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The impact of the light exposure on the morphological properties of selected photoresists

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In this paper we present the investigation aimed at the photoresist roughness change determination as a reliable estimator of the exposition rate in the processing verification in semiconductor industry. By employing atomic force microscopy as the 3D high resolution surface imaging tool, we tested twelve popular photoresists in terms of the morphological properties changes, while the following radiation doses were applied. Basing on high precision, and repetitive sample positioning, it was possible to perform the tests with high degree of confidence and observe the roughness change dynamics. Various profiles of roughness changes were observed, showing the need for individual study of each material. Moreover, it was possible to select the photoresists which due to poor homogeneity and small roughness changes are not suitable to such a verification. According to our knowledge, no such study was performed so far.

Keywords: photolitography, polymer degradation, atomic force microscopy.

1. Introduction

The properties changes of polymers due to the light exposition, is one of the phenomena that in general may cause unwanted results, such a degradation. Yet, some industrial applications benefit from the sensitivity of polymer films to the radiation in visible or near visible range of wavelength. Such a materials are the photoresists utilized in photolitography process in semiconductor industry. The pursuit of high resolution and efficiency in photolithography for semiconductor industry leads to various approaches aimed at process optimization and better control. One of the proposed solutions concerning the verification of the quality of the photolithography process, that can be performed before the development of the photoresist, is its surface morphology imaging and quantitative description by means of atomic force microscopy (AFM) [1]. A similar idea in terms of resists used in electron lithography was formulated as well [2].

Yet, one has to be aware that every polymer reveals individual response to radiation, including non-monotonic behavior [3–7]. It has to be underlined that a number of studies allowed to show practical usability of the AFM technique in observation of various materials properties changes due to the UV light, temperature or heavy ions [8–11].

Concerning various kinds of photoresists used for certain applications, one has to assume that the AFM measurement may provide different roughness values due to their individual photochemical properties. Therefore in order to apply this method in a reliable fashion, the study revealing specific sensitivities and roughness changes trends must be performed. We present the study, basing on the analysis of the measurements performed on 12 popular photoresists exposed to UV light. Due to the need of general recognition of the investigated phenomena at this research stage, the applied doses were not optimized in terms of typical photolitography process. It has to be noted that applied in this experiment radiation doses cover significantly a wider range than typically used, as the general behavior of the material was observed. The comparison of the dynamics of the morphological properties changes reveals unique properties of each photoresist. According to our knowledge, no such work was performed so far.

2. Experimental procedure

The silicon samples (approx. 10 mm × 10 mm in size) were prepared using standard methods of photoresists deposition. The list and basic parameters of used resists is in the Table. It should be mentioned that also the electro-litography resists were tested.

The data acquired with AFM provide 3D data useful in calculation of a number of roughness parameters. It should be underlined that in order to obtain accurate data, one needs to utilize approach providing a minimized impact of the surface non-homogeneities on the measurements results. Therefore the precise repetitive sample positioning was utilized, as a formerly successfully implemented approach [3–6]. The simplified diagram representing the idea of this approach is presented in Fig. 1.

During a single exposition, UV radiation 370 nm at energy about 256 mJ/cm^2 was delivered to the samples. The scan-exposure cycle was repeated 5 times after the initial scan revealing the $t = 0$ h state.

The measurements were made using DI3000 system, in intermittent contact mode, in ambient conditions. Based on previous experience, the scan area was set to 3 μm × 3 μm. By the imaging resolution 512 × 512 points, it provides a 5.8 nm distance between the pixels, therefore the observation of the surface degradation at the desired scale is possible. The data was processed using SPIP software from Image Metrology [12]. Following set of parameters was used to compare the surface parameters changes: S_q – root mean square roughness, S_{dr} – surface area ratio (measured area to scanning area ratio), and S_z – the peak–peak value within the height map.

For each sample and each exposure stage, 8 measurements were performed, providing statistical information about the morphology changes. As the results revealed

T a b l e. The list of used resists and their basic parameters.

