strict that fundamental understanding of pattern formation reactions is strongly needed for the development of resist materials acceptable to mass production lines.

The resolving power of lithography has been improved by the repeated replacement of exposure tools toward shorter wavelength. With this trend, the energy of exposure tools has gradually increased and will exceed the ionization potential of resist materials by the deployment of extreme ultraviolet (EUV). In previous study, clear differences between the reaction mechanisms of photoresists and electron beam (EB) resists have been observed.[1]

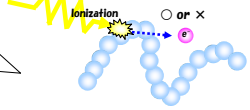




In chemically amplified EB and EUV resists, the energy of radiation is mostly deposited on the polymer matrices via ionization processes.[2] When EUV photons enter resist materials, polymers are ionized. By ionization, polymer radical cations and electrons are generated. The ejected electron further induces ionization. The ejected electrons react with acid generators after their energy has been lost sufficiently. Through the reaction with electrons, the acid generators release counter anions of acids. Protons of acids are generated through the deprotonation of polymer radical cations.

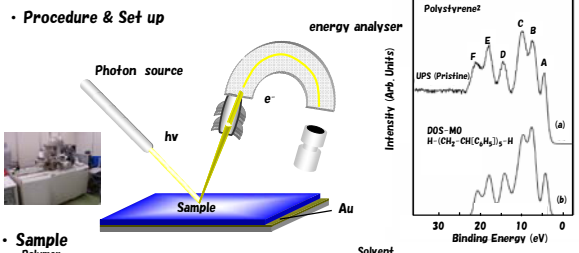
Therefore, it is essential to know the ionization mechanisms of backbone polymers and understand the reaction mechanism in details in order to accomplish high sensitivity and ultra-fine pattern in EUV lithography. In this study, we investigated the photoelectron spectra of typical backbone polymers for chemically amplified EUV resists using ultraviolet photoelectron spectroscopy (UPS).

Whether Ionization occurs or not is very important for typical backbone polymers for chemically amplified EUV resists .

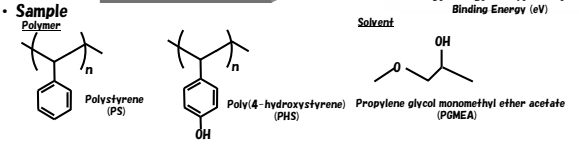


Experimental

- Procedure & Set up



- Sample



In this study, PHS and PS were used as polymers, PGMEA was used as a casting solvent, PS and PHS solutions were spin-coated on gold-coated Si wafers to form ultrathin films. The thickness of the polymer films was estimated to be less than 20 nm. The sample film is thin enough to prevent any sample-charging problem arising from its electric non-conductive nature. The samples were introduced into JPS 9010MC XPS/UPS system. The base pressure of the system was lower than 1×10^{-5}Pa. The cleanliness and structure change of samples was confirmed by XPS. The UPS spectra were recorded using SPECS UVS-300 UPS Source, He I radiation ($h\nu$=21.2 eV). The energy resolution of analyzer is less than 0.2 eV, estimated from the Fermi edge of the Au-coated wafer.

Results and Discussion

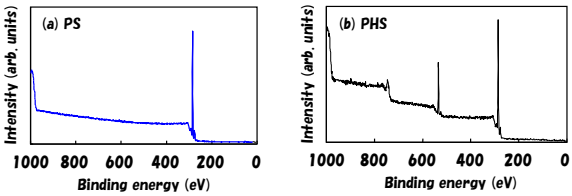


Figure 1. XPS spectra of (a) polystyrene (PS) and (b) poly(4-hydroxystyrene) (PHS) films. They were obtained with Mg Kα (1253.6 eV).

