Cost-Effective Sub-20 nm Lithography: Smart Chemicals to the Rescue

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The increasing cost of the lithographic process, which is driven both by process complexity and by the increasing price of moving to smaller exposure wavelengths, makes approaches that use “smart chemicals” and “bottom up” patterning processes that employ molecular scale assembly processes ever more attractive. The technology that is closest to implementation in IC manufacturing is directed self-assembly (DSA) of block copolymers for contact hole shrink and line space multiplication. The current delays and limitations in EUV lithography provide further incentive to pursue DSA technology, which can be both complementary (such as in contact shrink) as well as a competitor (such as for fine line patterning). Current results indicate that DSA structure quality, line roughness measures, and defectivity are in a range that allows development work for integration into existing production to begin. Contact hole shrink may be closest to implementation, since its process integration is very similar to existing shrink material schemes. A first application for line frequency multiplication may be the replacement of multiple patterning processes with DSA schemes which have the potential to provide compelling cost and technical advantages.

Keywords: Photoresist improvement rate, equivalent NA, EUV lithography, Directed Self Assembly (DSA), contact hole shrink, line frequency multiplication, grapho-epitaxy, chemi-expitaxy.

1. Introduction

The IC industry’s ability to continuously shrink feature sizes is at the core of Moore’s Law.¹ This ability to print ever smaller features is often seen as mainly deriving from improvements and innovations in the hardware of IC manufacture, in particular in the exposure tools of optical lithography that have been used to define the features of almost all computer chips ever made. According to Rayleigh’s equation (Eq. 1),

$$\text{max. resolution} = k_1 \frac{\lambda}{NA} \quad (1)$$

improvements in resolution capability of these exposure tools can be achieved by either decreasing the exposure wavelength or by increasing their numerical aperture (NA).

Historically, the industry has followed both paths, increasing the NA of tools for a given wavelength to the maximum useful level, and then switching to a shorter wavelength and beginning the NA upgrade cycle again. In this way, the industry has switched

from broadband mask aligners to g-line (435 nm, max. NA 0.45) to i-line (365 nm, max. NA 0.54) to DUV (248 nm, max. NA 0.80) to ArF excimer (193 nm, max. NA 0.93) lithography, and, after an abortive attempt at 157 nm lithography, introducing water as an immersion medium and going to ArF immersion (193 nm and max. NA 1.35). The final technology for optical lithography is seen as Extreme UV (EUV) lithography, with a wavelength of 13.4 nm that requires the use of all-reflective multi-layer mirror, vacuum optics. EUV lithography has the potential for high resolution due to its greatly decreased exposure wavelength, but the limitations of X-ray mirror optics limit the achievable NA to lower numbers, i.e., NA of 0.25 to 0.30 for initial tools and NAs of 0.40 to 0.45 for future advanced tools.² As a result, a possible switch to 6.7 nm wavelength is being discussed for future EUV generations.³

Along this path, the increasing complexity of optics and illumination systems, the heightened requirements for alignment and throughput, and increasing wafer size have led to an exponential increase in exposure tool cost (Fig. 1). Along the

timeline of tool development, the industry has achieved a wavelength reduction from ~450 nm (broadband mask aligner) to 13.4 nm (EUV), corresponding to a factor of 33, but at the expense of increasing tool cost by a factor of over 1,000, from ~\$0.1 million to \$100-120 million for an EUV exposure tool. Even for high volume devices for which packing density and smallest linewidth are critical for economics and performance, the rising cost of tools and of advanced mask sets using complex techniques for resolution enhancement has put a significant economic strain on device manufacturers. Already a segment of the industry has opted out of 193 nm dry lithography and stayed with device types that can be manufactured with 248 nm tools; similarly, 193 nm immersion lithography will not be adopted by everybody. It is anticipated that for EUV lithography, only the largest chip makers will be able to afford the cost of full implementation.

Figure 1: List price development of lithographic tools 1986 - 2011.⁴ From 1986 to 2007, tool cost has risen exponentially following a regression line of cost [\$ million] = $0.934 \cdot \exp(0.173 \cdot (\text{year} - 1986))$. This regression would predict billion dollar tools by 2026. 2011 data point (for EUV) is ~68% higher than expected from the regression.