Symbol	Type	Recommended thickness (4000 rpm)	Optimal exposure voltage/wavelength range	Recommended radiation dose
AR-P 617.06	e-beam, deep UV (248 nm)	0.29 μm	5–30 kV	20–100 μC/cm^2
AR-P 617.08	e-beam, deep UV (248 nm)	0.48 μm	5–30 kV	10–50 μC/cm^2
AR-P 679.02	e-beam, deep UV (248 nm)	0.09 μm	20–30 kV	50–150 μC/cm^2
AZ MIR 701	Positive, UV range	0.9 μm	310–440 nm	50–100 mJ/cm^2
ECI 3027_1.2	Positive, UV range	1.2 μm	320–440 nm	50–100 mJ/cm^2
AZ 9260	Positive, UV range	6.0 μm	310–410 nm	150–400 mJ/cm^2
ma-N1420	Negative, UV range	2.0 μm	320–440 nm	550 ± 30 mJ/cm^2
S1818	Positive, UV range	1.8 μm	350–450 nm	90–150 mJ/cm^2
AZ 4562	Positive, UV range	6.2 μm	320–440 nm	120–500 mJ/cm^2
S1805	Positive, UV range	0.5 μm	350–450 nm	50–100 mJ/cm^2
SU 8(2)	Negative, UV range	2 μm	350–400 nm	50–200 mJ/cm^2
AR-N 7520.11 neu	e-beam and UV exposure 248–365 nm, negative in the UV range	0.2 μm	5–30 kV	10–50 μC/cm^2

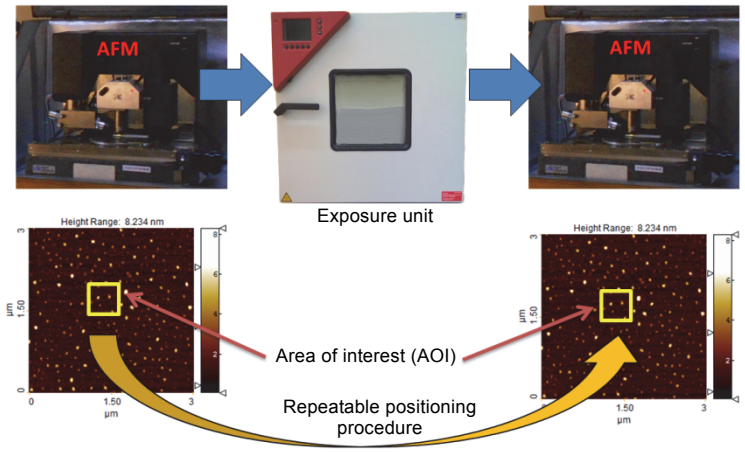

Fig. 1. The idea of repetitive scanning of specific area, while the sample is exposed to a certain factor.

