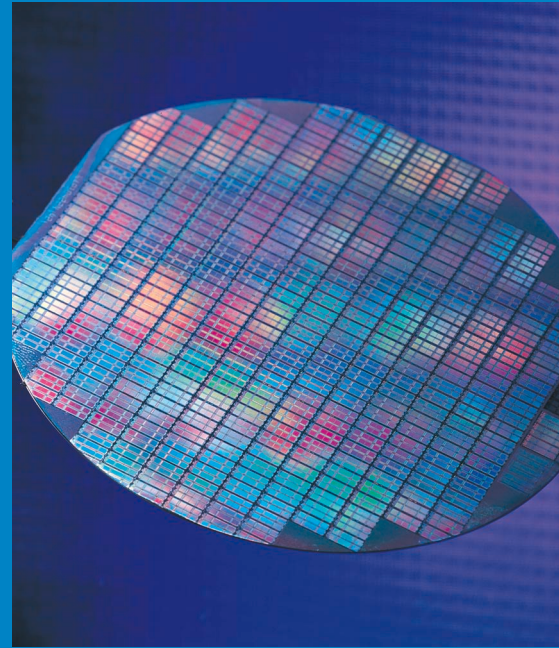


# **TECHNICAL DATA: BOE<sup>®</sup> BUFFERED OXIDE ETCHANTS**

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Clean, Uniform Etching for Semiconductor Devices



# BOE® PREMIXED ETCHANTS

## A complete range of useful thermal oxide etching rates



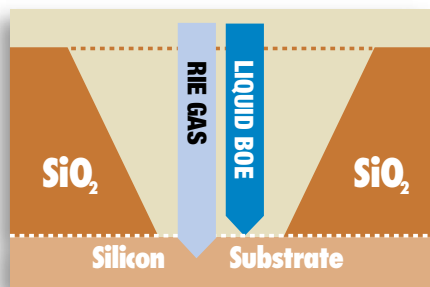
### ISO Registration

Our electronic grade chemicals are manufactured, analyzed, packaged, and distributed under strict ISO 9002 guidelines. The scope of our ISO registration, as noted on our certificate, is:

*“The manufacture of inorganic acids, bases, etchants, ammonia-based inorganic compounds, and custom blends of inorganic salts, bases, and acids. The purification of phosphoric acid, solvents, hydrogen peroxide, and inorganic bases to specifications... for the semiconductor industry.”*

ISO registration ensures that we pay continuous attention to quality, so you can expect superb purity and lot-to-lot consistency in all General Chemical electronic grade process chemicals.

General Chemical's premixed BOE® buffered oxide etchants provide a complete range of useful thermal oxide etching rates. All of our liquid BOE products etch silicon dioxide ( $\text{SiO}_2$ ) but not the silicon substrate. This selectivity allows etching to stop at the  $\text{Si}/\text{SiO}_2$  interface, unlike RIE gases, which can etch the silicon as well.



Superwet BOE products contain a surfactant additive, which improves wetting of the substrate face. This allows for greater uniformity and cleaner etching even in sub-one-micron geometries. There's no need for wafer prep in an aqueous surfactant solution, so the etchant will not be diluted by drag-in of the prep solution, thereby extending the bath life.

The surface tensions of Superwet BOE etchants fall in the range of 19 to 23 dynes/cm, which is equal to or below the interfacial tensions required to uniformly wet patterned substrates. As a result, the amount of overetch required for complete etching across the wafer is reduced, and lateral etch is also minimized. Superwet BOE etchants have a shelf life exceeding one year, and may be continuously filtered during usage without loss of uniform etching effectiveness.

Superwet BOE etchants are used in standard oxide etching procedures. No residual surfactant contaminants are left on the substrate after typical wafer cleaning procedures are completed. Particle counts on wafer surfaces etched with Superwet BOE etchants are substantially lower, providing fewer defects on the wafers and increasing yields.

Modified BOE products have lower freezing points than standard BOE products and greater solubility for oxide etching by-products. Residues are completely rinsable with water, minimizing residual crystals in etched windows. Modified BOE etchants provide uniform, predictable oxide etching rates. They are also available in the Superwet form.