The purpose of this paper is to advance a different paradigm based on materials science. If the current approach of transferring all information from the mask (“top down lithography”) runs into economic constraints, a “bottom-up” approach in which materials contribute to the definition of the smallest features becomes increasingly attractive, and, in the long run, maybe even mandatory. Going forward, materials chemistry faces the challenge of not only continuing to enable Moore’s Law but also reducing or avoiding the increasingly unaffordable cost of traditional “top down”

lithography paradigm, in which all pattern information is transmitted in hardware-based steps. The purpose of this paper is also to show that there is precedent for the development of lithographic materials playing a crucial role in advancing the industry’s ability to print smaller feature sizes, and that there are already options to extend their role to the definition of patterns significantly below 20 nm half-pitch that are beyond the reach of current mass production lithographic technologies.

1. The Role of Photoresist in Enabling Moore’s Law

In terms of Rayleigh’s equation (Eq. 1), the role of materials in enhancing resolution is usually expressed in terms of the factor k_1 , which is used as a lumped parameter that convolutes the effects of optics and resist process capability. No process can achieve k_1 values smaller than 0.25, at which point there is no more modulation in the aerial image, and manufacturable processes require higher k_1 factors. The industry has learned to decrease the k_1 values for manufacturable processes from $k_1 = 0.7$ for g-line to near 0.30 for current processes, and of course double patterning has added the capability to divide the k_1 factors by two, albeit at the expense of at least doubling the patterning cost.

This reduction in k_1 factors has been made possible by the improvements processing technology and more complex masks, but also in resist materials themselves and by the use of additional assist layers such as bottom antireflective coatings. A 2002 paper⁵ has tried to evaluate the relative contribution of materials and exposure tools to increasing resolution capability by analyzing a time series of resist resolutions and expressing the improvement rate in terms of an “equivalent NA” that can be directly compared to the rate of NA increase of exposure tools. In this paper, an initial example of i-line technology was used to introduce the concept of the equivalent NA (NA_{eq}) as follows:

Diazonaphthoquinone-based resists constituting the state of the art in 1984, 1990, and 1996 were imaged on the same i-line stepper ($NA=0.54$), and their resolutions compared (Fig. 2). Along the time series, k_1 factors decreased from 0.81 in 1984 to 0.55 in 1990 and 0.44 in 1996. In order to compare the resolution improvement due to resist optimization with stepper NA improvement, Rayleigh’s equation was used to determine what stepper NA would be needed to achieve the observed resist resolution with the 1984

reference k_1 factor 0.81. The result was that a near-unity NA_{eq} would be required to achieve the 1996 resolution (Fig. 3).

Fig. 3 shows the i-line data points to lie on a straight line with a slope of 0.037 NA_{eq} units per year. With three data points, this could be a coincidence; however, the same analysis was carried out by G. Jord-

Figure 2: Historical k_1 factors for i-line photoresist.

Figure 3: Plot of NA_{eq} for the data points of Fig. 2 and similar data for 248 nm lithography (G. Jordhamo⁶, IEEE 2000). The 2001 data point corresponds to an experimental resist, its deviation from the straight line indicates that DNQ i-line resist technology has reached a technical limit.

Figure 4: Master curve for photoresist development rate showing identical improvement rate of $\sim 0.037 NA_{eq}$ units per year for all technologies from i-line to EUV.

hamo of IBM for 248 nm lithography⁶ and gave the same linear rate of resist performance increase for this technology (Fig. 3). This prompted the more extensive

re-analysis including 193 nm lithography in the 2002 paper⁵ which showed that the rate of increase was indeed the same for i-line, 248 nm, and 193 nm resist technologies (Fig. 4). In this paper, recent data on EUV resist resolution capability⁷ have been added (Fig. 4) and are found to follow the same linear rate of increase in NA_{eq} . By comparing these numbers to the rate of exposure tool NA increase, the 2002 paper⁵ concluded that the contribution of materials technology had historically outperformed those of optics (Fig. 5). This conclusion does not hold for the more recent introductions of immersion and double patterning technologies, which achieved rates of NA_{eq} improve-

Figure 5: Historical development rate for optical tools and photoresists prior to the advent of immersion technology.⁵

ment of about 0.11 and 0.27 units per year, far above the historical resist improvement rate. While significant materials development was needed for 193 nm immersion resists, such as the development of non-leaching PAGs,⁸ more hydrophobic resist polymers⁹ and additive technology,¹⁰ and immersion top coats^{11,12} to enable defect-free high scan speeds, this development has not led to significant increases in resolution capability: 193 nm immersion resists do not show significant resolution improvements versus dry resists when imaged on a non-immersion tool.