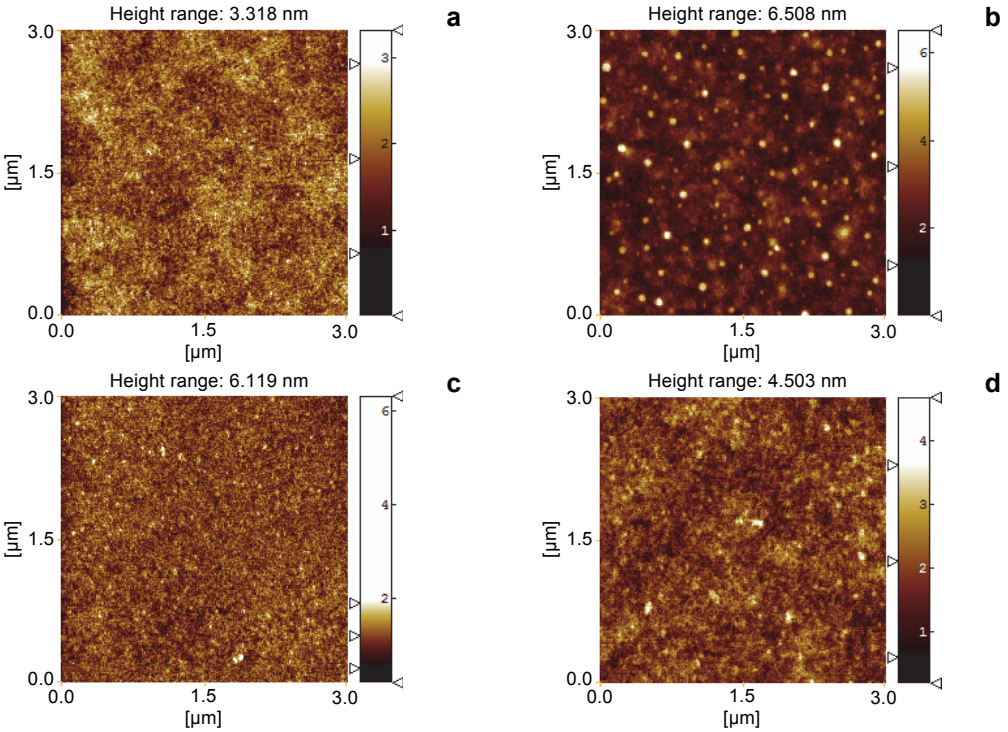

Fig. 2. Examples of acquired topography images of investigated samples: AR-P 617.06 (**a**), AR-P 679.02 (**b**), AZ 4562 (**c**), and AR-N 7520.11 neu (**d**).

that the homogeneity of various photoresists can differ significantly (Fig. 2), one needs to verify the standard deviation of the results acquired for specific sample at certain ageing stage.

3. Experimental results

The following analysis showed that some of investigated materials, due to roughness variations related to the non-homogeneity of the morphology, cannot be observed in terms of UV photolithography, while the roughness changes are smaller than the variations. Figure 3 shows the changes of S_q parameter for tested samples. As this particular factor is the most popular in terms of roughness determination, one could assume that it is the best tool for the evaluation of the exposition dose. One can see the diversity of the S_q changes, while following portions of energy were s applied. Similar behavior

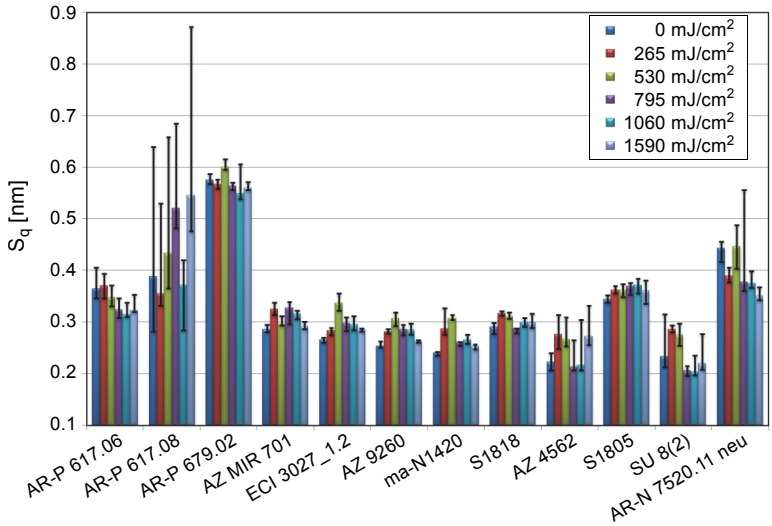

Fig. 3. Graph showing changes of S_q roughness parameter for investigated samples.

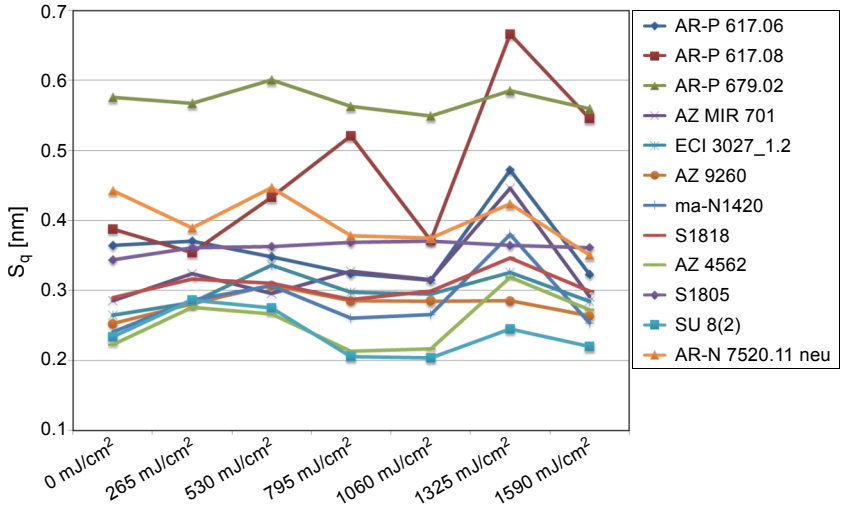

Fig. 4. Graph showing changes of S_q roughness parameter in mutual relations of the samples.