### CHARACTERISTICS

Buffered oxide etchants are blends of 49% hydrofluoric acid (HF) and 40% ammonium fluoride ( $\text{NH}_4\text{F}$ ) in various predetermined ratios. General Chemical's premixed BOE etchants are prepared in large volume lots, under controlled conditions. This minimizes the errors that can occur in preparing smaller volumes in a wafer processing area. Final composition of each lot of premixed BOE etchant is controlled and adjusted before packaging. Premixed BOE etchants are available in all commonly used ratios.

The use of premixed BOE etchants provides many benefits, including:

- consistent and correct etchant formulations, which yield reproducible etch rates lot-to-lot.
- guaranteed maximum impurity levels, assay and etch rates.
- the convenience of a ready-to-use product, which minimizes the handling of hazardous materials.

## SPECIFICATIONS

BOE etchants are prepared only from semiconductor grade components carefully adjusted to assure the proper formulation. General Chemical has established composition tolerances of  $\pm 0.15\%$  for HF content ( $\pm 0.05\%$  for BOE 50:1 etchants),  $\pm 0.5\%$  for  $\text{NH}_4\text{F}$  content in standard BOE etchants and  $\pm 0.3\%$  for  $\text{NH}_4\text{F}$  content in modified, low-freezing-point BOE etchants. Every BOE product specification includes a performance requirement based on thermal oxide etch rate at  $21^\circ\text{C}$ . The maximum allowable etch rate range is:

- $\pm 50 \text{ \AA}/\text{min}$ . for fast etchants (nominal etch rate of  $>1000 \text{ \AA}/\text{min}$ . at  $21^\circ\text{C}$ ).
- $\pm 35 \text{ \AA}/\text{min}$ . for intermediate etchants (nominal etch rate of 500 to  $1000 \text{ \AA}/\text{min}$ . at  $21^\circ\text{C}$ ).
- $\pm 25 \text{ \AA}/\text{min}$ . for slower etchants (nominal etch rate of 200 to  $500 \text{ \AA}/\text{min}$ . at  $21^\circ\text{C}$ ).
- $\pm 15 \text{ \AA}/\text{min}$ . for slow etchants (nominal etch rate of  $<200 \text{ \AA}/\text{min}$ . at  $21^\circ\text{C}$ ).

Maximum impurity levels in BOE etchants are superior to SEMI specifications and conform to General Chemical's high-purity requirements. Complete spec-

ifications for individual BOE products are available on request.

## APPLICATIONS

BOE buffered oxide etchants are used to etch window openings in silicon dioxide layers. The primary application is the etching of thermal oxide layers in IC production. The etch rates described in this brochure refer only to etching of thermal undoped oxides, not CVD or spun-applied glasses. These "non-thermal" oxides usually exhibit differing etch rates, which vary with deposition method, subsequent thermal treatment and dopant content.

Oxides containing large concentrations of boron usually etch much slower, while phosphorus-doped oxides etch faster than undoped oxides with equivalent thermal history. Arsenic-doped oxides etch faster than undoped oxides, but slower than phosphorus-doped oxides.

The trace amount of dopant found in thermal oxide that originates from substrate dopant content (0.1 ohm-cm or greater) has no measurable effect on etch rate. Undensified CVD glass or spun-on glass layers etch extremely fast. However, when such oxides are densified ( $>900^\circ\text{C}$ ), they behave more like thermal oxide.

## OUR ENVIRONMENTAL COMMITMENT



In addition to delivering a high-quality product, we are committed to managing our chemical processes and product supply systems within the guidelines of the American Chemical Council's Responsible Care® program. Full regulatory compliance ensures safe operation... and safety of supply to our customers.

## GENERAL CHEMICAL: *In Review*

General Chemical is a leading producer of performance chemicals for the environmental, technology, chemical processing, and pharmaceutical and healthcare markets. The company makes an array of value-added chemicals for technology-based sectors like semiconductors and disk drives, as well as such markets as papermaking, photography, petroleum refining, petrochemicals and foods.

### Broad Base in Electronic Chemicals

General Chemical is an established supplier of acids, solvents, bases and chemical blends for the electronics and related industries. It pioneered wet electronic-grade chemicals in the 1940s, and has maintained a strong presence in this area ever since. It currently operates a number of high-purity chemical facilities: an acid facility in Pittsburg, Calif.; sulfuric acid units in Richmond, Calif., and Newark, N.J.; and a solvent facility in Hollister, Calif. It has warehousing and distribution points across the United States, and sells its products throughout the world.