The linear increase of NA_{eq} as a function of time is an entirely empirical relationship; while it holds for multiple technologies over long time scales, its origin is unknown (although it has been speculated that it may result from characteristics of the materials development infrastructure, e.g. the amount of revenue resist manufacturers can spend on development). However, whatever its origin, it provides a valuable tool to extrapolate resist development progress into the future. Such a tool is of particular interest for examining progress in EUV lithography, where resist performance continues to be a limiting factor.

In a 2010 presentation,⁷ AMSL extrapolated resist performance on the NXE 2000 EUV scanner (NA 0.32, dipole illumination) and predicted that resists would achieve 18 nm resolution early in the first half of 2013.

A re-analysis of their data (Fig. 6) using extrapolation based on the equivalent NA technique indicates that this resolution would only be achieved over 2 years later, by mid-2015. This kind of a delay in resist performance improvement would have a significant impact on EUV technology availability for the 18 nm node. However, even this timeline may be overly optimistic: in a 2011 presentation at the SPIE Advanced Lithography conference,¹³ P. Naullaeu reported that resists had not shown resolution improvement on the Berkeley MET tool over the last three years. Fig. 7 shows a re-plot of his data, including a conversion to equiv. NA numbers. The plot indicates a leveling off effect that is reminiscent of the one seen for i-line lithography in Fig. 2, which could mean that a fundamental limit in chemically amplified resist (CAR) technology has been reached. The observed limit does not correspond to a limitation of the exposure tool, since 16 nm resolution has already been demonstrated under the same exposure conditions with non-CAR resists.

Fig. 6: Re-plot of 2010 ASML data⁷ and extrapolation using NA_{eq} scheme showing deviation from a simple power-law extrapolation.

Fig. 7: Re-plot of P. Naullaeu's 2011 data¹³ showing deviation from the expected improvement rate for EUV photoresists on the Berkeley MET.

EUV resist development requires a delicate balance and trade-offs between line width roughness,

resolution, and sensitivity,¹⁴ with the latter still being severely constrained by the low power of EUV sources. Since diffusion blur has been reduced to probably its lowest practical level with the introduction of polymer bound photoacids (PBPs),¹⁵ current proposed approaches focus on the increase of photon absorption in the resist by introducing more absorbing elements, such as fluorine. If such approaches should prove to be insufficient to achieve the required resolutions, and if CAR resists have indeed reached a fundamental limit, a completely new photoresist platform will be required to achieve the introduction of EUV lithography for sub-20 nm nodes. If history is any guide, the development of new resist platforms requires a significant amount of time. The delay in EUV readiness, partly caused by photoresist availability, will have to be made up by costly quadruple patterning schemes.

The above assessment is in marked contrast to the continued optimism of the EUV resist development community,¹⁶ who continue to predict that CAR EUV technology will be used down to the 16 nm node. However, whether the technical limits are reached at 20 or at 15 nm, it is clear that both from a technical and economical perspective, the ceilings of top-down lithography are in sight. This perspective provides additional incentive for a vigorous development of bottom-up approaches, in which feature size is no longer limited by resist structure definition.

2. Stages of Bottom-Up Materials Evolution

The purpose of the previous section has been twofold: for one, to show that materials development has historically been a somewhat equal partner in allowing continued feature size reduction as required by Moore's Law, and second, to show that the industry is nearing limits that may require a paradigm change from top-down lithography, in which materials react to information directly transferred from a mask or pattern generator, to bottom-up approaches in which materials themselves contain structural information. One example of such an approach is directed self assembly of block copolymers, in which the characteristic feature size is defined by the polymer blocks' molecular weight. Such materials are sometimes referred to as "smart chemicals", which incorrectly implies that the currently used materials are somehow "dumb".