can be found in case of: ECI 3027_1.2, AZ 9260, ma-N1420 and S1818. Another specific changes profile can be found for AR-P 679.02 and AZ MIR 701. On the other hand, due to large standard deviation bars, it would be difficult to recognize roughness changes for AR-P 617.08, AZ 4562, AR-N 7520.11 neu and SU 8(2).

The other method of S_q factor visualization is shown in Fig. 4. It allows to clearly see the dose-related changes, but in mutual relation of the investigated samples.

The analysis of S_{dr} parameter's changes (Fig. 5) allows to estimate its usability in determination of applied radiation doses. The changes dynamics in first few steps is

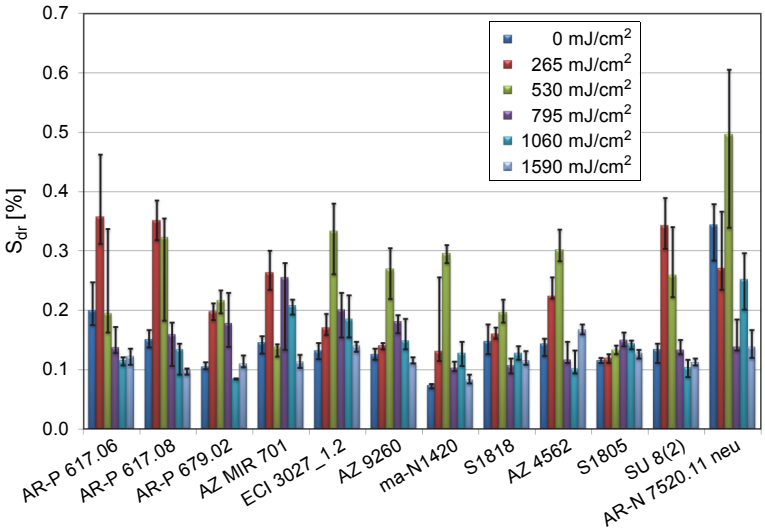

Fig. 5. Graph showing changes of S_{dr} roughness parameter for investigated samples.

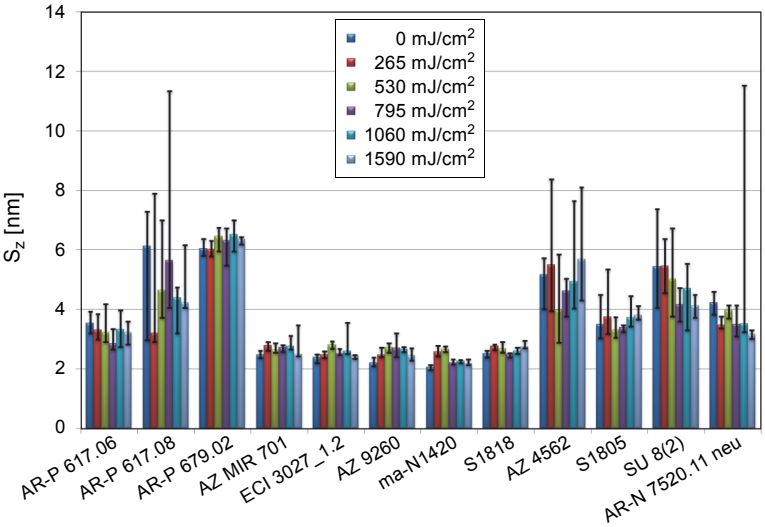

Fig. 6. Graph showing changes of S_z roughness parameter for investigated samples.

more significant. Yet, also the distribution is relatively high, therefore the dose estimation resolution can be significantly reduced for some materials. On the other hand, in case of materials disqualified for S_q estimation such as: AR-P 617.08, AZ 4562, AR-N 7520.11 neu and SU 8(2), it is possible to perform reliable distinction between some radiation doses.