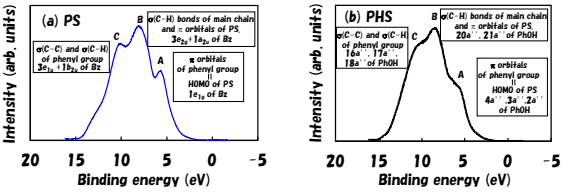
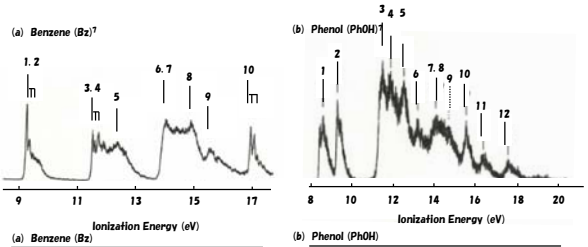


Figure 2. A typical He I ($h\nu$=21.2 eV) UPS spectra of (a) PS and (b) PHS films, respectively. Binding energy scaled to Au Fermi energy.

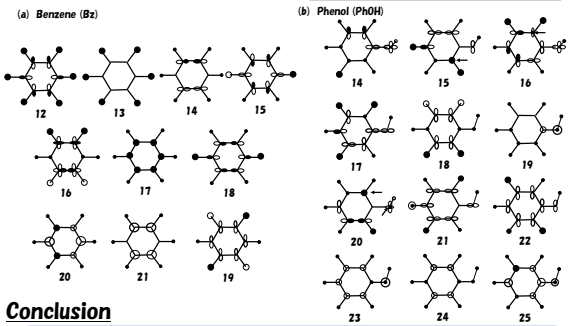


(a) Benzene (Bz)

	Exp't.	SCF MO [4-31G]			
	I_v(eV)	$-\varepsilon$(eV)	MO		Character
1	9.25	9.63	$1e_{1u}$	(21)	π_3
2				(20)	π_2
3	11.53	13.22	$3e_{2u}$	(19)	σ
4				(18)	σ
5	12.38	13.54	$1a_{1u}$	(17)	π_1
6	13.98	15.89	$3e_{1u}$	(16)	σ
7				(15)	σ
8	14.86	16.71	$1b_{1u}$	(14)	σ
9	15.46	17.32	$2b_{1u}$	(13)	σ
10	16.84	19.25	$3a_{1g}$	(12)	σ

(b) Phenol (PhOH)

	Exp't.	SCF MO [4-31G]			
	I_v(eV)	$-\varepsilon$(eV)	MO		Character
1	8.70	8.55	4a''	(25)	π_2
2	9.39	9.31	3a''	(24)	π_3
3	11.59	13.06	2a''	(23)	π_1, n_O
4	12.02	13.32	21a'	(22)	B(19)
5	12.61	13.93	20a'	(21)	B(18)
6	13.44	15.16	19a'	(20)	n_O
7	14.21	15.98	1a''	(19)	n_O
8	14.21	16.15	18a'	(18)	B(16)
9	(14.7)	16.68	17a'	(17)	B(15)
10	15.51	17.67	16a'	(16)	B(14)
11	16.36	18.63	15a'	(15)	B(13)
12	17.51	19.97	14a'	(14)	σ_{O-H}



Conclusion

The peaks labeled A-C in Figure2 (a) are assigned as follows. Peak A originates from π orbitals at pendant phenyl group, Peak B is ascribed to mainly σ(C-H) bonds from the main chain and partially from π orbitals at pendant group, Peak C involves σ(C-C) and σ(C-H) bonds from the pendant group. The measured first ionization potential (IP) of PS was 5.6 eV. This value is similar to the earlier publication of PS films measured with UPS (5.7 eV[2] and 6.95 eV[3]). On the other hand, The UPS spectra of PHS films was firstly obtained as shown in Figure 2(b) though it is not determined by precise level. The measured first ionization potential (IP) of PS was 5.4 eV. This difference in IP values between PS and PHS was observed as it is reported that IP in benzene and phenol are different in gas phase respectively.[6]

Reference

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