Photoresists play a key role in enabling the patterning process, acting as chemical rectifiers to

transform a sinusoidal aerial image with a large constant (a DC component in electrical engineering parlance) into a square wave (the photoresist relief image), and their ability is on a par with many electrical signal rectifiers. With the increasing complexity of patterning ever smaller features, photoresists needed to be supported by a large number of assisting materials in order to perform their function, such as

- Top antireflective coatings (T.A.R.C.s)¹⁷
- Bottom antireflective coatings (B.A.R.C.s),¹⁸ including developer-soluble B.A.R.C.s¹⁹
- Top protection coatings for immersion lithography^{11, 20, 21}
- Hardmasks (spin-on or deposited)²²
- Carbon-rich underlayers (spin-on or deposited)²³
- Anti-collapse rinses.²⁴

All of these materials are exceedingly well designed for their purpose, and certainly “smart” in that sense. For example, developer-soluble antireflective coatings¹⁹ need to be soluble in common resist casting solvents after spin-on, to provide spin bowl compatibility and allow the use of common edge bead removers; they then need to be transformed prior to photoresist application into a form that is insoluble in the photoresist solvent to avoid intermixing, which in one implementation of the technology is accomplished by crosslinking them. However, crosslinking would prevent dissolution in developer, so the crosslink formation has to be reversed during exposure and PEB. Acid-labile crosslinks meet this requirement, and also provide a mechanism in which the coating only becomes soluble only in the exposed areas, resulting in an anisotropic development rate that reduces undercut. All of the above targets need to be achieved while at the same time providing all of the usual B.A.R.C. functions, i.e, antireflection, low to no footing or undercut, and good collapse margin. As can be seen from this example, the design of “conventional” top-down lithographic materials can be intricate and complex.

Shrink materials²⁵ are applied to existing photoresist patterns in order to reduce the spaces left by resist patterning (Fig. 8). They form a chemical attachment layer around the resist, leading to smaller contact hole or trench dimensions than can be obtained by direct lithographic patterning. While this technique cannot reduce the features’ pitch, it enables the user to create dimensions inaccessible by current lithographies

or to use older and cheaper technology for their patterning. Both water-based reactive polymers and solvent-based approaches using polymer blends fall into this category. The attachment amount is determined by the chemistry (and process) of the attachment layer, so in a rudimentary sense a bottle of shrink material already contains feature size information, although it may still be somewhat dependent on the interaction with a particular photoresist’s chemistry. As such, shrink materials represent an early stage, intermediate step in the development of bottom-up lithography.

3. Directed Self-Assembly Of Block Copolymers

Materials for “bottom-up” lithography exhibit built-in “chemical intelligence” in which the feature size ultimately formed on the substrate is defined by

Fig. 8: Photoresist space reduction of trench structures using shrink materials. R607,SH114: AZ com. materials.

the material’s molecular parameters. The final feature size is largely independent of the initial feature which only serves as a guideline for placement. Recent developments in Directed Self Assembly (DSA) of block copolymers²⁶⁻³⁰ take lithography a significant step further towards such a bottom up approach. Lithographic guide patterns are still required to position and align the self assembly process: there currently is no viable path to avoid the “top down” information transfer of resist patterning to create the guiding features that define alignment and placement of the DSA features. Although “DSA on DSA” approaches have been reported that push the top-down process back one step,^{30,31} it is conceptually difficult to envisage processes that would not use some initial guiding feature. Ultimately the goal of bottom-up lithography must therefore be to minimize the amount of information that needs to be transferred top-down.

The intent of this paper is not to provide a review of the state of block copolymer lithography, but rather to point out its promise for bottom-up lithography.

However, to this purpose, a short overview of its technical features is required. This overview will concentrate mainly on a select few recent schemes which have focused on processes which are compatible with standard fab operations, and will in the interest of brevity have to exclude many other existing efforts in DSA of block copolymers³⁰ that are currently under way.