The utilization of S_z parameter (Fig. 6) may be justified for few materials such as: AZ MIR 701, ECI 3027_1.2, AZ 9260, ma-N1420, S1818. For other materials, the deviation of the parameter is too big to be used practically. It should be underlined that S_z factor is very sensitive to single events such pinholes, or grains that occurred in the scanned area. It can be however useful, as the indicator of possible technological fail-

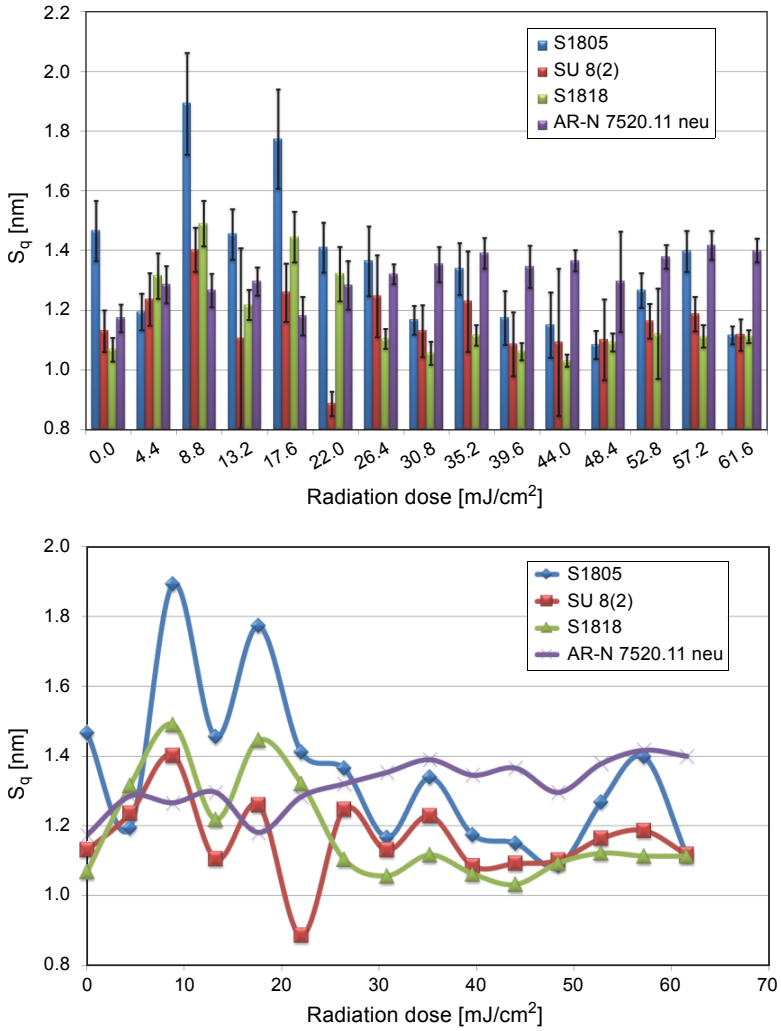

Fig. 7. Graph showing changes of S_q roughness parameter for investigated samples for standard radiation doses.

ures, as single defects may be critical to the quality and reliability of fine microelectronic structures.

Second set of measurements was performed for selected groups of photoresists that revealed a relatively good homogeneity, allowing to observe the roughness changes for small exposure doses. It allowed to observe the roughness changes for the UV radiation doses within a range of more relevant to standard lithography exposure.

Standard radiation doses for selected photoresists span from single mJ/cm^2 to *ca*. 50 mJ/cm^2. It may be observed that the roughness changes below 30 mJ/cm^2 (Fig. 7) are much more rapid than for the rest of the range. This behavior can be explained by intense generation of carboxylic acid as a photoproduct. Above 30 mJ/cm^2 this process is inhibited and the roughness is not increasing. However, for most photoresists when the radiation doses exceed 1000 mJ/cm^2 the carbonization process occurred that modified the surface and increased the roughness by 50%.