**Table I: Standard BOE Etchant Characteristics**

40% NH <sub>4</sub> F: 49% HF Volume Ratio	HF Conc., %	Specific Gravity @ 25°C	Etch Rate @ 21°C, Å/Min.	Freezing Point, °F
4:1	9.9-10.2	1.115	1740-1840	76
5:1	8.2-8.5	1.113	1020-1120	64
21:4	7.9-8.2	1.113	970-1070	63
6:1	7.0-7.3	1.112	860-930	56
25:4	6.8-7.1	1.112	830-900	53
13:2	6.5-6.8	1.111	790-860	52
34:5	6.3-6.6	1.111	765-835	50
7:1	6.1-6.4	1.111	735-805	49
8:1	5.4-5.7	1.110	640-710	44
9:1	4.9-5.2	1.110	575-645	40
10: 1	4.4-4.7	1.109	510-580	37
12: 1	3.8-4.1	1.109	435-505	32
15:1	3.0-3.3	1.108	345-395	30
20:1	2.3-2.6	1.107	265-315	26
25:1	1.8-2.1	1.107	205-255	25
30:1	1.5-1.8	1.106	185-215	22
40:1	1.1-1.4	1.106	140-170	21
50:1	1.0-1.1	1.105	125-145	20
100:1	.45-.55	1.105	65-85	20

**Table II: Modified BOE Etchant Characteristics**

Modified BOE Product	HF Conc., %	Specific Gravity @ 25°C	Etch Rate @ 21°C, Å/Min.	Freezing Point, °F
1235	8.1 -8.4	1.11	1150-1250	53
930	6.2-6.5	1.11	850-920	40
725	4.4-4.7	1.11	670-740	15
500	2.8-3.1	1.11	420-490	0

**ETCH RATE**

The etch rate of undoped thermal oxide by aqueous NH<sub>4</sub>F/HF solutions, with or without surfactant additives, depends on three primary factors: NH<sub>4</sub>F range, etching temperature, and specific HF content.

Standard BOE etchants (40% NH<sub>4</sub>F/ 49% HF blends) contain over 30% NH<sub>4</sub>F, a range where HF content has primary influence on etch rate (*Table I*).

It is observed that a variation of 0.1% HF can change the etch rate by 20 Å/min. or more. A temperature variation of 1°C can affect etch rate by as much as 100 Å/min. A constant temperature bath, or other suitable heating/cooling means, should be provided for maintaining ±0.5°C temperature control of the etchant bath. The etchant reaction is essentially nonexothermic.

Tables I and II give the HF concentration for premixed standard, Modified and Superwet BOE formulations. The tables also provide the specific gravity, etch rate range at 21°C and the freezing point of each formulation. The weight of standard BOE products ranges from 9.29 (BOE 4:1 etchant) to 9.22 (BOE 50:1 etchant) pounds per gallon at 25°C, while the weight of Modified and Superwet BOE products is about 9.25 pounds per gallon at 25°C.

**Recycling Programs**

As a basic manufacturer, we can recycle certain acids to our production units.

This not only benefits the environment, but it also reduces or eliminates neutralization costs for our customers.

We have decades of experience in acid recycling and processes that simplify the logistics of spent acid removal, as we supply you with high-purity materials.