Block copolymer phase separation is driven by the entropic factors, which become unfavorable for macromolecules. The Gibbs free energy of a polymer mixture is given by

$$\frac{\Delta G_{mix}}{kt} = \frac{f_A}{N_A} \ln(f_A) + \frac{f_B}{N_B} \ln(f_B) + f_A f_B \chi \quad (2)$$

where k is the Boltzmann constant, f_A and f_B are the relative volume fractions, N_A and N_B are the degrees of polymerization, and χ is the interaction parameter. For high molecular weight materials, the first two terms become very small, and only polymers for which the interaction with each other is more favorable than their self-interaction (negative χ factors) will mix. If the polymer blocks' self interaction is greater than the interaction with each other (positive χ factors), phase separation will result for sufficiently high molecular weight. Practically, phase separation will only occur above a minimum value of the segregation strength χN . Self-consistent field theory yields this value as $\chi N > 10.5$.³²

In block copolymers (BCPs), the polymer segments are linked by a chemical bond, which introduces constraints on the geometrical arrangement of the macromolecules. This leads to the formation of distinct phases which depend on the volume fractions of the blocks (shown in Fig. 9 for AB type binary copolymers). Of these phases, the cylindrical (locally hexagonal packed) and lamellar phases are of particular interest since they closely resemble lithographically useful contact hole and line/space structures. The period of the BCP structures is called the characteristic length L_0 (for example, a binary A-B BCP with block A lamellae of width 18 nm and block

B width 22 nm has $L_0 = 40$ nm). The characteristic length is a material constant, which means that the CD information will be delivered "in the bottle." This imposes design constraints since only a single feature size can be generated in a single layer, but on the other hand it offers opportunities to achieve unprecedented levels of CD control.

In the most advanced (in the sense of being closest to actual implementation) of the approaches currently under investigation, the cylindrical and lamellar phases are aligned at a right angle to the surface, one of the blocks is selected to be more dry etch resistant than the other, and the less resistant block is removed by dry etching. For a variety of technical and practical reasons, poly(styrene-*b*-methyl methacrylate), P(S-*b*-MMA), has been used for the majority of studies in this area. P(S-*b*-MMA) has a low χ factor of about 0.0028,³³ which means that this BCP requires high MW to achieve $\chi N > 10.5$. Therefore, P(S-*b*-MMA) is only capable of generating larger self-assembled structures in the range above ~20 nm characteristic length. Future implementations of DSA lithography will have to use different BCPs to achieve smaller features.

However, in the case of p(S-*b*-MMA), the interaction energy with air is about the same for both blocks, which removes the need to control the top of the block copolymer film in order to achieve the vertical orientation of the polymer domains. Annealing is performed in a bake step at high temperatures, and the polymer blocks need to move past each other to achieve the thermodynamically favored configuration. BCPs with lower χ factors tend to be easier to anneal since the movement of the polymer blocks encounters lower activation barriers. High χ factor BCPs, such as silicon-based copolymers,³⁴ are more difficult to anneal by a thermal bake only and typically require the use of solvent vapors to achieve pattern formation.³⁵ Even for p(S-*b*-MMA), early studies on the physics of block copolymer self-assembly frequently used annealing times of tens of hours to days; however, annealing times can be brought down to track-compatible times of two minutes or less.³⁶

Figure 9: Phases adopted by binary block copolymers as a function of composition. Volume fractions for cylindrical (rod) phases of monomer 1 are approximately from 0.2 to 0.3, for lamellar phases from 0.4 to 0.6.

The vertical alignment of the polymer domains is effected either by providing a three-dimensional relief structure as an orienting feature (grapho-epitaxy) or by providing a “orientation control layer” with equal affinity to both polymer blocks. Chemical patterns can then be defined on top of the orientation control layer to guide and align the polymer phases (chemi-epitaxy).

The chemistry of the orientation control layers is a critical part of the DSA process. If the layer under the BCP has a higher affinity to one of the blocks, the block copolymer domains may orient parallel to the surface rather than in perpendicular (vertical) orientation. While it is possible to use surface energy modifications to achieve alignment, the best results are achieved by using a grafted polymer layer that is a random copolymer of the BCP's monomers.³⁷

Two first applications of block copolymer DSA for microlithography are currently under investigation which allow either shrink of contact holes,²⁶ or the frequency multiplication of line/space patterns²⁷ that can serve as a low-cost alternative to triple, quadruple, or higher patterning.²⁸ DSA for contact hole lithography uses the relief image of a contact hole as a three-dimensional guiding pattern (grapho-epitaxy, cf. Figs. 10 and 11). In this application, a cylinder-forming block copolymer is used to form a central cylindrical domain within the topographic prepattern. Selective removal of the cylindrical domain affords a contact hole or via with reduced CD relative to the prepattern. The size of the contact hole obtained after the dry etch depends on the size of the cylindrical domain, which is largely determined by composition of the BCP material in the bottle delivered by the materials suppliers.