4. Conclusions

Obtained results revealed various morphological responses of investigated materials, therefore in order to practically use the AFM in the photoresists assessment in terms of appropriate light exposure, one needs to verify whether certain roughness correlates with observed changes. The non-monotonic changes of observed parameters require very careful interpretation, as in some cases the lack of precise knowledge about the absorbed energy ratio and the roughness changes may lead to false conclusions. In addition, one can easily notice that particular materials, due to the non-homogenous morphology, make such a diagnostic approach impossible. Further investigation aimed at identification of the morphological and mechanical properties changes of the photoresists due to exposition to radiation doses typical in the microelectronic processes is planned in order to verify in detail the behavior of selected materials. It must be underlined that due to the impact of the several processing parameters as well as the non-monotonic changes of investigated roughness factors, only roughness changes, relatively to the reference level, can be used, and it may be considered as useful in a relatively narrow range of energy. Yet, it will be investigated whether morphological parameters in connection with mechanical properties may be a better indicator of the resist exposition. Such experiments are planned to be performed in near future.

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References

[1] SIERAKOWSKI A., JANUS P., KOPIEC D., NIERADKA K., DOMANSKI K., GRABIEC P., GOTSZALK T., *Optimization method of photolithography process by means of atomic force microscopy*, Proceedings of SPIE **8352**, 2012, article ID 83520B, DOI: 10.1117/12.918024.

[2] INDYKIEWICZ K., *Zastosowanie litografii elektronowej do wytwarzania tranzystora AlGaN/GaN HEMT*, PhD Thesis, Wrocław University of Science and Technology, Poland 2018 (in Polish).

[3] Sikora A., Bednarz Ł., Fałat T., Wałecki M., Adamowska M., *Investigation of the impact of simulated solar radiation on the micro- and nanoscale morphology and mechanical properties of a sheet moulded composite surface*, Materials Science-Poland **34**(3), 2016, pp. 641–649, DOI: 10.1515/msp-2016-0080.

[4] Sikora A., Grabarek A., Moroń L., Wałecki M., Kryla P., *The investigation of the light radiation caused polyethylene based materials deterioration by means of atomic force microscopy*, IOP Conference Series: Materials Science and Engineering **113**, 2016, article ID 012016, DOI: 10.1088/1757-899X/113/1/012016.

[5] Sikora A., *The new approach to the investigation of the roughness changes of the non-uniform materials irradiated with UV light and imaged by means of atomic force microscopy supported with precise repetitive scanning area positioning*, Measurement Science and Technology **28**(3), 2017, article ID 034016, DOI: 10.1088/1361-6501/28/3/034016.

[6] Sikora A., *High accuracy and sensitivity method of the observation of the surface's morphology changes by means of atomic force microscopy with cyclic, precise sample positioning*, Nanoscience and Nanometrology **3**(1) 2017, pp. 6–11, DOI: 10.11648/j.nsnm.20170301.12.

[7] Sikora A., Moczała M., Boharewicz B., *Utilization of the precision samples positioning for the AFM assessment of the polystyrene/PC61BM nanocomposite surface degradation*, Materials Science -Poland, in print.

[8] Suresh B., Maruthamuthu S., Khare A., Palanisamy N., Muralidharan V.S., Ragunathan R., Kannan M., Pandiyaraj K.N., *Influence of thermal oxidation on surface and thermo-mechanical properties of polyethylene*, Journal of Polymer Research **18**(6), 2011, pp. 2175–2184, DOI: 10.1007/s10965-011-9628-0.

[9] Mikšová R., Macková A., Malinský P., Slepička P., Švorčík V., *A study of the degradation of polymers irradiated by C^{n+} and O^{n+} 9.6 MeV heavy ions*, Polymer Degradation and Stability **122**, 2015, pp. 110–121, DOI: 10.1016/j.polymdegradstab.2015.10.017.

[10] Nowicki M., Richter A., Wolf B., Kaczmarek H., *Nanoscale mechanical properties of polymers irradiated by UV*, Polymer **44**(21), 2003, pp. 6599–6606, DOI: 10.1016/S0032-3861(03)00729-8.

[11] Huaixi Wang, Huimin Xie, Zhenxing Hu, Dan Wu, Pengwan Chen, *The influence of UV radiation and moisture on the mechanical properties and micro-structure of single Kevlar fibre using optical methods*, Polymer Degradation and Stability **97**(9), 2012, pp. 1755–1761, DOI: 10.1016/j.polymdegradstab.2012.06.010.

[12] https://www.imagemet.com/ (accessed 01.06.2018).

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