## PROCEDURE

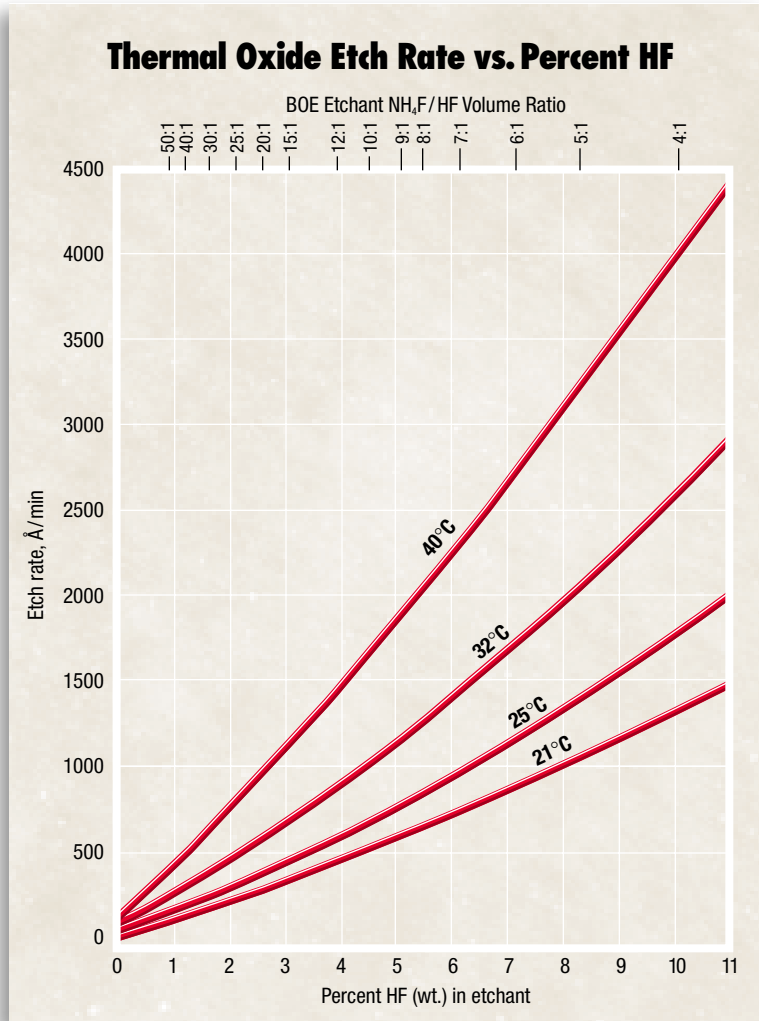
When using General Chemical's BOE products, standard etching procedures are applicable. Standard established resist processes and post-bake conditions are acceptable. The more important procedures affecting uniform etching are highlighted in this section.

Etching should be done in an etchant bath, which has excellent temperature control, preferably to within  $\pm 0.5^\circ\text{C}$  or better. A variation of  $1^\circ\text{C}$  results in a  $100 \text{ \AA}/\text{min.}$  variation in etch rate. Poor control of etchant temperature results in under- or overetching, and loss of the primary benefit of premixed etchants – consistent, complete etching in predictable etch times.

Continuous filtration of the etchant maintains cleanliness of the etchant bath, also providing greater etching uniformity with fewer defects. General Chemical's Superwet BOE etchants retain their low surface tension throughout the use of continuous 0.2-micron filtration procedures.

Etching a pilot wafer having an oxide thickness identical to that of the product wafers helps maximize the benefits of low surface tension etchants like Superwet BOE etchant. This procedure establishes the time required for just etching through the oxide layer. Product wafers may then be etched at 110% (10% overetch) of the time required for etching through the oxide. Experience suggests that 10% overetch with a Superwet BOE etchant will provide uniformly etched patterns, while etchants without surfactants may require 20 to 30% overetch for complete etch through all window areas.

Side wall taper caused by lateral etching is a characteristic of etchant composition and temperature. Superwet BOE products minimize the occurrence of lateral etch. Other techniques for controlling window taper include:

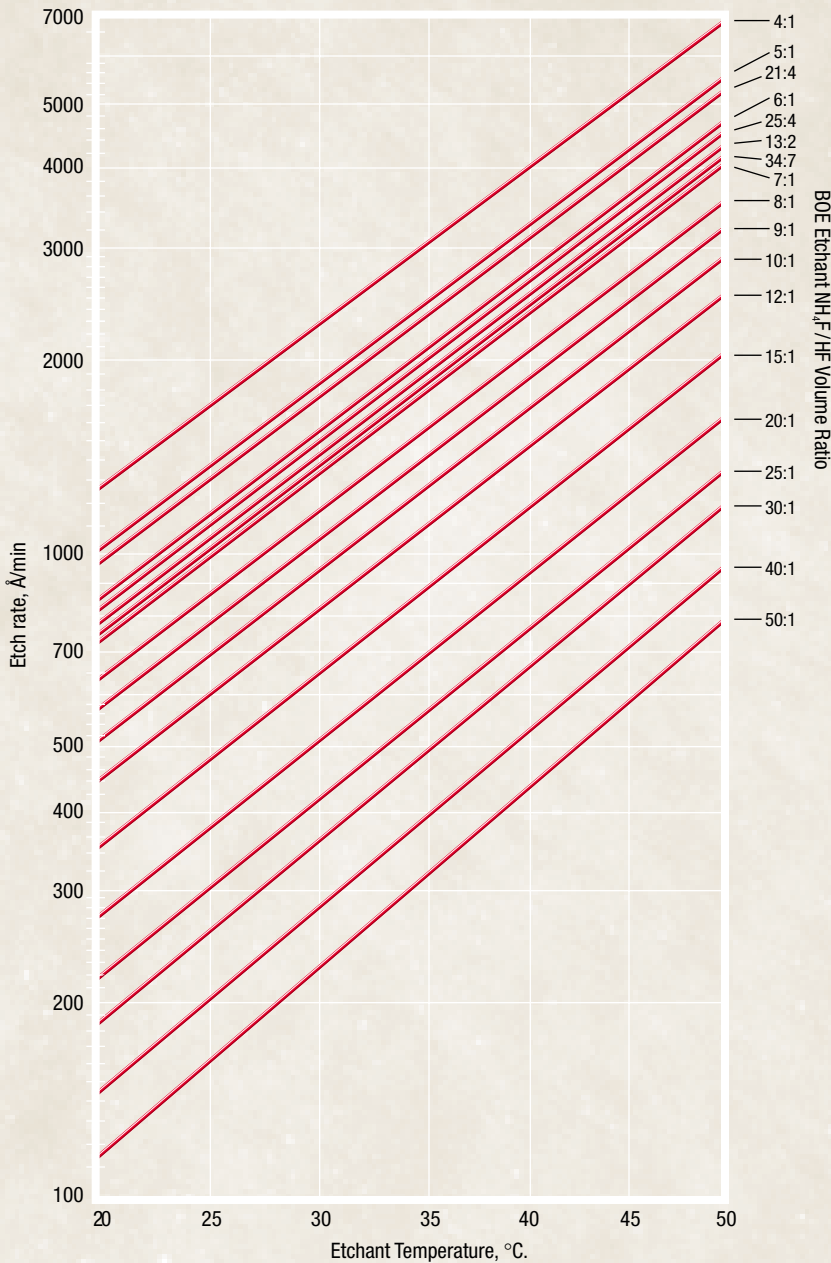


- modification of photoresist adhesion by reducing resist post-bake temperature.
- providing an upper few hundred Å of faster etching oxide.

(Techniques that achieve faster etching layers include phosphorus doping of the oxide, or application of undensified CVD oxide or spun-on glasses, either undoped or slightly phosphorus doped.)

## Thermal Oxide Etch Rate vs. Temperature

Standard BOE Etchants



### BATH LIFE

BOE etchants etch a minimum of 500 150-mm wafers, 300 200-mm wafers or 125 300-mm wafers (10,000 Å oxide) per gallon. Often, etchant baths are changed every shift because etch rate may decline slowly as HF is consumed.

Water carry-over from an aqueous surfactant/depredip step dilutes the HF, further reducing etch rate. The use of Superwet BOE etchants containing a surfactant is preferred, as it eliminates the need for wafer depredip. This avoids drag-in of depredip solution and the precipitate that may result from incompatible surfactants.

### RECIRCULATION

Continuous recirculation of the etchant bath through sub-micron filters can extend bath life by maintaining low particulate content in the etchant bath. Superwet BOE products are especially advantageous because the surfactant is not removed by 0.2-micron filtration. Etching capability remains uniform for as long as one week.

Additional Superwet BOE etchant may be added to maintain liquid level in the bath. Monitor wafers may be necessary to ascertain "current" etch rate.

### CRYSTALLIZATION AND RECONSTITUTION

The initial crystallization temperatures of all commonly used BOE etchants are given in Tables I and II. Many of these formulations crystallize at fairly high temperatures (40 to 70°F) and are difficult to redissolve. They should be stored in a warm area to minimize freezing concerns.

If crystallization occurs, the solution may be reconstituted by heating the etchant above the freezing point and providing agitation. Agitation is important to ensure a uniformly reconstituted solution. The use of a ball mill roller is a convenient method for remixing etchant contained in one-gallon bottles.