A limitation of this technique for contact hole lithography is that the volume fraction of the contact hole is limited by the volume fractions in which cylindrical phases form, placing constraints on the extent of shrink that can be achieved while maintaining the desired domain morphology. For example, if the prepattern is too large relative to the natural period of the block copolymer, complex morphologies may be formed.³⁸ For very large prepatterns, multiple domains will form within a single prepattern feature.

In the second application, DSA for line frequency multiplication, a chemi-epitaxy approach is preferred over grapho-epitaxy, since topographical guide structures take up valuable space on the substrate and because the line edge roughness of the guide structures is transferred to the DSA lines (whereas no such

Figure 10: Process flow for DSA CH pattern generation

Fig. 11: Results of DSA CH lithography (from ²⁶, figures courtesy of IBM Almaden R&D, with permission).

“telegraphing” of LER/LWR is observed for chemi-epitaxy).²⁷

One chemi-epitaxy approach developed by IBM has focused on integrating DSA with existing fab processes.²⁷ It uses 193 nm immersion lithography to create photoresist patterns at a relaxed pitch to define the chemical patterns for DSA as shown in Fig. 12. The patterned photoresist is used to mask the underlying surface during grafting of the orientation control material. Dissolving the resist material with standard TMAH creates a chemical pattern to which the MMA blocks align. As mentioned before, one of the advantages of this chemi-epitaxy process is that LWR of the guide structures is not transferred to the DSA pattern; as a matter of fact, the DSA process is

even able to “heal” and correct imperfections in the guide patterns.

A major concern with DSA has been the question of the inherent defectivity of the process. Since annealing relies on a thermodynamic driving force, it was conceivable that defects such as disclinations and dislocations would occur at a level higher than tolerable for IC lithography even at thermodynamic

Figure 12: 4x line frequency multiplication using DSA chemo-epitaxy lift-off approach (from²⁷, with permission).

equilibrium. Recently, the first attempts at measuring the full-wafer defectivity of a 4x line frequency multiplication DSA process on 300 mm wafers have been reported.³⁹ These experiments demonstrated promising initial defectivity level and put an upper bound of $< 25/\text{cm}^2$ on DSA specific defects, similar to the level seen for early immersion lithography efforts. While a considerable amount of work remains to determine other aspects of defectivity (such as overlay accuracy for example) which were not explored in this study, it is expected that further materials and process optimization will be able to bring down the gross defectivity levels in a manner similar to seen in other historical introductions of new lithographic materials.

4. Conclusion

The increasing cost of the lithographic process, which is driven both by process complexity and by the increasing cost of moving to smaller exposure wavelengths, makes approaches that use “smart chemicals” and “bottom up” patterning processes that employ molecular scale assembly processes ever more attractive. The technology that is closest to implementation in IC manufacturing is DSA of block

copolymers for contact shrink and line space multiplication. The current delays and limitations in EUV lithography provide further incentive to pursue DSA technology, which can be both complementary (such as in contact hole shrink) as well as a competitor (such as for fine line patterning). Current results indicate that DSA structure quality, line roughness measures, and defectivity are in a range that allows development work for integration into existing production to begin. DSA for contact hole formation may be closest to implementation, since its process integration is very similar to existing shrink material schemes. A first application for line frequency multiplication may be the replacement of multiple patterning processes with DSA schemes. A DSA-based process can provide significant cost and cycle time reductions over existing spacer schemes as well as other technical advantages.²⁸

Beyond replacing spacer patterning, the regular arrays of lines generated by DSA can also serve as templates for line cutting schemes⁴⁰ that have been proposed to generate more arbitrary patterns. DSA will require considerable additional work for process integration and mask fracturing/design, and it cannot be considered a simple drop-in even for current spacer multiple patterning. However, DSA’s potential cost and technical advantages make a compelling case for pursuing this technology.

The introduction of DSA technology will follow the same sequence historically seen for new patterning technologies: after initial development of the fundamental technology by academia and research institutions, commercial suppliers will take over the task of optimizing materials, providing them with consistent quality, and modifying them to meet specific customer requirements. The race is on for materials suppliers to carve out their niche in this new field.

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