Even though the BOE solution may appear clear, agitation before use is advisable, since the material may have crystallized in transit, redissolved unnoticed, and left a stratified etchant composition (weak, slower-etching material at the top and strong, faster-etching solution near the bottom).

Low surface tension etchants like Superwet BOE products are not permanently altered by freezing and thawing. They have been frozen and reconstituted with no change in expected characteristics.

### Physical and Chemical Properties

**Appearance** ..... Colorless liquid

**Color, APHA** ..... 10 maximum

**Specific gravity**

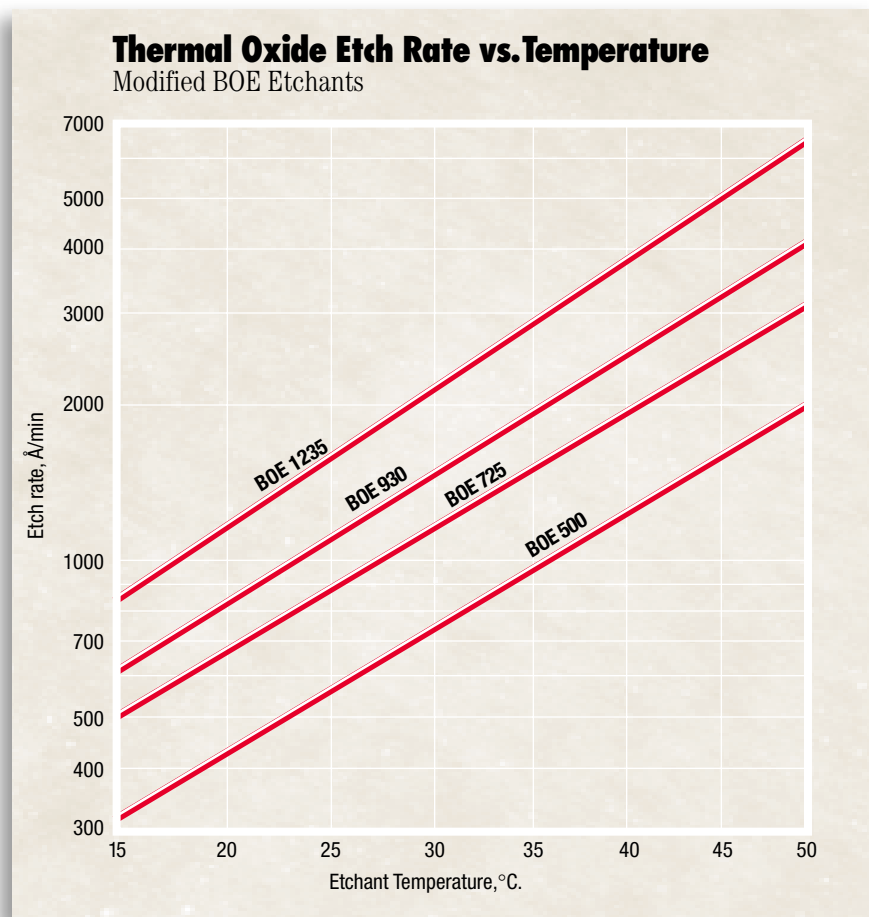
@ 25°C ..... 1.11 (approx.)

**Freezing point** .... Varies with BOE product ratio  
.....  
..... (Tables I and II)

**Surface tension:**

Modified and Standard BOE ..... 85 to 90 dynes/cm

Superwet BOE ..... 19 to 23 dynes/cm



### PACKAGING

General Chemical's Modified BOE etchants are available in 9-lb. polyethylene bottles and 475-lb. polyethylene-lined drums or in returnable polyethylene or PFA-lined drums. All standard and Modified BOE products are available in the Superwet version with surfactant added.

A complete line of acids, solvents, mixed acid etchants (MAE® products), phosphoric acid etchants (PAE® products), glass and polysilicon etchants, and other chemicals are available from General Chemical. For more information, call our Customer Service Center toll-free: (800) 956-7467.

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## HOW TO ORDER

To place an order, obtain samples or request technical information, call Customer Service toll-free at (800) 956-7467, or the Electronic Chemicals Group directly at (800) 247-4519.

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